Synthesis and Electrochemistry of Ferrocenylphthalocyanines

Ka-Wo Poon, Yan Yan, Xi-you Li, and Dennis K. P. Ng*

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, People's Republic of China

Received March 25, 1999

A series of phthalocyanines containing 4, 8, and 16 2-ferrocenylethoxy moieties on the periphery have been prepared and spectroscopically characterized. The UV−vis spectrum of the tetraferrocenyl phthalocyanine **4** shows an unusual long-wavelength band at ca. 760 nm in nonpolar solvents. When the spectral changes of this compound and its analogue [1,8,15,22-tetrakis(3-pentyloxy)phthalocyaninato]zinc(II) (**12**) are studied in different solvents and at various concentrations, along with their fluorescence spectra, it can be concluded that this band is not likely due to a slipped cofacial dimer as reported previously. Compound **4** is not emissive, which can be explained by the efficient quenching due to electron transfer from ferrocene to the excited phthalocyanine. The value of $\Delta G°$ for this photoinduced electron transfer has been estimated to be −0.48 eV. Electrochemical studies of these phthalocyanine−ferrocene conjugates by cyclic voltammetry have revealed that all the ferrocenyl redox centers attached to the macrocyclic core are electrochemically independent and undergo an oxidation at the same potential.

Introduction

In the past few years, there has been a growing interest in molecular systems containing multiple redox-active centers.[1−3] These molecules can act as potential candidates for multielectron redox catalysts[2] and serve as models for the studies of light-initiated intramolecular electron transfer that may shed light on complex but practically useful processes such as solar energy conversion and artificial photosynthesis.[1a,3] Ferrocene, owing to its chemical stability and well-defined electrochemistry, has been widely used in the construction of such multicomponent systems. Among the various frameworks that link the redox-active ferrocenyl units together,[4−7] porphyrins are of special interest because of their biological relevance and unique redox and photophysical properties.[3,8,9] Porphyrins with up to four ferrocenyl substituents have been reported, some of which are also capable of sensing anionic guest species.[9] Phthalocyanines are porphyrin analogues exhibiting intriguing but distinct physicochemical properties.[10] It is therefore worthwhile to investigate the related phthalocyanine−ferrocene conjugates, only a few examples of which have been reported so far, with a maximum number of four ferrocenyl units in a macrocycle.[11,12] We have recently extended this series of

---

[1] (a) Chow, H.-F.; Mong, T. K.-K.; Nongrum, M. F.; Wan, C.-W. *Tetrahedron* **1998**, *54*, 8543 and references therein. (b) Uno, M.; Dixneuf, P. H. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1714.

[2] (a) Steiger, B.; Anson, F. C. *Inorg. Chem.* **1994**, *33*, 5767. (b) Bard, A. J. *Nature* **1995**, *374*, 13.

[3] (a) Schmidt, E. S.; Calderwood, T. S.; Bruice, T. C. *Inorg. Chem.* **1986**, *25*, 3718. (b) Beer, P. D.; Kurek, S. S. *J. Organomet. Chem.* **1989**, *366*, C6. (c) Wagner, R. W.; Brown, P. A.; Johnson, T. E.; Lindsey, J. S. *J. Chem. Soc., Chem. Commun.* **1991**, 1463. (d) Giasson, R.; Lee, E. J.; Zhao, X.; Wrighton, M. S. *J. Phys. Chem.* **1993**, *97*, 2596 and references therein. (e) Uosaki, K.; Kondo, T.; Zhang, X.-Q.; Yanagida, M. *J. Am. Chem. Soc.* **1997**, *119*, 8367. (f) Thornton, N. B.; Wojtowicz, H.; Netzel, T.; Dixon, D. W. *J. Phys. Chem. B* **1998**, *102*, 2101.

[4] For systems containing multi-ferrocenyl units linked with polymers, see for example: (a) Casado, C. M.; Morán, M.; Losada, J.; Cuadrado, I. *Inorg. Chem.* **1995**, *34*, 1668. (b) Manners, I. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1602. (c) Watson, K. J.; Zhu, J.; Nguyen, S. T.; Mirkin, C. A. *J. Am. Chem. Soc.* **1999**, *121*, 462.

[5] For systems containing multi-ferrocenyl units linked with dendrimers, see for example: (a) Cuadrado, I.; Morán, M.; Casado, C. M.; Alonso, B.; Lobete, F.; García, B.; Ibisate, M.; Losada, J. *Organometallics* **1996**, *15*, 5278. (b) Deschenaux, R.; Serrano, E.; Levelut, A.-M. *Chem. Commun.* **1997**, 1577. (c) Valério, C.; Fillaut, J.-L.; Ruiz, J.; Guittard, J.; Blais, J.-C.; Astruc, D. *J. Am. Chem. Soc.* **1997**, *119*, 2588. (d) Castro, R.; Cuadrado, I.; Alonso, B.; Casado, C. M.; Morán, M.; Kaifer, A. E. *J. Am. Chem. Soc.* **1997**, *119*, 5760 and references therein. (e) Cuadrado, I.; Casado, C. M.; Alonso, B.; Morán, M.; Losada, J.; Belsky, V. *J. Am. Chem. Soc.* **1997**, *119*, 7613. (f) Köllner, C.; Pugin, B.; Togni, A. *J. Am. Chem. Soc.* **1998**, *120*, 10274.

[6] For systems containing diferrocenyl units linked with polyenes or poly(vinylene)phenylenes, see for example: (a) Ribou, A.-C.; Launay, J.-P.; Sachtleben, M. L.; Li, H.; Spangler, C. W. *Inorg. Chem.* **1996**, *35*, 3735. (b) Hradsky, A.; Bildstein, B.; Schuler, N.; Schottenberger, H.; Jaitner, P.; Ongania, K.-H.; Wurst, K.; Launay, J.-P. *Organometallics* **1997**, *16*, 392.

[7] For systems containing multi-ferrocenyl units linked with other moieties, see for example: (a) Fillaut, J.-L.; Linares, J.; Astruc, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2460. (b) Fillaut, J.-L.; Astruc, D. *New J. Chem.* **1996**, *20*, 945. (c) Deschenaux, R.; Monnet, F.; Serrano, E.; Turpin, F.; Levelut, A.-M. *Helv. Chim. Acta* **1998**, *81*, 2072.

[8] (a) Wollmann, R. G.; Hendrickson, D. N. *Inorg. Chem.* **1977**, *16*, 3079. (b) Hisatome, M.; Takano, S.; Yamakawa, K. *Tetrahedron Lett.* **1985**, *26*, 2347. (c) Beer, P. D.; Kurek, S. S. *J. Organomet. Chem.* **1987**, *336*, C17. (d) Kadish, K. M.; Xu, Q. Y.; Barbe, J.-M. *Inorg. Chem.* **1987**, *26*, 2565. (e) Xu, Q. Y.; Barbe, J.-M.; Kadish, K. M. *Inorg. Chem.* **1988**, *27*, 2373. (f) Maiya, G. B.; Barbe, J.-M.; Kadish, K. M. *Inorg. Chem.* **1989**, *28*, 2524. (g) Loim, N. M.; Abramova, N. V.; Sokolov, V. I. *Mendeleev Commun.* **1996**, 46. (h) Burrell, A. K.; Campbell, W.; Officer, D. L. *Tetrahedron Lett.* **1997**, *38*, 1249.

[9] (a) Beer, P. D.; Drew, M. G. B.; Hesek, D.; Jagessar, R. *J. Chem. Soc., Chem. Commun.* **1995**, 1187. (b) Beer, P. D.; Drew, M. G. B.; Jagessar, R. *J. Chem. Soc., Dalton Trans.* **1997**, 881.

[10] *Phthalocyanines−Properties and Applications*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH: New York, 1989; Vol. 1; 1993; Vol. 2; 1993; Vol. 3; 1996; Vol. 4.

[11] (a) Jin, Z.; Nolan, K.; McArthur, C. R.; Lever, A. B. P.; Leznoff, C. C. *J. Organomet. Chem.* **1994**, *468*, 205. (b) Cook, M. J.; Cooke, G.; Jafari-Fini, A. *J. Chem. Soc., Chem. Commun.* **1995**, 1715. (c) Dabak, S.; Bekaroglu, Ö. *New J. Chem.* **1997**, *21*, 267. (d) Silver, J.; Sosa-Sanchez, J. L.; Frampton, C. S. *Inorg. Chem.* **1998**, *37*, 411. (e) González, A.; Vázquez, P.; Torres, T. *Tetrahedron Lett.* **1999**, *40*, 3263.

10.1021/om990208x CCC: $18.00

complexes by preparing phthalocyanines connected on the periphery to 4, 8, and 16 ferrocenyl moieties with oxyethylene linkers. The synthesis and the spectroscopic and electrochemical properties of these novel macrocycles are reported herein.

Experimental Section

General Procedure. Reactions were performed under an atmosphere of nitrogen. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. *n*-Pentanol, *n*-hexanol, and *n*-octanol were distilled from sodium prior to use. *N*,*N*-Dimethylformamide (DMF) was predried over barium oxide and distilled under reduced pressure. Chromatographic purifications were performed on silica gel columns (Macherey-Nagel, 70−230 mesh) with the indicated eluents unless otherwise stated. Hexanes used in chromatography was distilled from anhydrous $CaCl_2$. The electrolyte $[Bu_4N][ClO_4]$ was recrystallized from dry acetone three times prior to use. All other reagents and solvents were of reagent grade and were used as received. 2-Ferrocenylethanol (**1**)[13] and 2-ferrocenylethyl *p*-toluenesulfonate (**5**)[14] were prepared according to literature procedures.

Melting points were uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 spectrometer (^1H, 300 MHz; ^{13}C, 75.4 MHz) in $CDCl_3$ unless otherwise stated. Spectra were referenced internally using the residual solvent (^1H: $CDCl_3$, δ 7.26; CD_3SOCD_3, δ 2.50; C_6D_6, δ 7.15) or solvent (^{13}C: $CDCl_3$, δ 77.0) resonances relative to $SiMe_4$. IR spectra were measured on a Nicolet Magna 550 FT-IR spectrometer as KBr pellets. UV−vis and fluorescence spectra were taken on a Hitachi U-3300 spectrophotometer and a Hitachi F-4500 spectrofluorometer, respectively. Liquid secondary-ion (LSI) mass spectra were recorded on a Bruker APEX 47e Fourier transform ion cyclotron resonance (FTICR) mass spectrometer with a 3-nitrobenzyl alcohol matrix. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) spectra were obtained on a Bruker bench TOF mass spectrometer equipped with a standard UV-laser desorption source, using α-cyano-4-hydroxycinnamic acid as matrix. Elemental analyses were performed by the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.

Electrochemical measurements were carried out on a BAS CV-50W voltammetric analyzer. The cell contained inlets for a platinum-sphere working electrode, a platinum-plate counter electrode, and a $Ag-AgNO_3$ (0.1 mol dm^{-3} in MeCN) reference electrode, which was connected to the solution by a Luggin capillary whose tip was placed close to the working electrode.[15] Typically, a 0.1 mol dm^{-3} solution of $[Bu_4N][ClO_4]$ in DMF (unless otherwise stated) containing 1.0 mmol dm^{-3} of sample was purged with nitrogen for 20 min; then the voltammograms were recorded at ambient temperature. Potentials were referenced to the $Ag-Ag^+$ couple in MeCN.

3-(2-Ferrocenylethoxy)phthalonitrile (3). A mixture of 2-ferrocenylethanol (**1**; 1.15 g, 5.0 mmol), 3-nitrophthalonitrile (**2**; 0.43 g, 2.5 mmol), and K_2CO_3 (0.69 g, 5.0 mmol) in DMF (3 mL) was stirred at room temperature for 21 h. The volatiles were then removed under reduced pressure, giving a brown residue which was subjected to chromatography using THF/hexanes (1:4) as eluent. Compound **3** was isolated as orange-yellow microcrystals (0.24 g, 27%; mp 163−166 °C). ^1H NMR (CD_3SOCD_3): δ 7.84 (dd, $J = 7.5$, 8.4 Hz, 1 H, Ar H), 7.66 (d, $J = 8.4$ Hz, 1 H, Ar H), 7.64 (d, $J = 7.5$ Hz, 1 H, Ar H), 4.32 (t, $J = 6.6$ Hz, 2 H, OCH_2), 4.23 (t, $J = 1.8$ Hz, 2 H, Fc), 4.15 (s, 5 H, Fc), 4.08 (t, $J = 1.8$ Hz, 2 H, Fc), 2.80 (t, $J = 6.6$ Hz, 2 H, $FcCH_2$). $^{13}C\{^1H\}$ NMR: δ 161.3, 134.4, 125.0, 117.0, 116.6, 115.3, 113.1, 104.9, 83.8, 70.6, 69.3, 69.0, 68.2, 29.6. IR (KBr): ν 2227 m cm^{-1} ($C{\equiv}N$). HRMS (LSI): m/z calcd for $C_{20}H_{16}{}^{56}FeN_2O$ (M^+) 356.0612, found 356.0607. Anal. Calcd for $C_{20}H_{16}FeN_2O$: C, 67.44; H, 4.53; N, 7.86. Found: C, 67.45; H, 4.54; N, 7.81.

[Tetrakis(2-ferrocenylethoxy)phthalocyaninato]zinc(II) (4). A mixture of **3** (100 mg, 0.28 mmol) and $Zn(OAc)_2 \cdot 2H_2O$ (22 mg, 0.10 mmol) in *n*-hexanol (3 mL) was heated to 90 °C; then 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.01 mL, 0.07 mmol) was added. The mixture was stirred at 150 °C for 16 h; then the volatiles were removed under reduced pressure. The resulting deep green residue was subjected to chromatography using $CHCl_3$ as eluent to give **4** as a green solid (80 mg, 77%). ^1H NMR: δ 8.38−8.98 (m, 4 H, Ar H), 7.66−8.08 (m, 4 H, Ar H), 7.00−7.64 (m, 4 H, Ar H), 4.54−4.92 (m, 8 H, OCH_2), 4.02−4.38 (m, 36 H, Fc), 2.86−3.50 (m, 8 H, $FcCH_2$). UV−vis (THF) [λ_{max}, nm (log ϵ)]: 316 (5.41), 347 (5.35), 629 (5.29), 664 (sh), 698 (5.94). MS (MALDI-TOF): an isotopic cluster peaking at m/z 1490.2 (M^+). Anal. Calcd for $C_{80}H_{64}Fe_4N_8O_4Zn$: C, 64.48; H, 4.33; N, 7.52. Found: C, 65.28; H, 4.63; N, 7.32.

3,6-Bis(2-ferrocenylethoxy)phthalonitrile (7). A mixture of 2,3-dicyanohydroquinone (**6**; 200 mg, 1.25 mmol) and K_2CO_3 (700 mg, 5.07 mmol) in DMF (4 mL) was stirred at room temperature for 15 min. Then 2-ferrocenylethyl *p*-toluenesulfonate (**5**; 1.0 g, 2.60 mmol) was added and the mixture was stirred at 90 °C for 2 days. The resulting dark brown solution was poured into H_2O (100 mL) and then extracted with $CHCl_3$ (3 × 50 mL). The combined extracts were dried with anhydrous Na_2SO_4 and evaporated in vacuo. The residue was purified by column chromatography using $CHCl_3$/hexanes (4:1) as eluent to obtain **7** as a yellow solid (400 mg, 55%; mp 198−200 °C). ^1H NMR: δ 7.04 (s, 2 H, Ar H), 4.21 (s, 4 H, Fc), 4.14 (s, 10 H, Fc), 4.11 (s, 4 H, Fc), 4.08 (t, $J = 6.3$ Hz, 4 H, OCH_2), 2.87 (t, $J = 6.3$ Hz, 4 H, $FcCH_2$). $^{13}C\{^1H\}$ NMR: δ 155.0, 118.2, 113.1, 105.3, 83.5, 70.8, 68.9, 68.6, 67.8, 29.7. IR (KBr): ν 2227 m cm^{-1} ($C{\equiv}N$). HRMS (LSI): m/z calcd for $C_{32}H_{28}{}^{56}Fe_2N_2O_2$ (M^+) 584.0849, found 584.0856. Anal. Calcd for $C_{32}H_{28}Fe_2N_2O_2$: C, 65.78; H, 4.83; N, 4.79. Found: C, 65.18; H, 4.67; N, 4.72.[16]

[1,4,8,11,15,18,22,25-Octakis(2-ferrocenylethoxy)phthalocyaninato]zinc(II) (8). A mixture of **7** (100 mg, 0.17 mmol) and $Zn(OAc)_2 \cdot 2H_2O$ (22 mg, 0.10 mmol) in *n*-pentanol (3 mL) was heated to 90 °C, then DBU (0.01 mL, 0.07 mmol) was added. The mixture was stirred at 150 °C overnight and then poured into a mixture of methanol and water (1:1, 50 mL). The precipitate formed was filtered off and chromatographed on a basic alumina column using $CHCl_3$/THF (5:1) as eluent to give **8** as a green powder (54 mg, 53%). ^1H NMR (C_6D_6): δ 7.48 (br s, 8 H, Ar H), 5.04 (br s, 16 H, OCH_2), 4.29 (s, 16 H, Fc), 4.07 (s, 40 H, Fc), 3.92 (s, 16 H, Fc), 3.27 (br s, 16 H, $FcCH_2$). UV−vis (THF) [λ_{max}, nm (log ϵ)]: 327 (5.15), 661 (5.04), 736 (5.72). MS (MALDI-TOF): an isotopic cluster peaking at m/z 2404.6 (M^+). Anal. Calcd for $C_{128}H_{112}Fe_8N_8O_8Zn$: C, 63.99; H, 4.70; N, 4.66. Found: C, 62.66; H, 4.71; N, 4.45.[16]

Tetrakis(2-ferrocenylethoxy)phthalonitrile (10). A mixture of **1** (1.38 g, 6.0 mmol), tetrafluorophthalonitrile (**9**; 0.10

---

[12] A few ferrocene-containing porphyrazines have also been reported: (a) Baumann, T. F.; Sibert, J. W.; Olmstead, M. M.; Barrett, A. G. M.; Hoffman, B. M. *J. Am. Chem. Soc.* **1994**, *116*, 2639. (b) Baumann, T. F.; Nasir, M. S.; Sibert, J. W.; White, A. J. P.; Olmstead, M. M.; Williams, D. J.; Barrett, A. G. M.; Hoffman, B. M. *J. Am. Chem. Soc.* **1996**, *118*, 10479.

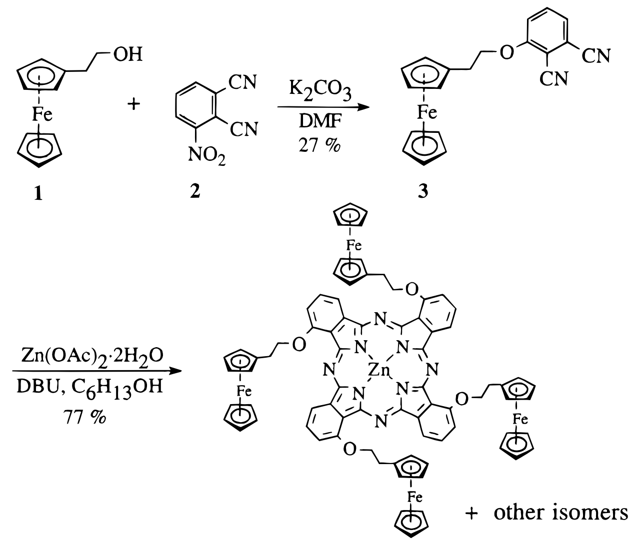
[13] Rinehart, K. L., Jr.; Curby, R. J., Jr.; Sokol, P. E. *J. Am. Chem. Soc.* **1957**, *79*, 3420.

[14] Lee, C. C.; Chen, S.-C.; Sutherland, R. G. *Can. J. Chem.* **1975**, *53*, 232.

[15] Sawyer, D. T.; Sobkowiak, A.; Roberts, J. L., Jr. *Electrochemistry for Chemists*, 2nd ed.; Wiley: New York, 1995; Chapter 6.

[16] The experimental carbon contents for **7** and **8** were marginal. Attempts to further purify these compounds by column chromatography and obtain better analytical data, unfortunately, were unsuccessful. The unsatisfactory data for **8** could be related to the fact that phthalocyanines are notoriously difficult to combust (see: Hu, M.; Brasseur, N.; Yildiz, S. Z.; van Lier, J. E.; Leznoff, C. C. *J. Med. Chem.* **1998**, *41*, 1789). The compounds were deemed to be pure by chromatographic and spectroscopic analyses.

Scheme 1



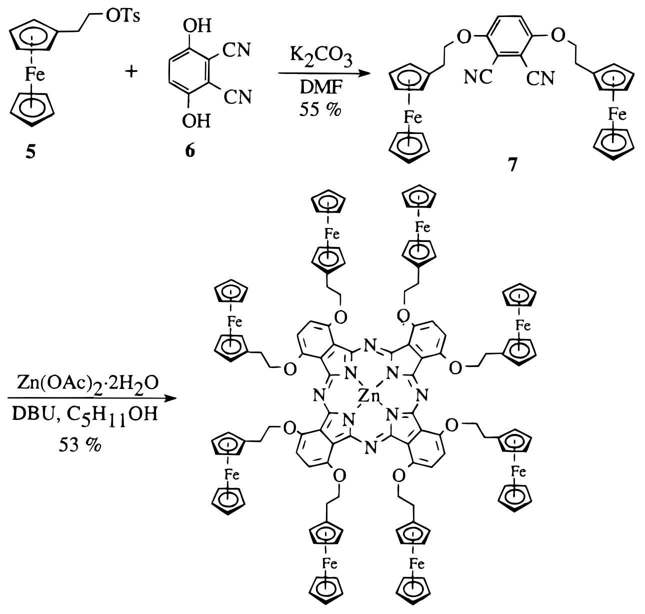
4

g, 0.5 mmol), and K_2CO_3 (0.83 g, 6.0 mmol) in DMF (5 mL) was stirred at 100 °C for 24 h and then poured into water (50 mL). The mixture was extracted with $CHCl_3$ (3 × 30 mL), and the combined extracts were dried over anhydrous Na_2SO_4 and rotary evaporated. The crude product was purified by column chromatography with toluene as eluent to afford a yellow solid (265 mg, 51%, mp 139−141 °C). ^1H NMR: δ 4.0−4.3 (m, 44 H, Fc & OCH_2), 2.76 (br s, 4 H, $FcCH_2$), 2.67 (br s, 4 H, $FcCH_2$). $^{13}C\{^1H\}$ NMR: δ 152.7, 150.7, 113.1, 104.5, 84.3, 83.8, 75.7, 74.9, 69.3, 69.2, 68.7, 68.2, 67.8, 30.5, 30.4. IR (KBr): ν 2231 m cm^{-1} ($C{\equiv}N$). MS (LSI): an isotopic cluster peaking at *m/z* 1040.14 (M^+). Anal. Calcd for $C_{56}H_{52}Fe_4N_2O_4$: C, 64.65; H, 5.04; N, 2.69. Found: C, 64.54; H, 5.06; N, 2.72.

Hexadecakis(2-ferrocenylethoxy)phthalocyanine (11). Lithium (10 mg, 1.44 mmol) was suspended in *n*-octanol (3 mL). The suspension was stirred at 150 °C until the solution became clear. The homogeneous solution was cooled to 90 °C, and then dinitrile **10** (100 mg, 0.10 mmol) was added. The temperature was increased to 120 °C, at which point the mixture was stirred for 4 h. Glacial acetic acid (3 mL) was then added, and the mixture was kept at this temperature for 15 min before being poured into a mixture of methanol and water (1:1, 50 mL). The precipitate formed was filtered off and chromatographed with $CHCl_3$/THF (10:1) as eluent to give **11** as a green powder (15 mg, 15%). ^1H NMR: δ 5.08 (br s, 16 H, OCH_2), 4.58 (br s, 16 H, OCH_2), 4.35 (br s, 16 H, Fc), 4.08−4.23 (m, 96 H, Fc), 3.98 (br s, 32 H, Fc), 3.18 (br s, 16 H, $FcCH_2$), 3.08 (br s, 16 H, $FcCH_2$). UV−vis (THF) [λ_{max}, nm (log ϵ)]: 323 (5.21), 349 (5.16), 386 (5.13), 669 (5.01), 692 (5.04), 732 (sh), 756 (5.62). MS (MALDI-TOF): an isotopic cluster peaking at *m/z* 4168.6 (M^+). Anal. Calcd for $C_{224}H_{210}Fe_{16}N_8O_{16}$: C, 64.62; H, 5.08; N, 2.69. Found: C, 64.31; H, 5.21; N, 2.66.

Results and Discussion

Scheme 2



8

Treatment of 2-ferrocenylethanol (**1**) with 3-nitrophthalonitrile (**2**) under alkaline conditions gave the dinitrile **3**, which underwent typical cyclization to afford the tetrasubstituted phthalocyanine **4** as a mixture of constitutional isomers, as revealed by ^1H NMR spectroscopy (Scheme 1). In an attempt to prepare a single 1,8,15,22-tetrasubstituted isomer, **3** was treated with lithium in *n*-octanol at lower temperature (70 °C).[17] After acidification with acetic acid, a deep green solid was obtained, the UV−vis spectrum of which showed the characteristic pattern for metal-free phthalocyanines (λ_{max} ($CHCl_3$): 320, 356, 629, 663, 695, 730 nm). Its ^1H NMR spectrum recorded in $CDCl_3$, however, exhibited complex multiplets for the phthalocyanine ring protons, indicating that a mixture of isomers was produced. It is worth noting that, under similar reaction conditions, a single isomer could be obtained for phthalocyanines containing substituents such as $-OCH_2C_6H_4{}^nBu$, $-OCH_2{}^tBu$, −OMe, and $-OCHEt_2$ at the 1,8,15,22-positions.[17,18] It appears that the steric as well as the electronic nature of the substituent is crucial in the formation of a single isomer in the cyclization of 3-substituted phthalonitriles.[17b,19]

The octaferrocenylphthalocyanine **8** was prepared by the route shown in Scheme 2. Reaction of the tosylate **5** with 2,3-dicyanohydroquinone (**6**) in the presence of K_2CO_3 afforded the dinitrile **7** in moderate yield. Upon treatment with zinc acetate and DBU, this compound was converted to **8**, which could only be purified by chromatography on basic alumina columns; the compound was unstable and turned yellow in silica gel columns.

The tetraferrocenyl dinitrile **10** was prepared using tetrafluorophthalonitrile (**9**) and **1** as the starting materials (Scheme 3).[20] Substitution occurred in the presence of K_2CO_3, giving **10** in moderate yield. Attempts to prepare the corresponding zinc phthalocyanine using the above procedure were not successful. The metal-free hexadecakis(2-ferrocenylethoxy)phthalocyanine (**11**), however, could be prepared using lithium in *n*-octanol followed by acid treatment. The reaction temperature was critical in the preparation of **11** and should be controlled at ca. 120−130 °C. Higher reaction

---

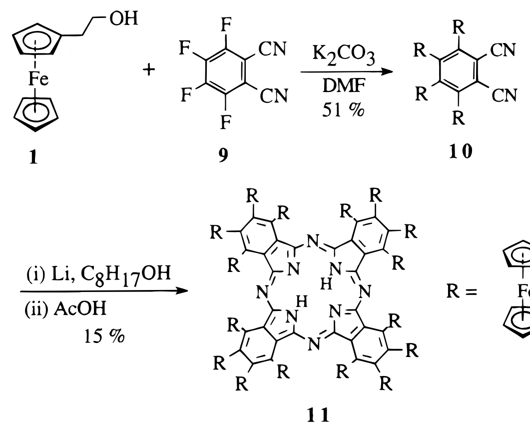
(17) (a) Leznoff, C. C.; Hu, M.; McArthur, C. R.; Qin, Y.; van Lier, J. E. *Can. J. Chem.* **1994**, *72*, 1990. (b) Leznoff, C. C.; Hu, M.; Nolan, K. J. M. *Chem. Commun.* **1996**, 1245.

(18) (a) Kasuga, K.; Kawashima, M.; Asano, K.; Sugimori, T.; Abe, K.; Kikkawa, T.; Fujiwara, T. *Chem. Lett.* **1996**, 867. (b) Kasuga, K.; Asano, K.; Lin, L.; Sugimori, T.; Handa, M.; Abe, K.; Kikkawa, T.; Fujiwara, T. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1859.

(19) Rager, C.; Schmid, G.; Hanack, M. *Chem. Eur. J.* **1999**, *5*, 280.

(20) Eberhardt, W.; Hanack, M. *Synthesis* **1997**, 95.

Scheme 3



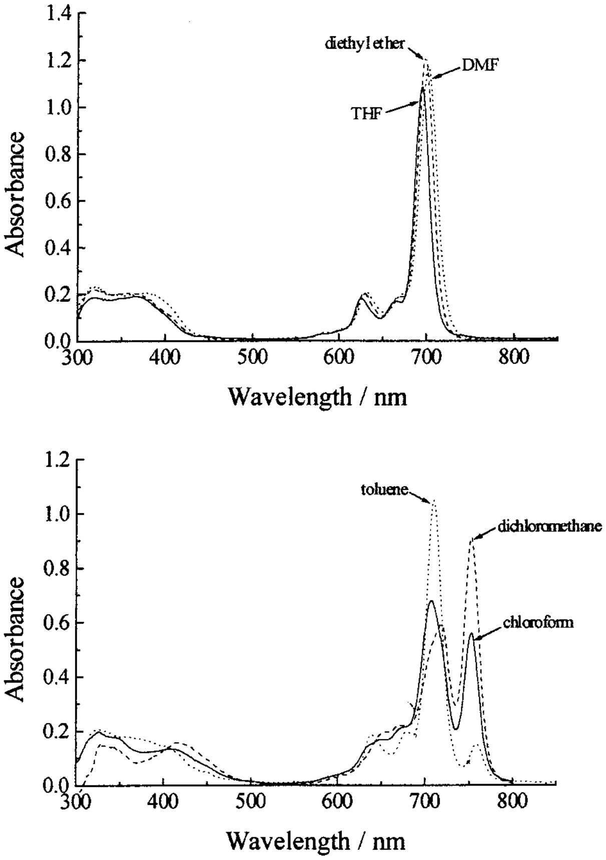


Figure 1. UV−vis spectra of **4** in THF, DMF, diethyl ether, toluene, $CHCl_3$, or CH_2Cl_2.

temperatures would lead to the formation of black mixtures with no indication of the presence of **11**.

All the new compounds were characterized by elemental analyses and various spectroscopic methods. The UV−vis spectra of **4** are peculiar and worth mentioning. As shown in Figure 1, the spectra of **4** are solvent-dependent. In THF, DMF, and diethyl ether solutions, the spectra show a typical Q-band at 695−701 nm along with broad signals at 316−379 nm due to the phthalocyanine (B band) and ferrocene. In less polar solvents such as toluene, $CHCl_3$, and CH_2Cl_2, the Q-band is broadened and slightly shifted to the red (707−718 nm), and an additional band emerges at 752−758 nm. Similar phenomena were observed previously for the Mg(II) and Zn(II) (**12**) complexes of 1,8,15,22-tetrakis-(3-pentyloxy)phthalocyanine, and the longest wavelength band was tentatively attributed to a slipped face-to-face dimer.[18b] To reveal the origin of this band, the concentration dependency of the absorption spectra of **4** and **12** was studied. For both compounds in toluene or CH_2Cl_2, the intensity of the "monomer" band at ca. 700 nm decreased while that of the "dimer" band at ca. 760 nm increased with decreasing concentration of phthalocyanines (from 1×10^{-5} to 2×10^{-7} mol dm^{-3}). Compound **12** showed fluorescence emission at 714 nm in CH_2Cl_2 upon excitation at 630 nm; no emission was observed at a wavelength longer than 760 nm, indicating that the species absorbing at 760 nm was not fluorescent. The spectral changes of a CH_2Cl_2 solution of **12** after ultrasonic treatment were also examined. The "dimer" band became more intense, while the "monomer" band together with the fluorescence at 714 nm was significantly weakened. All the observations suggested that the longer wavelength absorption may not be due to a cofacial dimer which is expected to be dominant in higher concentrations as in the cases of zinc(II)[21] and aluminum(III)[22] complexes of tetrasulfonatophthalocyanine in MeCN/H_2O and aqueous alcohol, respectively, which were also assumed to adopt a dimeric structure with a face-to-face slipped or tilted conformation. The dimer of the former zinc(II) complex was also found to be emissive, which again contradicts our results.[21] Thus, the exact nature of this band remains to be explored.

The electrochemical properties of all the ferrocenyl phthalonitriles and phthalocyanines were investigated by cyclic voltammetry, and the data are collected in Table 1. The voltammograms of the dinitriles **3**, **7**, and **10** in DMF showed two couples at ca. 0.0 and −2.0 V assignable to the ferrocene (oxidation to ferrocenium cation) and dicyanobenzene (reduction to the corresponding radical anion) moieties, respectively. By comparison of the reduction potentials of benzonitrile (−2.32 V vs SCE or −2.63 V vs Ag−Ag$^+$ in MeCN),[23,24] phthalonitrile, and these compounds (Table 1), it is clear that the electron-withdrawing cyano group greatly facilitates the addition of electrons to the π system while the electron-donating 2-ferrocenylethoxy group makes the reduction more difficult. On the basis of the separation between the anodic and cathodic potentials (ΔE) and the plots of peak current vs square root of the scan rate, which showed deviation from a straight line at higher scan rates, all these couples were regarded as quasi-reversible, except the phthalonitrile reduction of **10**, which was basically irreversible. Addition of ferrocene to the solution of **10** only increased the cathodic and anodic current without significantly shifting or splitting the potential. This indicated that the ferrocenyl units in **10** are electrochemically very similar to free ferrocene. The voltammogram of ferrocene was also recorded under identical conditions. The peak currents for the ferrocene−ferrocenium couple were much lower

---

(21) Kaneko, Y.; Arai, T.; Tokumaru, K.; Matsunaga, D.; Sakuragi, H. *Chem. Lett.* **1996**, 345.

(22) Yoon, M.; Cheon, Y.; Kim, D. *Photochem. Photobiol.* **1993**, *58*, 31.

(23) Bartak, D. E.; Houser, K. J.; Rudy, B. C.; Hawley, M. D. *J. Am. Chem. Soc.* **1972**, *94*, 7526.

(24) The potential of Ag−Ag$^+$ in MeCN was taken as +0.31 V vs the saturated calomel electrode (SCE), as determined for this system previously using ferrocene as an internal standard (see: Wong, Y.-L.; Ma, J.-F.; Law, W.-F.; Yan, Y.; Wong, W.- T.; Zhang, Z.-Y.; Mak, T. C. W.; Ng, D. K. P. *Eur. J. Inorg. Chem.* **1999**, 313).

Table 1. Electrochemical Data for Phthalonitriles and Phthalocyanines[a]

	ferrocene			phthalonitrile/phthalocyanine								
compd	$E_{1/2}$(ox)	ΔE^b	$\|i_{p,a}/i_{p,c}\|$	$E_{1/2}$(ox1)	ΔE^b	$\|i_{p,a}/i_{p,c}\|$	$E_{1/2}$(red1)	ΔE^b	$\|i_{p,a}/i_{p,c}\|$	$E_{1/2}$(red2)	ΔE^b	$\|i_{p,a}/i_{p,c}\|$
phthalonitrile							−1988	91	0.95			
3	43	79	1.02				−2008	93	0.89			
7	20	70	1.02				−2013	70	0.91			
10	63	76	0.97				−2078	154	0.53			
4[c]	44	72	1.01	288	56	0.54	−1306	72	1.12	−1784	104	0.63
8[d]	43	93	1.01	215	57	0.66	−1348	53	0.80	−1788	89	0.78
11[e]	79	226	0.37	342[f]			−1209	106	0.59	−1493	138	0.93

[a] Recorded with $[Bu_4N][ClO_4]$ as electrolyte in DMF (0.1 mol dm^{-3}) at ambient temperature with a scan rate of 100 mV s^{-1} unless otherwise stated. Potentials are expressed in mV vs Ag−Ag$^+$ in MeCN. [b] $\Delta E = |E_{p,c} - E_{p,a}|$. [c] $E_{1/2}$(red3) for phthalocyanine appeared at −1982 mV with ΔE = 111 mV. [d] The scan rate was 20 mV s^{-1}. $E_{1/2}$(ox2) for phthalocyanine appeared at 490 mV with ΔE = 43 mV. [e] In CH_2Cl_2. $E_{p,c}$(ox2) and $E_{p,c}$(red3) for phthalocyanine appeared at 610 and −1852 mV, respectively. [f] $E_{p,c}$.

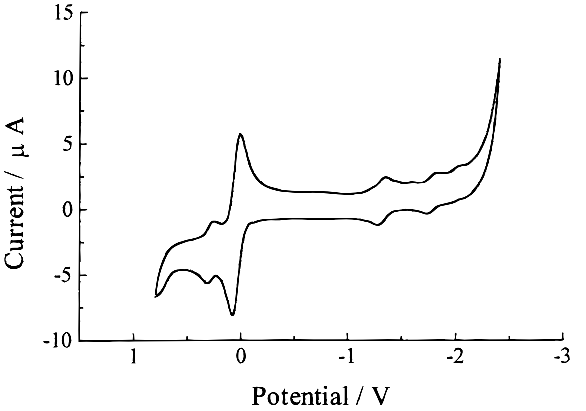


Figure 2. Cyclic voltammogram of **4** in DMF containing 0.1 mol dm^{-3} $[Bu_4N][ClO_4]$ at a scan rate of 100 mV s^{-1}.

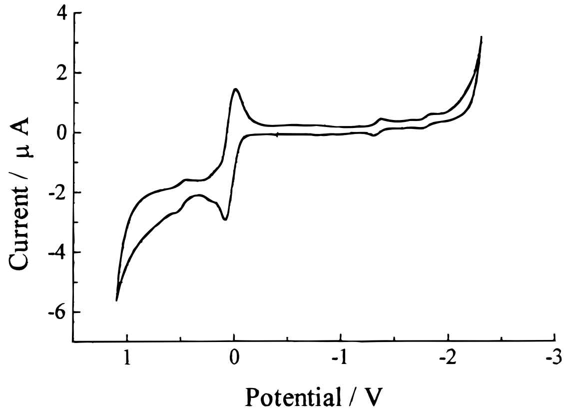


Figure 3. Cyclic voltammogram of **8** in DMF containing 0.1 mol dm^{-3} $[Bu_4N][ClO_4]$ at a scan rate of 20 mV s^{-1}.

than those of **10** at the same concentration, showing that **10** may undergo a multielectron redox process.

All the voltammograms of phthalocyanines **4** (Figure 2), **8** (Figure 3), and **11** (Figure 4) showed a quasi-reversible oxidation attributed to the ferrocenyl units together with one to two quasi-reversible oxidations and up to three quasi-reversible reductions due to the phthalocyanine π system (Table 1).[25] As **11** was not soluble in DMF, the voltammogram was recorded in CH_2Cl_2. The potential difference between the first oxidation and reduction couples for phthalocyanines is related to the energy gap between their highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO). The values for these ferrocenylphthalocyanines are very similar and fall in the normal region (1.5−1.7 V) reported for other phthalocyanines.[25] As shown in Figures 2−4, a remarkable trend is the increase of relative peak currents of the ferrocene couple with respect to either one of the phthalocyanine couples as the number of ferrocenyl units increased from 4 to 8 to 16 in a molecule. A sharp cathodic stripping peak was observed for the ferrocene couple of **11** with a peak current ratio $|i_{p,a}/i_{p,c}|$ much smaller than unity (0.37). This waveform suggested that adsorption of the oxidized product onto the electrode may occur, which was also seen for some ferrocene-containing dendrimers.[5a,e] Addition of a small amount of MeCN (1:5 v/v in relation to CH_2Cl_2) reduced the peak-to-peak separation (ΔE) of the ferrocene couple to 126 mV. This, however, could not solve the problem of adsorption ($|i_{p,a}/i_{p,c}|$ = 0.25), and the other redox couples for phthalocyanine turned to be even weaker. The voltammogram of **11** in THF gave a higher peak current ratio ($|i_{p,a}/i_{p,c}|$ = 0.57) for the ferrocene couple, showing that this solvent can better dissolve the oxidized product and relieve the adsorption. The couple, however, became less reversible, as shown by the large peak-to-peak separation (420 mV). In all cases, no splitting of the ferrocene couple was observed. Such splitting again was not seen in the differential pulse voltammograms of all these ferrocenylphthalocyanines recorded under the same conditions. It appears that all the ferrocenyl moieties attached to these phthalocyanines behave independently and are oxidized at the same potential.

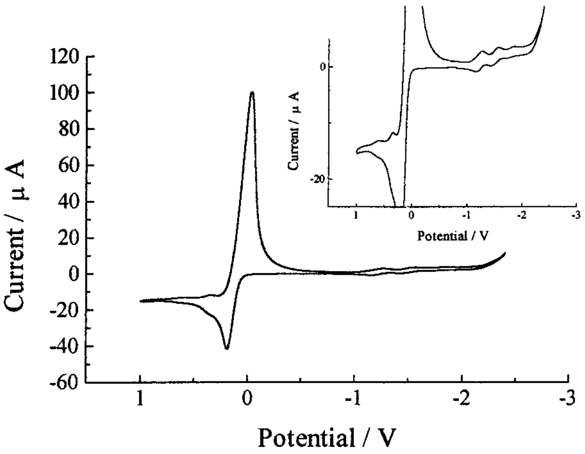


Figure 4. Cyclic voltammogram of **11** in CH_2Cl_2 containing 0.1 mol dm^{-3} $[Bu_4N][ClO_4]$ at a scan rate of 100 mV s^{-1}. An enlarged figure is shown in the inset.

The electronic interaction between the ferrocenyl units and the macrocyclic core in these ferrocenylphtha-

---

(25) Lever, A. B. P.; Milaeva, E. R.; Speier, G. In *Phthalocyanines: Properties and Applications*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH: New York, 1993; Vol. 3, pp 1−69.

locyanines also seemed to be insignificant at the ground state. This was based on the observation that the absorption spectrum of **12** mixed with 4 equiv of ferrocene was almost identical with that of **4** in $CHCl_3$. The ferrocenyl moieties, however, were very efficient in quenching the excited state of **4**, for which no fluorescence was observed. We attributed this quenching to a photoinduced electron transfer (PET) in which ferrocene behaves as an electron donor. The overall free energy change for this PET was determined by the Rehm–Weller equation:[26]

$$\Delta G° = e[E_{1/2}(D^{\bullet +}/D) - E_{1/2}(A/A^{\bullet -})] - \Delta E(0,0) - w_p$$

where e is the charge on the electron, $E_{1/2}$ is the half-wave reduction for potential for either the donor ($D^{\bullet +}$/D) or acceptor ($A/A^{\bullet -}$) couples in volts, $\Delta E(0,0)$ is the relevant singlet state energy, and w_p is a Coulombic interaction term between the oxidized donor and reduced acceptor. For polar solvents with a high dielectric constant, this term is usually small (<0.1 eV) and is neglected here.[3f] On the basis of the electrochemical data for **4** (Table 1) and the value of $\Delta E(0,0)$ for (phthalocyaninato)zinc(II) (1.83 eV),[27] the value of $\Delta G°$ was determined to be −0.48 eV, showing that this PET is a thermodynamically favorable process. The alternative quenching pathway by energy transfer from the phthalocyanine's S_1 state to ferrocene is excluded because of its endothermic nature (the S_1 state of ferrocene at 2.46 eV).[28] The estimated value of $\Delta G°$ for this system is of the same order with and lies between those of octamethylporphyrins linked with a ferrocenyl group at a meso position (ca. −0.1 eV)[3d] and the ferrocenylporphyrin containing three cationic pyridinum moieties at the meso positions (−0.66 eV).[3f]

To conclude, we have prepared and characterized three novel phthalocyanines with 4, 8, and 16 ferrocenyl units. The redox-active ferrocenyl groups appear to be independent, undergoing an electrochemical oxidation at the same potential and a rapid electron transfer to the excited phthalocyanine core.

Acknowledgment. We thank Prof. D. Chan's group for measuring the MALDI-TOF spectra and the Hong Kong Research Grants Council and The Chinese University of Hong Kong for financial support.

OM990208X

---

[26] Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

[27] Kavarnos, G. J. *Fundamentals of Photoinduced Electron Transfer*; VCH: New York, 1993; p 43.

[28] Sohn, Y. S.; Hendrickson, D. N.; Gray, H. B. *J. Am. Chem. Soc.* **1971**, *93*, 3603.