

# New peripherally-substituted naphthalocyanines: synthesis, characterisation and evaluation in dye-sensitised photoelectrochemical solar cells

Xiyou Li, Nicholas J. Long,\* John N. Clifford, Colin J. Campbell and James R. Durrant

Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London, UK SW7 2AY. E-mail: n.long@ic.ac.uk

Received (in London, UK) 4th February 2002, Accepted 14th May 2002

First published as an Advance Article on the web 26th June 2002

A series of novel tetra-substituted naphthalocyanines featuring hydroxy and carboxylate substituents in peripheral positions have been synthesised in reasonable yields and characterised by spectroscopic techniques. The photochemical properties of the tetra-acid derivative **7** were examined following immobilisation on a nanocrystalline TiO<sub>2</sub> surface and photoinduced dye cations were observed following optical excitation. **7** has a redox potential of 0.25 V (*vs.* Ag/AgCl), which is lower than is required for an efficient regeneration reaction and, therefore, results in limited photocurrent flow when **7** is used in photoelectrochemical solar cells.

## Introduction

Although the first preparation of metal naphthalocyanines (MNC) was reported in 1936,<sup>1</sup> there is still only limited chemical and physical data on these compounds, especially when compared to phthalocyanines (Pc). Nc are of interest because of the extension of the  $\pi$ -electron system, compared to Pc, which can effectively modify the optical spectra and other electronic properties such as redox potentials, electrical conductivity, photoconductivity and catalytic activity.<sup>2</sup> In unsubstituted Nc preparation, 1,2- and 2,3-dicyanonaphthalenes can be used as starting materials, though the former species will give rise to up to four isomers.<sup>3</sup> To avoid any difficulties associated with isomerism, the 2,3- starting material can be utilised.<sup>4</sup> (1,2-Naphthalocyaninato)iron(II) has been prepared and one of the isomers structurally characterised,<sup>5</sup> further derivatisation was carried out *via* axial substitution.<sup>6</sup> Other peripherally-substituted Nc (R = OC<sub>5</sub>H<sub>11</sub>) have been widely applied, most notably as IR-absorbing dyes.<sup>7–11</sup> A good deal of effort has also been directed towards the study of nonlinear optical (NLO) properties of Nc, *e.g.* InNc has a Q-band shifted to the near IR region at 800 nm, with a transmission window at 530–650 nm.<sup>12</sup> Axially-<sup>13</sup> and peripherally-substituted<sup>14</sup> Nc exhibit large third-order nonlinearities.

We are interested in dye-sensitised nanocrystalline solar cells as low cost alternatives to conventional solid-state photovoltaic devices.<sup>15</sup> Since phthalocyanines and naphthalocyanines give rise to intense absorption bands in the near IR region and, along with their excellent stability, this renders them attractive for photovoltaic applications.<sup>16</sup> We can now report (i) the synthesis of some novel peripherally- and tetra-substituted Nc featuring hydroxy and carboxylate substituents, and (ii) the first evaluation, as far as we are aware, of a naphthalocyanine dye in a photoelectrochemical solar cell *via* immobilisation on nanocrystalline TiO<sub>2</sub> and analysis of the electrochemical and photochemical properties.

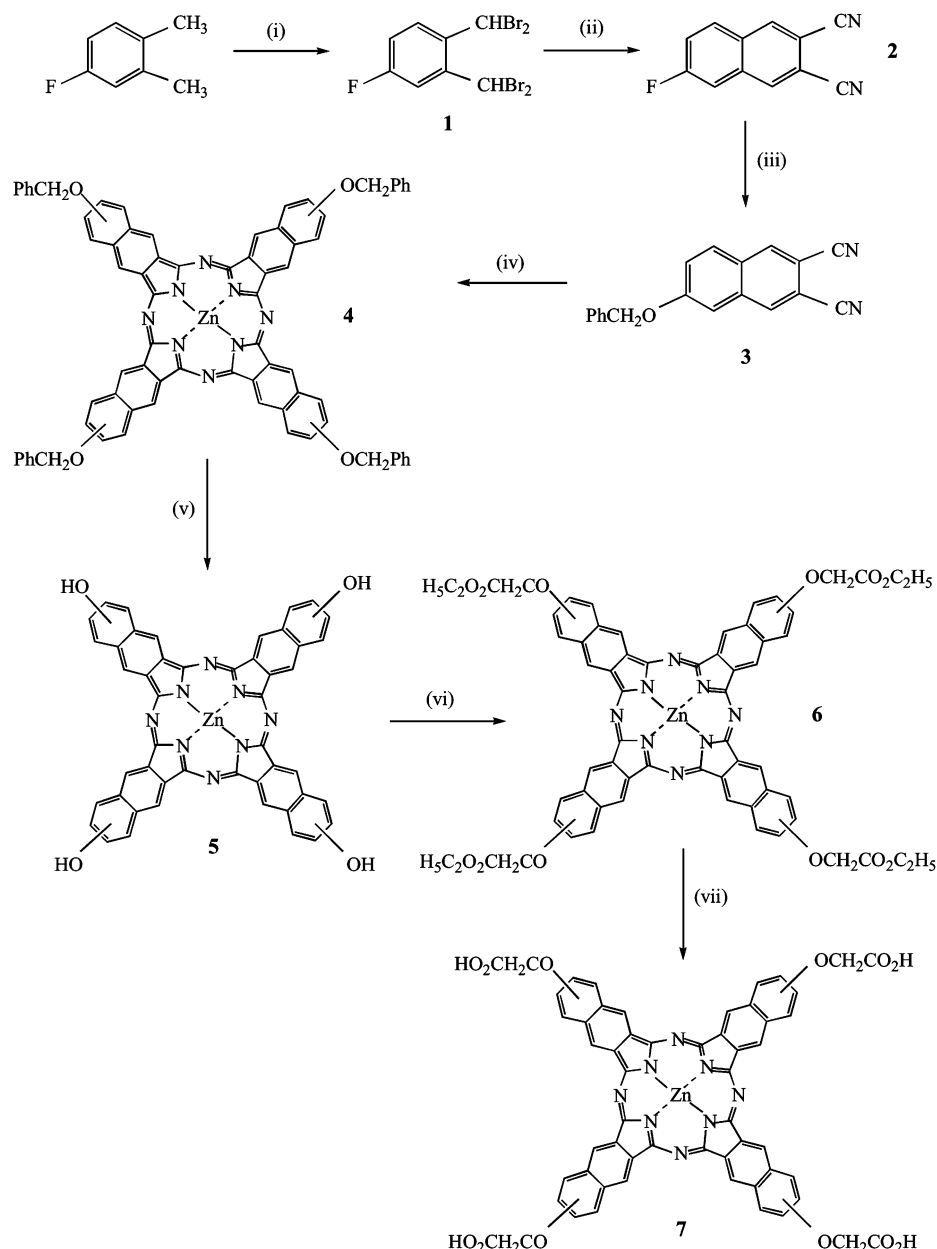
## Results

### Synthesis

Compound **1** was prepared from the bromination of 4-fluoroxylene (Scheme 1). A literature method<sup>9</sup> indicated that the reaction was efficiently carried out in the presence of *N*-bromosuccinimide. We found that the reaction was very slow and there was an incomplete bromination of starting material. However, irradiation with UV light along with reflux of the solution for 17 h enabled isolation of the product, after column chromatography (silica gel, hexane eluant), in good yield (60%). Compound **2** was synthesised following literature methods,<sup>10,17</sup> but using anhydrous sodium iodide and heating the reaction mixture at 70 °C for 18 h. This gave the off-white product in 95% yield. **2** was then treated with potassium carbonate and benzyl alcohol under N<sub>2</sub> and, after 72 h, the crude residue purified by column chromatography (silica gel, dichloromethane eluant). The product **3** was removed as the first fraction in 35% yield and characterised by <sup>1</sup>H NMR and mass spectrometry.

The cyclisation of **3** with zinc acetate in *n*-pentanol and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) resulted in the formation of **4**. The crude residue was washed thoroughly with methanol and subjected to column chromatography (silica gel, chloroform eluent), whereby a green fraction was collected and evaporated to dryness to give the product in 26% yield. Mass spectrometry (+ve FAB) showed the expected molecular ion and UV-vis spectroscopy indicated formation of the naphthalocyanine (Q-band at 765 nm, Soret band 330 nm).

Deprotection of the benzoxyl groups was effected by adding **4** to trifluoroacetic acid and tetramethylbenzene, followed by reflux of the solution. The crude residue was repeatedly washed with dichloromethane, and **5** was finally isolated *via* reprecipitation from THF and dichloromethane. Again, mass spectrometry indicated the presence of the molecular ion. To aid solubility and purification, the hydroxy substituents were replaced by ethyl acetate units *via* the reaction of **5** with ethyl



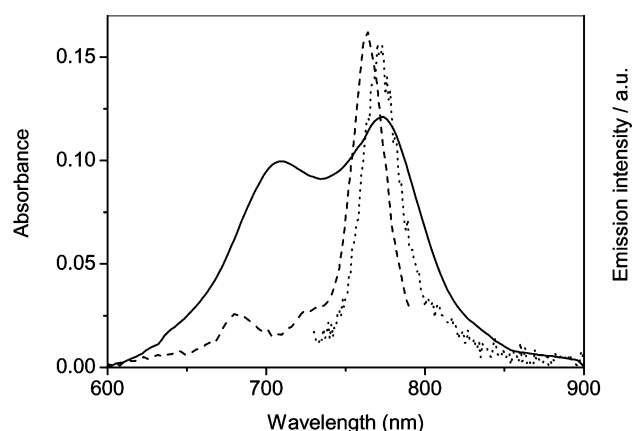
**Scheme 1** Reagents and conditions: (i) *N*-bromosuccinimide, AIBN,  $\text{CCl}_4$ , reflux, UV irradiation, 17 h; (ii) fumaronitrile, NaI, THF,  $70^\circ\text{C}$ , 18 h; (iii) benzyl alcohol,  $\text{K}_2\text{CO}_3$ , DMF,  $60^\circ\text{C}$ , 72 h; (iv)  $\text{Zn}(\text{OAc})_2$ , DBU, *n*-pentanol,  $80^\circ\text{C}$ ,  $\text{N}_2$ , 16 h; (v) trifluoroacetic acid, tetramethylbenzene, reflux, 16 h; (vi) ethylchloroacetate,  $\text{K}_2\text{CO}_3$ , DMF,  $60^\circ\text{C}$ ,  $\text{N}_2$ , 24 h; (vii) KOH (aq), THF, 3 h, then HCl (aq).

chloroacetate and potassium carbonate in DMF. The crude residue was washed thoroughly with methanol and purified by column chromatography on silica gel with chloroform–methanol (95:5) as eluent. A green fraction containing the product in 42% yield was isolated and fully characterised.

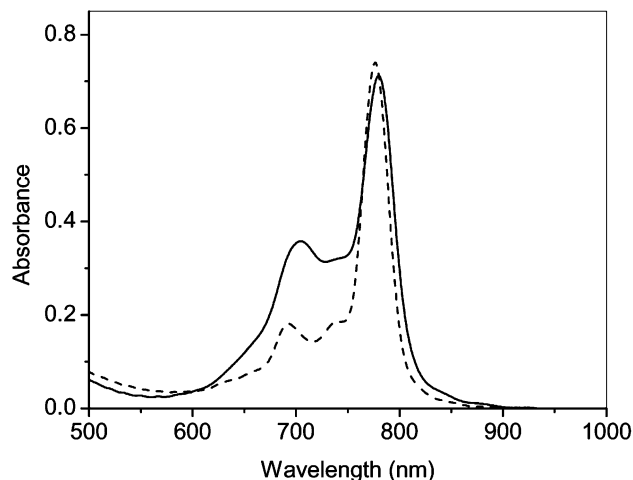
Finally, a THF solution of **6** was added to a solution of KOH in water. After stirring for 3 h, followed by acidification, a green solid, **7**, formed and was collected by filtration. This was dried and isolated in 61% yield, and characterised by mass spectrometry (high resolution), and IR and UV-vis spectroscopies.

#### Steady-state spectroscopy

The carboxylated Zn Nc **7** showed a strong tendency to aggregate in solution. Fig. 1 shows typical steady-state electronic absorption, excitation and emission spectra of **7** in DMF. The steady-state absorption spectra exhibits a broad band in the near infrared, with maxima at 700 and 780 nm, characteristic of extensive dye aggregation. In contrast, the fluorescence



**Fig. 1** Steady-state absorption (—), fluorescence excitation (---) and fluorescence emission (···) spectra of **7** in DMF. The excitation spectrum was recorded after excitation at 770 nm. The emission spectrum was recorded after excitation at 730 nm. Excitation and emission were normalised for comparative purposes.



**Fig. 2** Steady-state absorption spectra of **7** immobilised on 4  $\mu\text{m}$   $\text{TiO}_2$  film following sensitisation in a DMF solution only (—) and in a DMF solution with 15% 4-*tert*-butylpyridine, 5% DMSO and 75 mM 3 $\alpha$ ,7 $\alpha$ -dihydroxy-5 $\beta$ -cholic acid (---).

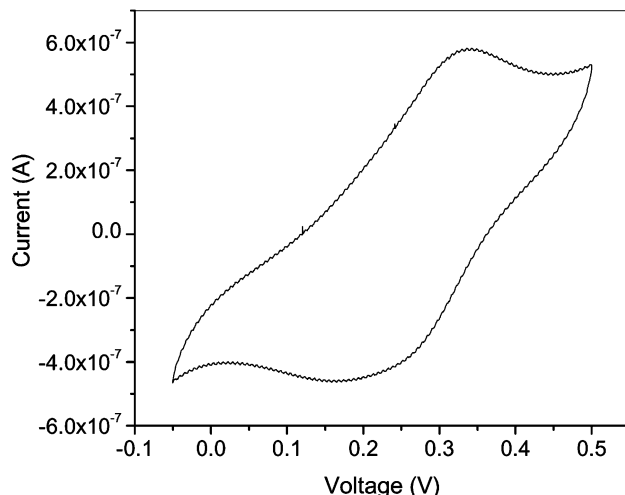
excitation and emission of this solution show spectra characteristic of monomeric Nc dyes. We conclude that, in this solution, the dye consists primarily as molecular aggregates, with a smaller proportion of monomeric dyes. The fluorescence of the molecular aggregates appears to be strongly quenched, as is typical of such aggregates. The fluorescence of the monomeric dyes is, however, not quenched and these dyes therefore dominate the observed excitation and emission spectra. Immobilisation of **7** on nanocrystalline  $\text{TiO}_2$  films was readily achieved by immersion of the unsensitised film in the dye solution for 3–4 h. Fig. 2 shows the electronic absorption spectra of **7** immobilised on nanocrystalline  $\text{TiO}_2$  film after exposure to two different sensitising solutions. It is apparent that the absorption spectrum of the dye immobilised on the nanocrystalline  $\text{TiO}_2$  film shows significantly less aggregation than that observed in solution. Aggregation of the immobilised dye was further reduced by the inclusion of 4-*tert*-butylpyridine, DMSO and 3 $\alpha$ ,7 $\alpha$ -dihydroxy-5 $\beta$ -cholic acid in sensitising solutions, as has been reported previously for the immobilisation of phthalocyanine sensitisers.<sup>18</sup> Under these sensitising conditions, the absorption spectrum appears to be that of monomeric dye, and is indistinguishable from the solution fluorescence excitation spectrum shown in Fig. 1.

### Solution electrochemistry

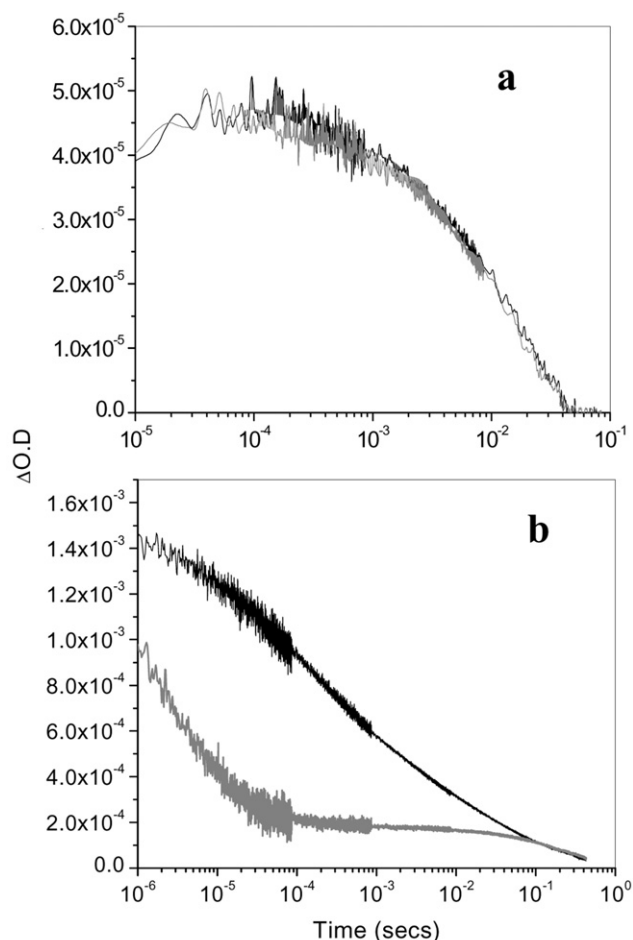
Electrochemical investigations of **7** were carried out in 0.1 M tetrabutylammonium perchlorate (TBAP) in DMF at a scan rate of 5  $\text{mV s}^{-1}$  (see Experimental). Fig. 3 shows a voltammogram for the oxidation of **7** under these conditions, showing reversible electrochemistry with oxidation and reduction peaks at 0.3 and 0.2 V *vs.* Ag/AgCl, respectively. We conclude that the dye/dye<sup>+</sup> mid-point potential of **7** is 0.25 V *vs.* Ag/AgCl. Comparison with the excitation and emission spectra shown in Fig. 1 indicates an excited-state oxidation potential for dye\*/dye<sup>+</sup> of –1.4 V *vs.* Ag/AgCl.

### Transient absorption spectroscopy

Transient absorption spectroscopy was employed to assess the ability of **7** to sensitise the nanocrystalline  $\text{TiO}_2$  to visible irradiation. Following pulsed laser excitation of the immobilised dye at 450 nm, a long-lived transient absorption signal was observed throughout the visible/near infrared. Typical data, at a probe wavelength of 850 nm are shown in Fig. 4(a). The spectrum of this signal is characteristic of the formation of Nc cation species, exhibiting a narrow ground-state bleach



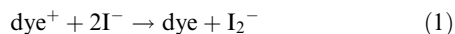
**Fig. 3** Cyclic voltammogram of **7** in 0.1 M TBAP in DMF at a scan rate of 5  $\text{mV s}^{-1}$ .



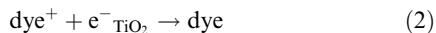
**Fig. 4** Transient absorption data monitoring charge recombination dynamics for  $\text{TiO}_2$  films sensitised with **7** (a) and  $[\text{Ru}(\text{dcbpy})_2(\text{NCS})_2]$  (b) in propylene carbonate solutions with 0.1 M  $\text{LiClO}_4$  (black) and 0.1 M  $\text{LiI}$  (grey). Probe wavelengths were 800 and 850 nm for  $[\text{Ru}(\text{dcbpy})_2(\text{NCS})_2]$  and **7**, respectively.

signal at 780 nm superimposed on a broad induced absorption assigned to photoinduced dye cation absorption (data not shown). No signal was observed for **7** in solution. This signal is therefore assigned to dye cations generated by photoinduced electron injection into the  $\text{TiO}_2$ .

In dye-sensitised photoelectrochemical cells, the dye ground state is typically regenerated from the photoinduced dye cation by the inclusion of iodide ions in the electrolyte ( $k_{RR}$ ):



For an efficient photoelectrochemical cell, this regeneration must compete effectively with the wasteful charge recombination reaction between the oxidised dye and electrons injected into the  $\text{TiO}_2$  ( $\text{e}^-_{\text{TiO}_2}$ ),  $k_{CR}$ :



The efficiency of the regeneration reaction can be monitored by transient optical spectroscopy, as we have shown previously<sup>19</sup> and as is illustrated in Fig. 4(b) for  $\text{TiO}_2$  films sensitised by the well-established sensitizer dye *cis*-[Ru<sup>II</sup>(dcbpy)<sub>2</sub>(NCS)<sub>2</sub>]- (dcbpy = 2,2'-bipyridyl-4,4'-dicarboxylate). In the absence of iodide ions in the electrolyte, a long-lived signal is observed and assigned to dye cation absorption. This signal decays with a half time,  $t_{50\%}$ , of 0.4 ms due to the charge recombination reaction  $k_{CR}$ . Following the addition of 0.1 M  $\text{I}^-$  to the electrolyte, the decay becomes biphasic. The fast phase ( $t_{50\%} \sim 4$   $\mu\text{s}$ ) has been assigned to the regeneration reaction  $k_{RR}$ . The slow phase has been assigned to  $\text{I}_2^-$  species generated by this regeneration reaction. It can be concluded that an efficient regeneration reaction  $k_{RR}$  in the presence of iodide ions can be monitored both by the detection of a large reduction in the lifetime of the dye cation photoinduced absorption and/or by the observation of long-lived  $\text{I}_2^-$  product species.

Comparison of Fig. 4(a) and (b) indicates that, in contrast to the data observed for the efficient sensitizer dye [Ru(dcbpy)<sub>2</sub>(NCS)<sub>2</sub>], the data observed for the  $\text{TiO}_2$  films sensitised with dye **7** are independent of the presence of iodide ions in the electrolyte, with a  $t_{50\%}$  of 8 ms. We conclude that, for dye **7**, the regeneration reaction  $k_{RR}$  is unable to compete effectively with the recombination reaction  $k_{CR}$ .

## Discussion

We have demonstrated the synthesis of a novel carboxylated naphthalocyanine dye and its immobilisation on a nanocrystalline  $\text{TiO}_2$  electrode. The strong red/near infrared absorption of this dye makes it, in principle, attractive as a sensitizer dye for dye-sensitised photoelectrochemical solar cells, complementing the strong blue/green absorption of existing efficient sensitising dyes.<sup>20</sup>

Following optical excitation of the immobilised dye, photoinduced dye cations are observed, attributed to electron injection into the  $\text{TiO}_2$  electrode. Such electron injection is consistent with the  $-1.4$  V excited-state oxidation mid-point potential determined for this dye from solution phase electrochemistry and spectroscopy, this potential being typical of that for other dyes employed successfully in dye-sensitised photoelectrochemical solar cells. We note, however, that the magnitude of the transient signals attributed to dye **7** cation formation was significantly smaller ( $> 20$  times) for this dye than that observed for our control dye [Ru(dcbpy)<sub>2</sub>(NCS)<sub>2</sub>]. It appears unlikely that this difference can be explained solely by a difference in cation extinction coefficients of these two dyes, nor by differences in laser excitation intensity, and most probably results from a significantly lower injection yield.

The primary limitation of the use of **7** in dye-sensitised photoelectrochemical cells employing an iodide/iodine redox couple is the inability of iodide to reduce photogenerated dye cations. This inability is consistent with dye ground-state oxidation potential, determined to be  $0.25$  V *vs.* Ag/AgCl in solution. Comparison with alternative, efficient sensitizer dyes, such as [Ru(dcbpy)<sub>2</sub>(NCS)<sub>2</sub>], indicates that a ground-state oxidation potential of  $> 0.85$  V is required for an efficient regeneration reaction  $k_{RR}$ .

Photoelectrochemical solar cells fabricated employing dye **7** yielded only negligible photocurrent, as expected from our transient absorption data. Our electrochemical and transient absorption studies have identified that the primary reason for this is the insufficiently positive oxidation potential of this dye. Attempts to synthesise alternative phthalocyanines with more positive oxidation potentials are currently in progress.

## Experimental section

All solvents were distilled over standard drying agents under nitrogen directly before use and, where stated, reactions were carried out under an atmosphere of nitrogen. Silica gel (grade II) was used for chromatographic separations.

All NMR spectra were recorded using a Delta upgrade on a Jeol EX270 MHz spectrometer operating at 250.1 MHz (<sup>1</sup>H) and chemical shifts are reported in  $\delta$  using  $\text{CDCl}_3$  (<sup>1</sup>H,  $\delta$  7.25 ppm) as the reference. Infrared spectra were recorded using NaCl solution cells ( $\text{CH}_2\text{Cl}_2$ ) with a Mattson Polaris Fourier Transform IR spectrometer and UV-vis absorption spectra were recorded on a Perkin-Elmer Lambda 20 UV-vis spectrometer. Excitation and emission spectra were recorded in DMF using a Spex Fluoromax spectrofluorometer. Mass spectra were recorded using positive FAB methods on an Autospec Q mass spectrometer. Microanalyses were carried out by the SACS, University of North London. Electrochemical data were obtained using an Autolab PGSTAT12 potentiostat and a standard three-electrode cell (platinum working and counter electrodes and an Ag/AgCl reference) at a scan rate of  $5$  mV  $\text{s}^{-1}$ . The voltammograms were recorded at room temperature in a solution of  $0.1$  M tetrabutylammonium perchlorate as the supporting electrolyte in DMF and all solutions were  $\text{N}_2$  purged.

Anatase phase nanocrystalline  $\text{TiO}_2$  films were prepared as described elsewhere on transparent conducting glass slides.<sup>21</sup> Dye immobilisation was achieved by immersion of  $1$  cm<sup>2</sup>  $4$   $\mu\text{m}$   $\text{TiO}_2$  films in dye solutions of at least  $10^{-6}$  M concentration with 15% 4-*tert*-butylpyridine, 5% DMSO and 75 mM 3 $\alpha$ ,7 $\alpha$ -dihydroxy-5 $\beta$ -cholic acid.

For transient absorption experiments, films were placed in a quartz cuvette at a fixed position and measurements carried out in  $0.1$  M  $\text{LiClO}_4$  and  $0.1$  M LiI propylene carbonate solutions. Details of the apparatus employed have been given previously.<sup>22</sup> All experiments were conducted at room temperature.

## Synthesis

Compounds **1** and **2** were synthesised following methods adapted from literature procedures.<sup>9,10,17</sup>

**2,3-Dicyano-6-benzyloxynaphthalene (3).** **2** (0.50 g, 2.55 mmol) was dissolved in dry DMF (30 cm<sup>3</sup>) and the solution was treated with  $\text{K}_2\text{CO}_3$  (2.00 g) and benzyl alcohol (1.00 g, 9.26 mmol) under  $\text{N}_2$ . The mixture was heated to  $60^\circ\text{C}$  for 72 h. The solvents were then evaporated to dryness under reduced pressure and the residue subjected to column chromatography on silica gel using  $\text{CH}_2\text{Cl}_2$  as eluent. The first fraction was collected and, after removal of the solvents, **3** was isolated in 35% yield (0.25 g). MS (EI)  $m/z$ : 284 ( $M^+$ ), 191 ( $M^+ - \text{C}_7\text{H}_7$ ); HRMS: found  $m/z$  284.0948, calculated for  $\text{C}_{19}\text{H}_{12}\text{N}_2\text{O}$   $m/z$  284.0950;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ): 8.24 (1 H, s,  $\text{C}_{10}\text{H}_5$ ), 8.17 (1 H, s,  $\text{C}_{10}\text{H}_5$ ), 7.85 (1 H, d,  $\text{C}_{10}\text{H}_5$ ), 7.30–7.50 (7 H, m, 2 of  $\text{C}_{10}\text{H}_5$ , 5 of  $\text{C}_6\text{H}_5$ ), 7.28 (1 H, d,  $\text{C}_{10}\text{H}_5$ ), 5.22 (2 H, s,  $\text{CH}_2$ ).

**Tetra(benzyloxy)-2,3-naphthalocyaninatozinc(II) (4).** **3** (0.10 g, 0.35 mmol) and zinc acetate (0.04 g, 0.19 mmol) were added to freshly distilled *n*-pentanol (10 cm<sup>3</sup>) and the mixture heated

to 80 °C under N<sub>2</sub>, several drops of DBU were then added. The mixture was heated to reflux for 16 h and the solvent evaporated to dryness under reduced pressure. The residue was washed thoroughly with methanol (4 × 25 cm<sup>3</sup>) and then purified by column chromatography on silica gel with CHCl<sub>3</sub> as eluent. A green fraction was collected, the solvent removed *in vacuo* and **4** was isolated in 26% yield (0.11 g). MS (FAB +ve) *m/z*: 1202 (*M*<sup>+</sup>); UV-vis (CHCl<sub>3</sub>)  $\lambda$ /nm: 765, 720, 675, 330.

**Tetra(hydroxy)-2,3-naphthalocyaninatozinc(II) (5). 4** (0.10 g, 0.08 mmol) was mixed with trifluoroacetic acid (10 cm<sup>3</sup>) and tetramethylbenzene (0.1 g, 0.75 mmol) and the mixture heated to reflux overnight. The solution was evaporated to dryness and the residue washed with CH<sub>2</sub>Cl<sub>2</sub> (3 × 25 cm<sup>3</sup>). The green solid was then reprecipitated from THF–CH<sub>2</sub>Cl<sub>2</sub>, collected by filtration and used directly in the next step. Yield: 55% (0.034 g). MS (FAB +ve) *m/z*: 776 (*M*<sup>+</sup>); UV-vis (THF)  $\lambda$ /nm: 772, 726, 680, 335.

**Tetra(ethoxycarbonylmethoxy)-2,3-naphthalocyaninatozinc(II) (6). 5** (0.05 g, 0.06 mmol) was dissolved in DMF (20 cm<sup>3</sup>) and potassium carbonate (0.5 g) and ethyl chloroacetate (1.00 g, 8.13 mmol) added. The mixture was heated to 60 °C for 24 h under N<sub>2</sub>. The solvent was then removed *in vacuo* and the crude residue washed with methanol (2 × 25 cm<sup>3</sup>) and subjected to column chromatography on silica gel using CHCl<sub>3</sub>–methanol (95:5) as eluent. A green fraction was collected which yielded the product in 42% yield (0.03 g). Found: C, 64.59; H, 4.02; N, 8.91; C<sub>64</sub>H<sub>48</sub>N<sub>8</sub>O<sub>12</sub>Zn requires C, 64.79; H, 4.08; N, 9.44%; MS (FAB +ve) *m/z*: 1186 (*M*<sup>+</sup> + H); UV-vis (CHCl<sub>3</sub>)  $\lambda$ /nm: 768, 720, 678, 333;  $\delta$ <sub>H</sub> (CDCl<sub>3</sub>): 9.10–7.25 (20 H, br, aromatic), 5.30–5.10 (8 H, br, OCH<sub>2</sub>), 4.40–4.20 (8 H, br, CH<sub>2</sub>), 1.55–1.30 (12 H, br, CH<sub>3</sub>).

**Tetra(hydroxycarbonylmethoxy)-2,3-naphthalocyaninatozinc(II) (7). 6** (0.03 g, 0.02 mmol) was dissolved in THF (20 cm<sup>3</sup>) and added to a solution of potassium hydroxide (0.20 g) in water (1 cm<sup>3</sup>). The mixture was stirred at room temperature for 3 h and then diluted by addition of water (20 cm<sup>3</sup>). The mixture was filtered and the solution acidified with conc. HCl, during which time a green solid formed. This was collected by filtration and dried *in vacuo* to yield **7** in 61% yield (0.013 g). MS (FAB +ve) *m/z*: 1073 (*M*<sup>+</sup>); HRMS: found *m/z* 1074.2691, calculated for C<sub>56</sub>H<sub>32</sub>N<sub>8</sub>O<sub>12</sub>Zn *m/z* 1074.2952; UV-vis (DMF)  $\lambda$ /nm: 765, 726, 682, 343. IR (KBr)  $\nu$ /cm<sup>–1</sup>: 3479 (w, OH), 2918 (s, CH<sub>2</sub>), 1717 (m, C=O), 1615 (s, C=O).

## Acknowledgements

We are very grateful to the EPSRC for funding. We thank Richard Willis and Thierry Lutz for fabrication of the TiO<sub>2</sub>

films, Richard Monkhouse for assistance with the transient absorption spectrometer and Emilio Palomares for help with excitation and emission studies.

## References

- 1 E. F. Bradbrook and R. P. Linstead, *J. Chem. Soc.*, 1936, 1744.
- 2 (a) H. S. Nalwa and J. S. Shirk, in *Phthalocyanines: Properties and Applications*, ed. C. C. Leznoff and A. B. P. Lever, VCH, 1996, vol. 4, ch. 3; (b) N. B. McKeown, *Phthalocyanine Materials: Synthesis, Structure and Function*, Cambridge University Press, Cambridge, 1998.
- 3 B. Grolach, M. Dachtler, T. Glaser, K. Albert and M. Hanack, *Chem. Eur. J.*, 2001, **7**, 2459 and references therein.
- 4 A. Vogler and H. Kunkely, *Inorg. Chim. Acta*, 1980, **44**, L209.
- 5 M. Hanack, G. Renz, J. Strahle and S. Schmid, *Chem. Ber.*, 1988, **121**, 1479.
- 6 M. Hanack, G. Renz, J. Strahle and S. Schmid, *J. Org. Chem.*, 1991, **56**, 3501.
- 7 M. J. Cook, A. J. Dunn, S. D. Howe, A. J. Thomson and K. J. Harrison, *J. Chem. Soc., Perkin Trans. I*, 1988, 2453.
- 8 E. I. Kovshev, V. A. Puchnova and E. A. Luk'yanets, *Zh. Org. Khim.*, 1971, **7**, 369.
- 9 R. Polley and M. Hanack, *J. Org. Chem.*, 1995, **60**, 8278.
- 10 A. N. Cammidge, I. Chambrier, M. J. Cook, A. D. Garland, M. J. Heeney and K. Welford, *J. Porphyrins Phthalocyanines*, 1997, **1**, 77.
- 11 (a) M. Brewis, G. J. Clarkson, P. Humberstone, S. Makheed and N. B. McKeown, *Chem. Eur. J.*, 1998, **4**, 1633; (b) P. Humberstone, G. J. Clarkson, N. B. McKeown and K. E. Treacher, *J. Mater. Chem.*, 1996, **6**, 315.
- 12 M. Hanack, T. Schneider, H. Heckmann and M. Barthel, *Eur. J. Org. Chem.*, 2001, 3055.
- 13 N. Q. Wang, Y. M. Cai, J. R. Hoflin, J. W. Wu, D. L. Rodenberger and A. F. Garito, *Polymer*, 1991, **32**, 1752.
- 14 (a) H. S. Nalwa, A. Kakuta and A. Mukoh, *Chem. Phys. Lett.*, 1993, **203**, 109; (b) H. S. Nalwa, A. Kakuta and A. Mukoh, *J. Phys. Chem.*, 1993, **97**, 1097; (c) Y.-O. Yeung, R. C. W. Liu, W.-F. Law, P.-L. Lau, J. Jiang and D. K. P. Ng, *Tetrahedron*, 1997, **53**, 9087.
- 15 (a) B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737; (b) S. A. Haque, Y. Tachibana, D. R. Klug and J. R. Durrant, *J. Phys. Chem. B*, 1998, **102**, 1745.
- 16 D. Wohrle and D. Meissner, *Adv. Mater.*, 1991, **3**, 129.
- 17 V. N. Koprannikov, E. A. Makarova and E. A. Luk'yanets, *Zh. Org. Khim.*, 1981, **17**, 358.
- 18 M. K. Nazeeruddin, R. Humphry-Baker, M. Grätzel and B. A. Murrer, *Chem. Commun.*, 1998, 719.
- 19 A. F. Nogueira, M. A. De Paoli, I. Montanari, R. Monkhouse, J. Nelson and J. R. Nelson, *J. Phys. Chem. B*, 2001, **105**, 7517.
- 20 K. Kalyanasundaram and M. Grätzel, *Coord. Chem. Rev.*, 1998, **77**, 347.
- 21 R. Willis, C. Olsen, B. O'Regan, T. Lutz, J. Nelson and J. R. Durrant, *J. Phys. Chem. B*, in press.
- 22 S. Haque, Y. Tachibana, D. R. Klug and J. R. Durrant, *J. Phys. Chem. B*, 1998, **102**, 1745.