

The Synthesis and Characterisation of a Free-Base Porphyrin–Perylene Dyad that Exhibits Electronic Coupling in Both the Ground and Excited States

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Abstract: A covalent dyad composed of a free-base porphyrin and a perylene diimide (**1**) was synthesised and characterised by NMR, HRMS, UV/Vis and fluorometric methods. UV/Vis spectrophotometric analysis indicated a moderate coupling between the components in the ground state. Fluorescence spectroscopy revealed that the emissive properties of the dyad showed that the quantum yield of emission from the porphyrin Soret band increased dramatically and could not be rationalised by a straightforward photoinduced energy (and/or electron) transfer, but rather a coupling of excited states.

Keywords: dyes/pigments • energy conversion • fluorescence • porphyrinoids • UV/Vis spectroscopy

Introduction

The study of covalent and noncovalent photoactive dyads and triads continues to be of interest due to the structural and functional similarities these constructs share with the reaction centre within the photosystem of purple photosynthetic bacteria.^[1,2] These particular constructs have been studied due to their ability to donate and accept electrons upon the absorption of light and it is this ability that has potential applications in the field of solar-energy conversion.^[3,4]

We have recently embarked on a study of multichromophoric arrays in the hope that these constructs will be utilised to realise artificial photosynthetic devices. As part of our investigation toward the synthesis of multichromophoric supramolecular triads and ternary systems, we have synthesised a covalently bound dyad composed of a free-base porphyrin and a tetraarylperylene diimide.

Free-base porphyrin–perylene dyads have featured in previous studies with the majority of reports utilising an imide-type connection between the chromophores, facilitated by the reaction of an amino-functionalised porphyrin and a perylene anhydride.^[5,6] Comprehensive studies have also been

performed on porphyrin–perylene dyads formed through alkynyl linkages between the two chromophores.^[7–9] These particular modes of connections between chromophores in previously reported dyads caused the arrays to behave as a supposition of the individual dye molecules, as observed through absorption spectroscopy. Recently, we have synthesised and characterised a dyad composed of a free-base porphyrin and a perylene diimide, in which the two components are connected covalently through a methylene amide spacer, pictured in Figure 1. The presence of the methylene spacer in this dyad is a unique aspect and it is this particular feature as that extends unorthodox spectroscopic properties to this molecule.

The utility of the perylene chromophore in dyad **1** is two-fold in this construct. Firstly, the presence of the 3,5-di-*tert*-butylphenoxy groups increases the solubility of the dyad. This is important as both porphyrin and perylene diimide molecules with low substitution are notorious for possessing low solubilities in organic solvents, as a result of cofacial aggregation.^[10,11] Secondly, the high fluorescence quantum yield associated with the perylene diimide family of molecules ensures that photoinduced events initiated by the singlet state of the perylene should correspondingly occur with high quantum efficiency.^[12]

Results and Discussion

Synthesis of the free-base porphyrin perylene dyad 1: The synthesis of **1** was performed by the coupling of respective porphyrin (**5**) and perylene (**10**) units, the syntheses of

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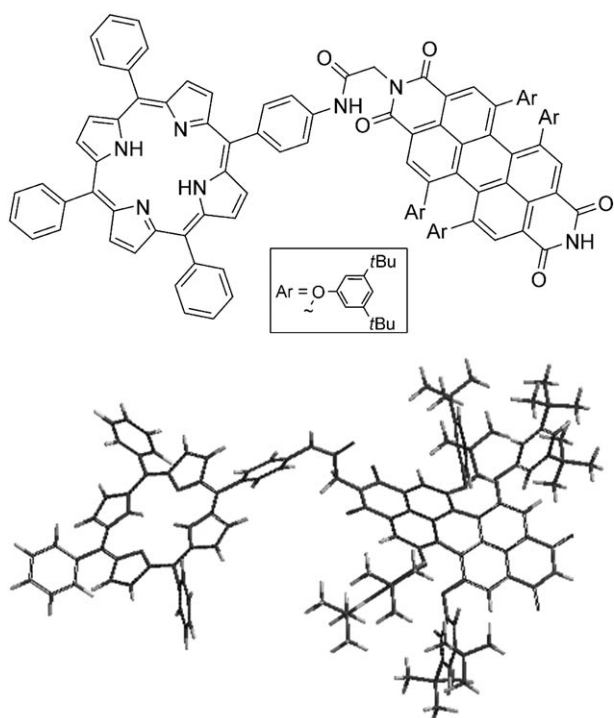
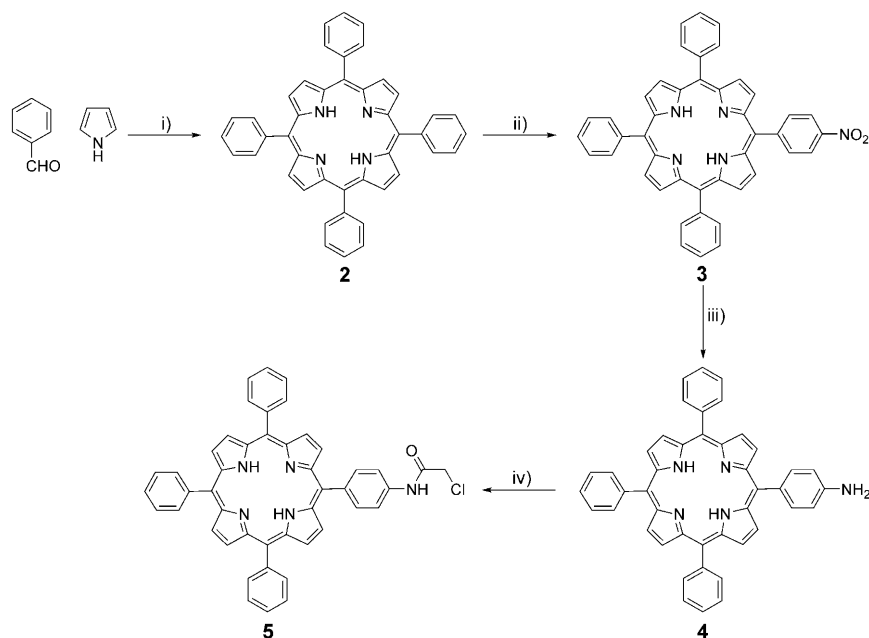


Figure 1. The schematic (top) and an AM1 optimised geometry (below) of the free-base porphyrin-perylene dyad **1**.

which are shown in Schemes 1 and 2. Porphyrin fragment **5** was synthesised by the regioselective mononitration and reduction of the tetraphenyl porphyrin **2**.^[13] This was followed by the acylation of **4** with chloroacetyl chloride, as shown in Scheme 1.



Scheme 1. The synthesis of porphyrin fragment **5**. Reaction conditions: i) propionic acid, reflux, 17%; ii) NaNO_2 , trifluoroacetic acid, 25 °C, 94%; iii) $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, conc. $\text{HCl}_{(\text{aq})}$, 80 °C, 27%; iv) 2-chloroacetyl chloride, CH_2Cl_2 , Et_3N , 25 °C, 97%.

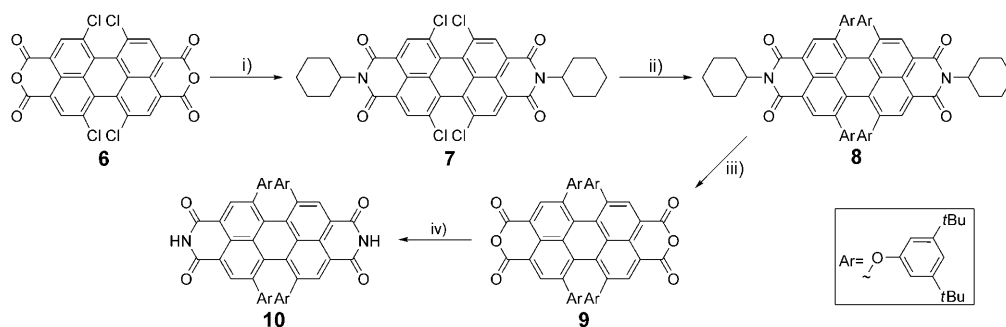
Perylene fragment **10** was synthesised over four steps, shown in Scheme 2, from the commercially available 1,6,7,12-tetrachloro-3,4:9,10-perylene dianhydride (**6**). Formation of the corresponding cyclohexyl diimide **7**, was followed by substitution of the halogen substituents of the perylene core by 3,5-di-*tert*-butylphenol/ K_2CO_3 in 1-methyl-2-pyrrolidone (NMP), affording the highly soluble tetraaryl-perylene diimide **8**.^[14] Anhydride **9** was formed by heating **8** in a solution of KOH in *tert*-BuOH/ H_2O . The desired perylene fragment **10** was synthesised by the imidation reaction of **9** by treatment with ammonium propionate in propionic acid at reflux.

The synthesis of dyad **1** was achieved by a nucleophilic substitution reaction between porphyrin **5** and the dianion of **10**, which was generated in situ by heating in NMP/ K_2CO_3 as outlined in Scheme 3. Slow addition of a solution of **5** in NMP and monitoring of the reaction by TLC ensured a reasonable yield (56%) of dyad **1**. The identity of **1** was confirmed by ^1H and ^{13}C NMR spectroscopy and high-resolution ESI-MS. Characterisation by UV/Vis and fluorescence spectroscopic methods were also performed and are discussed in the following section.

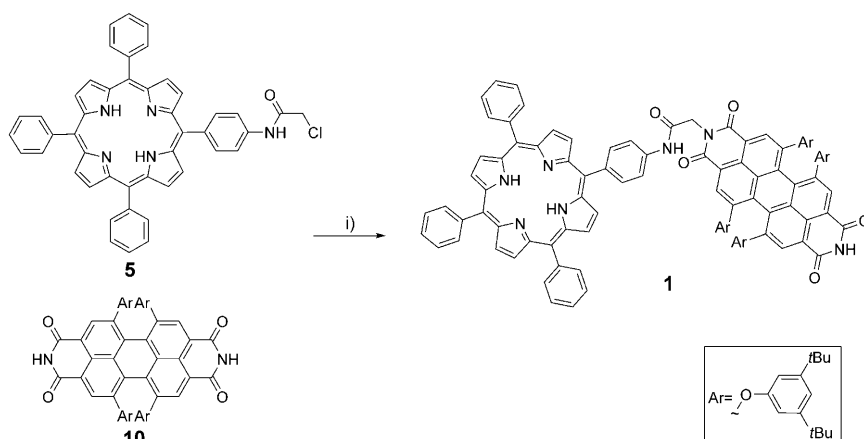
Spectrophotometric characterisation of dyad **1**

UV/Vis spectrophotometric analysis of dyad 1: The UV/Vis spectrum of **1**, along with that of porphyrin reference **2** and perylene reference **8**, are shown in Figure 2 and summarised in Table 1. The absorption spectrum of **1** possesses a porphyrin-derived Soret band at 420 nm and Q-bands at 519, 549 and 647 nm. A perylene-derived maximum at 590 nm is also apparent in the UV/Vis spectrum of **1**. The Soret absorption in porphyrin reference **2** appears at 418 nm and exhibits a molar absorptivity of $490\,000\text{ M}^{-1}\text{ cm}^{-1}$. Incorporation of a free-base porphyrin into dyad **1** causes red-shifting of the Soret band by 2 nm and a decrease of molar absorptivity to a value of $285\,000\text{ M}^{-1}\text{ cm}^{-1}$. In a similar manner, the Q-band of **2** at 650 nm exhibits a molar absorptivity of $5000\text{ M}^{-1}\text{ cm}^{-1}$ with the corresponding peak in the dyad experienced a blue shift of 3 nm and a decrease of molar absorptivity to $3000\text{ M}^{-1}\text{ cm}^{-1}$. Perylene reference **8** exhibits a maximum at 582 nm, but comparisons of molar absorptivities cannot be made due to an overlapping Q-band in the UV/Vis spectrum of **1**.

The reductions in the molar absorptivities of the absorption



Scheme 2. The synthesis of the perylene component **10**. Reaction conditions: i) cyclohexylamine, H₂O, reflux, 81 %; ii) 3,5-di-*tert*-butylphenol, K₂CO₃, NMP, 120 °C, 83 %; iii) KOH, H₂O, *tert*-BuOH, 98 %; iv) NH_{3(g)}, propionic acid, reflux, 87 %.



Scheme 3. The synthesis of dyad **1**. Reaction conditions: i) K₂CO₃, NaI, NMP, 80 °C, 56 %.

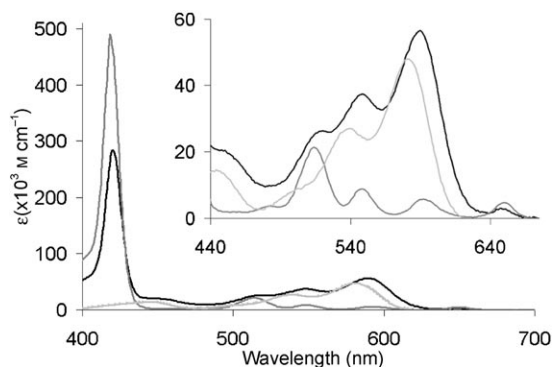


Figure 2. UV/Vis spectrum of **1** (black), **2** (dark grey), **8** (light grey) in toluene and enlargement of S₁ state transitions (inset).

bands in the UV/Vis spectra of dyad **1** and reference **2** are consistent with the presence of a ground-state interaction between electroactive components within the dyad.^[15] The width of the Soret band was analysed to further clarify the nature of the coupling. Events leading to aggregation can be identified by changes in the width and magnitude of the Soret absorption relative to **2**.^[16,17] As depicted in Figure 2, the Soret band of **1** exhibits no broadening behaviour, suggesting that the porphyrinic component exists in the monomeric form. Thus, it was concluded that the nature of the observed moderate coupling is a product of coupling between the porphyrin and perylene components of the dyad in the ground state.^[18]

Steady-state fluorometric analysis of dyad 1: The steady-state emission spectra of **1**, along with reference compounds **2** and **8** are presented in Figure 3 as well as Table 1. Excitation of solutions of the compounds in toluene at 585 nm allowed near-selective excitation (Abs₂/Abs₁ 12:1) of the perylene component within the dyad. Excitation of **1** at 585 nm resulted in a fluorescence spectrum with the maxima at 615 and 650 nm reminiscent of a perylene diimide. The slight shoulder at 720 nm in the emission spectrum of the dyad was assigned to emission from the free-base porphyrin within **1**. The perylene-derived fluorescence from **1** experienced quenching when compared to an optically matched solution of perylene reference compound **8**. Reference **8** produced an emission maximum at 606 nm, indicating that formation of the dyad was accompa-

Table 1. Absorbance and emission maxima with respective molar absorptivities and emission origins.

	1			2			3		
	λ [nm]	ϵ [M cm ⁻¹]		λ [nm]	ϵ [M cm ⁻¹]		λ [nm]	ϵ [M cm ⁻¹]	
absorbance maxima	420	276 000		418	490 000		444	4500	
	519	25 100		514	21 200		539	27 000	
	549	37 400		549	8700		582	48 000	
	590	56 500		592	5800				
	647	3000		650	4800				
emission maxima	615	perylene-type		653	porphyrin-type		606	perylene-type	
	660	porphyrin-type		719	porphyrin-type				

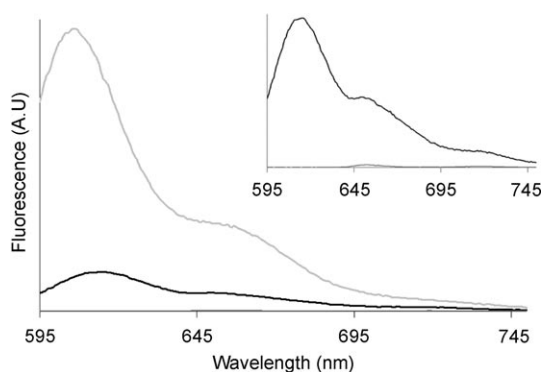


Figure 3. Emission spectrum of **1** (black, inset), **2** (dark grey, inset) and **8** (light grey) in toluene ($\lambda_{\text{em}} = 585$ nm) and enlargement of **1** and **2** (inset).

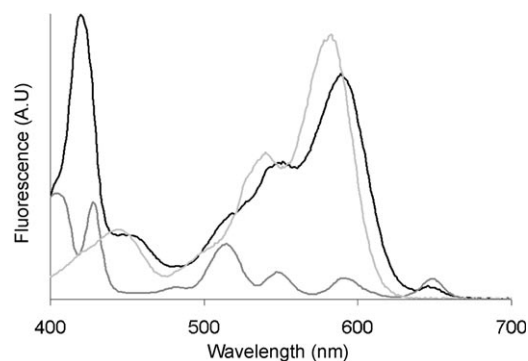


Figure 4. Excitation spectrum of **1** (black), **2** (dark grey) and **8** (light grey) in toluene ($\lambda_{\text{em}} = 715$ nm).

nied by a 9 nm red-shift in emission maximum. The emission spectrum of porphyrin reference **2** exhibited emission maxima at 653 and 719 nm. These maxima correlate well to the features of the lower energy emissions of **1** at 650 nm and the shoulder at 720 nm, respectively. The porphyrin-type emission from **1** is significantly enhanced when compared to the emission from an optically matched solution of reference compound **2**. The observation of fluorescence quenching of the perylene component and the corresponding enhancement of emission intensity from the porphyrin component of the dyad is indicative of excited-state coupling between the porphyrin and perylene components of the dyad. Thus the electronic coupling between chromophores identified in the UV/Vis spectrum of **1** is greater than indicated by the absorption spectrum, as the coupling regime extends into the excited state.

The blending of porphyrin and perylene excited states in **1** that yields an emission spectrum featuring the characteristic emission maxima of both components is possible if the observed porphyrinic emission intensity occurs at the expense of perylene emission intensity. The observation of decreased emission intensity from the perylene component of **1** is consistent with the occurrence of photoinduced energy transfer within the dyad.

Evidence of the moderate level of excitonic coupling was investigated further by obtaining excitation spectra by monitoring the emission intensity at 715 nm (corresponding to the maximum lowest energy emission from tetraphenylporphyrin) of **1**, **2** and **8** as depicted in Figure 4. Figure 4 shows that dyad **1** produced excitation maxima at 420, 551, 589 and 646 nm through reading the emission intensity at 715 nm. The peaks at 420, 551 and 646 nm clearly represent a contribution from the porphyrin (Soret and Q-band) absorptions within **1** as presented in Figure 4. The excitation spectrum of **2** possessed corresponding Soret and Q-band maxima at 428, 547 and 648 nm. The greatest difference between the excitation spectra of **1** and **2** are their respective emissions at 715 nm upon absorption of the Soret band. The ratio of excitation energy ($E_{\text{m1}}:E_{\text{m2}}$) provided by the Soret bands of **1** and **2** was calculated to be approximately 3:1. Thus, absorption by the Soret band in **1** gave a threefold

greater contribution to the porphyrin-derived emission at 715 nm than **2**, albeit the Soret absorption of **1** has a lowered molar absorptivity as ascertained from UV/Vis experiments. The contribution of the Soret band of **1** is in fact much larger than the additive contributions of **2** and **8** at 428 nm in producing emission at 715 nm. The excitation spectrum of the perylene reference **8** exhibits a maximum at 583 nm, correlating well to the perylene excitation maximum of **1** at 589 nm. In a similar fashion to the corresponding absorbance in the UV/Vis spectrum, formation of the dyad resulted in red-shifting of this perylene excitation maximum.

The observations from the excitation experiments indicate that dyad **1** emits with an enhanced quantum yield of fluorescence relative to **2**. The ground- and excited-state couplings between the components in **1** observed in the UV/Vis and fluorescence emission spectra allow the blending of emission properties to occur. As a result of the enhanced electronic interaction between the chromophores, the porphyrin component in **1** has adopted the high quantum yield characteristics of the perylene component at the porphyrinic Soret absorbance maximum.

The photoinduced behaviour of **1** is complex in nature, but explainable by the lowest lying excited state characteristics of the dyad being unified into a new single-quantum system. The changes in emission intensity in Figure 4 are not purely a product of photoinduced behaviour (photoinduced electron or energy transfer) between the two components within the dyad. A rationalisation of the degree of excitonic coupling observed in dyad **1** is depicted in Figure 5. The diagram shows two scenarios, one in which the coupling between components is strong and the compound behaves as a new single-quantum system (left) with the energy delocalised over the entire system. The other scenario depicted in Figure 5 is the weak coupling regime in which the electroactive components behave as separate entities (right), preserving their spectral properties and causing a photoinduced energy transfer from a donor to an acceptor.^[19] Although it has been proven that the components of **1** couple in the excited state, the excited state dynamics of dyad **1** is a median between these two depicted scenarios.

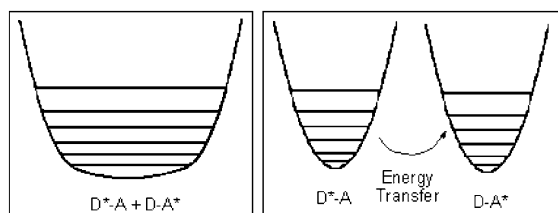


Figure 5. Depictions of the strong coupling regime (left) in which molecules in a dyad behave as a single quantum system and weak coupling (right) in which the molecules behave as separate entities (as observed spectroscopically).^[19]

The scenario between the two extreme cases in Figure 5 fits the photoinduced transitions observed in **1**. In the ground state of **1**, a weak interaction between electroactive centres of the dyad was established by UV/Vis spectroscopic analysis, but the lack of a charge-transfer band indicated that there was no significant electronic communication between the components. Upon absorption of light at 585 nm, **1** entered an excited state at which the moderate excitonic interaction caused partial delocalisation of energy over the whole system, resulting in diminished emission from the perylene component within the dyad is likely to originate from the corresponding blending of emission properties. The quenching can be rationalised through the blending of quantum yields for all the deactivation processes from both of the components. That is, although the emission from **1** is predominantly derived from the perylene component, the magnitude of the emission is dictated by a greater contribution by internal conversion and intersystem crossing contributions from the porphyrinic component of **1**. Likewise, the threefold enhancement of Soret absorption in the excitation spectrum of **1** (Figure 4) can be understood by the delocalisation of excitation energy across the whole molecule. This particular mode of photoinduced behaviour is highly unlikely if the dyad behaves as a superposition of the individual components and this is not the case for **1**. Similar observations have been made for the aggregation of molecules with the corresponding decrease in luminescence emission corresponding to increased phosphorescence.^[20]

Conclusion

A free-base porphyrin–perylene dyad possessing a unique methylene amide spacer has been synthesised and characterised. The spectroscopic properties of the dyad indicate the presence of appreciable levels of electronic coupling between the chromophores in both ground and excited states. Having studied the unusual spectrophotometric behaviour of the dyad, corresponding studies of a hybrid covalent/supramolecular triad can be performed utilising an appropriate hydrogen-bonded electron acceptor.^[21]

Experimental Section

1,6,7,12-Tetrachloro-3,4:9,10-perylene dianhydride (**6**) was purchased from Synthon Chemicals (Wolfen, Germany) and used without further purification. The remaining chemicals were purchased from Sigma-Aldrich. Chemicals were purified as recommended by Perrin^[22] and purified solvents for chromatography were stored under 4 Å molecular sieves. Thin-layer chromatography (TLC) was performed on pre-coated sheets of Merck silica gel 60 and visualised using UV light (254 nm). Column chromatography was carried out under a positive pressure of nitrogen using Merck silica gel (230–400 mesh). NMR spectra were acquired on a Varian Gemini 300 MHz spectrometer by using standard pulse sequences. Spectra were recorded at 298 K in CDCl₃ unless otherwise stated. Chemical shifts (δ) are reported as parts per million (ppm) with respect to tetramethylsilane (TMS) or CDCl₃. Abbreviations used in assigning spectra include: s, singlet; brs, broad singlet; d, doublet; t, triplet; q, quartet and m, multiplet. The assignments observed in various NMR data were confirmed by homonuclear (¹H–¹H) correlation spectroscopy (COSY) and heteronuclear (¹H–¹³C) correlation spectroscopy (HETCOR) when required. HRMS acquired at Monash University (Melbourne, Australia) by using electrospray ionisation (ESI-MS) or laser desorption/ionisation time-of-flight (LDI-ToF-MS) mass spectrometry. ESI-MS was performed on a Micromass Quattro II Triple-Quadrupole mass spectrometer. LDI-ToF-MS was performed on an Applied Biosystems Voyager-DE STR BioSpectrometry Workstation. The instrument was operated in positive-ion mode with the reflectron enabled for high-resolution analysis. Sample was spotted on a stainless steel sample plate and allowed to air dry. Data from 500 laser shots (337 nm nitrogen laser) were collected, signal averaged and processed with the provided Data Explorer software. UV/Vis experiments were performed at an ambient temperature of 25 °C by using a Varian Cary 50 Scan Spectrophotometer. The samples were analysed in a Quartz cuvette obtained from Starna Pty. Steady-state fluorescence experiments were conducted on a Varian Cary Eclipse fluorescence spectrophotometer equipped with a Varian single cell Peltier accessory used in conjunction with a Gilson MINIPULS3 peristaltic pump to aid temperature control of the sample. The samples were held in a quartz cuvette obtained from Sigma-Aldrich and stirred with a magnetic flea. Melting points were obtained on a Reichart hot-stage apparatus and are uncorrected. Calculations were performed on Spartan'02 for Macintosh by using the semi-empirical AM1 method.

5-(p-Chloroacetamidophenyl)-10,15,20-triphenylporphyrin (5): Compound **4** (63 mg, 0.1 mmol) was dissolved in Et₃N (1 mL) and CH₂Cl₂ (12.5 mL) under an atmosphere of nitrogen. Chloroacetyl chloride (0.105 mmol, 8.4 μ L) was added and the solution stirred for 1 h. Chloroacetyl chloride (1.26 mmol, 100 μ L) was added dropwise and the solution stirred for a further 2 h. The solvent was evaporated and the crude product subjected to column chromatography (silica, hexane then 1:2 EtOAc/hexane then 1:1 EtOAc/hexane) to afford the desired product (69 mg, 97%) as a purple solid. M.p > 300 °C; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = –2.73 (brs, 2H; NH), 4.35 (s, 2H; CH₂), 7.76–7.80 (m, 9H; Ar-H), 7.95 (d, *J* = 8.6 Hz, 2H; Ar-H), 8.22–8.28 (m, 8H; Ar-H), 8.58 (brs, 1H; NH), 8.90 ppm (s, 8H; β -H); ¹³C NMR (75 MHz, CDCl₃, 25 °C, TMS): δ = 43.01, 118.27, 119.08, 120.21, 120.26, 126.68, 127.72, 131.13, 134.53, 135.13, 136.40, 139.08, 142.08, 164.11 ppm; HRMS (ESI): *m/z* calcd for C₄₆H₃₃ClN₅O⁺ [*M*+H]⁺: 706.2368; found: 706.2366.

N,N'-Dicyclohexyl-1,6,7,12-tetrachloro-3,4:9,10-perylenediimide (7): Compound **6** (1 g, 2.0 mmol) and water (25 mL) were combined and, with vigorous stirring, cyclohexylamine (5 mL, 4.34 g, 43 mmol) was added dropwise. The resulting solution was heated to reflux for 10 h with stirring. After cooling, the solution was diluted with water (100 mL) and filtered onto a G4 sintered funnel. The solids were washed with water (50 mL) and dried in an oven at 85 °C for 15 h to afford the product as an orange solid (1.12 g, 81%). ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): δ = 1.31–1.94 (m, 16H; CH₂), 2.52 (m, 4H; CH₂), 5.02 (t, *J* = 12 Hz, 2H; CH), 8.63 ppm (s, 4H; pery-H); ¹³C NMR (75 MHz, CDCl₃, 25 °C, TMS): δ = 25.32, 26.47, 29.03, 29.09, 54.46, 123.32, 123.77, 128.37, 131.39, 132.87, 135.28, 152.62, 162.63 ppm.

N,N'-Dicyclohexyl-1,6,7,12-tetrakis(3,5-di-*tert*-butylphenoxy)-3,4:9,10-perylene diimide (8): Compound **7** (1.2 g, 1.73 mmol), anhydrous K_2CO_3 (2.61 g, 18.9 mmol) and 3,5-di-*tert*-butylphenol (3.63 g, 17.4 mmol) were combined in dry NMP (87 mL) under an inert atmosphere. The solution was heated to 120°C for 48 h (endpoint by TLC silica, $CHCl_3$). The solution was cooled and filtered through a G4 sintered funnel and the remaining solids stirred in water (200 mL). The product was filtered onto a G4 sintered funnel, washed with water and dried in an oven at 85°C overnight to give the pure product (1.97 g, 83%). 1H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 1.14 (s, 72H; CH_3), 1.2–2.0 (m, 16H; CH_2), 2.43 (m, 4H; CH_2), 4.92 (m, 2H; CH), 6.82 (d, J = 1.5 Hz, 8H; Ar-H), 7.14 (t, J = 1.5 Hz, 4H; Ar-H), 8.05 ppm (s, 4H; pery-H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ = 25.40, 26.49, 29.08, 31.27, 34.82, 53.79, 115.12, 118.47, 119.00, 119.59, 112.77, 132.83, 152.78, 154.39, 156.79, 163.91 ppm; UV/Vis (toluene): $\lambda_{max}(\epsilon)$ = 582 (48000), 539 (27000), 444 nm ($14000\text{ mol}^{-1}\text{ m}^3\text{ cm}^{-1}$); HRMS (ESI): m/z calcd for $C_{69}H_{14}NaO_4^+$ [$M+Na$] $^+$: 1393.8151; found: 1393.8154.

1,6,7,12-Tetrakis(3,5-di-*tert*-butylphenoxy)-3,4:9,10-perylene dianhydride (9): Compound **8** (0.892 g, 0.65 mmol) was added to *tert*-butanol (52.7 mL), potassium hydroxide (5.27 g, 80 mmol) and water (2.6 mL) and the resulting solution refluxed for 25 h. Hydrochloric acid (2N, 53 mL) was added to the cooled solution and stirring was continued for 6 h. The precipitate was filtered onto a G4 sintered funnel and washed thoroughly with water then dried at 85°C overnight to afford the anhydride as a red powder (770 mg, 98%). 1H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 1.15 (s, 72H; CH_3), 6.81 (d, J = 1.5 Hz, 8H; Ar-H), 7.19 (t, J = 1.5 Hz, 4H; Ar-H), 8.09 ppm (s, 4H; pery-H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ = 31.24, 34.91, 114.93, 118.50, 119.62, 120.30, 120.79, 121.11, 133.51, 153.27, 154.01, 157.17, 159.94 ppm; HRMS (ESI): m/z calcd for $C_{81}H_{93}O_{11}^+$ [$M+MeOH+H$] $^+$: 1241.6712; found: 1241.6720.

1,6,7,12-Tetrakis(3,5-di-*tert*-butylphenoxy)-3,4:9,10-perylene diimide (10): Compound **9** (291 mg, 0.240 mmol) was dissolved in propionic acid (15 mL) and anhydrous ammonia (2.01 g) was bubbled into the reaction. After sustaining the mixture overnight at reflux, the solution was cooled, hydrochloric acid (1N, 15 mL) was added and the mixture stirred for 8 h. The solids were filtered onto a G4 sintered funnel, washed with water and dried in an oven at 85°C. The solids were dissolved in minimal CH_2Cl_2 and separated by column chromatography (silica, 30% EtOAc/ CH_2Cl_2) to afford the desired product (251 mg, 87%) as a crimson solid. 1H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 1.15 (s, 72H; CH_3), 6.81 (d, J = 1.8 Hz, 8H; Ar-H), 7.16 (t, J = 1.8 Hz, 4H; Ar-H), 8.09 (s, 4H; pery-H), 8.38 ppm (brs, 2H; NH); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ = 31.27, 34.88, 114.99, 118.42, 119.21, 120.25, 122.19, 152.96, 154.31, 156.76, 163.05 ppm; HRMS (ESI): m/z calcd for $C_{80}H_{91}N_2O_8^+$ [$M+H$] $^+$: 1207.6769; found: 1207.6766.

Free-base porphyrin–perylene dyad (1): Compound **10** (100 mg, 0.08 mmol) was dissolved in NMP (10 mL) with K_2CO_3 (100 mg, 0.72 mmol) and NaI (100 mg, 0.67 mmol) at 80°C for 1 h under an inert atmosphere. Compound **5** (51 mg, 0.07 mmol) in NMP (5 mL) added dropwise over the course of 2 h. The reaction mixture was poured into water (200 mL) and extracted with toluene (5 × 20 mL). The organic extracts were washed with water (5 × 100 mL) dried (Na_2SO_4) and solvent evaporated. Chromatography (silica, hexane then 1:2 EtOAc/hexane then 1:1 EtOAc/hexane) afforded the product (73 mg, 56%) as a purple solid. M.p. > 300°C; 1H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = −2.80 (brs, 1H; NH), 1.17 (s, 36H; CH_3), 1.19 (s, 36H; CH_3), 5.00 (d, J = 15 Hz, 1H; CH_2), 5.19 (d, J = 15 Hz, 1H; CH_2), 6.87 (d, J = 1.5 Hz, 4H; Ar-H), 6.88 (d, J = 1.5 Hz, 4H; r-H), 7.19 (t, J = 1.5 Hz, 8H; Ar-H), 7.20 (t, J =

1.5 Hz, 2H; Ar-H), 7.68–7.78 (m, 9H; Ar-H), 7.87 (d, J = 8.6 Hz, 2H; Ar-H), 8.04 (brs, 1H; NH), 8.13 (d, J = 8.6 Hz, 2H; Ar-H), 8.15 (s, 2H; pery-H), 8.17–8.22 (m, 6H; Ar-H), 8.23 (s, 2H; pery-H), 8.54 (brs, 1H; NH), 8.82 (s, 4H; β -H), 8.84 ppm (s, 4H; β -H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C, TMS): δ = 31.28, 31.30, 34.88, 34.90, 114.98, 115.13, 117.94, 118.50, 119.14, 119.28, 119.41, 120.10, 120.18, 126.63, 127.66, 130.99, 133.06, 133.30, 134.50, 135.00, 137.18, 138.18, 142.09, 152.91, 152.98, 154.19, 154.35, 156.76, 156.97, 163.15, 163.59, 165.35 ppm; UV/Vis (toluene): $\lambda_{max}(\epsilon)$ = 590 (57000), 549 (37000), 520 (26000), 420 nm ($284000\text{ mol}^{-1}\text{ m}^3\text{ cm}^{-1}$); HRMS (ESI): m/z calcd for $C_{126}H_{122}N_7O_9^+$ [$M+H$] $^+$: 1876.9299; found: 1876.9286.

- [1] M. R. Wasielewski, *Chem. Rev.* **1992**, 92, 435–461.
- [2] D. Gust, T. A. Moore, A. L. Moore, *Acc. Chem. Res.* **2001**, 34, 40–48.
- [3] T. Hasobe, H. Imahori, P. V. Kamat, T. K. Ahn, S. K. Kim, D. Kim, A. Fujimoto, T. Hirakawa, S. Fukuzumi, *J. Am. Chem. Soc.* **2005**, 127, 1216–1228.
- [4] A. Kotiaho, R. M. Lahtinen, N. V. Tkachenko, A. Efimov, A. Kira, H. Imahori, H. Lemmetyinen, *Langmuir* **2007**, 23, 13117–13125.
- [5] C.-C. You, F. Wuerthner, *Org. Lett.* **2004**, 6, 2401–2404.
- [6] J. L. Hua, F. Ding, F. S. Meng, H. Tian, *Chin. Chem. Lett.* **2004**, 15, 1373–1376.
- [7] S. Prathapan, S. I. Yang, J. Seth, M. A. Miller, D. F. Bocian, D. Holten, J. S. Lindsey, *J. Phys. Chem. B* **2001**, 105, 8237–8248.
- [8] S. I. Yang, S. Prathapan, M. A. Miller, J. Seth, D. F. Bocian, J. S. Lindsey, D. Holten, *J. Phys. Chem. B* **2001**, 105, 8249–8258.
- [9] S. Ik Yang, R. K. Lammi, S. Prathapan, M. A. Miller, J. Seth, J. R. Diers, D. F. Bocian, J. S. Lindsey, D. Holten, *J. Mater. Chem.* **2001**, 11, 2420–2430.
- [10] G. Seybold, G. Wagenblast, *Dyes Pigm.* **1989**, 11, 303–317.
- [11] J. S. Lindsey, R. W. Wagner, *J. Org. Chem.* **1989**, 54, 828–836.
- [12] H. Langhals, W. Jona, *Angew. Chem.* **1998**, 110, 998–1001; *Angew. Chem. Int. Ed.* **1998**, 37, 952–955.
- [13] R. Luguia, L. Jaquinod, F. R. Fronczek, M. G. H. Vicente, K. M. Smith, *Tetrahedron* **2004**, 60, 2757–2763.
- [14] D. Dotcheva, M. Klapper, K. Muellen, *Macromol. Chem. Phys.* **1994**, 195, 1905–1911.
- [15] G. Hungerford, M. Van Der Auweraer, D. B. Amabilino, *J. Porphyrins Phthalocyanines* **2001**, 5, 633–644.
- [16] K. Procházková, Z. Zelinger, K. Lang, P. Kubat, *J. Phys. Org. Chem.* **2004**, 17, 890–897.
- [17] D. L. Akins, H.-R. Zhu, C. Guo, *J. Phys. Chem.* **1996**, 100, 5420–5425.
- [18] L. Flamigni, N. Armaroli, F. Barigelletti, J.-C. Chambron, J.-P. Sauvage, N. Solladie, *New J. Chem.* **1999**, 23, 1151–1158.
- [19] M. F. García-Parajó, J. Hernando, G. S. Mosteiro, J. P. Hoogenboom, E. M. H. P. van Dijk, N. F. van Hulst, *ChemPhysChem* **2005**, 6, 819–827.
- [20] E. G. McRae, M. Kasha, *J. Chem. Phys.* **1958**, 28–26, 721–722.
- [21] S. Mathew, M. R. Johnston, unpublished results.
- [22] D. D. Perrin, W. L. F. Armarego, D. R. Perrin, *Purification of Laboratory Chemicals*, Pergamon Press, Oxford, **1966**, p. 370.

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