APPROVAL

Name: Muriel Rakotomalala

Degree: Master of Science

Title of Thesis: Photochemistry of Benzo[2,3-g]quinoxaline Derivatives

Examining Committee:
  Chair Dr. David J. Vocadlo
         Assistant Professor, Department of Chemistry

          Dr. Vance E. Williams
          Senior Supervisor
          Associate Professor, Department of Chemistry

          Dr. Neil R. Branda
          Supervisor
          Professor, Department of Chemistry

          Dr. Steven Holdcroft
          Supervisor
          Professor, Department of Chemistry

          Dr. Peter D. Wilson
          Internal Examiner
          Associate Professor, Department of Chemistry

Date Defended/Approved: March 25, 2008
Declaration of Partial Copyright Licence

The author, whose copyright is declared on the title page of this work, has granted to Simon Fraser University the right to lend this thesis, project or extended essay to users of the Simon Fraser University Library, and to make partial or single copies only for such users or in response to a request from the library of any other university, or other educational institution, on its own behalf or for one of its users.

The author has further granted permission to Simon Fraser University to keep or make a digital copy for use in its circulating collection (currently available to the public at the “Institutional Repository” link of the SFU Library website <www.lib.sfu.ca> at: <http://ir.lib.sfu.ca/handle/1892/112>) and, without changing the content, to translate the thesis/project or extended essays, if technically possible, to any medium or format for the purpose of preservation of the digital work.

The author has further agreed that permission for multiple copying of this work for scholarly purposes may be granted by either the author or the Dean of Graduate Studies.

It is understood that copying or publication of this work for financial gain shall not be allowed without the author’s written permission.

Permission for public performance, or limited permission for private scholarly use, of any multimedia materials forming part of this work, may have been granted by the author. This information may be found on the separately catalogued multimedia material and in the signed Partial Copyright Licence.

While licensing SFU to permit the above uses, the author retains copyright in the thesis, project or extended essays, including the right to change the work for subsequent purposes, including editing and publishing the work in whole or in part, and licensing other parties, as the author may desire.

The original Partial Copyright Licence attesting to these terms, and signed by this author, may be found in the original bound copy of this work, retained in the Simon Fraser University Archive.

Simon Fraser University Library
Burnaby, BC, Canada
ABSTRACT

Since its discovery in 1867, the photodimerisation of anthracene has been one of most exploited reactions for reversibly connecting materials at a molecular level. The cumbersome synthesis of many substituted anthracene derivatives combined with their tendency to form endoperodixes when irradiated in presence of oxygen and the short wavelengths needed to convert the dimer to its monomer prohibit their use in practical applications. In an attempt to circumvent some of these problems, we undertook the synthesis and the investigation of the photochemistry of benzo[2,3-g]quinoxalines, which are structurally similar to anthracenes. Surprisingly, the photochemical behaviour of these molecules has not been investigated.

Upon irradiation, 2,3-diphenylbenzo[2,3-g]quinoxaline (DPBQ) and 2,3-di(2-dipyridyl)benzo[2,3-g]quinoxaline (DPyBQ) both underwent photodimerisation to yield di-DPBQ and di DPyBQ respectively. The head-to-tail structure of di-DPBQ was confirmed by X-ray crystallography. Preliminary studies suggested that the presence of ZnCl\textsubscript{2} and Zn(OAc)\textsubscript{2} reduced the yield of dimerisation of DPyBQ.
DEDICATION

To my parents and brother.

“Ny hazo no vanon ko lakana, ny tany naniriany no tsara”
ACKNOWLEDGEMENTS

First I would like to thank my senior supervisor, Dr. Vance Williams, for giving me the opportunity to join his group and his support and guidance throughout my Master's studies. I would also like to show my appreciation to the members of my supervisory committee, Dr. Neil Branda and Dr. Steven Holdcroft, for their time and helpful suggestions.

I would also like to show my appreciation to the past and present members of the Williams' lab, Dr. David Bailey, Mr. Oliver Calderon, Dr. Johan Foster, Ms. Christine Lavigne, Mr. Laura Stusiak and Maitre Emilie Voisin, for their help throughout the different aspects of my project and laughing to all my French jokes.

I am thankful to Dr. Daniel Spantulesku (Branda Lab) for the synthesis of 4,4'-dimethoxybenzil, Ms. Emilie Voisin for the crystallisation of the dimers, the DSC measurements and for the synthesis and characterisation of 2,3,6,7-tetrahexyloxybenzil and 2,3,6,7-tetraoctyloxybenzil, Dr. Cornelia Bohne and Tamara Pace (University of Victoria) for the lifetime measurements and Ms. Chirstine Lavigne and Mr. Michael Katz for crystallographic data, and the Holdcroft group for the GPC measurements.

I would also like to express my gratitude to Mrs. Marcy Tracey (NMR), Mr Colin Zhang (NMR), Dr. Andrew Lewis (NMR), Mr. Simon Wong (MS and CHN
microanalysis), Mr. Mikki Yang (CHN microanalysis) for their technical assistance.

Last but not least, I am grateful to Simon Fraser University and the Natural Sciences and Engineering Research Council of Canada for their financial assistance.
TABLE OF CONTENTS

Approval.................................................................................................................................... ii
Abstract........................................................................................................................................ iii
Dedication....................................................................................................................................... iv
Acknowledgements.......................................................................................................................... v
Table of Contents ............................................................................................................................ vii
List of Figures.................................................................................................................................. ix
List of Equations ............................................................................................................................... xiii
List of Schemes................................................................................................................................. xiv
List of Abbreviations......................................................................................................................... xvi

Chapter 1: General Introduction...................................................................................................... 1
  1.1 Introduction ............................................................................................................................. 1
  1.2 Photochromism ....................................................................................................................... 1
    1.3 Bimolecular photochromism ................................................................................................. 4
    1.3.1 Common bimolecular systems ....................................................................................... 4
    1.3.2 Anthracene photochemistry ............................................................................................ 7
  1.4 Reversibly cross-linked polymers ............................................................................................ 9
    1.4.1 Applications of reversible photo-cross-linking ............................................................... 9
    1.4.2 Previous efforts towards photo-reversibly cross-linked polymers ................................. 10
    1.4.3 Anthracene containing polymers .................................................................................... 10
    1.4.4 Influence of the substitution pattern ............................................................................... 11
    1.4.5 Possible heterocyclic candidates for bimolecular photochromism ................................ 13
  1.5 Pyrazine-containing molecules ............................................................................................... 15
    1.5.1 Common pyrazine containing molecules ..................................................................... 15
  1.6 Objectives ............................................................................................................................... 17

Chapter 2: Photochromic Properties of substituted benzoquinoxaline .................................. 18
  2.1 Introduction ............................................................................................................................. 18
    2.1.1 Reactivity of benzo[2,3-g]quinoxalines .......................................................................... 19
    2.1.2 Objectives ...................................................................................................................... 19
  2.2 Results and discussion ............................................................................................................. 21
    2.2.1 Photochromism of 2,3-Diphenylbenzo[2,3-g]quinoxaline ............................................... 21
    2.2.2 Influence of Substitution at the 2- and 3-positions ....................................................... 35
    2.2.3 2,3-Di(pyridin-2-yl)benzo[2,3-g]quinoxaline ................................................................. 49
2.3 Conclusion ........................................................................................................... 52

Chapter 3: Towards stimuli-responsive photochromism ......................................... 54
3.1 Introduction: ........................................................................................................... 54
3.2 Result and Discussion: ......................................................................................... 54
3.2.1 Influence on optical properties ........................................................................ 55
3.2.2 Photochemical studies ...................................................................................... 66
3.3 Conclusion: ............................................................................................................ 70

Chapter 4: Selective formation of photoadduct ......................................................... 72
4.1 Introduction: ........................................................................................................... 72
4.2 Results and Discussion: ......................................................................................... 75
4.2.1 [4+4] Photocycloaddition .................................................................................. 76
4.2.1.1 [4+4] Photocycloaddition ............................................................................. 76
4.2.1.2 Cross [4+4] photocycloaddition ................................................................... 79
4.3 Conclusion ............................................................................................................. 84

Chapter 5: efforts towards photoresponsive materials containing
benzo[2,3-g]quinoxalines .............................................................................................. 85
5.1 Benzo[2,3-g]quinoxaline-functionalised polymer .................................................. 85
5.1.1 Introduction ....................................................................................................... 85
5.1.2 Result and Discussion ....................................................................................... 86

Chapter 6: Conclusion and Future work ..................................................................... 89
6.1 Conclusion ............................................................................................................. 89
6.2 Future Work ......................................................................................................... 92
6.2.1 Benzo[2,3-g]quinoxaline-functionalised polymers ............................................. 92
6.2.1 Stimuli responsive gels ..................................................................................... 94

Chapter 7: Experimental: ......................................................................................... 96
7.1 Materials and methods .......................................................................................... 96
7.2 Experimental for chapter 2 ................................................................................... 97
7.2.1 Synthesis of diketone derivatives ..................................................................... 97
7.2.2 Synthesis of benzoquinoxaline derivatives: ..................................................... 100
7.2.3 Photochemical Experiments .......................................................................... 102
7.3 Experimental for chapter 4 .................................................................................. 106
7.3.1 Synthesis ......................................................................................................... 106
7.3.2 Photoadduct formation ..................................................................................... 107
7.4 Experimental for chapter 5 .................................................................................. 109

Reference List .......................................................................................................... 111

Appendix 1: Crystallographic data for di-DPBQ .......................................................... 116
Appendix 2: Liquid crystal characterisation of THPQ ............................................... 123
LIST OF FIGURES

Figure 1.1: Numbering of positions of anthracene .................................................. 9
Figure 1.2: Exhaustive list of diazaanthracene reported to undergo successful [4+4] photocycloaddition ................................................................. 14
Figure 1.3: Structures of anthracene (A), benzo[2,3-g]quinoxaline (BQ) and pyrazo[2,3-g]quinoxaline (PQ) .............................................................. 15
Figure 1.4: Different pyrazine (P) containing moieties, quinoxaline (Q), benzophenazine (BP) and benzo[2,3-g]quinoxaline (BQ) ....... 15
Figure 1.5: 2,3-substituted benzo[2,3-g]quinoxaline ................................................. 16
Figure 2.1: Structure of anthracene (A) and benzo[2,3-g]quinoxaline (BQ) ........... 18
Figure 2.2: Orbital representation of HOMO (bottom) and LUMO (top) of anthracene (A) and benzoquinoxaline (BQ) calculated at the AM1 level .................................................. 19
Figure 2.3: "H-NMR spectra of DPBQ recorded in CDCl₃ before (top) and white solid isolated by decantation of CH₃CN after 150 min of irradiation (bottom) ................................................................. 24
Figure 2.4: UV-Vis absorption spectra of a 5.0 μM solution of DPBQ and a 10.0 μL solution of di-DPBQ recorded at room-temperature in CH₃CN ................................................................. 25
Figure 2.5: Crystal structure of ht-di-DPBQ ................................................................. 26
Figure 2.6: Plot of absorbance versus of concentration of DPBQ in CH₃CN recorded at 25 °C .............................................................................. 29
Figure 2.7: UV-Vis spectra monitoring the photodissociation of di-DPBQ when irradiated with 328 nm light at room temperature. Inset: zoom-in isobestic points ................................................................. 33
Figure 2.8: Variation of UV-Visible absorption spectra of a 1.0 mM solution of di-DPBQ in CH₃CN heated at 150 °C ...................................................... 34
Figure 2.9: Comparison of UV-Vis spectra of DPBQ, PBQ and BQ recorded at room-temperature in CH₃CN ................................................................. 37
Figure 2.10: "H-NMR spectra of BQ recorded in CDCl₃ before (top) and after 150 min of irradiation (bottom). New peaks associate with the photoadduct are emphasised with stars ......................... 39
Figure 2.11: $^1$H-NMR spectra of PBQ recorded in CDCl$_3$ before (top) and after 150 min of irradiation (bottom) (stars emphasise new peaks)........................................................................................................ 41

Figure 2.12: Comparison of UV-Vis spectra of BQ, MoPBQ and DMoPBQ recorded at room temperature in CH$_3$CN...................................................... 44

Figure 2.13: $^1$H-NMR of DMoPBQ recorded in CDCl$_3$; (top), after 150 min of irradiation (bottom). New peaks associated with the photoproduct are emphasised with stars, while the unidentified impurities present in traces prior to irradiation are emphasised by triangles........................................................................................................ 46

Figure 2.14: $^1$H-NMR spectrum of MoPBQ recorded in CDCl$_3$ before (top) and after 150 min of irradiation (bottom). New peaks are emphasised with stars. ........................................................................................................ 48

Figure 2.15: UV-Vis absorption spectra of DPBQ, DPyBQ and DMoBQ solutions in CH$_3$CN recorded at room-temperature. ........................................ 50

Figure 2.16: $^1$H-NMR spectrum of DPyBQ recorded in CDCl$_3$ before (top) and white solid isolated after 150 min of irradiation (bottom). ............... 52

Figure 3.1: Influence of chemicals on the luminescence of a solution of DPyBQ in CH$_3$CN (3.02 x 10$^{-4}$ M). Samples viewed under UV light........................................................................................................ 55

Figure 3.2: Absorption spectra of a solution of 0.1 mM = [DPyBQ] + [ZnCl$_2$] with varying [Zn$^{2+}$]/[DPyBQ] in CH$_3$CN measured at room temperature. .......................................................................... 57

Figure 3.3: Job's plot obtained from the change of absorption intensity at 380 nm of a solution of DPyBQ and ZnCl$_2$ measured at room temperature. ........................................................................ 58

Figure 3.4: Emission spectra of a series of solutions made of 0.1 $\mu$M solution of DPyBQ and ZnCl$_2$ in CH$_3$CN excited at 380 nm with varying molar ratio of ZnCl$_2$ such that [DPyBQ] + [Zn$^{2+}$] = 0.1 M but [Zn$^{2+}$]/[DPyBQ] varies measured at room-temperature. .................... 59

Figure 3.5: Job's plot obtained from change of luminescence intensity at 486 nm of a 0.1 $\mu$M of DPyBQ in CH$_3$CN with addition of ZnCl$_2$ measured at room temperature. ..................................................... 60

Figure 3.6: Influence of ZnCl$_2$ on the absorption of a 1.07 x 10$^{-4}$ M solution of DPyBQ in CH$_3$CN measured at room-temperature. .......................... 62

Figure 3.7: Job's plot of change of absorbance at 295 nm with molar fraction of Zn$^{2+}$ added to a constant volume of DPyBQ solution (1 x 10$^{-4}$ M). ........................................................................................................ 62

Figure 3.8: Fluorescence titration of a constant volume of DPyBQ solution (1x10$^{-6}$ M) in CH$_3$CN with addition of a small volume of ZnCl$_2$ solution (1 x 10$^{-5}$ M) measured at room-temperature. .................. 63
Figure 3.9: Absorption spectra of a solution of 0.1 mM = [DPyBQ] + [Zn(OAc)$_2$] with varying [Zn$^{2+}$]/[DPyBQ] in CH$_3$CN measured at room temperature .................................................. 65

Figure 3.10: Job’s plot obtained from the change of absorbance at 380 nm of a 0.1 mM solution of DPyBQ in CH$_3$CN measured at room-temperature .................................................. 65

Figure 3.11: Change of luminescence of a constant volume of DPyBQ solution in CH$_3$CN with addition of a solution of Zn(OAc)$_2$ in CH$_3$CN, recorded at room-temperature .................................................. 66

Figure 3.12: UV-Vis absorption spectra a solution of DPyBQ and ZnCl$_2$ in CH$_3$CN containing 0.37 molar ratio of ZnCl$_2$ before (full line) and after (dashed line) irradiation, measured at room-temperature .......... 67

Figure 3.13: UV-Vis absorption spectra a solution of DPyBQ and Zn(OAc)$_2$ in CH$_3$CN containing 0.30 molar ratio of Zn(OAc)$_2$ before (full line) and after (dashed line) irradiation (150 min), measured at room-temperature .......... 67

Figure 3.14: Percent conversion of DPyBQ after 150 min of irradiation in the Rayonet photoreactor without filter .......... 69

Figure 4.1: 2,3,6,7-Tetraphenylanthracene (TPA) and 2,3,7,8-tetraphenylpyrazo[2,3-g]quinoxaline (TPPQ) .......... 74

Figure 4.2: HOMO (bottom) and LUMO (top) of A and PQ calculated at the AM1 level .......... 74

Figure 4.3: Structural similarities between anthracene (A), benzo[2,3-g]quinoxaline (BQ) and pyrazo[2,3-g]quinoxaline (PQ) .......... 75

Figure 4.4: UV-Vis absorption spectra of TPPQ and TPA .......... 76

Figure 4.5: 2,3,7,8-Tetrakis(3,4-bis(hexyloxy)phenyl)-pyrazo[2,3-g]quinoxaline (THPQ) and polarised micrograph showing the C$_6$ symmetry taken at 106 °C with 400 x magnification .......... 79

Figure 4.6: $^1$H-NMR of a mixture of 0.2 mM solutions of TPPQ and A (5.0 +5.0 mL) in CH$_3$CN after 150 min of irradiation, dried in vacuo and recorded in CDCl$_3$. TPPQ (diamond), AO$_2$ (five-point star), di-A (triangle), new photoproduct (four-point star), unknown impurity (*) .......... 81

Figure 4.7: $^1$H-NMR of a mixture of 0.2 mM solutions of TPPQ and DMA (5.0 +5.0 mL) in CH$_3$CN after 150 min of irradiation, concentrated in vacuo and recorded in CDCl$_3$. TPPQ (diamond), DMA (five-point star), new photoproduct (four-point star) .......... 83

Figure 6.1: Synthesis of PS functionalised with a benzo[2,3-g]quinoxaline with a glycol linkage .......... 93

Figure 6.2: Proposed synthesis of co-benzoquinoxaline styrene polymer .......... 94
Figure 6.3: Proposed synthesis of polyamide polymer based on 2,3-diphenylbenzo[2,3-g]quinoxaline. ............................................................... 94

Figure 6.4: Structural similarities between (i) dialkoxyanthracene (DAOA), (ii) dialkoxyphenazine and (iii) dialkoxybenzoquinoxaline (DABQ). ........................................................................................................... 95

Figure A-7.1: Metling transition of THPQ determined by DSC. ......................... 123
LIST OF EQUATIONS

Equation 1.1: Light-stimulated reversible interconversion between state A and B. ........................................................................................................... 2

Equation 1.2: Formation of dianthracene (di-A) under UV light exposure of anthracene (A) and reversion from di-A to A through light \( h_{v1}>h_{v2} \) or heat. ........................................................................................................... 7

Equation 1.3: Possible isomers resulting from irradiation of a 9-substituted anthracene ........................................................................................................... 12

Equation 4.1: Photocycloaddition of 9,10-dimethylandanthracene and 2,3,6,7-tetraphenylanthracene ........................................................................................................... 73

Equation 4.2: Synthesis of TPPQ ...................................................................................................................................................................................... 76

Equation 4.3: Result of UV exposure of TPPQ ...................................................................................................................................................................................... 77

Equation 4.4: Cross-dimer formation resulting from irradiation of a mixture of TPPQ and A ........................................................................................................... 81

Equation 4.5: Cross-dimer formed from irradiation of a mixture of DMA and TPPQ ........................................................................................................... 83

Equation 5.1: Synthesis of poly(styrene-co-4-vinylbenzyl chloride) by free-radical polymerization ........................................................................................................... 87
LIST OF SCHEMES

Scheme 1.1: Examples of common unimolecular photochromic systems:
Azobenzene (1), spiropyran (2), dithienylethene (3) and rhodospin (4) ................................................................. 4

Scheme 1.2: Common systems undergoing [2+2]-photocycloaddition when exposed to UV irradiation: Phenanthrene (5), acetonaphthylene (6), cinnamate acid (7) and thymine (8) ................................................................. 5

Scheme 1.3: Examples of molecules undergoing [4+4] cycloaddition under UV irradiation: Tetracene (9), anthracene (10), naphthalene (11), pentacene (12), 2-aminopyridine (13), 2-pyridone (14) and acridizinium (15) ............................................................................................................. 6

Scheme 1.4: Paths of relaxation of anthracene in its singlet excited state:
Internal conversion (i), inter-system crossing (ii), luminescence (iii), non-radiative deactivation (iv), concentration quenching (v), dimerisation (vi) and dissociation (vi) ............................................................................................................. 8

Scheme 1.5: Formation of endoperoxide (AO$_2$) when anthracene (A) is irradiated in presence of oxygen ............................................................................................................. 9

Scheme 1.6: Synthesis of 1,2-diphenylquinoxaline ............................................................................................................. 16

Scheme 1.7: Synthesis of alkpyrazines from a-hydroxyimino ketones .......................................................... 16

Scheme 2.1: Possible isomers resulting from [4+4] photocycloaddition of a 2,3-disubstituted benzo[2,3-g]quinoxaline ............................................................................................................. 20

Scheme 2.2: Formation of $ht$-dimer after [4+4] photocycloaddition of 2,3-diphenylanthracene ............................................................................................................. 21

Scheme 2.3: Synthesis of DPBQ ............................................................................................................................. 22

Scheme 2.4: Photodimerisation of DPBQ ............................................................................................................. 24

Scheme 2.5: Synthesis of BQ ............................................................................................................................. 35

Scheme 2.6: Synthesis of PBQ ............................................................................................................................. 36

Scheme 2.7: [4+4]photocycloaddition of BQ ............................................................................................................. 39

Scheme 2.8: Possible isomers resulting from dimerisation of PBQ.$(X\text{=Ph}, Y\text{=H or } X\text{=H}, Y\text{=Ph})$ ............................................................................................................. 42

Scheme 2.9: Synthesis of DMoPBQ ............................................................................................................................. 43

Scheme 2.10: Synthesis of MoPBQ ............................................................................................................................. 43

Scheme 2.11: Synthesis of DPyBQ ............................................................................................................................. 50

xv
Scheme 5.1: Synthesis of benzo[2,3-g]quinoxaline functionalised poly styrene. ........................................................................................................... 88
LIST OF ABBREVIATIONS

δ Chemical shift
ºC Degree Celsius
A Anthracene
BP Benzophenazine
BQ Benzo[2,3-g]quinoxaline
Br Broad
Cm Centimetre
D Doublet
di-A Di-anthracene
DMA 9,10-Dimethylanthracene
DMF N,N'-Dimethylformamide
DMoBQ 2,3-Di(4-methoxyphenyl) benzo[2,3-g]quinoxaline
DMSO Dimethylsulfoxide
DPBQ 2,3-Diphenylbenzo[2,3-g]quinoxaline
DPyBQ 2,3-Di(2-pyridyl)benzo[2,3-g]quinoxaline
DSC Differential Scanning calorimetry
EtOH Ethanol
FT-IR Fourier Transform Infrared
g Gram
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>GPC</td>
<td>Gas permeation chromatography</td>
</tr>
<tr>
<td>h</td>
<td>Hours</td>
</tr>
<tr>
<td><em>hh</em></td>
<td>Head-to-head</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td><em>ht</em></td>
<td>Head-to tail</td>
</tr>
<tr>
<td>Hz</td>
<td>Hertz</td>
</tr>
<tr>
<td>hv</td>
<td>Irradiation with light</td>
</tr>
<tr>
<td><em>J</em></td>
<td>Coupling constant</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>m</td>
<td>Multiplet</td>
</tr>
<tr>
<td>M</td>
<td>Mol per litre</td>
</tr>
<tr>
<td>m.p.</td>
<td>Metling point</td>
</tr>
<tr>
<td>m/z</td>
<td>Mass to charge ratio</td>
</tr>
<tr>
<td>MALDI-TOF</td>
<td>Matrix assisted laser desorption ionisation time of flight</td>
</tr>
<tr>
<td>MeOH</td>
<td>Methanol</td>
</tr>
<tr>
<td>mg</td>
<td>Milligram</td>
</tr>
<tr>
<td>MHz</td>
<td>Megahertz</td>
</tr>
<tr>
<td>min</td>
<td>Minutes</td>
</tr>
<tr>
<td>mL</td>
<td>Millilitre</td>
</tr>
<tr>
<td>mmol</td>
<td>Millimole</td>
</tr>
<tr>
<td>MoBQ</td>
<td>2-(4-Methoxyphenyl) benzo[2,3-g]quinoxaline</td>
</tr>
<tr>
<td>mol</td>
<td>Mole</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------------------------------------------</td>
</tr>
<tr>
<td>MS</td>
<td>Mass spectroscopy</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometre</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>OAc</td>
<td>Acetate</td>
</tr>
<tr>
<td>P</td>
<td>Pyrazine</td>
</tr>
<tr>
<td>PBQ</td>
<td>2-phenylbenzo[2,3-g]quinoxaline</td>
</tr>
<tr>
<td>Ph</td>
<td>Phenyl</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>PQ</td>
<td>Pyrazo[2,3-g]quinoxaline</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>Q</td>
<td>Quinoxaline</td>
</tr>
<tr>
<td>S</td>
<td>Singlet</td>
</tr>
<tr>
<td>T</td>
<td>Triplet</td>
</tr>
<tr>
<td>TLC</td>
<td>Thin layer chromatography</td>
</tr>
<tr>
<td>TPA</td>
<td>2,3,6,7-tetraphenylanthracene</td>
</tr>
<tr>
<td>TPPQ</td>
<td>2,3,7,8-tetraphenylpyrazo[2,3-g]quinoxaline</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultraviolet-visible</td>
</tr>
<tr>
<td>λ</td>
<td>Wavelength</td>
</tr>
<tr>
<td>μL</td>
<td>Microlitre</td>
</tr>
</tbody>
</table>
CHAPTER 1: GENERAL INTRODUCTION

1.1 Introduction

The focus of this thesis was the investigation of the photochromic properties of benzo[2,3-g]quinoxaline derivatives, which we anticipated would undergo [4+4] photocycloaddition reactions. The present chapter will introduce photochromism in general and the photochemical properties of molecules that are structurally related to our target compounds.

1.2 Photochromism

Light represents an attractive stimulus for chemical reactions as it is a clean and easily tunable source of energy that can be focused on small areas without significant diffusion. The interaction of light with unsaturated organic molecules may induce photophysical and photochemical changes in the molecule in question. In the case of photochromic molecules, absorption of a photon of given energy $E = h\nu$ will induce a reversible change in the electronic properties of the chromophore resulting in a change of colour (Equation 1.1).\(^1\) The colour can then be reverted either thermally or photochemically.
Equation 1.1: Light-stimulated reversible interconversion between state A and B.¹

Several photochromic systems were investigated as a mean to introduce change of properties at the macroscopic level using a light as a stimulus. One of the most extensively studied systems is the azobenzene system (1). As shown in Scheme 1.1, azobenzenes undergo cis-trans isomerisation across the N=N double bond upon irradiation with UV-light. The change of geometry accompanying the isomerisation, has been used to photo-induce change in volume in polymers and liquid crystals.²,³ However, such systems suffer from the high thermal instability of the cis form. The lack of thermal stability combined with the small difference UV-Vis absorption between the two isomers represent drawbacks for potential applications such as optical data storage.³ Other systems based on electrocyclic photocyclisation such as spiropyrans (2) and diarylethenes (3) (Scheme 1.1) have also the subject to extensive research.⁴,⁵ In these systems, the change of conjugation induced by the cyclisation is translated in large change in UV-Vis absorption that could potentially be used for protective lenses.⁵-⁷ Spiropyrans (2) have been more extensively studied than diarylethenes (3), however they suffer from a lack of thermal stability accompanied by a low fatigue resistance which prevents their use in practical application requiring cycling.⁸
The focus of this thesis will be molecules that undergo intermolecular cycloaddition reactions to yield photodimers. Similarly to the unimolecular systems shown in Scheme 1.1, irradiation of bimolecular systems leads to a change of UV-Vis absorption and other physical properties. However, such systems have the advantage of enabling the use of light to reversibly assemble materials at the molecular level. A non-exhaustive list of attempts to use such systems in materials will be described in Chapter 1.4.
Scheme 1.1: Examples of common unimolecular photochromic systems: Azobenzene (1), spiropyran (2) and dithienylethene (3).¹

1.3 Bimolecular photochromism

1.3.1 Common bimolecular systems

The most common bimolecular photochromic systems undergo either [2+2] or [4+4] cycloaddition reactions leading to dimerisation of the photochromic moiety when exposed to UV or visible light. Non-exhaustive lists of molecules known to undergo [2+2] and [4+4] cycloadditions are shown in Scheme 1.2 and Scheme 1.3 respectively.
Cycloaddition involving four $\pi$ electrons, yielding a cyclobutane ring through a [2+2] cycloaddition of ethene containing chromophores, tends to induce only a small shift in absorption spectra.$^{1,9}$ This makes these systems less attractive for material applications such as photochromic lenses and optical data storage, which are focused on the change of colour. Materials containing cinnamate moieties (6) have been investigated for printing, lithography and photoresist applications.$^{10,11}$ The dimerisation of thymine (7) has been extensively investigated, as it has been shown to cause lesions in DNA leading to apoptosis, immuno-suppression and carcinogenesis.$^{12,13}$
The first example of a [4+4] cycloaddition was reported for the dimerisation of tetracene (9) in 1867 by Fritzsche.\textsuperscript{14} Since then, other conjugated systems such as naphthalene (11) and more recently pentacene (12), as well as heterocyclic systems such as acridizinium (15) were reported to undergo [4+4] photocycloaddition reactions.\textsuperscript{15-17} Anthracene (10) and its derivatives remain the most studied systems and several reviews concerning their photochromic properties have been published.\textsuperscript{18,19} Thus, anthracene will be used to illustrate the mechanism of [4+4] photocycloaddition reactions.
1.3.2 Anthracene photochemistry

The photochromic properties of anthracene were first reported by Fritzsche in 1867, when he exposed an extract of tar to sun light and observed an insoluble white powder adhering on the walls of the glassware.\textsuperscript{14}

\begin{equation}
\begin{array}{c}
2 \text{A} \\
\xrightarrow{h\nu_1} \text{di-A} \\
\xleftarrow{h\nu_2/\Delta} \text{A}
\end{array}
\end{equation}

\textbf{Equation 1.2:} Formation of dianthracene (di-A) under UV light exposure of anthracene (A) and reversion from di-A to A through light $h\nu_1 > h\nu_2$ or heat.

Luther and Weigert reported the first investigation of the mechanism of dimerisation of anthracene in 1905.\textsuperscript{20,21} However, it was not until the 1950's, along with the emergence of systematic studies on the mechanistic aspects of photochemical reaction processes, that Förster and Kasper discovered the formation of excimers (excited dimers).\textsuperscript{22} The discovery of excimer formation combined with the Woodward-Hoffman rules in 1965 generated interest in the mechanism of anthracene dimerisation. As shown in Scheme 1.4, once a molecule of anthracene interacts with a photon, it is excited to the singlet state $^1A^*$ which can then relax via several competing paths. Thus, as observed by Bowen and coworkers, an increase in dimerisation will be accompanied by a decrease in fluorescence.\textsuperscript{23} The formation of an excimer during anthracene dimerisation was first proposed by Ferguson in 1974 and confirmed by Cohen \textit{et al.} in 1976.\textsuperscript{24-26}
Scheme 1.4: Paths of relaxation of anthracene in its singlet excited state: (i) Internal conversion, (ii) Inter-system crossing, (iii) luminescence, (iv) non-radiative deactivation, (v) dimerisation and (vi) dissociation.

The [4+4] photocycloaddition across the central ring of two anthracenes results in the formation of two new sigma bonds at the 9- and 10-positions (Figure 1.1) which are the most reactive positions of the anthracene core as most of the electron density is located on the central ring. Along with the competing photophysical processes shown in Scheme 1.4, other photochemical events can occur resulting in a reduction of the dimerisation efficiency. It was demonstrated that when irradiated at low concentration in presence of molecular oxygen, anthracene undergoes photooxidation to yield 9,10-epidoxioanthracene (AO2 endoperoxide) (Scheme 1.5). AO2 is formed by reaction of singlet oxygen, sensitised by the triplet state of anthracene, at the 9- and 10-positions of anthracene (Scheme 1.5). Thus, to avoid the formation of the endoperoxide, the dimerisation of anthracene must often be carried out in a rigorously deoxygenated solvent, which makes anthracene dimerisation less attractive than other photochromic systems for practical applications such as holographic memory or photoinduced patterning.
Figure 1.1: Numbering of positions of anthracene.

Scheme 1.5: Formation of endoperoxide (AO₂) when anthracene (A) is irradiated in presence of oxygen.

1.4 Reversibly cross-linked polymers

1.4.1 Applications of reversible photo-cross-linking

The changes of physical properties (e.g. refractive index or solubility) involved with the dimerisation via either [2+2] and [4+4] processes can be exploited for practical applications. For instance, Tomlinson and co-workers investigated the dimerisation of several systems for holographic applications with non-destructive read-out. Kuckling and co-worker used the change in solubility associated with the dimerisation of acridizinium salt of a poly(N-isopropyl-acrylamide) to induce hydrogel formation and consequently photoinduced patterning of thin films at the picometer scale in aqueous media. It should however be noted that the application of photochromic systems has to overcome several practical limitations including fatigue.
resistance, competition of absorption between two or more chromophores species and thermal stability.¹

1.4.2 Previous efforts towards photo-reversibly cross-linked polymers

The use of photodimerisation as a tool to induce cross-linking in polymers has been widely studied.³² Most studies focused on the dimerisation of cinnamate-based polymers, which suffer from the competing E/Z isomerisation resulting in a decrease in dimerisation efficiency.²⁹,³³ Other systems based on [2+2] photocycloaddition such as coumarin or thymine labelled polymers have been reported.³⁴ However, only a limited number of reports have described the [4+4] photocycloaddition of systems other than anthracene (Scheme 1.3).¹⁶

1.4.3 Anthracene containing polymers

Several anthracene-containing polymers have been reported to undergo successful cross-linking through [4+4] photocycloaddition in solution.³²,³⁵-³⁸ Coursan and co-workers reported the photoreversible cross-linking of anthracene end-capped polystyrene.³⁶ However, both Zheng and Matsui independently observed that the irradiation of the cross-linked polymer with shorter wavelengths (< 300 nm) only partially regenerated the anthracene.²⁹,³⁷ Zheng and co-workers suggested that the lack of reversibility was due to the competing absorption by the carbonyl functionality, but the change from an ester to an ether functionality did not lead to improved reversibility.²⁹ They also observed a decrease in rate of photoreaction for both forward and backward reactions in solid thin films.²⁹ This
reduced photoreactivity was ascribed to the lack of flexibility in the solid state, where anthracene cannot align optimally for photodimerisation. In order to, one day, witness the use of anthracene dimerisation in practical applications, studies have been focusing in overcoming the limitations that have been presented earlier, that is to say, the limited efficiency of the dimerisation, the tendency to form photooxidation product and the high energy required for the photodissociation step.

1.4.4 Influence of the substitution pattern

Research on dimerisation of anthracene derivatives has focused on compounds with substituents at the 9- and 10- positions, which are generally the most synthetically accessible derivatives as the carbon atoms on the central ring are the most reactive positions. However, it has been demonstrated that the added steric bulk at these sites reduces the thermal stability of the photoadduct; hence, 9,10-disubstituted anthracenes do not tend to form homodimers, whereas 9-substituted derivatives form only the less sterically encumbered of two possible regioisomers (Equation 1.3). Thus, changing the substitution to the peripheral 1-8-position could potentially lead to more thermally stable dimers. However, functionalisation at the 2- and 3-positions is not straightforward since the peripheral positions of the anthracene core are not as reactive. The development of a system with synthetically accessible functionalisation that also undergoes [4+4] cycloaddition would enable the design of a reversibly cross-linked polymer based on bimolecular photochromism.
Equation 1.3: Possible isomers resulting from irradiation of a 9-substituted anthracene.

One potential solution to the lack of reversibility observed by Zheng\textsuperscript{29} and Matsui\textsuperscript{37} would be to tailor the anthracene moiety such that its dimer absorbs light above 300 nm. Indeed, reducing the energy necessary for the photodissociation would in turn decrease the number of possible photochemical events occurring upon irradiation and render the dissociation more efficient. As shown in Equation 1.3, groups at the 9- and 10- positions will only have a small effect on the absorption properties of the dimer since such groups do not contribute to the conjugated $\pi$-system in the dimer. Thus, substitution of the outer rings would be preferred to ensure the thermal stability of the dimer and red-shift its absorption as a result of the extended conjugated system. Such system would be more advantageous for material applications.

When a mixture of 2 anthracene compounds A and B is irradiated, three photoadducts can be formed: two dimers AA and BB and one cross-adduct AB. Previous work in our laboratory successfully exploited steric demands in anthracene dimerisation as a tool for selective photoadduct formation.\textsuperscript{39} As part of this work, synthetic routes to peripherally substituted anthracene via Diels-Alder reactions of appropriate disubstituted sulfones or cyclopentadienones with
benzoquinones were developed. These approaches were used to synthesise a variety of substituted anthracenes, albeit in low yields and over several steps. Such time-consuming synthetic routes combined with the low yields prevent such systems from being extensively investigated and in turns delays their use in material application. It is therefore necessary to develop a photochromic system that would be more synthetically accessible.

1.4.5 Possible heterocyclic candidates for bimolecular photochromism

Another approach to overcome the limitations of anthracene photochromism, is to introduce heteroatoms in the core while keeping it isoelectronic to anthracene. The most extensively studied nitrogen-containing analogues of anthracenes are acridiziums (15). Bradscher and co-workers reported that UV irradiation of a solution bromo acrizidinium salt yielded a photoadduct that was formed by [4+4] cycloaddition across the central ring of two acridizinum moieties. Diazaanthracenes are systems where two carbons in the anthracene core were replaced by two nitrogens. To the best of our knowledge, only three isolated diazaanthracenes were reported to undergo successful [4+4] photocycloaddition in a similar manner to anthracene. Stimulated by the development of rigid framework containing pyrimidine base components, Warrener and co-workers reported dimerisation of 1,3-diazaanthracene (16) which was the first example of diazaanthracene [4+4] photocycloaddition. However, neither the photodissociation of 16 nor the investigation of the photochemistry of its parent molecules was reported. Jouvenot and co-workers investigated the photochromic properties of 2,7-diazaanthracene 17 in an effort
to develop responsive ligands that could be employed to switch interactions between coordination centres. More recently, Berni and co-workers reported the photochromic properties of 4,5-diazaanthracene 18 in an effort to capture helical foldamers in helice-like molecules. Even though such diazaanthracenes possess interesting properties, their synthesis requires time-consuming multistep approach.

Figure 1.2: Exhaustive list of diazaanthracene reported to undergo successful [4+4] photocycloaddition.

In order to develop a photochromic system that can be easily functionalised at the peripheral positions (i.e. not the 9- and 10-), we turned our attention to pyrazine containing polycyclic molecules. The structural similarity between benzo[2,3-g]quinoxaline (BQ), pyrazo[2,3-g]quinoxaline (PQ) and anthracene (A) led us to investigate the former two compounds as possible photochromic molecules (Figure 1.3). This work constitutes the major body of this thesis. The following sections will briefly introduce the chemistry of these and related molecules.
1.5 Pyrazine-containing molecules

1.5.1 Common pyrazine containing molecules

Although pyrazines are synthetically accessible, their natural occurrence is fairly limited. The dialkylated pyrazine rings are present in fused oils or flavour constituents in foodstuffs and these compounds are produced from proteins during fermentation. Pyrazines represent important intermediates in fragrance or agricultural chemicals.

The synthesis of pyrazine rings is typically achieved by condensation of unsaturated 1,2-diamine and a 1,2-diketone. For instance, refluxing a mixture of o-phenylenediamine and benzil in ethanol quantitatively yields 1,2-diphenylquinoxaline (Scheme 1.6).
Scheme 1.6: Synthesis of 1,2-diphenylquinoxaline.

Symmetrically substituted pyrazines can also be obtained by self-condensation of α-amino carbonyl compounds. This method is not optimum for unsymmetrical pyrazines as it yields a mixture of regioisomers. Thus, Buchi and Galindo developed a route to obtain alkylpyrazines from α-hydroxyimino ketones (Scheme 1.7).

Scheme 1.7: Synthesis of alkylpyrazines from α-hydroxyimino ketones.

A wide variety of substituted pyrazines such as 2,3-substituted benzo[2,3-g]quinoxaline have been synthesised by condensation of 2,3-diaminonaphthalene with 2,3-diketones (Figure 1.5). The photochemistry of these compounds has yet to be reported.

Figure 1.5: 2,3-substituted benzo[2,3-g]quinoxaline.
1.6 Objectives

This thesis will describe synthesis and the study of the photochromic properties of benzo[2,3-g]quinoxaline derivatives in an attempt to overcome the limitations encountered with the anthracene systems. 2,3-Diphenylbenzo[2,3-g]quinoxaline (DPBQ) will be synthesised and its photochromic properties investigated. To investigate the influence of substituents, the groups at the peripheral positions will be modified and their the photochemical properties will be compared to those of DPBQ. Finally, in order to develop a more selective photochromic system, the photochemical properties of tetraphenylpyrazo[2,3-g]quinoxaline will be investigated.
CHAPTER 2: PHOTOCHROMIC PROPERTIES OF SUBSTITUTED BENZOQUINOXALINE

2.1 Introduction

As was discussed in the previous chapter, bimolecular photochromic reactions offer unique opportunities for creating dynamic materials. Anthracene derivatives have been the most extensively studied bimolecular photochromic systems. However, these systems have many practical limitations, such as their often cumbersome synthesis and a tendency to form endoperoxides when irradiated in presence of oxygen. The structural similarity between anthracene and benzo[2,3-g]quinoxaline, along with the relative ease of synthesis of the latter compound, led us to investigate the possible dimerisation of this class of heterocycles (Figure 2.1). The photochromic properties of a series of quinoxaline derivatives will be presented and will be compared with their anthracene analogues.

![Figure 2.1: Structure of anthracene (A) and benzo[2,3-g]quinoxaline (BQ).](image)

Figure 2.1: Structure of anthracene (A) and benzo[2,3-g]quinoxaline (BQ).
2.1.1 Reactivity of benzo[2,3-g]quinoxalines

Prior to the synthesis of the targeted benzo[2,3-g]quinoxaline derivatives, the electron density of the HOMO and LUMO of benzo[2,3-g]quinoxaline (BQ) were calculated using semi-empirical calculations at the AM1 level and compared to those of anthracene. Like anthracene, both the HOMO and LUMO of BQ are predicted to have large coefficients at the 9- and 10- positions of the tricyclic core (Figure 2.2). This preliminary calculation suggested that BQ could undergo [4+4] cycloaddition upon irradiation.

![Figure 2.2: Orbital representation of HOMO (bottom) and LUMO (top) of anthracene (A) and benzoquinoxaline (BQ) calculated at the AM1 level.](image)

2.1.2 Objectives

According to the information provided by the preliminary AM1 calculations, benzo[2,3-g]quinoxaline was expected to undergo [4+4] photocycloaddition across the central ring upon UV-irradiation. 2,3-Disubstituted benzo[2,3-
g]quinoxalines can potentially undergo [4+4] photocycloaddition to produce six isomers (Scheme 2.1).

Scheme 2.1: Possible isomers resulting from [4+4] photocycloaddition of a 2,3-disubstituted benzo[2,3-g]quinoxaline.

When R' and R'' are identical, the possible number of isomers is reduced to two stereoisomers, referred to as head-to-head hh (c and d) and head-to-tail ht (a, b, e and f). A previous study in our group demonstrated that irradiation of a degassed solution of 2,3-diphenylanthracene (DPA) in CH$_3$CN with 350 nm light led to the formation of only one photoadduct. It was suggested that the less sterically hindered ht-photoadduct was formed (Scheme 2.2).$^{18,27,52}$ Hence, we could expect that irradiation of 2,3-disubstituted benzo[2,3-g]quinoxaline would also lead to the least hindered photoproduct.
2.2 Results and discussion

2.2.1 Photochromism of 2,3-Diphenylbenzo[2,3-g]quinoxaline

2,3-Diphenylbenzo[2,3-g]quinoxaline (DPBQ) was chosen to investigate whether benzo[2,3-g]quinoxaline derivatives could undergo [4+4] photocycloaddition upon UV-irradiation as it was expected to lead to only two possible photoadducts (hh and ht). DPBQ was synthesised according to literature procedure by condensation of the commercially available 2,3-diaminonaphthalene and benzil\(^{53}\) (Scheme 2.3) and characterised by \(^1\)H-NMR and UV-Vis absorption spectroscopy as well MALDI-TOF mass spectroscopy. The UV-Vis absorption spectrum of this compound in CH\(_3\)CN reveals a strong absorbance centred at 270 nm and a less intense set of bands at longer wavelengths (\(\lambda_{\text{max}} = 380\) nm)(Figure 2.4), which suggested that UV irradiation could lead to a photochemical reaction.
2.2.1.1 [4+4] Photocycloaddition of DPBQ

In order to study its photochemical behaviour, a 4.4 mM solution of DPBQ in CH$_3$CN was irradiated with 350 nm lamps in a Rayonet® photochemical reactor. After 2.5 h of irradiation, a white powder was formed on the side of the reaction vessel. This is consistent with the behaviour of anthracene dimers which tend to have lower solubility than their monomeric forms. Unlike anthracene dimers, which tend to be ionised and break apart during mass spectrometry experiments, the MALDI-TOF spectrum of the photoadduct of DPBQ exhibited a peak at m/z = 665, corresponding to the dimer (M+1) peak in addition to a more intense peak corresponding to DPBQ. The insoluble white powder was isolated from the reaction medium by decantation of CH$_3$CN and characterised by $^1$H-NMR spectroscopy. The singlet corresponding to the protons at the 9- and 10-positions shifted from 8.75 to 5.06 ppm, which is consistent with the change of hybridization from sp$^2$ to sp$^3$ as a bridgehead was formed between the central rings in the benzo[2,3-g]quinoxaline moieties (Figure 2.3).$^{18}$ The presence of a single peak at 5.06 ppm is consistent with the presence of only one photoadduct, which was tentatively inferred to be the ht-
dimer for steric reasons. The observed peak at 52.7 ppm in the $^{13}$C-NMR spectrum of the photoadduct was consistent with the shift observed for di-DPA with respect to DPA (from 141.5 to 53.4 ppm). The UV-Vis absorption spectrum of di-DPBQ is blue-shifted with respect to that of DPBQ, with an absorption maximum at 328 nm (Figure 2.4). This is consistent with the reduction of delocalisation of the $\pi$-electrons as the dimerisation results in a change of hybridisation of the carbon atoms in the central ring from sp$^2$ to sp$^3$. Like anthracene dimers, di-DPBQ does not absorb in the visible region, but its absorption is significantly red-shifted with respect to that of di-DPA. Such red-shift in absorption represents an advantage over the anthracene analogue as the photodissociation would require less energy and in turn reduce the number of other possible photochemical events occurring in solution.
Scheme 2.4: Photodimerisation of DPBQ.

Figure 2.3: \(^1\)H-NMR spectra of DPBQ recorded in CDCl\(_3\) before (top) and white solid isolated by decantation of CH\(_3\)CN after 150 of irradiation (bottom).
Figure 2.4: UV-Vis absorption spectra of a 5.0 μM solution of DPBQ and a 10.0 μL solution of di-DPBQ recorded at room-temperature in CH₃CN.

2.2.1.2 Crystal structure of di-DPBQ

The identification of this photoproduct as *ht-di-DPBQ* was confirmed by X-ray crystallography of single crystal obtained by slow evaporation of a 1:1 CH₃CN:CHCl₃ solution (Figure 2.5). Under these conditions, the di-DPBQ crystallizes in the monoclinic space group *P2₁/n*. The bond lengths between the sp³-hybridized bridgehead carbons are 1.61(6) Å, which are longer than for a

---

*Crytal data for di-DPBQ: C₄₈H₃₄N₄, M.W. = 664.79, monoclinic, space group *P 1 2₁/n 1, a = 8.6132(9), b = 18.4915(17), c = 10.9618(16) Å, β = 96.550(6), V = 1734.5(4) Å³, T = 293 K, Z = 2, ρ_{calcld} = 1.273 g·cm⁻³, μ(Cu-Kα) = 0.580, T = 293 K, 3014 unique reflections, 2639 observed (I > 2.5σ(I)). The final R_F = 0.0436 and R_{W_F} = 0.0645 (observed data). Apendix I for full crystallographic data.*
typical carbon-carbon single bond, but similar to the lengths of the corresponding bonds in dianthracene (1.624 Å) and related systems.\textsuperscript{18}

\textbf{Figure 2.5:} Crystal structure of ht-di-DPBQ

\textbf{2.2.1.3 Formation of Endoperoxide}

To test the sensitivity of DPBQ dimerisation to O\textsubscript{2}, three samples of a 4.4 mM solution of DPBQ in CH\textsubscript{3}CN were irradiated in the Rayonet\textsuperscript{®} photochemical reactor with different levels of air in the reaction vessel. One sample was degassed by three freeze-pump-thaw cycles and irradiated under N\textsubscript{2}; the second sample was not deoxygenated, but was irradiated under ambient conditions, while air was bubbled through the third sample during irradiation. The effect influence of oxygen was quantified by \textsuperscript{1}H-NMR analysis of the concentrated solutions after 150 min of irradiation. Similar ratios of DPBQ to di-DPBO in \textsuperscript{1}H-NMR spectra of all three samples confirmed that unlike anthracene derivatives, the dimerisation of DPBQ was not sensitive to the presence of oxygen yielding only di-DPBO (21 %). No additional products were observed in the presence of
O₂, suggesting that DPBQ can be irradiated in presence of oxygen without formation of endoperoxide or singlet oxygen, which represents a significant advantage in terms of fatigue resistance and performance relative to anthracene. The above results suggest that photodimerisation occurs from the singlet excited state, since triplets would likely undergo quenching by oxygen.²⁷ As shown in Scheme 1.5, the formation of endoperoxide is dependent on the sensitisation of O₂ by the excited molecule of DPBQ in its triplet state.

In an effort to better understand the mechanism of photodimerisation, the excited state lifetimes of DPBQ were determined by single-photon counting for the singlet excited state and by laser flash photolysis for the triplet state by Dr. Cornelia Bohne and Tamara Pace (University of Victoria, BC, Canada). The singlet state lifetime was found to be 1.9 ± 0.1 ns in CH₃CN and less than 0.5 ns in cyclohexane. The triplet lifetime is long (~10 µs) in CH₃CN and cyclohexane. The singlet excited state of anthracene has a lifetime of approximately 5.3 ns. In comparison, the lifetime of the singlet excited state of DPBQ is very short, thus the efficiency of dimerisation is expected to be reduced. Indeed, when two degassed solutions of A and DPBQ are irradiated in the same conditions, di-A is formed in 86 %, whereas di-DPBQ is formed in 21 %. Even though the triplet lifetime of DPBQ is relatively long lived, the unsuccessful sensitisation of O₂ by

---

²² Fluorescence spectra were measured with a PTI QM-2 spectrometer and the singlet excited state lifetimes were measured with a OB920 single photon counter from Edinburgh. The excitation wavelength was 380 nm and emission spectra were collected between 395 and 700 nm (slit bandwidth of 3 nm), while decays were collected at 460 or 490 nm (slit bandwidth of 16 nm). For a description of the laser flash photolysis system. Samples were excited with a Nd:YAG laser at 266 nm and the kinetics was monitored at 400-410 and 460 nm. For all photophysical experiments samples were deoxygenated by bubbling nitrogen for 20 min.
Excited DPBQ in its triplet state can be rationalized by the fact that there are competing photophysical events occurring in solution (Scheme 1.4).

Assuming that the photodimerisation occurs through a singlet state, the efficiency of dimerisation is dependent on the probability of an excited molecule \( *A \) interacting with another molecule in its ground state \( A \) to form the intermediate \( *A-A \). This process, also called quenching, is diffusion limited.\(^{55}\) Assuming a steady state of the concentration of \( *A-A \), the rate constant for the dimerisation \( k_d \) can be expressed as followed:

\[
\begin{align*}
  *A + A & \xrightleftharpoons[k_d]{k_d} *A-A \\
  & \xrightarrow{k_{de}} \text{dimer}
\end{align*}
\]

\[ k_q = \frac{k_d k_{de}}{k_d + k_{de}} \]

Assuming that the deactivation of the excited state \( *A \) is a competition between the monomolecular processes (fluorescence \( k_f \) and non-radiative processes \( k_{nr} \)) and bimolecular processes, the change of intensity of emission can be expressed by the Stern-Volmer equation expressed below:

\[
\frac{I^0}{I} = 1 + \left( \frac{k_q}{k_0} \right) [A]
\]

\[ k_0 = k_f + k_{nr} = \frac{1}{\tau_0} \]

The Stern-Volmer constant \( K_{SV} \) is defined as:

\[ K_{SV} = \frac{k_q}{k_0} = k_q \tau_0 \]
Thus, the efficiency of the bimolecular reaction is directly proportional to the lifetime of the excited state $\tau_0$. This may explain why less di-DPBQ was produced when two equimolar degassed solutions of A and DPBQ were irradiated simultaneously.

In order to rule out that dimerisation resulted from preassociation of DPBQ, UV-Vis absorption spectra of DPBQ in CH$_3$CN were recorded at concentrations ranging from $1.00 \times 10^{-4}$ to $1.00 \times 10^{-6}$ M. The linear plot of absorbance versus concentration confirmed that the Beer-Lambert law was obeyed, suggesting that no pre-association was taking place over this concentration range (Figure 2.6).

![Figure 2.6: Plot of absorbance versus of concentration of DPBQ in CH$_3$CN recorded at 25 °C.](image)

According to the Stern-Volmer equation, the amount of dimer formed should be proportional to the initial concentration of DPBQ in solution as well as
the number of incident photons. The 350 nm lamps that were used emit a non-negligible amount of light around 330 nm, the wavelength of light absorbed by the dimer. It is therefore possible that the dimer is being dissociated during the irradiation in the Rayonet® fitted with 350 nm lamps.

In an effort to further understand the effect of 350 nm lamps on the dimerisation of DPBQ, a solution of di-DPQB in CH₃CN was irradiated in the Rayonet® photochemical reactor. After 15 min, the dimer was fully dissociated back to the monomer. This result implied that the photoreactor produced enough light around 330 nm to dissociate the dimer during dimerisation of DPBQ, resulting in a reduced yield of dimerisation. It should however be pointed out that during the dimerisation experiments the lamps used also emit light at 350 nm where di-DPQB has only a reduced absorption, which enables the formation of di-DPQB which precipitated at of solution. Thus, the use of a monochromatic light source should improve the yield of the dimerisation of DPBQ. To that end, a 1.00 mM solution of DPBQ in CH₃CN was irradiated using a fluorimeter as a monochromatic light source (λ = 378 nm, slid width 5 nm). The progress of the reaction was followed by UV-Vis spectroscopy, which imposed a limitation on the concentration used for irradiation with the fluorimeter to 1.00 mM instead of 4.4 mM when the Rayonet® photoreactor was used. No change was observed in the UV-Vis spectrum with irradiation time; it therefore was concluded that the dimerisation using a selective light source was unsuccessful. The photodissociation studies of di-DPQB (vide infra) demonstrated that the light source used for monochromatic irradiation was less effective than the Rayonet®
photoreactor® likely because of the lower flux. The lack of dimer formation of DPBQ under the same conditions can be associated with the reduced lifetime of the excited state with respect to anthracene. Consequently, the use of a more powerful monochromatic light source or the use of cut-off filters should improve the yield of dimerisation.

In order to demonstrate that the use of a cut-off filter would improve the yield of dimerisation DPBQ, a 2.00 M solution of KNO₃ in water was used to block wavelength under 340 nm. In order to verify that the filter reduced the effectively prevented the dissociation of di-DBPQ in solution during the irradiation in the Rayonet®, a solution of di-DPBQ in CH₃CN was immersed in the KNO₃ solution and irradiated in Rayonet® photochemical reactor for 15 min. ¹H-NMR analysis of the concentrated solution did not show any DPBQ. A solution of DPBQ immersed in this filter solution was irradiated simultaneously with an identical sample without a filter solution in the Rayonet® photochemical reactor. After 150 min of irradiation, integration of the diagnostic peaks in ¹H-NMR spectra for di-DBPQ and DPBQ, at 5.1 and 8.8 ppm, respectively, in a ratio of 3.6: 1 indicated yield of photoadduct of 78 %, whereas irradiation without filter only yields 72 % of photoadduct with a peak ratio of 2.6 : 1. This confirmed that light under 340 nm influences the yield of photocycloaddition likely by partially dissociating di-DPBQ formed in solution.

In order to study the influence of the solvent used during irradiation of a DPBQ solution, DPBQ was dissolved in benzene, acetonitrile, chloroform, dichloromethane, deuterated chloroform and deuterated acetonitrile. A degassed
1.3 mM solution of DPBQ yielded 19% of dimer in CH$_3$CN whereas only 14% of dimer was formed in benzene when irradiated for 150 min in the Rayonet® photochemical reactor. However, irradiation of DPBQ in halogenated and deuterated solvent did not yield any dimer. The lack of any photoadduct formation after irradiation in halogenated solvent might be associated with the quenching of the excited DPBQ by the solvent. Dissociative charge transfer in halogenated solvents during photochemical reactions has been previously reported.\textsuperscript{57,58} Hence, CH$_3$CN is better suited as a solvent for the dimerisation of DPBQ.

**2.2.1.4 Photodissociation of di-DPBQ**

In order to investigate the photodissociation of di-DPBQ, a 1.00 mM solution of di-DPBQ in CH$_3$CN was selectively irradiated with 328 nm light.\textsuperscript{c} A continuous decrease in absorbance at 328 nm, along with an increase at 380 nm in the UV-Vis spectra demonstrated that di-DPBQ dissociates to the corresponding monomer when irradiated at 328 nm (Figure 2.7). After 240 min of irradiation, no more changes in absorption were observed, confirming that the dissociation had reached completion. The presence of isobestic points at 321 nm and 345 nm suggests that the dissociation from di-DPBQ to DPBB occurs in one step. This assumption is only valid if there are no other species absorbing in the region of the isobestic point generated during the photoreaction.

\textsuperscript{c} This irradiation was carried out in 1 cm quartz cell and a fluorimeter was used as a selective light source allowing narrow excitation wavelength.
2.2.1.5 Thermal dissociation of di-DPBQ

The thermal stability of di-DPBQ was studied by heating 25 mL aliquots of a 1 mM solution in DMSO at 80, 100, 120 and 150 °C. The effects of temperature were followed by UV-Vis absorption spectroscopy. For the samples heated for over five hours at 80, 100 and 120 °C, the lack of absorption in the 400 nm region associated with the absorption of the monomer indicated that di-DPBQ is stable at these temperatures for a prolonged period of time and did not undergo dissociation. As observed in the photodissociation study, the continuous decrease of absorption at 328 nm and a corresponding increase at 380 nm, with
increased heating time demonstrated that di-DPBQ started decomposing back to DPBQ after 1 h at 150 °C (Figure 2.8). After 150 min, a 73 % decrease in absorption at 328 nm and an increase at 380 nm in the UV-Vis spectrum were observed. Inconveniently, the thermal dissociation could not be carried out to completion as a result of an amount insufficient stock solution. None the less, the presence of two isobestic points at 323 nm and 347 nm shows that the dissociation of di-DPBQ proceeds without side product formation, similar to anthracene. This suggested that longer exposure to heat would lead to full reversion of di-DPBQ to DPBQ.

![Absorption Spectra](image)

**Figure 2.8:** Variation of UV-Visible absorption spectra of a 1.0 mM solution of di-DPBQ in CH₃CN heated at 150 °C.
2.2.2 Influence of Substitution at the 2- and 3-positions

2.2.2.1 Phenyl groups

2.2.2.1.1 Synthesis

Once DPBQ was shown to undergo [4+4] photocycloaddition, we turned our attention to other derivatives. In order to further understand the influence of the substitution on the photodimerisation of benzo[2,3-g]quinoxaline derivatives, 2-phenylbenzo[2,3-g]quinoxaline (PBQ) and benzo[2,3-g]quinoxaline (BQ) were synthesised and their photochemical behaviours were investigated (Scheme 2.5 and Scheme 2.6).\textsuperscript{59}

The unsubstituted benzo[2,3-g]quinoxaline core BQ was synthesised in two steps from glyoxal and 2,3-diaminonaphthalene (Scheme 2.5).\textsuperscript{60}

\begin{align*}
\text{HO}
\text{HO} & + \text{H} \text{COH} \xrightarrow{\text{benzene}} \text{HO} \text{HO} \\
\text{NH}_2 \text{NH}_2 & + \text{HO} \text{HO} \text{O} \text{O} \xrightarrow{\text{EtOH}} \text{BQ} \text{H}_2 \text{O} + \text{HO} \text{COH} \\
\end{align*}

Scheme 2.5: Synthesis of BQ

The desired phenylglyoxal necessary for the synthesis of PBQ was synthesised by oxidation of acetophenone. Several literature procedures for the oxidation of benzophenone were examined. To avoid the use of carcinogenic
dioxane, the oxidation of benzophenone was achieved on silica using microwave
irradiation, but separation of the phenylglyoxal from the silica was cumbersome.\textsuperscript{61}
The use of SeO\textsubscript{2} in dioxane solution\textsuperscript{42} only yielded 35\% of the target compound,
which was not as attractive as the use of HBr as an oxidating agent, which led to
the product in 87\% yield.\textsuperscript{59,62} PBQ was then obtained in 92\% yield by
condensation of phenylglyoxal with 2,3-diaminonaphthalene.

\begin{center}
\begin{align*}
\text{O} & \text{C} \quad 48 \% \text{HBr, DMSO} \quad \text{HO} & \text{C} \\
\text{H} & \text{O} \quad 53 \% \quad \text{HO} & \text{OH} \\
\text{NH}_{2} & \text{NH}_{2} \quad \text{H} & \text{O} \quad \text{EtOH} \quad \text{N} & \text{N} \quad 92 \%
\end{align*}
\end{center}

\textit{Scheme 2.6: Synthesis of PBQ}

The UV-Vis absorption spectrum of BQ showed two strong peaks at 222
and 258 nm, and a less intense set of peaks centred at 359 nm, while the UV-Vis spectrum of PBQ was very similar to DPBQ (Figure 2.9). The absorption at the
maximum wavelength of PBQ is less intense and blue-shifted relative to those of
dPBQ but more intense and red-shifted with respect to BQ. This change in
absorption is consistent with the reduced delocalisation of the \pi electrons. This
shift to shorter wavelength from DPBQ to BQ was similar to the observations
made between 2,3-diphenylanthracene and anthracene.\textsuperscript{39}
2.2.2.1.2 Photochemical studies

**BQ** exhibits a much lower solubility than **DPBQ** in CH$_3$CN, which necessitated carrying out photochemical experiments at lower concentrations than had been used for the latter compound. Irradiation of a 1.40 mM non-deoxygenated solution of **BQ** in spectral grade CH$_3$CN for 150 min did not lead to the formation of a precipitate. However, $^1$H-NMR analysis of the concentrated reaction mixture showed a new peak at 4.41 ppm, which can be ascribed to a change of hybridisation of the central ring and new peaks in the aromatic region, demonstrating that **BQ** was reacting under UV-irradiation. Integration of the diagnostic peaks for **BQ** and the formed photoproduct at 8.77 and 4.85 ppm respectively, enabled us to determine that the photoproduct was formed in 41 %
yield, assuming that it was the dimer (Figure 2.10). MALDI-TOF MS showed two major peaks, the strongest at m/z = 180 corresponding to BQ and a second less intense peak at m/z = 391 associated with the M(di-BQ+K+). Simultaneous irradiation of a 1.39 mM non-deoxygenated solution of DPBQ in CH₃CN in the same conditions yielded 40 % of di-DPBQ. This suggested that addition of phenyl groups at the peripheral position did not appreciably influence the photoreactivity of benzo[2,3-g]quinoxaline derivatives. Unfortunately, the low solubility of BQ also made isolation of the photoproduct more difficult. In the case DPBQ, isolation of the photoadduct was achieved by decantation of the solution containing the soluble unreacted monomer from the insoluble product. The similar solubility of the monomer and product precluded this approach, and isolating a sufficient amount of the photoproduct to carry out characterisation could not be achieved.
Scheme 2.7: [4+4] photocycloaddition of BQ.

Figure 2.10: $^1$H-NMR spectra of BQ recorded in CDCl$_3$ before (top) and after 150 min of irradiation (bottom). New peaks associate with the photoadduct are emphasised with stars.

Unlike DPBQ, no white solid was observed after irradiation of a 1.39 mM non-deoxygenated solution of PBQ. The MALDI-TOF mass spectrum of the solution showed two peaks; the heaviest fragment at m/z = 551 associated to M(di-PBQ+K)$^+$ (R.I= 117) and a more intense peak at m/z = 258 corresponding
to $\text{M(PBQ)}^+$ (R.I= 346), which is in accordance with results obtained after irradiation of a solution of DPBQ under the same conditions. $^1$H-NMR analysis of the concentrated reaction mixture showed a new set of peaks in the aromatic region as well as two singlets at 5.1 and 5.09 ppm associated with the change a hybridisation on the central ring, which was consistent with the shifts observed for both DPBQ and BQ (Figure 2.11). The $^1$H-NMR spectrum also showed another new peak at 9.5 ppm, which was assigned as the protons at the 3 and 3' position of the dimer. Assuming that the product was the dimer, integration of the diagnostic resonances of the PBQ at 9.3 ppm and the photoproduct at 9.5 ppm enabled us to determine a yield of 45 % for the product. On the other hand, integration of the two singlets (at 8.69 and 8.65 ppm) associated with PBQ versus the two singlets at 5.1 and 5.09 ppm associated with di-PBQ suggests a 13 % yield. It is therefore likely that another photoreaction is occurring under those conditions leading to a second photoproduct. Unfortunately, neither recrystallisation from acetone nor flash column chromatography were successful at separating PBQ from the photoproduct. Hence, the structures of the photoproducts could not be confirmed by X-ray crystallography. However, both MALDI mass spectrum and $^1$H-NMR analysis suggest that the irradiation of a solution of PBQ in CH$_3$CN results in the formation of a di-PBQ. When irradiated in the same conditions, DPBQ and A yielded 40% and 44 % of dimer respectively but A also yielded 44 % of endoperoxide.
Figure 2.11: $^1$H-NMR spectra of PBQ recorded in CDCl$_3$ before (top) and after 150 min of irradiation (bottom) (stars emphasise new peaks).

As a result of the unsymmetrical substitution pattern, the two protons on the central ring of PBQ are not equivalent. This difference in electronic environment was confirmed by $^1$H-NMR analysis of PBQ, as two singlets were observed at 8.69 and 8.65 ppm. The formation of the bridgehead across the central rings of two molecules of PBQ would lead to two different kinds of sp$^3$ protons in the dimer. Thus, two doublets or two singlets would be expected between 6 and 5 ppm in $^1$H-NMR spectrum of hh-PBQ and ht-PBQ, respectively. As observed in the $^1$H-NMR spectrum of PBQ, the two protons are still in different environments with respect to each other but the lack of splitting suggest that the
photoadduct formed under these conditions is either \textit{ht-di-PBQ} or \textit{hh-di-PBQ}
with \(X = \text{Ph}\) and \(Y = \text{H}\) (Scheme 2.8).

\begin{center}
\begin{tikzpicture}
    \node (a) at (0,0) {\textbf{2}};
    \node (b) at (1,0) {\textbf{ht-PBQ}};
    \node (c) at (2,0) {\textbf{hh-PBQ}};
    \draw[->] (a) -- (b);
    \draw[->] (a) -- (c);
    \node (d) at (-1,0) {\textbf{Scheme 2.8: Possible isomers resulting from dimerisation of PBQ. (X=Ph, Y=H or X=H, Y=Ph).}};
\end{tikzpicture}
\end{center}

\textbf{2.2.2.2 Influence of 4-methoxyphenyl groups}

\textbf{2.2.2.2.1 Synthesis}

In order to use the photochromism of benzo[2,3-g]quinoxaline derivatives in practical applications such as optical data storage, such system should be incorporated in polymer matrices such as polystyrene and their reactivity in solid state should be investigated. In order to graft benzo[2,3-g]quinoxaline derivatives on polystyrene polymers 2,3-di(4-methoxyphenyl)benzo[2,3-g]quinoxaline (DMoPBQ) and 2-(4-methoxyphenyl)benzo[2,3-g]quinoxaline (MoPBQ) were synthesised as shown in Scheme 2.9 and Scheme 2.10, respectively. These methoxy groups have the advantage that they could act as synthetic “handles” for incorporating benzo[2,3-g]quinoxalines into polymers as well as allowing us to study the effect of functional groups, if any, on the photochemistry.
Scheme 2.9: Synthesis of DMoPBQ.

Like 2-phenylglyoxal, 2-(4-methoxyphenyl)glyoxal was synthesised by oxidation of 1-(4-methoxyphenyl)ethanone in a 48 % HBr solution. The resulting 2-(4-methoxyphenyl)glyoxal was then condensed with 2,3-diaminonaphthalene to form MoPBQ in 76 % yield.

Scheme 2.10: Synthesis of MoPBQ

As observed for DPBQ, PBQ and BQ, the extension of the π-conjugated system resulted in a shift of absorption towards longer wavelengths. The addition of methoxy groups on the phenyl substituent resulted in a shift of absorption from 381 to 396 nm for the disubstituted compound and from 379 to 384 nm for the monosubstituted derivatives (Figure 2.12 and Figure 2.9). This red-shift in the UV-Vis absorption is consistent with the addition of electron donating group on
benzene ring which results in a destabilisation of the HOMO and inducing a smaller HOMO-LUMO gap.\textsuperscript{63-65}

![Graph showing UV-Vis spectra of BQ, MoPBQ, and DMoPBQ](image)

**Figure 2.12**: Comparison of UV-Vis spectra of BQ, MoPBQ and DMoPBQ recorded at room temperature in CH\textsubscript{3}CN

### 2.2.2.2 Photochemical Studies:

Similarly to PBQ and BQ, after irradiation of a 1.33 mM non-deoxygenated solution of DMoPBQ in CH\textsubscript{3}CN in the Rayonet® photoreactor for 150 min, no precipitate was observed. However, unlike the derivatives presented earlier in this chapter, MALDI- TOF MS did not show a peak related to di-DMoPBQ, which suggested that irradiation of DMoPBQ did not lead to any dimer. \textsuperscript{1}H-NMR characterisation of the concentrated reaction mixture showed peaks corresponding to the starting material as well as a new set of peaks in the
aromatic region similar to the di-DPBQ and a new peak at 5.45 ppm (Figure 2.13). The presence of this new peak in the diagnostic region for bridgehead protons suggested that DMoPBQ was undergoing a photochemical reaction involving a change of hybrisation at the central ring. Assuming the photoproduct is the dimer, integration of the peak at 5.45 ppm versus the singlet at 8.27 ppm suggested a 10 % yield. However, the formation of a dimer could not be confirmed by MALDI-TOF MS. Moreover, attempts to separate the photoproduct from DMoPBQ via flash column chromatography were not successful; thus, further characterisation of the photoproduct using X-ray crystallography could not be achieved. It is therefore not possible at this time to confirm that DMoPBQ undergoes dimerisation when irradiated under the same condition as DPBQ, PBQ, BQ and A. However, efforts towards characterisation of the photoproduct should be pursued.
Figure 2.13: $^1$H-NMR of DMoPBQ recorded in CDCl$_3$; (top), after 150min of irradiation (bottom). New peaks associated with the photoproduct are emphasised with stars, while the unidentified impurities present in traces prior to irradiation are emphasised by triangles.

Similarly to DMoPBQ, no precipitate was observed after irradiation of a 1.36 mM non-deoxygenated solution of MoPBQ. MALDI-TOF MS of the solution only showed the (MoPBQ)$^+$ and no (di-MoPBQ)$^+$ ion peak, which was consistent with the results obtained with the disubstituted analogue. $^1$H-NMR characterisation of the concentrated reaction mixture showed peaks corresponding to the starting material as well as a new set of peaks in the aromatic region similar to that of di-PBQ. Two small singlets at 5.44 and 5.42 ppm within the diagnostic region for the bridge-head of photoproduct formed
suggest that MoPBQ undergoes a photoreaction that involves a change of hybridisation at the central ring of the benzo[2,3-g]quinoxaline moiety. For the unsymmetrical MoPBQ, similarly to PBQ, another new singlet at 9.4 ppm associated with the proton on the 3 position of the benzo[2,3-g]quinoxaline core of the photoproduct is observed (Figure 2.14). This new singlet at 9.4 ppm can therefore be used as the diagnostic peak to determine that the product was formed in 37% yield, assuming that it was the dimer. However, integration of the singlets in the diagnostic region for bridgehead protons suggests that the photoproduct was only formed in 8% yield. The lack of consistency between the singlet a 9.4 ppm and the singlets at 5.44 and 5.42 ppm implies that there were more than one photoproduct formed when MoPBQ was irradiated. Unfortunately, attempts to separate with photoproduct from MoPBQ by recrystallisation were not successful. Thus, the photoadduct could not be identified by X-ray crystallography. Other purification methods should be investigated in order to obtain the pure photoproduct and confirm that irradiation of a MoPBQ solution in CH$_3$CN results in di-MoPBQ. However, neither MALDITOF nor $^1$H-NMR spectroscopy are sufficient to confirm that dimerisation is occurring in a similar fashion to DPBQ.

Unlike DPBQ, DMoPBQ only has limited absorption around 350 nm. Hence, the lack of reactivity of DMoPBQ could be rationalised by the use of the inappropriate energy to excite the molecule. Therefore, the effect of irradiation with a light source centred at longer wavelength should be investigated. As demonstrated with DPBQ, the use of a filter was necessary to prevent the
photodissociation of di-DPBQ in solution during the irradiation experiments. The addition of methoxy groups results in red-shift in absorption in the monomeric unit from DMoPBQ to DPBQ and from MoPBQ to PBQ, such shift should also be reflected in their respective dimers. Therefore, it is possible that both DMoPBQ and MoPBQ form dimers that absorb light around 350 nm, leading to their photodissociation in solution. Considering that DMoPBQ and MoPBQ did not behave as ideally as DPBQ, and due time to constraints, their photochemistry was not studied as thoroughly as the latter. Nonetheless, further studies should be carried out to understand the influence of methoxyphenyl groups on the photochemistry of benzo[2,3-g]quinoxaline.

![Figure 2.14: 1H-NMR spectrum of MoPBQ recorded in CDCl3 before (top) and after 150 min of irradiation (bottom). New peaks are emphasised with stars.](image)
2.2.3 2,3-Di(pyridin-2-yl)benzo[2,3-g]quinoxaline

2,3-Di(pyrid-2-yl)benzo[2,3-g]quinoxaline was synthesised in order to investigate the influence of heteroatoms on the photochemical properties of a benzo[2,3-g]quinoxaline. As shown in Scheme 2.11, 1,2-dipyridylethanedione was synthesised by oxidation of the product of the benzoin condensation of picolinaldehyde. The dione was then condensed with 2,3-diaminonaphthalene to yield 2,3-di(pyrid-2-yl)benzo[2,3-g]quinoxaline (DPyBQ) in 73 % yield.
In order to investigate whether **DPyBQ** would undergo [4+4] photocycloaddition in a similar manner to anthracene and **DPBQ**, a solution of **DPyBQ** was prepared...
1.33 mM of \textbf{DPyBQ} in CH$_3$CN was irradiated in the Rayonet\textsuperscript{®} photoreactor for 2.5 h. Similarly to \textbf{DPBQ}, MALDI TOF MS of the solution showed the m/z 668 (R.I= 461) corresponding to the M(di-DPyBQ)$^+$, and a more intense peak a m/z = 336 (R.I= 665) corresponding to M(DPyBQ+2)$^d$. $^1$H-NMR analysis of the evaporated reaction mixture showed a new set of peaks in the aromatic region and accompanied by a singlet at 5.15 ppm associated with the formation of the bridgehead protons across the central ring of two benzo[2,3-g]quinoxaline moieties (Figure 2.16). The $^1$H-NMR analysis combined with the MALDI-TOF mass spectrum confirmed that irradiation of solution of \textbf{DPyBQ} in CH$_3$CN was undergoing [4+4] photocycloaddition in a similar manner to that of anthracene. The photoadduct formed could be separated from \textbf{DPyBQ} on slow evaporation of CH$_3$CN.

\textsuperscript{d} The uncertainty may result from a calibration error
Figure 2.16: $^1$H-NMR spectrum of DPyBQ recorded in CDCl$_3$ before (top) and white solid isolated after 150 min of irradiation (bottom).

2.3 Conclusion

We demonstrated that benzo[2,3-g]quinoxaline derivatives with phenyl and pyridyl substituent on the 2- and 3- positions, which are more synthetically accessible than their anthracene equivalents, can undergo dimerisation when irradiated in the Rayonet® photochemical reactor. X-ray diffraction studies enabled us to determine that irradiation of a solution of DPBQ results in the [4+4] photocycloaddition across the central ring of two benzo[2,3-g]quinoxaline derivatives to yield the ht-dimer. MALDI-TOF MS suggested that PBQ and BQ also formed dimers upon irradiation however, their structures could not be fully
characterised as a result of the limited solubility of the starting materials, which complicated their separation from their photoproducts. MALDI-TOF MS of MoPBQ and DMoPBQ, on the other hand, did not show the presence of any dimer but $^1$H-NMR spectroscopy showed that both produced a photoproduct upon irradiation that could not be isolated or fully characterised. The absence of dimer after irradiation could be due the failure to excite the chromophore as both MoPBQ and DMoPBQ absorb at longer wavelengths than the other benzo[2,3-g]quinoxaline derivatives studied. The red-shift in absorption could also be observed in the dimer. This would lead to photodissociation during the irradiation experiments. When irradiated under the same conditions (without prior deoxygenation), anthracene forms dianthracene in similar yields, but 44 % of endoperoxide is also formed. Moreover, their facile synthesis enables the electronic properties of 2,3-benzo[2,3-g]quinoxaline to be tuned by variation of the substituents. Other derivatives should be synthesised and their photochemical properties should also be investigated. Such systematic studies will deepen the understanding of the influence of substitution on the photochemistry of benzo[2,3-g]quinoxalines and enable the rational design of a new sub-class of photochromic system based on this type of [4+4] cycloaddition reaction.
CHAPTER 3: TOWARDS STIMULI-RESPONSIVE PHOTOCHROMISM

3.1 Introduction:

The presence of the pyridine substituents on the benzo[2,3-g]quinoxaline, enables DPyBQ to coordinate to metals to form transition metal complexes. The potential ability to modify the efficiency of the photodimerisation of DPyBQ by the addition a transition metal species could lead to the development of a new class of hybrid photochromic systems. Even though some of the binding properties of DPyBQ has been previously reported, the influence of chemical species on its photochemical properties has not been investigated. In order to develop a photochromic system whose reactivity could be tuned by the presence of other chemical species, we investigated the influence of a variety of cations on the photophysical properties and efficiency of the dimerisation of DPyBQ.

3.2 Result and Discussion:

An excited molecule can relax to its ground state through different paths (e.g. fluorescence) or undergo chemical reactions (e.g. dimerisation). Prior to investigating the influence of cations on the photodimerisation of DPyBQ, we observed their influence on the luminescence of a stock solution of DPyBQ in CH$_3$CN. After qualitative investigation of the effect of different cations on the luminescence of a solution of DPyBQ in CH$_3$CN, it was concluded that Zn$^{2+}$
affected the optical properties of DPyBQ most dramatically as the luminescence was visibly increased (Figure 1.1).

![Image of luminescence experiments](image)

**Figure 3.1**: Influence of chemicals on the luminescence of a solution of DPyBQ in CH$_3$CN (3.02 x 10$^{-4}$ M). Samples viewed under UV light.

### 3.2.1 Influence on optical properties

In order to better understand the interaction between DPyBQ and Zn$^{2+}$, the variation in luminescence with increasing amount of Zn$^{2+}$ was investigated. A series of solutions was prepared by mixing aliquots of equimolar solutions of DPyBQ and ZnCl$_2$ in CH$_3$CN to maintain a total molarity [Zn$^{2+}$]+[DPyBQ] constant while varying [Zn$^{2+}$]/[DPyBQ]. This was achieved by mixing a volume $x$ of a 0.1 mM solution of DPyBQ in CH$_3$CN with a volume (1-$x$) of a 0.1 mM solution of ZnCl$_2$ in CH$_3$CN. The UV-Vis absorption spectra of this series were recorded. As shown in Figure 3.2, increasing the ratio of Zn$^{2+}$ resulted in a
decrease of absorption intensity, which is expected due to the dilution of DPyBQ. This reduction in absorption is also accompanied by a shift towards longer wavelengths that is consistent with enhanced conjugation of DPyBQ as a complex is formed with Zn$^{2+}$. Figure 3.3 shows the variation at the maximum absorption wavelength $\lambda = 380$ nm with molar ratio. This continuous addition method, also known as Job's method, enables us to determine that the complex formed in solution was the major absorbing specie when the concentration of Zn$^{2+}$ represent 50% of the total molarity of Zn$^{2+}$ + DPyBQ.\textsuperscript{72}
Figure 3.2: Absorption spectra of a solution of 0.1 mM \([\text{DPyBQ}] + [\text{ZnCl}_2]\) with varying \([\text{Zn}^{2+}] / [\text{DPyBQ}]\) in \(\text{CH}_3\text{CN}\) measured at room temperature.
Figure 3.3: Job's plot obtained from the change of absorption intensity at 380 nm of a solution of DPyBQ and ZnCl$_2$ measured at room temperature.

In order to study the influence of ZnCl$_2$ on the luminescence of a 0.1 mM solution of DPyBQ, a series of solutions containing ZnCl$_2$ and DPyBQ were prepared such that [Zn$^{2+}$/[DPyBQ] varies but [Zn$^{2+}$]+[DPyBQ] stays constant and their luminescence was measured.$^7_2$ Similarly to the UV-Vis absorption, the fluorescence intensity decreased with increasing molar ratio of Zn$^{2+}$ (Figure 3.4). As shown in Figure 3.5, the change in luminescence enabled us to determine that under these conditions, the major complex is formed when ZnCl$_2$ and DPyBQ are present in equal ratio in solution, which is consistent with the absorption data.
Figure 3.4: Emission spectra of a series of solutions made of 0.1 μM solution of DPyBQ and ZnCl₂ in CH₃CN excited at 380 nm with varying molar ratio of ZnCl₂ such that [DPyBQ] + [Zn²⁺] = 0.1 μM but [Zn²⁺]/[DPyBQ] varies measured at room-temperature.
In order to confirm the data obtained above, the addition of a small volume of a 0.2 mM solution of ZnCl₂ in CH₃CN to a constant volume (3.00 mL) of a 0.1 mM solution of DPyBQ in CH₃CN was monitored by UV-Vis spectroscopy. As shown in Figure 3.6, addition of ZnCl₂ resulted in an increase in absorption at 295 nm. However, after addition of 225 µL of ZnCl₂ solution, further addition of ZnCl₂ solution resulted in a reduction of absorption at 295 nm. Figure 3.7 shows that the maximum change of absorption was reached at an equimolar ratio of ZnCl₂ to DPyBQ. Thus, we concluded that the complex formed between Zn and DPyBQ was ZnCl₂(DPyBQ). Attempts to further characterise the structure of the complex were not successful. Indeed, the isolated precipitate formed if a large

![Figure 3.5: Job's plot obtained from change of luminescence intensity at 486 nm of a 0.1 µM of DPyBQ in CH₃CN with addition of ZnCl₂ measured at room temperature.](image)
amount of Zn$^{2+}$ is added to a solution of DPyBQ did not crystallise. Hence, the structure could not be confirmed by X-ray crystallography. Figure 3.7 also shows that a change in absorption of less than 5 % was observed with a molar ratio of 10 part DPyBQ to 1 part ZnCl$_2$. Thus, this system would not likely be useful in sensor applications.

The change in luminescence of a constant volume of DPyBQ solution in CH$_3$CN (1 x 10$^{-6}$ M) with addition of a small volume of ZnCl$_2$ solution (1 x 10$^{-5}$ M) in CH$_3$CN can be seen in Figure 3.8. In agreement with the UV-Vis absorption, the luminescence increases upon the addition of ZnCl$_2$ to a solution of DPyBQ, presumably due to an increase of rigidity in the ZnCl$_2$(DPyBQ) complex (Figure 3.8). After addition of 1 equivalent of ZnCl$_2$ for 1 DPyBQ, the fluorescence increased to such an extent that the upper limit of the detector was reached, thus the formula of the complex formed in these conditions could not be extrapolated using the Job's plot. The small change of fluorescence intensity observed at low molar ratio of Zn$^{2+}$ was consistent with the UV-Vis data discussed above and confirmed that such a system would not be optimal for sensing applications.
Figure 3.6: Influence of ZnCl₂ on the absorption of a 1.07 x 10⁻³ M solution of DPyBQ in CH₃CN measured at room-temperature.

Figure 3.7: Job’s plot of change of absorbance at 295 nm with molar fraction of Zn²⁺ added to a constant volume of DPyBQ solution (1 x 10⁻⁴ M).
In order to study the influence of the counter-ion on the fluorescence of a solution DPyBQ, a series of solutions were prepared by mixing equimolar solutions of Zn(OAc)$_2$ and DPyBQ in CH$_3$CN such that [Zn(OAc)$_2$]/[DPyBQ] varies but [Zn(OAc)$_2$]+[DPyBQ] = 0.1 mM. As shown in Figure 3.9, a decrease in absorbance is observed with increasing ratio of Zn(OAc)$_2$ which is consistent with the dilution of DPyBQ. As was the case for ZnCl$_2$, a shift to longer wavelengths in the UV-Vis spectrum with increasing concentration of Zn(OAc)$_2$ was observed, perhaps as a result of the increased conjugation of DPyBQ induced by the formation of a complex. Figure 3.10 shows that the absorption at 379 nm decreases with increasing molar ratio of Zn(OAc)$_2$ and enables us to determine that the major complex formed under those experimental conditions is present when Zn(OAc)$_2$ and DPyBQ in equimolar amount in solution. Attempts to isolate
the complex formed in solution were not successful. Indeed, attempts to crystallize the formed complexes by slow diffusion in order to further understand the coordination of DPyBQ to Zn$^{2+}$ were not successful. Hence, the structure of the complex cannot be confirmed to be Zn(DPyBQ)(OAc)$_2$. However, this experiment did not show that the counter-ion had a specific influence on the complex formed in solution.

In order to confirm the results obtained from the continuous addition method, a small volume of Zn(OAc)$_2$ solution in CH$_3$CN (1x10$^{-6}$ M) was added to a constant volume of DPyBQ in CH$_3$CN (1x10$^{-7}$ M). As shown in Figure 3.11, addition of Zn(OAc)$_2$ resulted in an increase in fluorescence, accompanied by a shift to longer wavelength, which is again consistent with the formation of a complex with increased planarity.
Figure 3.9: Absorption spectra of a solution of 0.1 mM $[\text{DPyBQ}] + [\text{Zn(OAc)}_2]$ with varying $[\text{Zn}^{2+}]/[\text{DPyBQ}]$ in CH$_3$CN measured at room temperature.

Figure 3.10: Job’s plot obtained from the change of absorbance at 380 nm of a 0.1 mM solution of DPyBQ in CH$_3$CN measured at room-temperature.
Figure 3.11: Change of luminescence of a constant volume of DPyBQ solution in CH$_3$CN with addition of a solution of Zn(OAc)$_2$ in CH$_3$CN, recorded at room-temperature.

3.2.2 Photochemical studies

The titration studies of a solution of DPyBQ in CH$_3$CN with zinc in the presence of different counter-ions discussed above showed that both ZnCl$_2$ and Zn(OAc)$_2$ resulted in an increase in the fluorescence. A series of solutions containing different molar ration of Zn$^{2+}$ to DPyBQ was prepared by mixing 0.1 M solutions DPyBQ and Zn$^{2+}$ in CH$_3$CN such that [Zn$^{2+}$]/[DPyBQ] varies but ([Zn$^{2+}$]+[DPyBQ]) stays constant (0.1 mM) was irradiated in the Rayonet® photochemical reactor for 150 min. As shown in Figure 3.12 and Figure 3.13, UV irradiation resulted in a decrease in absorption at 280 and 380 nm for both series. This decrease in absorption can be ascribed to the dimerisation of DPyBQ in solution.
Figure 3.12: UV-Vis absorption spectra a solution of DPyBQ and ZnCl$_2$ in CH$_3$CN containing 0.37 molar ratio of ZnCl$_2$ before (full line) and after (dashed line) irradiation, measured at room-temperature.

Assuming that no other species absorbs at 380 nm, the efficiency of dimerisation can be calculated by comparison of the absorbances of the
solutions of **DPyBQ** before and after irradiation. The percent conversion of **DPyBQ** for both ZnCl₂ and Zn(OAc)₂ series discussed earlier, were calculated by dividing of absorbance of the solution by the initial absorbance at 380 nm. As shown in Figure 3.14, irradiation of a solution of **DPyBQ** in CH₃CN at initial concentrations [**DPyBQ**]ᵢ ranging from 0.05 mM to 0.1 mM yielded 55-70 % of dimer. However, when irradiated in the same conditions in presence of 10-50 mol% of Zn²⁺, dimerisation efficiency was reduced to 40-55% for Zn(OAc)₂ and 50-55 % for ZnCl₂. No significant difference was observed between Zn(OAc)₂ and ZnCl₂ over the studied range of concentrations, suggesting that the counter ion does not appreciably influence the photochemistry of **DPyBQ** in presence of Zn²⁺. Figure 3.14 also shows that the difference in conversion stays almost constant between each series. This suggests that the increasing molar ratio of Zn²⁺ does not influence the dimerisation efficiency of **DPyBQ**, nor does the change in concentration of **DPyBQ** alter the results appreciably over this concentration range. However, the luminescence studies discussed above revealed that the addition Zn²⁺ to a solution of **DPyBQ** resulted in an increase in luminescence (Figure 3.8). In the dimerisation process, one molecule of **DPyBQ** in its ground state acts as a quencher to another molecule of **DPyBQ** in its excited state. However, when Zn²⁺ acts as a competing quencher for the excited state, a concentration increase in Zn²⁺ would be expected to reduce the dimerisation efficiency as the efficiency of dimerisation is dependent on the efficiency of the other photochemical events occurring in solution (Chapter 1:). Irradiation studies in different conditions such as keeping a constant
concentration of one of the components or working with more concentrated solutions should be undertaken in order to better understand the influence of Zn\(^{2+}\) on the dimerisation of DPyBQ. It is also important to replicate these experiments to establish the experimental error.

As shown in Figure 3.1, the addition of HCl resulted in the quenching of the fluorescence of a solution of DPyBQ. Thus, HCl was chosen in order to study the influence of acid on the dimerisation of DPyBQ. After 150 min of irradiation, a solution of DPyBQ in CH\(_3\)CN (0.81 mM) containing 10 mol% of HCl yielded 12 % of di-DPyBQ. Irradiation under the same conditions of a control solution of DPyBQ in CH\(_3\)CN (0.81 mM) yielded 20 % of di-DPyBQ. Thus, it was
concluded that the presence of a small amount of HCl during the irradiation of a DPyBQ solution did not result in a significant decrease in the amount of di-DPyBQ formed. Other chemical stimuli should be investigated in order to better understand the factors affecting the dimerisation of DPyBQ.

3.3 Conclusion:

In an attempt to develop a stimuli-responsive photochromic system based on the [4+4] photocycloaddition reaction, we investigated the influence of ZnCl₂ and Zn(OAc)₂ on the optical properties of DPyBQ, which was shown to undergo dimerisation upon irradiation. Addition of Zn²⁺ ion to a solution of DPyBQ results in a red shift in the UV-Vis absorption as well as an increase of absorbance at 290 nm, which is ascribed to the formation of a complex. Job’s method enabled us to determine that a complexes of Zn:DPyBQ were formed when both species are in equal concentration in solution.

In order to assess the influence of Zn²⁺ on its photochemical properties, a solution of DPyBQ was irradiated in the presence of different molar ratios of Zn²⁺. These preliminary studies revealed that the dimerisation of DPyBQ was slightly reduced by the presence of ZnCl₂ and Zn(OAc)₂ when present in 10-50 mol% in solution, however the nature of the counter ion did not appear to affect the yield of dimerisation. The results discussed earlier demonstrate that addition of Zn²⁺ did not result in complete suppression of the dimerisation of DPyBQ.

In order to gain a better understanding of the quenching mechanism of Zn²⁺ taking place during the dimerisation of DPyBQ, the complex formed in solution
should be isolated and its photochemical and photophysical properties investigated. To that same purpose, the photochemical properties of solutions of DPyBQ containing 51-99% of Zn$^{2+}$ should also be investigated. Working to the limit of solubility of complex should clarify whether the quenching in caused by the sole presence of the complex having competing photochemistry or if the reduced efficiency of dimerisation is only caused by the decreased amount of DPyBQ present in solution as the complex crashes out of solution.
CHAPTER 4: SELECTIVE FORMATION OF PHOTOADDUCT

4.1 Introduction:

Recently, the Williams' group reported a method for enforcing the selectivity of [4+4] photocycloadditions through careful control of steric interactions. 9,10-Dimethylanthracene (DMA) is known to not form a stable photodimer due to high steric hindrance across the newly formed sigma bond in the dimer. Similarly, 2,3,6,7-tetraphenylanthracene (TPA) does not readily form its photodimer due to the steric bulk associated with the phenyl groups. However, when DMA and TPA were irradiated together in solution with 350 nm lamps, a cross-photoadduct DMA-TPA was produced as the exclusive product, as shown in Equation 4.1. Stimulated by this selective photoadduct formation, the photochromic properties of tetraphenylpyrazo[2,3-\(g\)]quinoxaline (TPPQ) as a heterocyclic equivalent to TPA were initiated (Figure 4.1).
Equation 4.1: Photocycloaddition of 9,10-dimethylanthracene and 2,3,6,7-tetraphenylanthracene.

Modelling of the HOMO and LUMO of pyrazo[2,3-g]quinoxaline (PQ) were carried out at the AM1 level and were found to be qualitatively similar to those of anthracene (Figure 4.2). Thus it was anticipated that pyrazo[2,3-g]quinoxaline would undergo \([4+4]\) cycloaddition across the central ring when irradiated with UV light.
Like the benzo[2,3-\textit{g}]quinoxaline derivatives discussed in Chapter 2, tetra-substituted pyrazo[2,3-\textit{g}]quinoxalines were more synthetically accessible than their peripherally functionalized anthracene counter-parts. In this chapter, our attempts to demonstrate that \textbf{TPPQ} undergoes $[4+4]$ photocycloaddition with anthracene compounds substituted at the 9- and 10-positions will be described.
4.2 Results and Discussion:

In order to test the photoreactivity of the pyrazo[2,3-g]quinoxaline core, PQ was synthesized following a literature procedure.\textsuperscript{74} Similarly to BQ, PQ could not be purified to the same extent as the substituted quinoxaline derivatives and the final product was a dark brown solid instead of the yellow product reported in the literature.\textsuperscript{74} Unfortunately, the exceedingly low solubility of PQ rendered the investigation of its photochromic properties impractical.

![Structural similarities between anthracene (A), benzo[2,3-g]quinoxaline (BQ) and pyrazo[2,3-g]quinoxaline (PQ).](image)

**Figure 4.3**: Structural similarities between anthracene (A), benzo[2,3-g]quinoxaline (BQ) and pyrazo[2,3-g]quinoxaline (PQ).

TPPQ was synthesized in one step by condensation of benzil with tetraaminobenzene tetrahydrochloride salt (Equation 4.2) in 84 \% yield.\textsuperscript{75} The UV-Vis absorption spectra in CH\textsubscript{3}CN revealed a strong absorption at 264 nm and a set of less intense peaks with a maxima at 406 nm (Figure 4.4).
Equation 4.2: Synthesis of TPPQ.

\[
\text{H}_2\text{N} \begin{array}{c} \text{NH}_2 \\ \text{H}_2\text{N} \end{array}.4\text{HCl} + \begin{array}{c} \text{Ph} \\ \text{NH} \end{array}\text{O} \rightarrow \begin{array}{c} \text{Ph} \\ \text{NH} \end{array}
\text{NaOAc, EtOH} \rightarrow \begin{array}{c} \text{Ph} \\ \text{NH} \end{array}
\text{TPPQ 84%}
\]

Figure 4.4: UV-Vis absorption spectra of TPPQ and TPA.

4.2.1 \([4+4]\) Photocycloaddition

A 1.96 mM solution TPPQ in CH\(_3\)CN was irradiated in the Rayonet® photochemical reactor fitted with 350 nm lamps. After 2.5 h of irradiation, no photoproducts were observed. This lack of reactivity could be caused by the low
concentration that was necessitated by the low solubility of TPPQ in CH₃CN. This compound was much more soluble in benzene; hence irradiation of a 3.82 mM benzene solution was also examined. After 2.5 h of irradiation, no photoadduct was isolated suggesting that the reactivity of TPPQ was similar to that of TPA. In order to verify that the apparent lack of reactivity was not caused by cycloreversion of the dimer, a 0.1 mM solution of TPPQ in CH₃CN was irradiated in the Rayonet® photochemical reactor fitted with 419 nm lamps. After 2.5 h of irradiation, no photoadduct was observed by ¹H-NMR spectroscopy. The absence of photoadduct suggested that the enhanced steric bulk present at the peripheral positions inhibits the formation of photodimer (Equation 4.3). Thus, TPPQ could potentially be used to form cross-dimer in a similar manner as TPA, when irradiated in the presence of anthracene or DMA.

\[
\text{TPPQ} \quad \xrightarrow{\text{hv}} \quad \text{di-TPPQ}
\]

**Equation 4.3:** Result of UV exposure of TPPQ.

In order to improve the solubility of TPPQ, 2,3,7,8-tetrakis(3,4-bis(hexyloxy)phenyl)-pyrazo[2,3-g]quinoxaline (THPQ) (Figure 4.5) was synthesised by condensation of 1,2,4,5-tetraminobenzene tetrahydrochloride and 3,3',4,4'-tetrahexyloxybenzil. However, the solubility of THPQ in CH₃CN was not
improved compared to TPPQ. After a 1.34 x 10^{-4} M solution of THPQ was irradiated in the Rayonet® photochemical reactor for 170 min, no photoadduct was observed by ¹H-NMR spectroscopy. While this compound does not appear to undergo [4+4] photocycloaddition, THPQ was found to be liquid crystalline. DSC analysis showed that THPQ was liquid crystalline between 90 and 109 °C (see appendix 2). Polarised optical microscopy indicated that this liquid crystalline phase was columnar hexagonal (colₜ) phase. X-Ray crystallography data confirmed the hexagonal packing during slow cooling of THPQ from its isotropic liquid state. The relative accessibility of this new mesogenic compound combined with high fluorescence makes tetradialkoxyphenylpyrazo[2,3-g]quinoxaline derivatives potentially attractive for electroluminescent devices applications.⁷⁶
4.2.1.2 Cross [4+4] photocycloaddition

To investigate whether TPPQ could react like TPA, a 0.1 mM of TPPQ (5.00 mL) and a 0.1 mM solution of anthracene (A) (5.00 mL) in CH$_3$CN were mixed and irradiated in the Rayonet® photochemical reactor with 350 nm lamps for 2.5 h without prior deoxygenation. MALDI-TOF mass spectrum showed peaks at m/z=177, 489 and a less intense peak at m/z=664 corresponding to M(A)$^+$, M(TPPQ+3)$^+$ and M(A-TPPQ)$^+$, respectively. The last peak suggested that UV-irradiation of a concentrated solution containing equimolar amounts of TPPQ and A yielded and TPPQ-A cross-dimer. $^1$H-NMR analysis of the concentrated solution revealed peaks associated with TPPQ but only traces of A. Another set of peaks composed of two peaks in the aromatic region at 8.3 and 7.8 ppm and a singlet at 4.1 ppm, were ascribed to the formation of anthracene.

---

$^e$ Improper calibration of the MALDI instrument lead to a margin of error the ion peaks observed.
endoperoxide. A singlet at 4.55 ppm along with two peaks at 6.86 and 6.70 ppm suggested that di-A was also present in solution. When a 0.05 mM solution of A (10.00 mL) was irradiated simultaneously, endoperoxide was also produced quantitatively. This suggests that deoxygenating will be necessary for future photochemical studies of a mixture of TPPQ and A at millimolar concentration. 

$^1$H-NMR analysis of the concentrated solution also showed two doublets in a 1:1 ratio at 3.75 and 3.20 ppm suggesting that a fifth species present after irradiation possesses two adjacent sp$^3$ carbons in different environments which is consistent with the bridgehead protons of TPPQ-A (Equation 4.4). As seen in Figure 4.6, this third photoproduct is only present in minute amounts, thus attempts to assign the remaining peaks in the aromatic region were not successful. As encountered in earlier chapter, the lack of solubility of the starting material prevented separation of the photoproduct from the starting materials through crystallisation or column chromatography. Although MALDI-TOF MS suggested that TPPQ and A formed TPPQ-A upon irradiation, $^1$H-NMR spectroscopy did not provide enough evidence to confirm that this photoadduct results from the [4+4] photocycloaddition across the central rings of both TPPQ and A. Irradiation of larger volumes of more concentrated solution of TPPQ and A should be carried out in order to separate sufficient amounts of the photoadduct and determine its structure.
Equation 4.4: Cross-dimer formation resulting from irradiation of a mixture of TPPQ and A.

Figure 4.6: $^1$H-NMR of a mixture of 0.2 mM solutions of TPPQ and A (5.0 +5.0 mL) in CH$_3$CN after 150 min of irradiation, dried in vacuo and recorded in CDCl$_3$. TPPQ (diamond), AO$_2$ (five-point star), di-A (triangle), new photoproduct (four-point star), unknown impurity (*)

To demonstrate that TPPQ could form a heterodimer with DMA in a similar manner to TPA$^{52}$, a 0.1 mM solution of TPPQ in CH$_3$CN (5.00 mL) was mixed
with a 0.1 mM solution of DMA in CH₃CN (5.00 mL) and irradiated for 2.5 h in the Rayonet® photochemical reactor. MALDI-TOF MS showed peaks at m/z = 206 and 489 associated with DMA and TPPQ respectively, and a peak at m/z= 698 which corresponds to the TPPQ-DMA cross-cyclomer (Equation 4.5). ¹H-NMR spectroscopy revealed that the major species present in solution was unreacted TPPQ. The ¹H-NMR spectrum also showed a set of peaks composed of a singlet at 2.95 ppm and two peaks at 8.30 and 7.80 ppm corresponding to DMA. Other peaks were also present in the ¹H-NMR spectra, but due to the high signal-to-noise ratio the structure could not be further characterised (Figure 4.7). Once again, the low solubility of TPPQ limited the characterisation of the photoproduct formed upon irradiation however trace amounts a third compound were present. When 0.05 mM solutions of TPPQ and DMA where irradiated under the same conditions, no photoadduct was observed for either sample. Thus, the unknown photoadduct was associated with the photoreaction of TPPQ with DMA. The lack of characteristic peak in the diagnostic bridgehead region suggests that another kind of photoreaction is occurring under these experimental conditions. Similar to the previous experiment, the low solubility of TPPQ represents the main limitation to the characterisation of the photoproduct; hence, the use of more concentrated solution or larger volumes for irradiation should be attempted to form larger amounts of the product.
Equation 4.5: Cross-dimer formed from irradiation of a mixture of DMA and TPPQ.

Figure 4.7: $^1$H-NMR of a mixture of 0.2 mM solutions of TPPQ and DMA (5.0 +5.0 mL) in CH$_3$CN after 150 min of irradiation, concentrated in vacuo and recorded in CDCl$_3$. TPPQ (diamond), DMA (five-point star), new photoproduct (four-point star).
4.3 Conclusion

Similar to its anthracene analogue TPA, TPPQ did not yield any photoproduct when irradiated by itself. This suggested that the steric bulk at the peripheral positions prevented its dimerisation although at this point, we cannot rule out its lack of reactivity on electronic grounds as we still have not measured the lifetime of its excited state. Motivated to develop a selective photochromic system based on the control of steric interactions, TPPQ was irradiated in the presence of A and DMA. TPPQ was shown to undergo a photoreaction upon irradiation when equimolar amounts of A were present in solutions. However, the low solubility of TPPQ limited us to work at low concentrations, which in turn impeded the isolation and characterisation of the photoproduct.
CHAPTER 5: EFFORTS TOWARDS PHOTORESPONSIVE MATERIALS CONTAINING BENZO[2,3-\textit{g}]QUINOXALINES

5.1 Benzo[2,3-\textit{g}]quinoxaline-functionalised polymer

5.1.1 Introduction

The readily accessible benzo[2,3-\textit{g}]quinoxaline derivatives discussed in Chapter 2 were shown to have similar photochromic properties to their anthracene analogues. However, the absorption spectra for these systems were red-shifted, which could be advantageous when used in a polystyrene matrix. Indeed one of the reasons preventing anthracene functionalized polystyrene-based materials from being used in practical applications is the poor efficiency of the backward reaction (photodissociation); in fact, the polystyrene backbone and the incorporated dianthracene both absorb at similar wavelength (light under 300 nm) rendering the photodissociation inefficient.

Our approach was to graft benzo[2,3-\textit{g}]quinoxaline derivatives on a polystyrene backbone and compare the photochromic properties of this photoactive polymer with an anthracene analogue.
5.1.2 Result and Discussion

The benzo[2,3-g]quinoxaline moiety potentially can be grafted onto a polystyrene backbone by nucleophilic substitution on the benzylic position. To that purpose two polymers with different 4-chloromethylstyrene content were synthesised.

Our attempts to chloromethylate a commercially available polystyrene (PS) of known chain length and polydispersity using monochloromethyl ether were unsuccessful.77,78 Thus, a polydisperse polymer was synthesised via free radical polymerisation of styrene and 4-chloromethystyrene (Equation 5.1).79,80 After 18 h at 100 °C, a white solid was formed in the reaction vessel. 1H-NMR spectroscopy of this product (PS1) revealed a peak at 4.5 ppm which was associated with the benzylic position of the vinylbenzyl chloride unit of the polymer. Integration of this diagnostic peak with respect to the proton at the 4-position of the styrene repeat unit enabled us to determine a ratio of one chloromethylstyrene unit per two styrene units. GPC analysis determined an average molecular weight of 38 kDa and a polydispersity of 1.69. The high chloromethyl content would then lead to high level of cross-linking. In order to obtain a polymer with lower chloromethylstyrene content and the temperature of polymerisation was decreased to 70 °C and AIBN was added as a radical initiator. These experimental conditions yielded a copolymer PS2 composed of one unit of chloromethyl styrene per fifty unit styrene, with an average molecular weight of 71 kDa with a polydispersity of 1.74.
Equation 5.1: Synthesis of poly(styrene-co-4-vinylbenzyl chloride) by free-radical polymerization.

In order to functionalise the PS2 with a benzo[2,3-g]quinoxaline, 4-(benzo[2,3-g]quinoxalinyl)phenol (BQP) was synthesised by demethylation of MoPBQ with 48 % HBr solution. Polymer PS2 of known chain length and broad polydispersity was then grafted with BQP in the presence of a base (Scheme 5.1). The obtained polymer was however very insoluble and tended to form gels in several solvents such as acetonitrile, chloroform, benzene, dichloromethane, cyclohexane and toluene. The low insolubility suggested that other reactions occurred during the functionalisation of the polymer backbone resulting in a high cross-linking density within the polymer.
Scheme 5.1: Synthesis of benzo[2,3-g]quinoxaline functionalised polystyrene.

As a result of its poor solubility, the solution photochemistry of the modified polymer could not be investigated. Prior to the investigation of the photochemical properties of benzo[2,3-g]quinoxaline functionalised polystyrene, other synthetic routes such as polymerisation of functionalised monomer or inserting ethylene glycol chain in the back bone to increase the solubility should be investigated.
CHAPTER 6: CONCLUSION AND FUTURE WORK

6.1 Conclusion

The synthesis and studies of the photochemical properties of a series of benzo[2,3-g]quinoxaline and pyrazo[2,3-g]quinoxaline derivatives were described in this thesis. The 2,3-disubstituted benzo[2,3-g]quinoxaline derivatives represent easily synthetically accessible heterocyclic analogue to 2,3-disubstituted anthracene compounds, and were found to display similar photochromic properties. Such compounds therefore allow a facile investigation of the factors influencing the photochemistry of compounds undergoing [4+4] photocycloaddition upon irradiation.

Upon irradiation, anthracene derivatives are known to undergo [4+4] photocycloaddition to form a dimer. The dimer can then be dissociated back to the monomer using light of higher energy, which also promotes other photochemical events that prevent systems based on the photochromism of anthracenes to be used in practical applications. To overcome such phenomenon anthracene can be substituted on the peripheral ring rather than at the central ring using cumbersome multistep synthesis. A series of peripherally substituted benzo[2,3-g]quinoxaline derivatives was synthesised. As predicted, extension of the conjugation on the benzo[2,3-g]quinoxaline core resulted in a shift in UV-Vis absorption towards longer wavelengths. The effect of UV irradiation of these
compounds was investigated in solution and monitored by NMR spectroscopy, UV-Vis absorption spectroscopy and MALDI-TOF MS. All compounds synthesised underwent photoreactions upon UV-irradiation however, only the photoadducts of DPBQ and DPyBQ could be isolated and were confirmed to be dimers. The photochemistry of DPBQ was studied in more detail than the other derivatives. Both PBQ and BQ formed photoadduct upon irradiation however, the structure of the photoadduct could not be identified due to their poor solubility. The addition of methoxy group resulted in a red-shift in UV-Vis absorption but no dimer was observed for both DMoPBQ and MoPBQ. This lack of reactivity could be associated to the photodissociation of the dimers being formed during irradiation. Indeed, the addition of the methoxy group would lead to a red-shift in the dimers and the light source used during the irradiation experiment could provide enough energy to dissociate the photoadduct.

Table 6-1: Summary of characterisation of benzo[2,3-g]quinoxaline derivatives synthesised.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Yield (%)</th>
<th>Mw (g/mol)</th>
<th>m.p (°C)</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon$ (M$^{-1}$.cm$^{-1}$)</th>
<th>$\delta^a$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPBQ</td>
<td>72</td>
<td>332</td>
<td>185-186</td>
<td>381</td>
<td>12349</td>
<td>8.87</td>
</tr>
<tr>
<td>DPyBQ</td>
<td>73</td>
<td>334</td>
<td>185-187</td>
<td>378</td>
<td>7922</td>
<td>8.83</td>
</tr>
<tr>
<td>DMPBQ</td>
<td>66</td>
<td>392</td>
<td>185-187</td>
<td>396</td>
<td>8899</td>
<td>8.72</td>
</tr>
<tr>
<td>MPBQ</td>
<td>76</td>
<td>286</td>
<td>179 (d)</td>
<td>384</td>
<td>7612</td>
<td>9.37</td>
</tr>
<tr>
<td>PBQ</td>
<td>92</td>
<td>256</td>
<td>155-157</td>
<td>379</td>
<td>9502</td>
<td>9.34</td>
</tr>
<tr>
<td>BQ</td>
<td>&gt; 95</td>
<td>180</td>
<td>125-126</td>
<td>360</td>
<td>4899</td>
<td>8.77</td>
</tr>
</tbody>
</table>

$^a$ diagnostic peak in $^1$H-NMR spectrum
Table 6-2: Characterisation of concentrated solutions of benzo[2,3-g]quinoxaline derivatives after 150 min of irradiation.

<table>
<thead>
<tr>
<th>monomer</th>
<th>Mw (g mol⁻¹)</th>
<th>MALDI-TOF m/z</th>
<th>M</th>
<th>δᵇ</th>
<th>yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPBQ</td>
<td>664</td>
<td>665</td>
<td>M+</td>
<td>5.06</td>
<td>40</td>
</tr>
<tr>
<td>DPyBQ</td>
<td>668</td>
<td>668</td>
<td>M+</td>
<td>5.17</td>
<td>40</td>
</tr>
<tr>
<td>DMoPBQ</td>
<td>784</td>
<td>394</td>
<td>M+2</td>
<td>5.45</td>
<td>10</td>
</tr>
<tr>
<td>MoPBQ</td>
<td>572</td>
<td>288</td>
<td>M+2</td>
<td>5.42</td>
<td>8</td>
</tr>
<tr>
<td>PBQ</td>
<td>512</td>
<td>551</td>
<td>M(K⁺)</td>
<td>5.1</td>
<td>13</td>
</tr>
<tr>
<td>BQ</td>
<td>360</td>
<td>182</td>
<td>M+2</td>
<td>4.41</td>
<td>41</td>
</tr>
<tr>
<td>A</td>
<td>356</td>
<td>180</td>
<td>M+2</td>
<td>4.57</td>
<td>44</td>
</tr>
</tbody>
</table>

ᵇ diagnostic peak in the ¹H-NMR spectrum.

The pyridyl substituent enabled the study of the influence of Zn²⁺ on the dimerisation efficiency of DPyBQ. The presence of Zn²⁺ in solution decreased the efficiency of dimerisation, but changing the counter-ion did not have any detectable effect.

In order to develop more selective systems based on the dimerisation of anthracene derivatives, tetrasubstituted pyrazo[2,3-g]quinoxaline derivatives were synthesised and their ability to undergo [4+4] cycloaddition was investigated. Similarly to its anthracene analogue, TPPQ did not undergo dimerisation when irradiated in solution. However, when TPPQ was irradiated in the presence of less sterically hindered anthracene derivatives, cross-photoadduct were observed by ¹H-NMR-spectroscopy.

The studies described above demonstrate that benzo[2,3-g]quinoxaline derivatives possess interesting photochemical properties that had not been reported prior to this work. They proved to be a viable alternative to anthracene
derivatives and have many advantages over them such as the ease of their synthesis, their tolerance to the presence of oxygen during dimerisation, and the fact that their dissociation is triggered at longer wavelengths.

6.2 Future Work

6.2.1 Benzo[2,3-g]quinoxaline-functionalised polymers

In the interest of further understanding the photochemistry of benzo[2,3-g]quinoxalines, more derivatives should be synthesised and their photochemistry should be investigated. More precisely, the influence of electron donating and/or drawing groups, and the effect of polarisation and steric hindrance should be investigated.

In order to further understand the influence of transition metals and other chemicals on the dimerisation of DPyBQ, the isolation and characterisation of the complex formed with Zn^{2+} should be pursued. To that same purpose, the influence of pH on this compound and its photochemistry should also be further investigated. Such chemo-responsive systems could lead to the use of [4+4] cycloaddition as a sensor.

In an effort to develop light responsive materials based on the photochemistry of benzo[2,3-g]quinoxaline, future research should focus on trying to implement polymeric materials functionalised with benzo[2,3-g]quinoxalines. Indeed, most applications using photochromic systems require solid state devices.
Our preliminary efforts to functionalise polystyrene did not lead to a processable polymer. In order to yield more soluble benzo[2,3-\(g\)]quinoxaline functionalised polystyrene materials, polyethylene glycol chains could be added between the chromophore and the vinylic backbone. Other synthetic approaches to obtain anthracene-functionalised polysterene should be investigated. One possible alternative route could be to include the **DPBQ** in the polymer backbone by co-polymerising styrene with a vinylic derivative of **DPBQ** (Figure 6.2). Polyamide polymers could also represent a new variety of photoresponsive polymer (Figure 6.3).

![Figure 6.1: Synthesis of PS functionalised with a benzo[2,3-\(g\)]quinoxaline with a glycol linkage.](image)

---

93
6.2.1 Stimuli responsive gels

The ability to reversibly change the state of matter using external stimuli has motivated chemists and material scientists to develop photoresponsive gels. Serendipitously, Bouas-Laurent and Desvergne discovered the gelating properties of 2,3-dialkoxyanthracenes (DAOA) in different polar solvents. Replacing two CH groups in the central ring of anthracene by two N atoms to form phenazine also resulted in an effective gelator. Dialkoxphenazine was also reported to be pH-sensitive. Inspired by the theoretically easily accessible
dialkoxybenzoquinoxalines (DABQ), we attempted to develop photoreversible
gelator (Figure 6.4).

![Chemical structures](image)

**Figure 6.4:** Structural similarities between (i) dialkoxyanthracene (DAOA), (ii) dialkoxyphenazine and (iii) dialkoxybenzoquinoxaline (DABQ).

In order to study the photochemical properties of DABQ, a systematic
synthetic route should be developed. After overcoming those synthetic
limitations, a series of DABQ derivatives should be synthesised in order to study
the influence of alkoxy chains in systematic manner and the gelling properties of
these compounds. This would in turn, allow the rational design of
photoresponsive gels based on the underexploited dimerisation of anthracene-
like molecules.
CHAPTER 7: EXPERIMENTAL:

The methods used in synthesis, purification; and characterisation of the compounds reported in the previous chapters is presented in this chapter.

7.1 Materials and methods

All chemicals were used as purchased from supplier without further purification. Benzil was purchased from Matheson Coleman & Bell and Potassium cyanide from Merck. All other chemicals were purchased from Aldrich.

NMR characterisation of products was carried out using either a Bruker AMX-400 400MHz spectrometer (400 MHz $^1$H and 100 MHz $^{13}$C) or a Varian Unity Inova 500 MHz spectrometer equipped with a 5 mm inverse detection probe (500 MHz $^1$H and 125 MHz $^{13}$C) as specified. Low resolution mass spectra were recorded on a Hewlett Packard 5985 mass spectrometer (EI 70 eV) by Mr. Philip Ferreira and Mr. Simon Wong. MALDI-TOF mass spectra were performed using a Perspective Voyager-DE STR from PE Applied Biosystems with a nitrogen laser (337 nm) and using 2,5-dihydroxybenzoic acid as the matrix. Melting points were determined either on a Fisher Johns or a Gallenkamp melting point apparatus. Fluorimetry was performed on a PTI C60
spectrofluorimeter and UV-Visible spectroscopy was recorded on a Cary 100 UV-Vis spectrophotometer. Microanalyses (C, H and N) were performed at Simon Fraser University by Mr. Miki Wang and Mr Simon Wong. Infrared spectra were recorded with a Thermo Nicolet Nexus 670 FT-IR E.S.P. spectrometer; samples were prepared as compressed KBr pellets.

All calculations were performed using the Spartan '02 molecular modeling program. Geometry optimizations were performed at the AM1 semiempirical level. Structures were optimized without any constraints. Calculation of the HOMO/LUMO potential surfaces were performed at the AM1 level using geometry-optimized structures.

7.2 Experimental for chapter 2

7.2.1 Synthesis of diketone derivatives

7.2.1.1 Symmetrical precursor

Apart from benzil, which was commercially available, all symmetrical diketones were synthesised by benzoin condensation of the corresponding aryl-aldehyde followed by oxidation. 4,4'-(Dimethoxy)benzil was graciously provided by Dr. Daniel Spantulescu.

2-Hydroxy-1,2-di(pyridine-2-yl)ethanone: Picolinaldehyde (3.22 g, 30.0 mmol), and potassium cyanide (1.92 g, 30.0 mmol) were dissolved in ethanol (5 mL) and water (20 mL) and heated to reflux. After 4 h, TLC analysis (hexane: ethyl acetate 1:1) showed that all picolinaldehyde was consumed and the hot reaction mixture was poured over crushed ice. The resulting brown suspension
was filtered with a Buchner funnel and washed with cold ethanol to yield 2-hydroxy-1,2-di(pyridine-2-yl)ethanone (3.07 g, 14.3 mmol, 95 %) which was used without further purification. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$H (ppm) = 8.47 (d, $J$ = 5.0 Hz, 2.0 H), 7.93-7.88 (m, 2 H), 7.84 (dt, $J_1$ = 8.2, $J_2$ = 1.8 Hz, 2 H), 7.19 (ddd, $J_1$ = 7.3, $J_2$ = 5.0, $J_3$ = 1.2 Hz, 2 H)

1,2-di(pyridin-2-yl)ethane-1,2-dione: 2-Hydroxy-1-(pyridine-2-yl)ethanone (1.61 g, 7.50 mmol) was dissolved in pyridine (25 mL). To this solution was added a solution of CuSO$_4$ (1.87 g, 7.50 mmol) in H$_2$O (10 mL). Once the addition was completed, the reaction mixture was stirred at reflux for 1 h. The hot reaction was poured over crushed ice and filtered using a Buchner funnel yielding 0.857 9 of pure 1,2-di(pyridine-2-yl)ethanone-1,2-dione (0.86 g, 4.04 mmol, 54%) as a shiny yellow crystalline solid. $^1$H-NMR (500 MHz, CDCl$_3$) $\delta$H (ppm) = 8.60 (d, $J$ = 4.7 Hz, 2.0 H), 8.23 (d, $J$ = 7.8 Hz, 2 H), 7.94 (dt, $J$ = 7.7, 1.8 Hz, 2 H), 7.50 (ddd, $J_1$ = 7.6, $J_2$ = 4.8, $J_3$ =1.2 Hz, 2 H); m.p. = 155-157 °C (Lit.$^{85}$ 156-157 °C) m/z (EI) = 213 (M+1)

1,4-Dioxane-2,3-diol: 1,4-dioxane-2,3-diol was prepared as per literature procedure.$^{60}$ Oxalaldehyde (5.31 g, 91.5 mmol) and ethane-1,2-diol (2.33 g, 37.5 mmol) were dissolved in benzene (10 mL) in a 25 mL round bottom flask fitted with a Dean-Stark trap and a condenser and heated to reflux. After removal of 2.7 mL of water, the reaction was cooled down to room temperature. The top layer formed in the round bottom flask was decanted and the viscous lower layer
was triturated with acetone (6 mL). The resulting syrupy suspension was filtered to yield the target compound as a shiny white powder (4.50 g, 37.5 mmol, quant.) that was used without further purification. $^1$H-NMR (400 MHz, DMSO-$d_6$) $\delta_H$ (ppm) = 6.45 (d, $J = 5.6$ Hz, 2 H), 4.29 (d, $J = 5.5$ Hz, 2 H), 3.80 (d, $J = 8.5$ Hz, 2 H$_2$), 3.38 (d, $J = 8.5$ Hz, 2 H); m.p. = 101-103 °C (Lit. 60-100-103 °C).

7.2.1.2 Unsymmetrical diketones

2-Oxo-2-phenylacetalddehyde: 48% aqueous HBr (17.0 mL, 150 mmol) was slowly added to a stirred solution of acetophenone (6.0 g, 50.0 mmol) in DMSO (85 mL). The reaction mixture was then heated in an oil bath at 55 °C. After 25 h, no more starting material was observed by TLC (hexane: ethyl acetate 2:3), the hot reaction mixture was poured over crushed ice. The resulting suspension was extracted with EtOAc (3 x 100 mL). The combined organic extract were dried over MgSO$_4$ and evaporated in vacuo yielding a mixture anhydrous 2-oxo-2-phenylacetalddehyde and 2-oxo-2-phenylacetalddehyde monohydrate in a 3:2 ratio (5.80 g, 43.2 mmol, 87%) as a yellow viscous liquid, which was used immediately without further purification. $^6$ $^1$H-NMR (500 MHz, CDCl$_3$) $\delta_H$ (ppm) = 9.68 (s, 1 H), 8.16-8.10 (m, 2 H), 8.21 (dd, $J_1 = 8.3$, $J_2 = 1.4$ Hz, 3 H), 8.00 (dd, $J_1 = 8.3$, $J_2 = 1.4$ Hz, 4 H), 7.53 (dd, $J_1 = 9.5$, $J_2 = 6.2$ Hz, 1 H), 5.97 (s, 3 H), 7.70-7.60 (m, 1 H).

2-(4-Methoxyphenyl)2-oxoacetalddehyde: 48% aqueous HBr (8.5 mL, 75.0 mmol) was slowly added to a stirred solution of 1-(4-methoxyphenyl)ethanone (3.75 g, 25.0 mmol) in DMSO (42.5 mL). The reaction
mixture was then heated in an oil bath at 55 °C. After 24 h, no more starting material was observed by TLC (1:1 hexane:ethyl acetate), the hot reaction mixture was poured over crushed ice. The resulting suspension was extracted with EtOAc (3 x 100 mL). The combined organic extract were dried over MgSO₄ and evaporated *in vacuo* yielding the target compound (3.57 g, 21.7 mmol, 87%) as a yellow solid, which was used without further purification.\(^\text{1}\)H-NMR (500 MHz, CDCl₃) \(\delta_H (ppm) = 8.10 (d, J = 9.4 Hz, 2 H), 6.93 (d, J = 9.4 Hz, 2 H), 6.30 (s, 1 H), 3.86 (s, 3 H); m.p.= 95-98 °C (Lit.\(^\text{87}\) 96-99 °C) m/z (EI) = 165 (M⁺)

7.2.2 Synthesis of benzoquinoxaline derivatives:

**2,3-Diphenylbenzo[2,3-g]quinoxaline (DPBQ):** A solution of 2,3-diaminonaphthalene (0.316 g, 2.000 mmol) and benzil (0.423 g, 2.000 mmol) in acetic acid (10 mL) was heated under reflux overnight. Reaction progress was monitored by TLC (toluene). Once all 2,3-diaminonaphtalene was consumed, the hot reaction mixture was poured over crushed ice. The resulting brown suspension was then neutralised with saturated aqueous solution of NaHCO₃. The aqueous solution was extracted with dichloromethane (3 x 80 mL). The combined organic extracts were dried over MgSO₄, filtered and evaporated *in vacuo* yielding a dark yellow powder (0.585 g, 88%). The product was purified by flash column chromatography (silica gel, dichloromethane) and recrystallised from hot ethanol to yield DPBQ (0.497 g, 75%) as a yellow crystalline powder. \(^1\)H-NMR (400 MHz, CDCl₃) \(\delta_H (ppm) = 8.75 (s, 2 H), 8.13 (dd, J₁ = 3.3, J₂ = 6.4 Hz, 2 H), 7.57 (m, 6 H), 7.37 (m, 6 H); m.p. = 184-185 °C (Lit.\(^\text{53}\) 187-189 °C).
Benzo[2,3-g]quinoxaline (BQ): BQ was synthesised as per literature procedure. The product was purified by flash column chromatography (silica gel, ethyl acetate: dichloromethane 1:3) and recrystallised from hot ethanol to yield the target compound (85%) as brown powder. $^{1}$H-NMR (400 MHz, CDCl$_3$) $\delta_H$ (ppm) = 8.95 (s, 2 H), 8.80 (s, 2 H), 8.17 (dd, $J_1 = 3.3, J_2 = 6.5$ Hz, 2 H), 7.65 (dd, $J_1 = 3.2, J_2 = 6.6$ Hz, 2 H); m.p. = 126-130 °C ($^{Lit.}$60 125-126 °C).

2-Phenylbenzo[2,3-g]quinoxaline (PBQ): PBQ was synthesised as per literature procedure. The product was purified by flash column chromatography (silica gel, ethyl acetate) yielding PBQ (92%) as shiny yellow needles. $^{1}$H-NMR (400 MHz, CDCl$_3$) $\delta_H$ (ppm) = 9.41 (s, 1 H), 8.76 (s, 1 H), 8.72 (s, 1 H), 8.28 (d, $J = 7.0$ Hz, 2 H), 8.14 (dd, $J_1 = 4.0, J_2 = 5.6$ Hz, 2 H), 7.65-7.60 (m, 5 H); m.p. = 155-157 °C ($^{Lit.}$88 163 °C); m/z (Cl) = 256 (M+1)

2,3-Di(pyridin-2-yl)benzo[2,3-g]quinoxaline (DPyBQ): DPyBQ was synthesised as per literature procedure. The product was recrystallised from hot ethanol yielding DPyBQ (73%) as shiny yellow crystals. $^{1}$H-NMR (400 MHz, CDCl$_3$) $\delta_H$ (ppm) = 8.80 (s, 2 H), 8.36 (d, $J = 4.8$ Hz, 2 H), 8.15 (m, 2 H), 8.09 (d, $J = 7.8$ Hz, 2 H), 7.87 (dt, $J_1 = 1.7, J_2 = 7.7$ Hz, 2 H), 7.61 (m, 2 H), 7.26 (m, 4 H); m.p. = 183-185 °C ($^{Lit.}$66 184-185 °C); m/z (Cl) = 335 (M+1)
2,3-di(4-methoxyphenyl)benzo[2,3-g]quinoxaline (DMoPBQ): DMoPBQ was prepared as per literature procedure. DMoPBQ (66%) was obtained as a shiny crystalline product. No further purification was necessary. $^1$H-NMR (400 MHz, CD$_2$Cl$_2$) $\delta$H (ppm) = 8.68 (s, 2H), 8.09 (m, 2 H), 7.55 (m, 6 H), 6.89 (m, 4 H), 3.84 (s, 6 H); m.p. = 183-186 °C (Lit 185-187 °C); MALDI-TOF m/z = 361 (M-OMe)

2-(4-methoxyphenyl)benzo[2,3-g]quinoxaline (MoPBQ): MoPBQ was prepared according to the method described for DMoPBQ. MoPBQ (76%) was isolated as a yellow-greenish powder was obtained. EA found (submitted C, H, N; ) Calc for C$_{19}$H$_{14}$N$_2$O C, 79.7;H, 4.93;N, 9.78; $^1$H-NMR (500 MHz, CD$_2$Cl$_2$) $\delta$H (ppm) = 9.4 (s, 1 H), 8.86 (s, 1H), 8.73 (s, 1 H), 8.31 (d, $J$ = 8.2 Hz, 2 H), 8.13 (m, 2H), 7.61 (m, 2 H), 7.13 (d, $J$ = 8.4 Hz, 2 H), 3.93 (s, 3 H); $^{13}$C-NMR (125 MHz, CD$_2$Cl$_2$) $\delta$C (ppm) = 161.9, 151.6, 144.7, 139.1, 138.2, 134.5, 133.6, 129.6, 129.4, 128.8, 128.6, 127.76, 126.75, 127.1, 126.8, 114.9, 55.74, 55.73; m/z (El) = 286 (M$^+$); IR (KBr) v = 3053, 2993, 2956, 2919, 2845, 1607, 1249 cm$^{-1}$; UV-Vis $\lambda_{\text{max}}$/nm (e/M.cm$^{-1}$): 234 (17687), 268 (24170), 309 (17560), 318 (17950), 384 (7612).

7.2.3 Photochemical Experiments

Examples of typical photochemical experiments are described in this section.

di-DPBQ: 3.3 mg of DPBQ was dissolved in spectral grade benzene (1.5 mL) and deoxygenated by a minimum of three freeze-pump-thaw cycles. The
sample was then irradiated in a Rayonet® photochemical reactor for 2 h. After irradiation, a white powder precipitated onto the side of the glass.

The solution was decanted and the white product was collected. EA Found: C, 86.61; H, 4.98; N, 8.15. Calc. for C_{48}H_{32}N_{4} C, 86.72; H, 4.85; N, 8.43; \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta_H\) (ppm) = 7.23 (m, 16 H), 7.14 (m, 8 H), 7.03 (m, 4 H), 5.05 (s, 4 H); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)) \(\delta_C\) (ppm) = 156.3, 148.7, 140.4, 138.8, 129.4, 128.1, 128.0, 126.9, 52.7 (Note: due to the limited solubility of this compound, we were unable to observe the signals for quaternary carbons) MALDI-TOF m/z = 665 (M+1); IR (KBr) \(\nu\) = 3057, 2959, 2919, 2849, 1389, 1144 cm\(^{-1}\); UV-Vis \(\lambda_{\text{max}}\)/nm (\(\epsilon/M cm^{-1}\)): 230 (47543), 270 (17967), 308 (23337), 328 (29242).

For the experiments in which a filter solution was employed, 3.3 mg \textbf{DPBQ} was dissolved in 0.75 ml of CH\(_3\)CN. The solution was transferred to an NMR tube and immersed in a test tube filled with a 2.0 M solution of KNO\(_3\) in water. The sample was irradiated in the Rayonet® photochemical reactor for 150 min. The solvent was then removed \textit{in vacuo}.

Irradiation of \textbf{BQ : BQ} (3.8 mg, 0.02 mmol) was dissolved in spectral grade CH\(_3\)CN (15.0 mL). A 6.0 mL aliquot was then immersed in a 2.0 M aqueous KNO\(_3\) solution and irradiated in the Rayonet® photochemical reactor for 2.5 h. After irradiation, no white powder precipitated onto the side of the glass. The sample was dried \textit{in vacuo} (41 %). \(^1\)H-NMR (500 MHz, CDCl\(_3\)) \(\delta_H\) (ppm) =
9.12 (s, 1 H), 8.9 (s, 2 H), 8.72 (s, 2 H), 8.46 (dd, $J_1 = 3.3$, $J_2 = 5.7$ Hz, 2 H), 8.15 (dd, $J_1 = 3.3$, $J_2 = 6.5$ Hz, 3 H), 7.93 (dd, $J_1 = 3.3$, $J_2 = 5.8$ Hz, 2 H), 7.62 (dd, $J_1 = 3.2$, $J_2 = 6.6$ Hz, 3 H), 7.26 (CHCl$_3$), 4.85 (s, 2 H); MALDI-TOF m/z = 394 (di-BQ+Na$^+$).

Irradiation of **PBQ : PBQ** (5.3 mg, 0.02 mmol) was dissolved in spectral grade CH$_3$CN (15.0 mL). A 6.0 mL aliquot was then immersed in a 2.0 M aqueous KNO$_3$ solution and irradiated in the Rayonet® photochemical reactor for 2.5 h. After irradiation, no white powder precipitated onto the side of the glass. The sample was dried *in vacuo* (13%). $^1$H-NMR (400 MHz, CDCl$_3$) $\delta_H$ (ppm) = 9.45-9.43 (m, 1 H), 9.35 (s, 2.1 H), 8.69 (s, 2 H), 8.65 (s, 3 H), 8.41-8.36 (m, 2 H), 8.21 (d, $J = 7.05$ Hz, 6 H), 8.10-8.05 (m, 8 H), 8.03-7.99 (m, 2 H), 7.99-7.95 (m, 2 H), 7.88-7.83 (m, 3 H), 7.77-7.73 (m, 4 H), 7.67-7.63 (m, 1 H), 7.58-7.44 (m, 1 H), 7.42-7.37 (m, 5 H), 5.42-5.39 (m, 1 H), 5.05-5.03 (s, 0.4 H), 5.03-5.01 (s, 0.3 H); MALDI-TOF m/z= 551 M(di-PBQ+K$^+$), 258 M(PBQ)$^+$

Irradiation of **DMoBQ : DMoPBQ** (7.8 mg, 0.02 mmol) was dissolved in spectral grade CH$_3$CN (15.0 mL). A 6.0 mL aliquot was then immersed in a 2.0 M aqueous KNO$_3$ solution and irradiated in the Rayonet® photochemical reactor for 2.5 h. After irradiation, no white powder precipitated onto the side of the glass. The sample was dried *in vacuo* (13%). $^1$H-NMR (500 MHz, CDCl$_3$) $\delta_H$ (ppm) = 8.72 (s, 8 H), 8.47-8.43 (m, 3 H), 8.16-8.10 (m, 9 H), 8.08-8.03 (m, 4 H),
7.97 (d, $J = 8.95$ Hz, 8 H), 7.93-7.89 (m, 4 H), 7.83-7.78 (m, 4 H), 7.73-7.68 (m, 6 H), 7.64-7.60 (m, 6 H), 7.52-7.48 (m, 5 H), 6.99 (d, $J = 8.9$ Hz, 12 H), 6.97-6.95 (m, 6 H), 6.92 (d, $J = 8.8$ Hz, 18 H), 6.91-6.89 (m, 3 H), 5.48-5.46 (m, 1 H), 3.91 (s, 10 H), 3.90-3.86 (m, 40 H).

Irradiation of MoPBQ: MoPBQ (5.8 mg, 0.02 mmol) was dissolved in spectral grade CH$_3$CN (15.0 mL). A 6.0 mL aliquot was then immersed in a 2.0 M aqueous KNO$_3$ solution and irradiated in the Rayonet® photochemical reactor for 2.5 h. After irradiation, no white powder precipitated onto the side of the glass. The sample was dried in vacuo (8 %). $^1$H-NMR (500 MHz, CDCl$_3$) $\delta_H$ (ppm) = 9.45-9.42 (m, 4 H), 9.37 (s, 11 H), 8.70 (s, 11 H), 8.67 (s, 11 H), 8.46-8.41 (m, 9 H), 8.31-8.28 (m, 9 H), 8.26 (d, $J = 8.8$ Hz, 22 H), 8.14-8.09 (m, 25 H), 7.92-7.87 (m, 6 H), 8.05-8.01 (m, 12 H), 7.58 (d, $J = 3.6$ Hz, 30 H), 7.12 (d, $J = 8.9$ Hz, 23 H), 7.10-7.08 (m, 7 H), 6.97-6.94 (m, 11 H), 5.64-5.63 (m, 1 H), 5.44-5.42 (m, 2 H), 3.86 (s, 12 H).

di-DPyBQ: DPyBQ (6.6 mg, 0.02 mmol) was dissolved in spectral grade CH$_3$CN (15.0 mL). A 6.0 mL aliquot was then immersed in a 2.0 M aqueous KNO$_3$ solution and irradiated in the Rayonet® photochemical reactor for 2.5 h. After irradiation, a white powder precipitated onto the side of the glass. The sample was dried in vacuo (40 %). $^1$H-NMR (500 MHz, CDCl$_3$) $\delta_H$ (ppm) = 8.43 (d, $J = 4.8$ Hz, 2 H), 7.69-7.63 (m, 2 H), 7.45-7.37 (m, 2 H), 7.25 (dd, $J_1 = 5.4$, $J_2$
= 3.3 Hz, 2 H), 7.21-7.14 (m, 1H), 7.00 (dd, J1 = 5.4, J2 = 3.2 Hz, 2 H), 5.16 (s, 2 H); 13C-NMR (125 MHz, CDCl3) δC (ppm) = 157.3, 156.9, 149.1, 147.9, 140.0, 136.2, 128.0, 127.31, 124.3, 122.6, 109.7, 52.7; MALDI-TOF m/z = 669 (M+1)

7.2.4 Dissociation of photodimer:

**Photodissociation of di-DPBQ:** A 1x10⁻⁴ M solution of di-DPBQ in CH₃CN was irradiated at 328 nm in a quartz cuvette in the fluorimeter. Dissociation progress was followed by UV-Vis spectroscopy at 30 min intervals.

**Thermal dissociation of di-DPBQ:** di-DPBQ (6.6 mg, 0.01 mmol) was dissolved in 100 mL of DMSO in a 100 mL volumetric flask. 20 mL of this 1.00 x 10⁻⁵ M solution of di-DPBQ were transferred into four 25 mL glass vials. The open vials were then heated in oil baths at 60, 80, 100, 150 °C for a maximum of 4 h. The dissociation was followed by UV-Vis spectroscopy at 30 min intervals.

7.3 Experimental for chapter 4

7.3.1 Synthesis

**Tetraphenylpyrazo[2,3-g]quinoxaline:** Tetraaminobenzene tetrahydrochloride salt (0.144 g, 0.5 mmol), benzil (0.210 g, 1.0 mmol) and sodium acetate (0.780 g, 5.0 mmol) were dissolved in ethanol (20 mL). Upon addition of AcONa the resulting purple solution turned red. After 3 h at reflux the hot solution was poured over crushed ice and the aqueous orange suspension was extracted with dichloromethane (3 x 100 mL). The organic phases were
combined, dried over MgSO$_4$ and concentrated \textit{in vacuo} yielding the crude target compound as a yellow powder (0.478 g). The powder was recrystallised from boiling ethanol yielding TPPQ (0.206 g, 0.424 mmol, 42\%) as yellow crystals. 

$^1$H-NMR (500 MHz, CDCl$_3$) $\delta_H$ (ppm) = 9.04 (s, 2 H) 7.55 (d, $J = 6.7$ Hz, 8 H) 7.33 (m, 12 H)

2,3,7,8-tetrakis(3,4-bis(hexyloxy)phenyl)-pyrazo[2,3-g]quinoxaline

THPQ: Tetraaminobenzene tetrahydrochloride (0.150 g, 0.5 mmol), tetrahexyloxybenzil (0.487 g, 1.0 mmol) and sodium acetate (0.708 g, 5.0 mmol) were dissolved in 95\% ethanol (50 mL). After 17 h at reflux, the hot reaction mixture was poured over crushed ice (200 g) and the brown suspension was filtered using a Buchner funnel. The brown powder collected was then purified by flash column chromatography (silica gel, toluene) yielding an orange powder which was recrystallised from methanol and dichloromethane (10 vol\%) (8\%). 

$^1$H-NMR (500 MHz, CDCl$_3$) $\delta_H$ (ppm) = 8.90 (s, 2 H), 7.22 (dd, $J_1 = 2.5$, $J_1 = 8.8$ Hz, 3.64 H), 6.87 (d, $J = 8.4$ Hz, 4.6 H), 4.03 (t, $J_1 = 6.7$, $J_2 = 6.7$ Hz, 8.1 H), 3.7 (t, $J_1 = 6.7$, $J_2 = 6.7$ Hz, 7.67 H), 1.80 (m, 20.7 H), 1.47 (m, 15.3 H), 1.35 (m, 25.8 H), 0.9 (t, 19.1 H); $^{13}$C-NMR (125 MHz, CDCl$_3$) $\delta_C$ (ppm) = 194.05, 155.18, 149.49, 126.39, 126.36, 69.43, 69.33, 31.78, 31.73, 29.25, 29.11, 25.92, 25.88, 25.82, 22.84, 22.80, 14.28, 14.26, 14.23.

7.3.2 Photoadduct formation

**Irradiation of TPPQ:** different solutions of TPPQ were irradiated in the Rayonet® photochemical reactor fitted with lamps centred at 350 nm for 150 min.

- (9.2 mg, 0.019 mmol) in spectral grade CH$_3$CN (100 mL)
- (5.0 mg, 0.010 mmol) in spectral-grade CH$_3$CN (100 mL)
- (9.3 mg, 0.019 mmol) in spectral-grade benzene (5 mL)

The solutions was concentrated in vacuo. $^1$H-NMR (500 MHz, CDCl$_3$) $\delta$ (ppm) = 9.04 (s, 2 H), 7.61(dd, 8 H), 7.38-7.42(m, 12 H) ppm.

**Anthracene-2,3,6,7-tetraphenylpyrazoquinoxaline (A-TPPQ):** 5.00 mL of a 0.2 mM solution of TPPQ in CH$_3$CN was mixed with 5.00 mL of a 0.2 mM solution of A in CH$_3$CN. The resulting mixture was irradiated in the Rayonet photoreactor® for 150 min. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ (ppm)= 9.05 (s, 14 H), 8.36-8.34 (m, 5 H), 8.33-8.32 (m, 2 H), 7.94-7.91 (m, 3 H), 7.85-7.82 (m, 4 H), 7.76-7.72 (m, 5 H), 7.66-7.62 (m, 51 H), 7.59-7.55 (m, 5 H), 7.45-7.39 (m, 80.8 H), 7.31 (dd, $J_1 = 5.3$, $J_2 = 3.1$ Hz, 8 H), 6.95-6.93 (m, 4 H), 6.84-6.82 (m, 4 H), 5.84-5.83 (m, 1 H), 5.82-5.81 (m, 1 H), 5.80-5.79 (m, 1 H), 5.57-5.54 (m, 2 H), 4.57-4.56 (m, 2 H); MALDI-TOF m/z= 488.4 (M(TPPQ)+2), 331 (M(TPPA-A)+2), 178 (M(A)+)

**9',10'-Dimethylanthracene-2,3,6,7-tetraphenylpyrazoquinoxaline (DMA-TPPQ):** 5.00 mL of a 0.2 mM solution of TPPQ in CH$_3$CN was mixed with 5.00 mL of a 0.2 mM solution of DMA in CH$_3$CN. The resulting mixture was irradiated in the Rayonet® photochemical reactor for 150 min The solution was irradiated in the Rayonet® photochemical reactor for 150 min. $^1$H-NMR (500 MHz, CDCl$_3$) $\delta$ (ppm)= 9.05 (s, 6 H), 8.38-8.32 (m, 3 H), 8.12-8.08 (m, 1 H), 7.87-7.86 (m, 3 H), 7.86-7.82 (m, 1 H), 7.74-7.71 (m, 1 H), 7.64 (d, $J = 7.0$ Hz, 29 H), 7.57-7.53 (m, 2.4 H), 7.47-7.38 (m, 57 H), 7.30 (dd, $J_1 = 5.45$, $J_2 = 3.2$ Hz, 11
H), 6.92-6.90 (m, 1 H), 6.86-6.81 (m, 2 H), 6.71-6.68 (m, 1 H), 6.77-6.74 (m, 1 H), 4.99-4.97 (m, 1 H), 4.91-4.88 (m, 1 H), 4.72-4.68 (m, 1 H), 3.82-3.80 (m, 1 H), 3.77-3.74 (m, 1 H), 3.47-3.44 (m, 1 H), 3.33-3.31 (m, 1 H), 2.17 (s, 17 H); MALDI-TOF m/z = 698 (M(TPPQ-DMA)\(^+\)), 489 (M(TPPQ)+(3), 206 (M(DMA)\(^+\)).

7.4 Experimental for chapter 5

The molecular weights of the copolymers were estimated by gel permeation chromatography (GPC) at 50 oC in DMF (0.01 M LiBr) using Waters Styragel HT columns (HT3, HT4, HT5), a Waters 1515 isocratic HPLC pump, a Waters 2414 differential refractometer and a Water 2487 dual \(\lambda\) absorbance detector set at 254 nm. Polystyrene standards were used for calibration.

**BQP:** was synthesised according to literature procedure.\(^{81}\) BQP was obtained as yellow powder (quant.). \(^1\text{H}-\text{NMR} (500\text{ MHz, CDCl}_3) \delta_{\text{H}} (\text{ppm}) = 9.37 (s, 1 \text{ H}), 8.74-8.66 (m, 2 \text{ H}), 8.24-8.19 (m, 2 \text{ H}), 8.12 (dd, J_1 = 6.1, J_2 = 3.4 \text{ Hz, 2.5 H}), 7.59 (td, J_1 = 5.9, J_2 = 3.3 \text{ Hz, 2 H}), 7.10-7.03 (m, 2 \text{ H}).

**Poly (Co-styrene-chloromethylstyrene) 1:** Chloromethylstyrene (0.15 g, 0.96 mmol) and styrene (1.01 g, 9.60 mmol) were heated in an oil bath at 100 oC for 18 h. The off-white solid was dissolved in dichloromethane and reprecipitated in a large excess of ethanol 5 times, yielding a solid after filtration (0.42 g). GPC determined a M\(w = 38169\text{ g/mol with a polydispersity of 1.74. The ratio of 1
chloromethylstyrene to 2 styrene units in the final pure polymer was determined by $^1$H-NMR spectroscopy. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta_H$ (ppm) = 7.10 (br, 7 H), 6.57-6.46 (br, 8 H), 4.5 (br, 2 H) 2.2 (br, 2 H) 1.8 (br, 5 H) 1.42 (br, 5 H) 1.26 (s, 2 H).

**Poly (Co-styrene-chloromethylstyrene) 2:** chloromethylstyrene (2.00 mL, 13.15 mmol) and styrene (20.03 g, 192.31 mmol) were heated in an oil bath at 70 °C for 6 days. After 6 days, $^1$H-NMR analysis only showed the starting materials in solution hence, AIBN (3.0 mg, mmol) was added to the reaction mixture. After 6 days, the reaction was cooled down as a thick off-white solid had precipitated. The off-white solid was dissolved in dichloromethane and reprecipitated in large volume of ethanol 5 times, yielding a solid after filtration (16.94 g). GPC determined a Mw= 426987 g/mol with a polydispersity of 1.58. The ratio of 1 chloromethylstyrene to 42 styrene units in the final pure polymer was determined by $^1$H-NMR spectroscopy. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta_H$ (ppm) = 7.10 (br, 133 H), 6.58-6.46 (br, 79 H), 4.5-4.3(br, 2 H) 2.2 (br, 2 H) 2.05 (br, 33 H) 1.42 (br, 87 H) 1.26 (s, 3 H).

**PS2BQ:** A mixture of 4-(benzo[2,3-g]quinoxaly)phenyl (7.0 mg, 0.03 mmol) and PS2 (0.108 g, 0.25 mmol) and K$_2$CO$_3$ (17.7 mg, 0.128 mmol) were dissolved DMF (3 mL) and heated under reflux. After 2 days, the reaction was quenched with water (5 mL). The resulting pale yellow milky solution was filtered to yield a white solid (84.7 mg, 84%).
REFERENCE LIST


(84) Wenz, G. Makromolekulare Chemie-Rapid Communications 1985, 6, 577-584.


APPENDIX 1: CRYSTALLOGRAPHIC DATA FOR di-DPBQ

Crystals of di-DPBQ were obtained by slowly evaporating a solution of this compound in chloroform and acetonitrile (1:1). Under these conditions, di-DPBQ crystallizes in the monoclinic system P 2₁/n. Analysis of the structure shows the presence of head-to-tail dimers of DPBQ with a bridge-head carbon to carbon distance of 1.605 Å.

Crystallographic data for di-DPBQ is summarised in Table A-1. A pale yellow crystal of di-DPBQ having dimensions 0.34 x 0.23 x 0.23 mm³ was mounted on a glass fibres using epoxy adhesive. The data range 9.4 ° ≤ 2θ ≤ 144.4 ° was recorded at room temperature on a Rigaku RAXIS RAPID image plate area detector with Cu Kα radiation. The data was corrected by integration for the effects of absorption using a numerical absorption correction (transmission range: 0.8704 – 1.000). Data reduction included corrections for Lorentz and polarization effects. Final unit-cell dimensions were determined based on 597 well-centred reflections with range 9.4 ° ≤ 2θ ≤ 144.4 °.

The coordinates and anisotropic displacement parameters for all non-hydrogen atoms were refined. Hydrogen atoms were placed in calculated positions (d C-H 0.95 Å) and refined with coordinate shifts linked with those of the respective carbon atoms. Isotropic thermal parameters for the hydrogen
atoms were initially assigned proportionately to the equivalent isotropic thermal parameters of their respective carbon. Subsequently, the isotropic thermal parameters for the C-H hydrogen atoms were constrained to have identical shifts during refinement. Selected bond lengths and angles for di-DPBQ are found in Table A-2.

The software package Crystal Clear (d*trek, Rigaku) was used for all absorption corrections, data reduction and processing.\(^1\) All structures were solved using Sir 92,\(^2\) expanded using Fourier techniques and refined using CRYSTALS.\(^3\) Complex scattering factors for neutral atoms were used in the calculation of structure factors.\(^4\) Diagrams were made using Mercury 1.4.2 and Material Studio 1.1.

---
<table>
<thead>
<tr>
<th><strong>Table A-1 Summary of crystallographic data</strong></th>
<th><strong>di-DPBQ</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
<td>( \text{C}<em>{48}\text{H}</em>{32}\text{N}_{4} )</td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
<td>664.79</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>Monoclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>( \text{P} \ 1 \ 2_1/\text{n} \ 1 )</td>
</tr>
<tr>
<td><strong>a, Å</strong></td>
<td>8.6132(9)</td>
</tr>
<tr>
<td><strong>b, Å</strong></td>
<td>18.4915(17)</td>
</tr>
<tr>
<td><strong>c, Å</strong></td>
<td>10.9618(16)</td>
</tr>
<tr>
<td><strong>( \alpha, \degree )</strong></td>
<td>90</td>
</tr>
<tr>
<td><strong>( \beta, \degree )</strong></td>
<td>96.550(6)</td>
</tr>
<tr>
<td><strong>( \gamma, \degree )</strong></td>
<td>90</td>
</tr>
<tr>
<td><strong>V, Å(^3)</strong></td>
<td>1734.5(4)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>2</td>
</tr>
<tr>
<td><strong>T, K</strong></td>
<td>293</td>
</tr>
<tr>
<td><strong>( \lambda, \text{Å} )</strong></td>
<td>1.5418</td>
</tr>
<tr>
<td><strong>( \rho_{\text{calc}}, \text{g\cdot cm}^{-3} )</strong></td>
<td>0.16</td>
</tr>
<tr>
<td><strong>( \mu, \text{mm}^{-1} )</strong></td>
<td>0.580</td>
</tr>
<tr>
<td><strong>( R^a, (I &gt; 2.5\sigma(I)) )</strong></td>
<td>0.0436</td>
</tr>
<tr>
<td><strong>( R_w^a, (I &gt; 2.5\sigma(I)) )</strong></td>
<td>0.0645</td>
</tr>
<tr>
<td><strong>Goodness of fit</strong></td>
<td>1.4097</td>
</tr>
</tbody>
</table>

\(^a\)Function minimized \( \Sigma w[(F_o \ - \ |F_c|)^2] \) where \( w^{-1} = [\sigma^2(F_o) + (0.020*F_o)^2] \), \( R = \Sigma |F_o| - |F_c| / \Sigma |F_o| \), \( R_w = [\Sigma w[(F_o \ - \ |F_c|)^2] / \Sigma w|F_o|^2]^{1/2} \).
<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1) - C(2)</td>
<td>1.5168(19)</td>
<td>C(2) - C(9)</td>
<td>1.605(2)</td>
</tr>
<tr>
<td>C(2) - C(3)</td>
<td>1.518(2)</td>
<td>C(8) - C(9)</td>
<td>1.516(2)</td>
</tr>
<tr>
<td>C(9) - C(10)</td>
<td>1.5095(19)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(2) - C(1) - C(10)</td>
<td>117.38(12)</td>
<td>C(1) - C(2) - C(9)</td>
<td>111.67(12)</td>
</tr>
<tr>
<td>C(1) - C(2) - C(3)</td>
<td>107.02(12)</td>
<td>C(9') - C(2) - C(3)</td>
<td>112.12(11)</td>
</tr>
<tr>
<td>C(2) - C(3) - C(4)</td>
<td>123.06(15)</td>
<td>C(2) - C(3) - C(8)</td>
<td>117.13(14)</td>
</tr>
<tr>
<td>N(2) - C(1) - C(2)</td>
<td>120.72(13)</td>
<td>C(3) - C(8) - C(9)</td>
<td>117.81(14)</td>
</tr>
<tr>
<td>C(7) - C(8) - C(9)</td>
<td>122.74(15)</td>
<td>C(8) - C(9) - C(2')</td>
<td>111.95(11)</td>
</tr>
<tr>
<td>C(8) - C(9) - C(10)</td>
<td>107.63(12)</td>
<td>C(2') - C(9) - C(10)</td>
<td>111.23(12)</td>
</tr>
<tr>
<td>C(9) - C(10) - C(1)</td>
<td>117.84(13)</td>
<td>C(9) - C(10) - N(1)</td>
<td>120.35(13)</td>
</tr>
</tbody>
</table>

*a Symmetry transformations: *, -x+1, -y+1, -z+1*
### Table A-3

Fractional atomic coordinates and equivalent isotropic thermal parameters \([U(\text{iso}) \text{ (Å}^2\text{)]}\) for di-DPBQ.

<table>
<thead>
<tr>
<th>Atom</th>
<th>(X)</th>
<th>(Y)</th>
<th>(Z)</th>
<th>([U(\text{iso}) \text{ (Å}^2\text{)]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)</td>
<td>0.48296(14)</td>
<td>0.34968(6)</td>
<td>0.35530(11)</td>
<td>0.0466</td>
</tr>
<tr>
<td>N(2)</td>
<td>0.20574(14)</td>
<td>0.43059(6)</td>
<td>0.32918(11)</td>
<td>0.0463</td>
</tr>
<tr>
<td>C(1)</td>
<td>0.32400(17)</td>
<td>0.44634(8)</td>
<td>0.41392(14)</td>
<td>0.0443</td>
</tr>
<tr>
<td>C(2)</td>
<td>0.31328(17)</td>
<td>0.50948(8)</td>
<td>0.50088(13)</td>
<td>0.0463</td>
</tr>
<tr>
<td>C(3)</td>
<td>0.36389(18)</td>
<td>0.48176(8)</td>
<td>0.62963(14)</td>
<td>0.0484</td>
</tr>
<tr>
<td>C(4)</td>
<td>0.2846(2)</td>
<td>0.49799(10)</td>
<td>0.72951(15)</td>
<td>0.06</td>
</tr>
<tr>
<td>C(5)</td>
<td>0.3396(3)</td>
<td>0.47138(11)</td>
<td>0.84533(17)</td>
<td>0.0713</td>
</tr>
<tr>
<td>C(6)</td>
<td>0.4724(3)</td>
<td>0.42996(11)</td>
<td>0.86168(17)</td>
<td>0.0694</td>
</tr>
<tr>
<td>C(7)</td>
<td>0.5530(2)</td>
<td>0.41379(9)</td>
<td>0.76254(16)</td>
<td>0.0583</td>
</tr>
<tr>
<td>C(8)</td>
<td>0.49958(18)</td>
<td>0.43905(8)</td>
<td>0.64614(14)</td>
<td>0.0478</td>
</tr>
<tr>
<td>C(9)</td>
<td>0.58271(18)</td>
<td>0.42330(8)</td>
<td>0.53439(14)</td>
<td>0.0468</td>
</tr>
<tr>
<td>C(10)</td>
<td>0.45989(17)</td>
<td>0.40407(8)</td>
<td>0.43001(14)</td>
<td>0.0451</td>
</tr>
<tr>
<td>C(11)</td>
<td>0.36580(17)</td>
<td>0.33411(8)</td>
<td>0.26561(14)</td>
<td>0.0453</td>
</tr>
<tr>
<td>C(12)</td>
<td>0.22449(17)</td>
<td>0.37278(8)</td>
<td>0.25626(13)</td>
<td>0.0449</td>
</tr>
<tr>
<td>C(13)</td>
<td>0.39976(18)</td>
<td>0.27493(8)</td>
<td>0.18031(15)</td>
<td>0.0501</td>
</tr>
<tr>
<td>C(14)</td>
<td>0.4881(2)</td>
<td>0.21621(10)</td>
<td>0.2260(2)</td>
<td>0.0669</td>
</tr>
<tr>
<td>C(15)</td>
<td>0.5233(3)</td>
<td>0.16116(11)</td>
<td>0.1467(2)</td>
<td>0.0837</td>
</tr>
<tr>
<td>C(16)</td>
<td>0.4738(3)</td>
<td>0.16526(12)</td>
<td>0.0230(2)</td>
<td>0.0858</td>
</tr>
<tr>
<td>C(17)</td>
<td>0.3869(3)</td>
<td>0.22321(13)</td>
<td>-0.0225(2)</td>
<td>0.0796</td>
</tr>
<tr>
<td>Atom</td>
<td>x</td>
<td>y</td>
<td>z</td>
<td>Ueq</td>
</tr>
<tr>
<td>-------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>C(18)</td>
<td>0.3498(2)</td>
<td>0.27806(10)</td>
<td>0.05457(16)</td>
<td>0.0627</td>
</tr>
<tr>
<td>C(19)</td>
<td>0.08309(17)</td>
<td>0.35184(8)</td>
<td>0.17286(14)</td>
<td>0.0474</td>
</tr>
<tr>
<td>C(20)</td>
<td>0.0063(2)</td>
<td>0.40208(10)</td>
<td>0.09361(16)</td>
<td>0.0623</td>
</tr>
<tr>
<td>C(21)</td>
<td>-0.1259(2)</td>
<td>0.38283(12)</td>
<td>0.01701(19)</td>
<td>0.0773</td>
</tr>
<tr>
<td>C(22)</td>
<td>-0.1866(2)</td>
<td>0.31346(12)</td>
<td>0.02260(19)</td>
<td>0.0759</td>
</tr>
<tr>
<td>C(23)</td>
<td>-0.1120(2)</td>
<td>0.26390(11)</td>
<td>0.10057(17)</td>
<td>0.0666</td>
</tr>
<tr>
<td>C(24)</td>
<td>0.02266(19)</td>
<td>0.28243(9)</td>
<td>0.17523(15)</td>
<td>0.0547</td>
</tr>
<tr>
<td>H(21)</td>
<td>0.20731(17)</td>
<td>0.52452(8)</td>
<td>0.49635(13)</td>
<td>0.0533(16)</td>
</tr>
<tr>
<td>H(41)</td>
<td>0.1932(2)</td>
<td>0.52712(10)</td>
<td>0.71896(15)</td>
<td>0.0705(16)</td>
</tr>
<tr>
<td>H(51)</td>
<td>0.2847(3)</td>
<td>0.48205(11)</td>
<td>0.91354(17)</td>
<td>0.0846(16)</td>
</tr>
<tr>
<td>H(61)</td>
<td>0.5092(3)</td>
<td>0.41225(11)</td>
<td>0.94109(17)</td>
<td>0.0811(16)</td>
</tr>
<tr>
<td>H(71)</td>
<td>0.6453(2)</td>
<td>0.38530(9)</td>
<td>0.77443(16)</td>
<td>0.0670(16)</td>
</tr>
<tr>
<td>H(91)</td>
<td>0.64916(18)</td>
<td>0.38269(8)</td>
<td>0.55171(14)</td>
<td>0.0537(16)</td>
</tr>
<tr>
<td>H(141)</td>
<td>0.5245(2)</td>
<td>0.21346(10)</td>
<td>0.3110(2)</td>
<td>0.0788(16)</td>
</tr>
<tr>
<td>H(151)</td>
<td>0.5820(3)</td>
<td>0.12044(11)</td>
<td>0.1783(2)</td>
<td>0.1000(16)</td>
</tr>
<tr>
<td>H(161)</td>
<td>0.4998(3)</td>
<td>0.12794(12)</td>
<td>-0.0306(2)</td>
<td>0.1039(16)</td>
</tr>
<tr>
<td>H(171)</td>
<td>0.3520(3)</td>
<td>0.22573(13)</td>
<td>-0.1078(2)</td>
<td>0.0955(16)</td>
</tr>
<tr>
<td>H(181)</td>
<td>0.2898(2)</td>
<td>0.31816(10)</td>
<td>0.02193(16)</td>
<td>0.0742(16)</td>
</tr>
<tr>
<td>H(201)</td>
<td>0.0449(2)</td>
<td>0.45015(10)</td>
<td>0.09202(16)</td>
<td>0.0714(16)</td>
</tr>
<tr>
<td>H(211)</td>
<td>-0.1752(2)</td>
<td>0.41702(12)</td>
<td>-0.03941(19)</td>
<td>0.0880(16)</td>
</tr>
<tr>
<td>H(221)</td>
<td>-0.2797(2)</td>
<td>0.30058(12)</td>
<td>-0.02776(19)</td>
<td>0.0873(16)</td>
</tr>
<tr>
<td>H(231)</td>
<td>-0.1528(2)</td>
<td>0.21631(11)</td>
<td>0.10381(17)</td>
<td>0.0779(16)</td>
</tr>
<tr>
<td>H(241)</td>
<td>0.07421(19)</td>
<td>0.24724(9)</td>
<td>0.22851(15)</td>
<td>0.0637(16)</td>
</tr>
</tbody>
</table>
Figure A-1: Crystal structure of di-DPBO showing 1 x 1 x 1 unit cell. View along the a axis.
APENDIX 2: LIQUID CRYSTAL CHARACTERISATION OF THPQ

**Figure A-7.1**: Melting transition of THPQ determined by DSC.

**Table A-4**: X-Ray Diffraction Data of THPQ.

<table>
<thead>
<tr>
<th>temperature (°C)</th>
<th>Miller index (hkl)</th>
<th>d-spacing (Å)</th>
<th>Lattice Constant (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>(100)</td>
<td>23.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(110)</td>
<td>13.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(200)</td>
<td>11.5</td>
<td></td>
</tr>
<tr>
<td>alkyl halo</td>
<td></td>
<td>4.5</td>
<td>27.1</td>
</tr>
<tr>
<td>π-π stacking</td>
<td></td>
<td>3.5</td>
<td></td>
</tr>
</tbody>
</table>