Preparation, solution behaviour and electrical properties of octasubstituted phthalocyaninato and 2,3-naphthalocyaninato oxotitanium(IV) complexes

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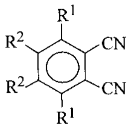
The octasubstituted oxo(phthalocyaninato)titanium(IV) complexes TiO[Pc′($CH_2OC_5H_{11}$)$_8$] (Pc′ = 2,3,9,10,16,17,23,24-octasubstituted phthalocyaninate) and TiO[Pc″(OC_4H_9)$_8$] (Pc″ = 1,4,8,11,15,18,22,25-octasubstituted phthalocyaninate) and the first 2,3,-naphthalocyaninato titanium complex TiO[Nc′(C_6H_{13})$_8$] (Nc′ = 2,5,11,14,20,23,29,32-octasubstituted naphthalocyaninate) have been prepared by treating the corresponding dicyano-benzenes or -naphthalene with titanium(IV) ethoxide and urea in *n*-pentanol. These compounds and their analogues TiO[Pc′(R)$_8$] (R = C_7H_{15}, OC_5H_{11}) tend to form molecular aggregates in solutions and the effects of solvent and concentration on their aggregation behaviour were investigated by UV–VIS and ^{1}H NMR spectroscopy. The electrochemistry and electrical properties of these compounds were also studied.

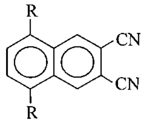
Oxo(phthalocyaninato)titanium(IV) (TiOPc) is a well known, near-IR-active photoconductive dye used practically as xerographic photoreceptors in copiers and GaAs laser printers.[1] The use of this material in optical disk information recording[2] and as a p-type semiconductor in photovoltaic cells[3] has also been documented. Owing to its poor solubility in usual organic solvents, the purification of TiOPc usually requires tedious procedures such as train sublimation[4] and acid pasting,[5] and most of the studies have been concentrated on its physical properties in the solid state such as single crystals[6,7] and thin solid films.[3,7,8] The solution properties of this compound, however, remain relatively unexplored.[9] Substitution on the periphery of phthalocyanine will not only enhance its solubility that may facilitate the fabrication of homogeneous thin films, but will also provide entries to tailor the properties of this material. Surprisingly, substituted TiOPc complexes are still scarce.[10,11] Here, we describe the preparation of a series of octasubstituted phthalocyaninato and 2,3-naphthalocyaninato oxotitanium(IV) complexes along with their spectroscopic and electrochemical behaviour in solutions. The electrical properties of thin films of TiO[Pc′(C_7H_{15})$_8$] and TiO[Nc′(C_6H_{13})$_8$] are also discussed.

Results and Discussion

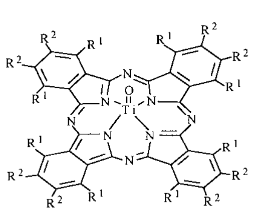
Treatment of substituted dinitriles **1**, **5** and **6** with titanium(IV) ethoxide and urea in *n*-pentanol led to the formation of the corresponding metallophthalocyanines **7** and **10**, and 2,3-naphthalocyanine **11**, respectively. The method was similar to that reported by Pac and co-workers in the synthesis of unsubstituted TiOPc,[12] but the yields were considerably lower (12–25%) for substituted analogues. It is noteworthy that compound **11**, to our knowledge, represents the first titanium complex of 2,3-naphthalocyanine reported. Reaction of dinitrile **2** under similar conditions afforded a dark green powder. Although its UV–VIS spectrum in $CHCl_3$ showed characteristic B and Q bands at 351 and 700 nm, respectively, other spectroscopic methods [^{1}H NMR, IR and liquid secondary ion (LSI) MS] and elemental analyses did not support the formation of TiO[Pc′(CH_2OPh)$_8$]. This unknown species seemed to be highly aggregated in solutions which hampered the purification and characterisation processes. The heptyl (**8**) and pentyloxy (**9**) analogues could however be prepared by either using this method or treating the corresponding dinitriles with $TiCl_4$ followed by hydrolysis.[11] All of these macrocycles could be purified by column chromatography or simply washing with appropriate solvents.



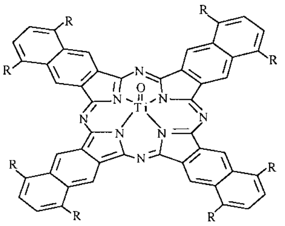
1 $R^1 = H, R^2 = CH_2OC_5H_{11}$
2 $R^1 = H, R^2 = CH_2OC_6H_5$
3 $R^1 = H, R^2 = C_7H_{15}$
4 $R^1 = H, R^2 = OC_5H_{11}$
5 $R^1 = OC_4H_9, R^2 = H$



6 $R = C_6H_{13}$



7 $R^1 = H, R^2 = CH_2OC_5H_{11}$
8 $R^1 = H, R^2 = C_7H_{15}$
9 $R^1 = H, R^2 = OC_5H_{11}$
10 $R^1 = OC_4H_9, R^2 = H$



11 $R = C_6H_{13}$

The UV–VIS spectra of these complexes displayed a typical Q band and a Soret band which are attributed to the π–π* transitions of the macrocycles. As shown in Table 1, the Q

Table 1 UV–VIS data of the oxotitanium complexes **7**–**11** in $CHCl_3$

compound	λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1})
7	352 (4.90), 631 (4.55), 665 (4.60), 700 (5.28)
8	347 (4.80), 639 (4.48), 680 (4.42), 710 (5.27)
9	348 (4.68), 439 (4.37), 631 (4.28), 669 (4.28), 702 (5.12)
10	340 (4.63), 479 (3.99), 704 (4.46), 791 (5.10)
11	337 (4.85), 451 (4.23), 734 (4.56), 782 (4.58), 826 (5.31)

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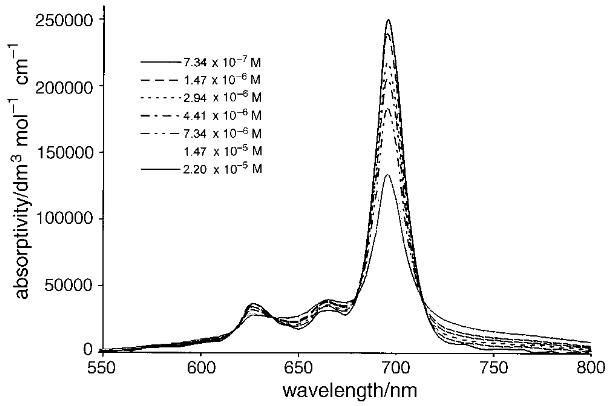

Fig. 1 Concentration dependence of UV–VIS spectra of **8** in hexanes

band absorption of 1,4-substituted phthalocyanine **10** shows a bathochromic shift ($\lambda_{max} = 791$ nm) in comparison with those of 2,3-substituted analogues **7**–**9** ($\lambda_{max} = 700$–710 nm). The Q band absorption of naphthalocyanine **11** is even more red-shifted ($\lambda_{max} = 826$ nm) owing to the more extended π conjugation.

It is well known that phthalocyanines, even in dilute solution, tend to form molecular aggregates such as dimers, trimers and oligomers. These aggregated species may have very different characteristics from the corresponding monomer and the degree of association is largely dependent on the polarity of the solvent and the concentration of the solution.[13] We measured the absorption spectra of compounds **7**–**11** in $CHCl_3$ over the concentration range of 10^{-6}–10^{-5} M and found no significant spectral change with concentration. The species exhibited spectra typical of monomeric phthalocyanines. Thus, it is apparent that aggregation is not important for these complexes in $CHCl_3$ in these concentrations. In contrast, the absorption spectra of **7** and **8** in hexanes were concentration dependent. Fig. 1 shows the variation of the UV–VIS spectrum of **8** with concentration ranging from 7.34×10^{-7} to 2.20×10^{-5} M. The Q band absorption maximum at 696 nm is unshifted but broadened as the concentration increases. Since further spectral change was not observed at concentrations lower than 7.34×10^{-7} M, the spectrum observed in this concentration can be attributed to the purely monomeric **8**. Compound **7** behaved similarly and the absorption spectrum due to monomeric species was obtained at concentrations below 3.25×10^{-6} M.

We assumed that a one-step equilibrium between phthalocyanine monomer (Pc) and aggregated phthalocyanine (Pc_n) exists [eqn. (1)], where K is the aggregation constant and n is the aggregation number.

$$n\mathrm{Pc} \overset{K}{\rightleftharpoons} \mathrm{Pc}_n \qquad (1)$$

By following the treatment described by Mataga,[14] eqn. (2) could be derived in which C_t is the total concentration of phthalocyanine, ε and ε_m are the observed molar absorptivity and the corresponding value for pure monomer, respectively.

$$\log[C_t(1-\varepsilon/\varepsilon_m)] = \log(nK) + n\log[C_t(\varepsilon/\varepsilon_m)] \qquad (2)$$

Plots of $\log[C_t(1-\varepsilon/\varepsilon_m)]$ *vs.* $\log[C_t(\varepsilon/\varepsilon_m)]$ for **7** and **8** gave straight lines from which the values of n and K were determined to be 2.07 and 6.84×10^4 (for **7**) and 2.34 and 1.75×10^6 (for **8**), respectively. The aggregation numbers for both complexes are close to two suggesting that dimer of these compounds may be the dominant species in hexanes solution. The higher value of K for **8** indicates that this compound has a higher aggregation tendency than compound **7** in hexanes and the value is comparable with the dimerisation constants determined for some other substituted phthalocyanines in non-polar solvents.[13a,d] The increased aggregation of these complexes in hexanes can be rationalised by the fact that hexanes, having a lower relative permittivity ($\varepsilon_r = 1.89$) than $CHCl_3$ ($\varepsilon_r = 4.81$),[15] has a weaker screening effect to disrupt the Pc–Pc interactions. For compounds **9** and **10**, such spectral analysis could not be performed because of their poor solubility in hexanes. The naphthalocyaninato complex **11**, as expected, is even more highly aggregated in hexanes solution. No absorption spectrum assignable to the monomeric species could be obtained. However, by gradual addition of $CHCl_3$ into dilute hexanes solution of **11**, the initial broad band around 770 nm became sharpened giving a characteristic spectrum of metallonaphthalocyanines (Fig. 2).

As revealed by UV–VIS spectroscopy, the aggregation of compounds **7**–**11** in $CHCl_3$ appears to be insignificant. However, at sufficiently high concentration, these complexes still have a tendency to form aggregates as shown by ^{1}H NMR spectroscopy. We recorded the ^{1}H NMR spectra of **7**–**10** in $CDCl_3$ over the concentration range 1×10^{-3}–2×10^{-2} M. Fig. 3 shows the concentration dependence of chemical shift of the aromatic ring protons for **7**–**10**. The resonances for 2,3-substituted phthalocyanines **7**–**9** shift upfield by 0.3–0.4 ppm as the concentration approaches 2×10^{-2} M. It is likely that the cone of aromaticity generated by the ring current of one phthalocyanine macrocycle causes upfield shifts of its aggre-

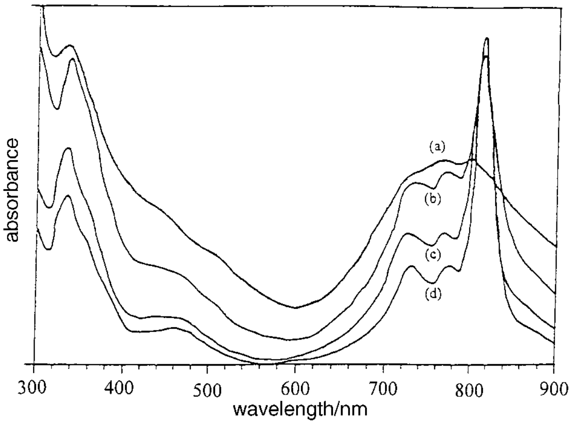

Fig. 2 UV–VIS spectral change of **11** in hexanes upon addition of $CHCl_3$; (a) hexanes only, gradual addition of $CHCl_3$ from (b) to (d)

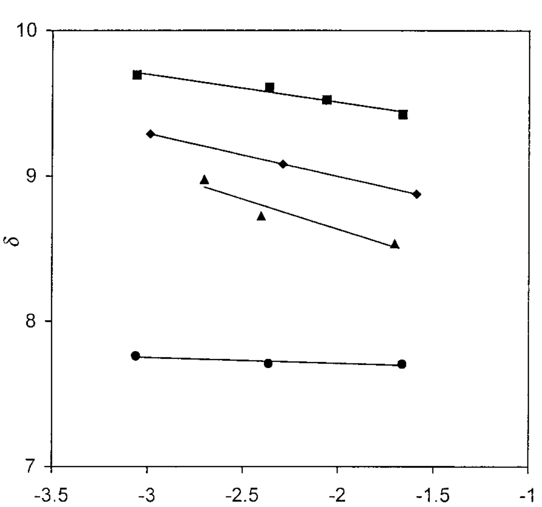

Fig. 3 Chemical shift of aromatic protons of **7**–**10** in $CDCl_3$ as a function of log (concentration); (■) **7**, (◆) **8**, (▲) **9**, (●) **10**

gated partners.[16] However, for the 1,4-substituted phthalocyanine **10**, the chemical shift of ring protons is essentially independent of concentration. This may be attributed to the fact that the ring protons are farther away from the core of phthalocyanine or a weaker aggregation occurs for this substitution pattern. The ^1H NMR spectrum of naphthalocyanine **11** in $CDCl_3$ showed only broad bands for the hexyl side chains; the aromatic protons' signals were not observed. However, by adding a few drops of [$^2H_5$]pyridine, a broad band at δ 9.42 and a relatively sharp singlet at δ 7.36 appeared which could be ascribed to H^1 and H^3, respectively. Thus pyridine is able to disrupt the interactions among these macrocycles to some extent.

The electrochemistry of compounds **7**–**11** was examined by cyclic voltammetry in CH_2Cl_2. The voltammograms for **8** (Fig. 4) and **9** revealed two reversible one-electron reduction couples, one quasi-reversible one-electron oxidation couple, together with one irreversible oxidation which may be associated with decomposition. Compound **7** gave a similar voltammogram except that an extra quasi-reversible reduction wave was observed, while for compound **10**, the second oxidation also appeared to be quasi-reversible. The voltammogram for naphthalocyanine **11** also displayed two reversible reductions, but the oxidation waves were poorly defined. The reversibility of the reduction waves of **7**–**11** was judged by the separations between the anodic and cathodic potentials (62–84 mV) which were almost invariable with scan rates of 50–200 mV s^{-1}, the cathodic to anodic peak current ratios (i_{pc}/i_{pa}) which approached unity and the linear plots of peak current *vs.* square root of the scan rate. A summary of the electrochemical data for these compounds is given in Table 2. All of these redox couples are attributed to the macrocyclic ligand as $Ti^{IV}{=}O$ can be considered as a redox inactive moiety.[17]

The potential difference between the first reduction and oxidation couples, which resembles the energy gap between the highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO), for 2,3-substituted TiO[Pc′(R)$_8$] **7**–**9** was found to be 1.54–1.57 V. These values are in the range (1.5–1.7 V) reported for the HOMO–LUMO separation of phthalocyanines.[17] The corresponding difference for 1,4-substituted analogue **10** was however smaller (1.29 V) which is in accord with the bathochromic shift of Q band in its UV–VIS spectrum. According to the electrochemical data, the narrowing of the HOMO–LUMO gap in **10** was due to an increase of the HOMO level. The data for **7**–**9** were also consistent with the electron donating ability of the substituents which follows the order $OC_5H_{11} > C_7H_{15} > CH_2OC_5H_{11}$.

The solubility of the substituted macrocyclic compounds **7**–**11** in organic solvents renders these compounds suitable for deposition with technique such as spin-coating. Fig. 5 shows the absorption spectra of spin-coated films of **8** and **11** (thickness: *ca.* 500 Å). In comparison with the solution spectra, the Q bands are significantly broadened, in particular for compound **11**. In addition, the λ_{max} for **11** (*ca.* 775 nm) shows a hypsochromic shift while that for **8** (*ca.* 715 nm) remains relatively unchanged. These observations may also indicate that the naphthalocyanine **11** has a higher columnar stacking tendency.[18]

The electrical properties of the films of **8** and **11** were also briefly examined. The dark conductivity increased with temperature and followed the Arrhenius equation of temperature dependence of conductivity [$\sigma = \sigma_1 \exp(-E_1/kT) + \sigma_2 \exp(-E_2/kT)$]. The Arrhenius plots for both compounds (Fig. 6) show two linear regions of different activation energies (Table 3) with no indication of sharp transition. Since the samples were not intentionally doped, the low activation energies (E_1 *ca.* 0.04 and 0.24 eV for **8** and **11**, respectively) indicate that extrinsic conduction, which may arise from structural defects, dominates in the low-temperature regime. Both complexes exhibited semiconducting properties with room-temperature conductivity in the range 10^{-8}–10^{-9} Ω^{-1} cm^{-1} which seem to be higher than the values reported for related phthalocyanines.[10c] As all the conductivity measurements were carried out in complete darkness, we exclude the possibility of extra charge carrier generations due to photo-absorption. On the other hand, it is well known that

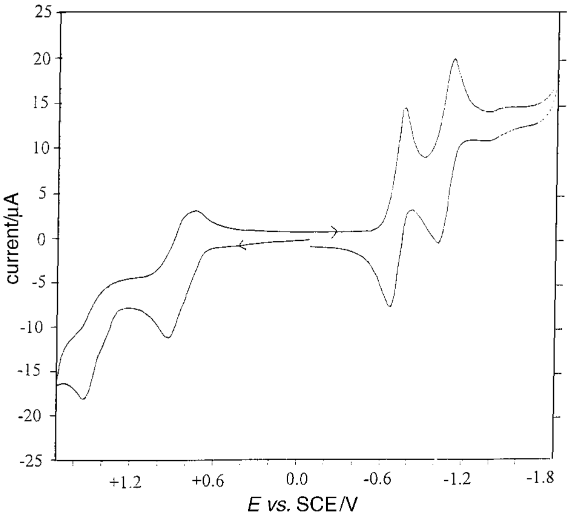

Fig. 4 Cyclic voltammogram of **8** in CH_2Cl_2 containing 0.1 M [NBu_4][PF_6] at a scan rate of 50 mV s^{-1}

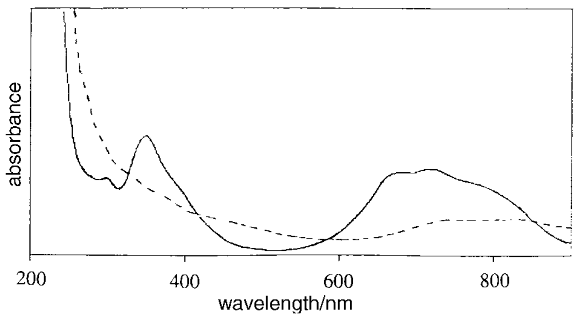

Fig. 5 UV–VIS spectra of spin-coated films of **8** (—) and **11** (– – –) with a thickness of *ca.* 500 Å

Table 2 Redox potentials for the oxotitanium complexes **7**–**11**[a]

compound	$E_{pa}{}^{b}$(ox.2)	$E_{1/2}{}^{c}$(ox.1)	$E_{1/2}$(red.1)	$E_{1/2}$(red.2)	$E_{1/2}$(red.3)
7	1.54	0.96	−0.58	−0.93	−1.39
8	1.54	0.86	−0.71	−1.06	—
9	1.40	0.80	−0.77	−1.11	—
10	1.00	0.59	−0.70	−1.06	—
11	—	—	−0.65	−0.97	—

[a] Recorded with [NBu_4][PF_6] as electrolyte in CH_2Cl_2 (0.1 M) at ambient temperature. Scan rate = 50 mV s^{-1}. Expressed in volts relative to SCE. [b] Anodic peak potential. [c] Half-wave potential.

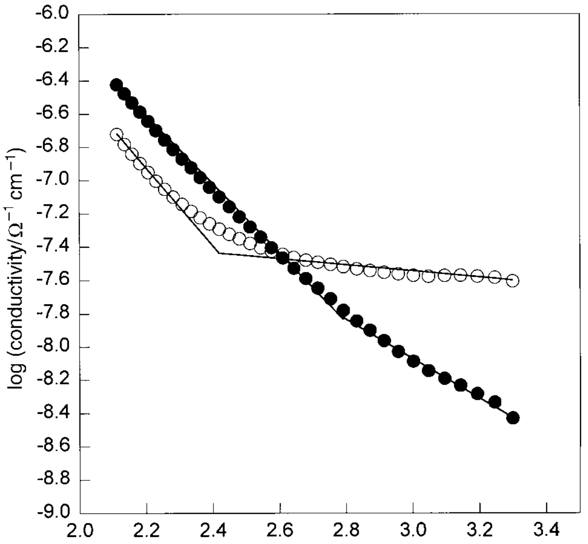

Fig. 6 Plots of log (conductivity) *vs.* 10^3 T^{-1} for spin-coated films of **8** (○) and **11** (●)

physical properties of thin film materials depend strongly on their film structures, which may exhibit vast differences as a result of different preparation methods and conditions, and of any subsequent thermal treatments.[19] A direct comparison of these data should thus be made with great care.

Experimental

General

n-Pentanol and hexanes were distilled from sodium and anhydrous calcium chloride, respectively. Chromatographic purifications were performed on silica gel columns (Merck, 70–230 mesh). Dichloromethane used for electrochemical studies was freshly distilled from calcium hydride and the electrolyte $[NBu_4][PF_6]$ was recrystallised from tetrahydrofuran. All other reagents and solvents were of reagent grade and used without prior purification. The compounds 1,2-dicyano-4,5-bis(pentyloxymethyl)benzene **1**,[20] 3,6-bis(butyloxy)-1,2-dicyanobenzene **5**,[21] and 2,3-dicyano-5,8-dihexylnaphthalene **6**[22] were prepared according to the literature procedures.

NMR spectra were recorded on a Bruker WM 250 spectrometer (250 MHz for ^{1}H and 62.9 MHz for ^{13}C) with $Si(CH_3)_4$ as an internal standard ($\delta = 0$). UV–VIS spectra were measured on a Hitachi U-3300 spectrophotometer. IR spectra were recorded on a Perkin Elmer 1600 or a Nicolet Magna 550 spectrometer as KBr pellets. LSI mass spectra were taken on a Bruker APEX 47e Fourier transform ion cyclotron resonance spectrometer with 3-nitrobenzyl alcohol as matrix. Elemental analyses were performed by the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.

Electrochemical measurements were carried out with a BAS CV-50W potentiostat using a conventional three-electrode cell equipped with a glassy carbon disc working electrode (3 mm diameter), a platinum wire counter electrode and a silver wire pseudo-reference electrode. Typically, experiments were performed in CH_2Cl_2 containing 0.1 M $[NBu_4][PF_6]$ at ambient temperature under a dry nitrogen atmosphere. The concentrations were in the range 10^{-4} M. All potentials were referenced to the ferrocenium–ferrocene couple (internal standard) at +0.45 V relative to the saturated calomel electrode (SCE).

Thin films of **8** and **11** were prepared by dissolving the compounds in tetrahydrofuran and $CHCl_3$, respectively, then spin-coating the solutions on Corning 7059 glass substrates with a spin-coater (Cost Effective Equipment, Model 100 CB) at a spinning rate of 6000 rev min^{-1} for 30 s. The films were baked at 70 °C for 30 min prior to subsequent measurements. The thicknesses of the films were determined by a film thickness profiler (Tencor Instrument, α-step 500). For conductivity measurements, silver electrodes which defined a gap width of *ca.* 2 mm were first evaporated onto the samples, then the resistances of the samples were measured in a dynamic vacuum (*ca.* 10^{-6} Torr) with an electrometer (Keithley, Model 617) in the V–I mode. The measuring processes started at 200 °C with a ramping down rate of 0.5 °C min^{-1} to 30 °C.

$TiO[Pc'(CH_2OC_5H_{11})_8]$ 7

A mixture of 1,2-dicyano-4,5-bis(pentyloxymethyl)benzene **1** (200 mg, 0.61 mmol) and urea (19 mg, 0.31 mmol) was dissolved in *n*-pentanol (0.5 ml) to which titanium(IV) ethoxide (0.04 ml, 0.18 mmol) was added *via* a micropipette. The mixture was refluxed under nitrogen for 20 h, then mixed with methanol (15 ml). After refluxing for a further 15 min, the mixture was filtered and the residue was washed with methanol (10 ml), water (10 ml), and methanol (5 ml) again. The resulting dark blue solid was chromatographed with ethyl acetate–hexanes (1 : 1) as eluent giving a greenish blue band which was collected and rotary evaporated. The greenish blue solid was dried *in vacuo*. Yield 53 mg (25%). ^{1}H NMR ($CDCl_3$, 1.6×10^{-2} M): δ 9.49 (s, 8 H, Pc′*H*), 5.14–5.26 (m, 16 H, Pc′C*H*$_2$), 3.84 (t, *J* 6.7 Hz, 16 H, OCH_2), 1.83–1.95 (m, 16 H, CH_2), 1.42–1.65 (m, 32 H, CH_2), 1.02 (t, *J* 7.0 Hz, 24 H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 151.6, 140.4, 136.3, 123.4, 71.3 (two overlapping signals), 29.7, 28.6, 22.7, 14.2. IR: $\nu = 978$ cm^{-1} (Ti=O); MS (LSI): an isotopic envelope peaking at *m*/*z* 1376.82 (100%) {calc. for M$^+$ based on ^{48}Ti, 1376.81}; Anal. Calc. for $C_{80}H_{112}N_8O_9Ti$: C, 69.74; H, 8.19; N, 8.13. Found: C, 67.17; H, 8.16; N, 7.68%.

$TiO[Pc''(OC_4H_9)_8]$ 10

To a mixture of 3,6-bis(butyloxy)-1,2-dicyanobenzene **5** (200 mg, 0.73 mmol) and urea (22 mg, 0.37 mmol) in *n*-pentanol (1 ml) was added titanium(IV) ethoxide (0.05 ml, 0.23 mmol). The mixture was refluxed under nitrogen for 48 h, then mixed with methanol (20 ml). After refluxing for a further 30 min, the mixture was cooled to room temperature then filtered, and the solid was washed with diethyl ether (3 × 10 ml). The resulting fine dark brown microcrystals were collected and dried *in vacuo*. Yield 26 mg (12%). ^{1}H NMR ($CDCl_3$, 2.2×10^{-2} M): δ 7.70 (s, 8 H, Pc″*H*), 4.80–5.05 (m, 16 H, OCH_2), 2.16–2.31 (m, 16 H, CH_2), 1.60–1.78 (m, 16 H, CH_2), 1.10 (t, *J* 7.4 Hz, 24 H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 151.6, 151.2, 127.0, 118.4, 71.7, 31.5, 19.4, 14.1. IR: $\nu = 966$ cm^{-1} (Ti=O); MS (LSI): an isotopic envelope peaking at *m*/*z* 1153.59 (100%) {calc. for MH$^+$ based on ^{48}Ti, 1153.56}; Anal. Calc. for $C_{64}H_{80}N_8O_9Ti$: C, 66.65; H, 6.99; N, 9.72. Found: C, 65.12; H, 6.97; N, 9.48%.

Table 3 Electrical properties of thin films of compounds **8** and **11**

compound	temp. range	E_1/eV	temp. range	E_2/eV	σ_{303}/Ω^{-1} cm^{-1}
8	303–413 K	0.04	413–473 K	0.47	2.5×10^{-8}
11	303–353 K	0.24	353–473 K	0.41	2.2×10^{-9}

$TiO[Nc'(C_6H_{13})_8]$ 11

A mixture of 2,3-dicyano-5,8-dihexylnaphthalene **6** (200 mg, 0.58 mmol) and urea (18 mg, 0.30 mmol) was dissolved in *n*-pentanol (0.5 ml). Then titanium(IV) ethoxide (0.04 ml, 0.18 mmol) was introduced *via* a micropipette. The mixture was refluxed under nitrogen for 20 h, then methanol (20 ml) was added. After refluxing for a further 30 min, the mixture was cooled to room temperature and decanted. The black residue was dissolved in hexanes (20 ml) and precipitated with methanol (10 ml). The solid was chromatographed with $CHCl_3$ as eluent. The dark green band developed was collected and rotary evaporated to give a dark green solid which was dried *in vacuo*. Yield 50 mg (24%). ^1H NMR {$CDCl_3$ + *ca.* 0.6 M [$^2H_5$]pyridine, 4.0×10^{-3} M): δ 9.42 (br s, 8 H, Nc'*H*), 7.36 (s, 8 H, Nc'*H*), 3.29 (br s, 16 H, Nc'CH_2), 2.00 (br s, 16 H, CH_2), 1.66 (br s, 16 H, CH_2), 1.47 (br s, 32 H, CH_2), 0.95 (t, *J* 6.9 Hz, 24 H, CH_3). IR: $\nu = 970\ cm^{-1}$ (Ti=O); MS (LSI): an isotopic envelope peaking at *m/z* 1449.94 (100%) {calc. for M^+ based on ^{48}Ti, 1449.91}; Anal. Calc. for $C_{96}H_{120}N_8OTi$: C, 79.52; H, 8.34; N, 7.73. Found: C, 77.74; H, 8.27; N, 7.31%.

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