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Tetrapyrrole Derivatives Substituted with Ferrocenylethynyl Moieties. Synthesis and Electrochemical Studies†

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Up to eight redox-active ferrocenyl units have been incorporated, through the unsaturated ethynyl linkers, on the periphery of a series of cyclic tetrapyrrole derivatives including zinc(II) phthalocyanine and 2,3-naphthalocyanine, and nickel(II) *meso*-diphenylporphyrin. The synthesis of the former two macrocycles **4** and **7** involves the Sonogashira coupling reaction of ferrocenylethyne with 4,5-dichlorophthalonitrile (**1**) or 6,7-dibromonaphthalonitrile (**5**), respectively, followed by a base-promoted cyclization. The *meso*-bis(ferrocenylethynyl)porphyrin **11** has been prepared from the dibromo analogue **10** also by a palladium-catalyzed coupling reaction. These novel macrocyclic compounds have been spectroscopically and electrochemically characterized. As revealed by cyclic voltammetry, the ferrocenyl moieties appear to be electrochemically independent in these complexes and there is no significant electronic coupling among the iron(II) centers.

Introduction

Studies of electronic interactions in systems containing multiple redox-active centers are of fundamental importance in the development of molecular-based electronic devices.[1] Owing to the high stability, ease of functionalization, and well-defined electrochemistry, ferrocene has been widely used as the redox-active centers which are linked together with a wide variety of structural units such as saturated and unsaturated carbon bridges,[2] delocalized fused rings,[2] and polymeric and dendritic backbones.[3,4] Although different extents of metal−metal interactions have been revealed for some of these systems, examples showing electronic coupling between the ferrocenyl units through a two-dimensional π system are extremely rare.[5] Several porphyrin and phthalocyanine derivatives incorporated with up to four ferrocenyl groups have been reported,[6,7] but none of them shows significant metal−metal coupling. We have recently prepared a novel series of phthalocyanines connected on the periphery to four, eight, and 16 ferrocenyl units with oxyethylene linkers.[8] Electrochemical studies show that the redox centers are again electrochemically independent, which may be attributed to the saturated nature of the linkers. To examine the effects of the connection units, we have prepared a series of cyclic tetrapyrrole derivatives in which the ferrocenyl moieties are linked to the macrocycles with unsaturated ethynyl bridges. These linkers should impose a coplanar orientation between the macrocycle and the ferrocenyl groups, thereby enabling effective electronic interactions within the molecule.[9] They thus may serve as better candidates than other unsaturated linkers such as the ethenyl moieties.[10,11] This paper describes the synthesis and electrochemical behavior of these novel ferrocenylethynyl macrocyclic compounds.

Experimental Section

Experimental details concerning the purification of solvents, spectroscopic measurements, and electrochemical studies were described elsewhere.[8] Chromatographic purifications were

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† Dedicated to Dr. Tze-Lock Chan on the occasion of his retirement.

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performed on silica gel columns (Macherey-Nagel, 70−230 mesh) with the indicated eluents. 4,5-Dichlorophthalonitrile (**1**),[12] ferrocenylethyne (**2**),[13] 6,7-dibromonaphthalonitrile (**5**),[14] 4-[3′,4′,5′-tris(*n*-dodecyloxy)benzyloxy]phthalonitrile (**8**),[15] and (5,15-dibromo-10,20-diphenylporphyrinato)nickel(II) (**10**)[16] were prepared according to literature procedures.

4,5-Bis(ferrocenylethynyl)phthalonitrile (3). A mixture of dinitrile **1** (100 mg, 0.51 mmol), ferrocenylethyne (**2**) (426 mg, 2.03 mmol), $Pd(PPh_3)_2Cl_2$ (20 mg, 0.03 mmol), and CuI (3 mg, 0.02 mmol) in triethylamine (10 mL) was stirred at 90 °C overnight. The resulting suspension was filtered, and the red solid collected was washed with hexanes and purified by column chromatography using $CHCl_3$/hexanes (4:1) as eluent (210 mg, 76%; mp 219−220 °C). ^1H NMR (300 MHz, $CDCl_3$): δ 7.83 (s, 2 H, ArH), 4.62 (s, 4 H, Fc), 4.40 (s, 4 H, Fc), 4.28 (s, 10 H, Fc). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 135.8, 130.8, 115.1, 112.9, 101.1, 82.9, 72.1, 70.4, 70.1, 62.9. IR (KBr): v 2204 s cm^{-1} (C≡N and C≡C). UV−vis (THF) [λ_{max}, nm (log ϵ)]: 312 (4.89), 494 (4.20). HRMS (LSI): m/z calcd for $C_{32}H_{20}{}^{56}Fe_2N_2$ (M^+) 544.0325, found 544.0329. Anal. Calcd for $C_{32}H_{20}Fe_2N_2$: C, 70.62; H, 3.70; N, 5.15. Found: C, 70.38; H, 3.61; N, 4.98. Crystallographic data: $C_{32}H_{20}Fe_2N_2$, fw 544.20, monoclinic space group $P2_1/n$ (no. 14), with $a = 16.170(4)$ Å, $b = 9.424(2)$ Å, $c = 17.487(4)$ Å, $\beta = 110.050(4)^o$, $V = 2503.2(9)$ Å^3, and $D_{calcd} = 1.444$ g cm^{-3} for $Z = 4$. The structure was solved by direct methods and refined by a full-matrix least-squares procedure using 2708 data points to a conventional R value of 0.0850 ($R_w = 0.2043$).

[2,3,9,10,16,17,23,24-Octakis(ferrocenylethynyl)phthalocyaninato]zinc(II) (4). A mixture of dinitrile **3** (200 mg, 0.37 mmol), $Zn(OAc)_2{\cdot}2H_2O$ (33 mg, 0.15 mmol), and a few drops of DBU in *n*-pentanol (10 mL) was heated at 150 °C for 12 h. The resulting dark green solution was evaporated in vacuo, and the residue was chromatographed using $CHCl_3$/MeOH (2:1) as eluent. The crude product was further purified by repeated chromatography using $CHCl_3$/MeOH (9:1) as eluent (27 mg, 13%). ^1H NMR (300 MHz, THF-d_8, ca. 6.4 × 10^{-4} mol dm^{-3}): δ 9.4 (br s, 8 H, ArH), 4.92 (s, 16 H, Fc), 4.48 (two overlapping signals, 56 H, Fc). IR (KBr): v 2200 m cm^{-1} (C≡C). UV−vis (THF) [λ_{max}, nm (log ϵ)]: 378 (4.97), 661 (4.55), 702 (sh), 737 (5.24). MS (MALDI-TOF): an isotopic cluster peaking at m/z 2242.6 (M^+).

6,7-Bis(ferrocenylethynyl)naphthalonitrile (6). A mixture of dinitrile **5** (0.40 g, 1.20 mmol), ferrocenylethyne (**2**) (1.00 g, 4.76 mmol), $Pd(PPh_3)_2Cl_2$ (60 mg, 0.09 mmol), and CuI (10 mg, 0.07 mmol) in triethylamine (10 mL) was stirred at 90 °C for 12 h. The resulting brown solid was filtered and washed with hexanes and a small amount of $CHCl_3$ to give an orange solid, which was further purified by column chromatography using $CHCl_3$ as eluent (0.54 g, 76%; dec 213 °C). ^1H NMR (300 MHz, $CDCl_3$): δ 8.22 (s, 2 H, ArH), 8.05 (s, 2 H, ArH), 4.67 (s, 4 H, Fc), 4.40 (s, 4 H, Fc), 4.32 (s, 10 H, Fc).[17] IR (KBr): v 2235 m, 2203 s cm^{-1} (C≡N and C≡C). UV−vis (THF) [λ_{max}, nm (log ϵ)]: 315 (5.16), 391 (4.32), 465 (4.19). HRMS (LSI): m/z calcd for $C_{36}H_{22}{}^{56}Fe_2N_2$ (M^+) 594.0482, found 594.0428. Anal. Calcd for $C_{36}H_{22}Fe_2N_2$: C, 72.76; H, 3.73; N, 4.71. Found: C, 72.48; H, 3.75; N, 4.60.

[3,4,12,13,21,22,30,31-Octakis(ferrocenylethynyl)naphthalocyaninato]zinc(II) (7). A mixture of dinitrile **6** (100 mg, 0.17 mmol), $Zn(OAc)_2{\cdot}2H_2O$ (12 mg, 0.05 mmol), and a few drops of DBU in *n*-pentanol (5 mL) was heated at 150 °C for 10 h to give a dark brown solution. The volatiles were removed under reduced pressure, then the residue was chromatographed using THF as eluent. A brown solution was obtained which was concentrated and chromatographed again using THF/hexanes (2:1) as eluent. A greenish-brown band was developed which was collected and evaporated to give the product as a greenish-brown solid (28 mg, 27%). ^1H NMR (300 MHz, THF-d_8, ca. 1.2 × 10^{-3} mol dm^{-3}): δ 9.1 (br s, 8 H, ArH), 8.5 (br s, 8 H, ArH), 4.89 (s, 16 H, Fc), 4.52 (s, 16 H, Fc), 4.45 (s, 40 H, Fc). IR (KBr): v 2200 m cm^{-1} (C≡C). UV−vis (THF) [λ_{max}, nm (log ϵ)]: 366 (5.10), 495 (4.43), 704 (4.76), 751 (4.77), 789 (5.40). MS (MALDI-TOF): an isotopic cluster peaking at m/z 2442.1 (M^+). Anal. Calcd for $C_{144}H_{88}Fe_8N_8Zn$: C, 70.81; H, 3.63; N, 4.59. Found: C, 69.34; H, 3.99; N, 4.36.

[2-[3′,4′,5′-Tris(*n*-dodecyloxy)benzyloxy]-10,11,19,20,-28,29-hexakis(ferrocenylethynyl)tribenzophthalocyaninato]zinc(II) (9). A mixture of dinitrile **6** (213 mg, 0.36 mmol), dinitrile **8** (19 mg, 25 μmol), $Zn(OAc)_2{\cdot}2H_2O$ (30 mg, 0.14 mmol), and a few drops of DBU in *n*-pentanol (20 mL) was heated at 150 °C for 12 h. After a brief cooling, the volatiles were removed under reduced pressure. The residue was chromatographed using THF/hexanes (2:1) as eluent giving two green bands containing the unsymmetrical tribenzophthalocyanine **9** (21 mg, 32%) and the symmetrical naphthalocyanine **7** (44 mg, 20%), respectively, which were collected, evaporated, and dried in vacuo. ^1H NMR (300 MHz, THF-d_8, ca. 6.3 × 10^{-4} mol dm^{-3}): δ 9.1 (br s, 6 H, ArH), 8.6 (br s, 9 H, ArH), 7.1 (br s, 2 H, ArH), 5.6 (br s, 2 H, OCH_2), 4.86 (s, 12 H, Fc), 4.45 (two overlapping signals, 42 H, Fc), 4.2 (br s, 6 H, OCH_2), 1.9 (br s, 6 H, CH_2), 1.6 (br s, 6 H, CH_2), 1.3 (br s, 48 H, CH_2), 0.85−0.96 (m, 9 H, CH_3). IR (KBr): v 2204 m cm^{-1} (C≡C). UV−vis (THF) [λ_{max}, nm (log ϵ)]: 363 (5.04), 681 (4.61), 733 (4.82), 763 (5.35). MS (MALDI-TOF): an isotopic cluster peaking at m/z 2634.9 (M^+).

[5,15-Bis(ferrocenylethynyl)-10,20-diphenylporphyrinato]nickel(II) (11). A mixture of dibromide **10** (305 mg, 0.45 mmol), ferrocenylethyne (**2**) (370 mg, 1.76 mmol), $Pd(PPh_3)_2Cl_2$ (20 mg, 0.03 mmol), CuI (3 mg, 0.02 mmol), and triethylamine (2 mL) in THF (8 mL) was stirred at room temperature overnight. The volatiles were then removed in vacuo, and the residue was chromatographed using hexanes and then $CHCl_3$ as eluent to develop a green band which was collected and evaporated. The resulting green solid was further purified by reprecipitation in $CHCl_3$ using MeOH (277 mg, 66%). ^1H NMR (300 MHz, $CDCl_3$): δ 9.45 (d, $J = 4.5$ Hz, 4 H, β-H), 8.71 (d, $J = 4.5$ Hz, 4 H, β-H), 7.99 (poorly resolved d, $J = 7.2$ Hz, 4 H, Ph), 7.70 (s, 6 H, Ph), 4.94 (s, 4 H, Fc), 4.47 (two overlapping signals, 14 H, Fc). IR (KBr): v 2199 w cm^{-1} (C≡C). UV−vis (THF) [λ_{max}, nm (log ϵ)]: 433 (5.59), 564 (4.40), 624 (4.80). HRMS (LSI): m/z calcd for $C_{56}H_{36}{}^{56}Fe_2N_4{}^{58}Ni$ (M^+) 934.0992, found 934.0960.

Results and Discussion

Dialkynylphthalonitriles $C_6H_2(CN)_2(C{\equiv}CR)_2$, the precursors of octaalkynylphthalocyanines, have only been reported recently.[18] The preparation of these compounds usually involves the palladium-catalyzed coupling reaction of terminal alkynes with dibromo- or diiodophthalonitriles. We found that such coupling reactions could also proceed with the electron-deficient dichloro analogue

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(10) It has been found that for push−pull 5,15-diphenylporphyrins, ethynyl moiety is a better linker than ethenyl group to enhance electronic coupling across the system. This is due to the fact that the latter allows a tilted conformation between the porphyrin core and the electron donor/acceptor. See: Yeung, M.; Ng, A. C. H.; Drew, M. G. B.; Vorpagel, E.; Breitung, E. M.; McMahon, R. J.; Ng, D. K. P. *J. Org. Chem.* **1998**, *63*, 7143.

(11) Ferrocene-containing tetrapyrrole derivatives with other unsaturated linkers are also very rare. See: (a) Giasson, R.; Lee, E. J.; Zhao, X.; Wrighton, M. S. *J. Phys. Chem.* **1993**, *97*, 2596. (b) Burrell, A. K.; Campbell, W.; Officer, D. L. *Tetrahedron Lett.* **1997**, *38*, 1249. (c) Burrell, A. K.; Campbell, W. M.; Officer, D. L.; Scott, S. M.; Gordon, K. C.; McDonald, M. R. *J. Chem. Soc., Dalton Trans.* **1999**, 3349. (d) González, A.; Vázquez, P.; Torres, T. *Tetrahedron Lett.* **1999**, *40*, 3263.

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(14) Kovshev, E. I.; Puchnova, V. A.; Luk'yanets, E. A. *Zh. Org. Khim.* **1971**, *7*, 369.

(15) This dinitrile was prepared by treating 4-nitrophthalonitrile with 3,4,5-tris(*n*-dodecyloxy)benzyl alcohol in the presence of K_2CO_3 in DMF (Ng, A. C. H.; Ng, D. K. P. Manuscript in preparation).

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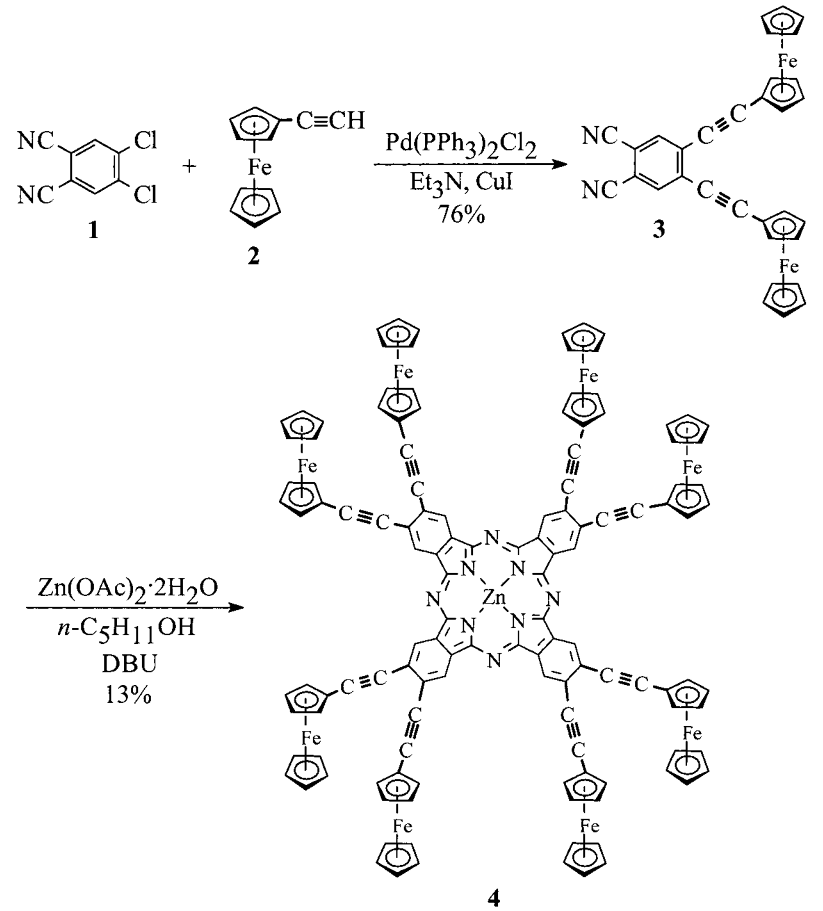
(17) The solubility of this dinitrile in common organic solvents was significantly lower than that of **3** which precluded the acquisition of a satisfactory ^{13}C NMR spectrum.

Scheme 1



1, which is easily accessible in large quantity from the commercially available 4,5-dichloro-1,2-benzenedicarboxylic acid in four steps.[12] Under typical Sonogashira reaction conditions,[19] **1** reacted with an excess of ferrocenylethyne (**2**) to give 4,5-bis(ferrocenylethynyl)phthalonitrile (**3**) in 76% yield. Cyclization of this dinitrile in the presence of $Zn(OAc)_2 \cdot 2H_2O$ and DBU in *n*-pentanol led to the formation of phthalocyanine **4** (Scheme 1). This compound was found to be highly aggregated, and its mobility in silica gel or alumina columns was extremely slow.[20] Purification could however be achieved by column chromatography using MeOH as a co-eluent, which probably can relieve the aggregation tendency of the macrocycle. The new phthalocyanine appears to be robust in the solid state, but is rather unstable in solutions and decomposes gradually in THF and $CHCl_3$ over several hours.

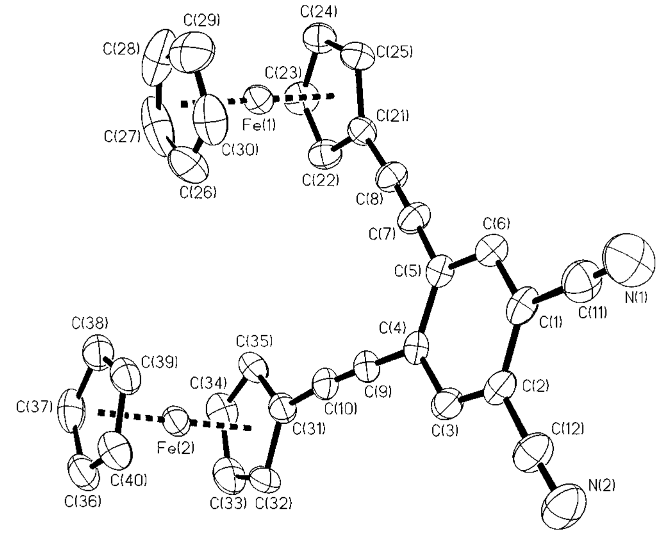


Figure 1. Molecular structure of **3** showing the atom labeling scheme. Hydrogen atoms are omitted for clarity.

The molecular structure of the dinitrile **3** was established by single-crystal X-ray diffraction analysis. As shown in Figure 1, the two ferrocenyl moieties lie on the same face of the benzene ring with an Fe−Fe separation of 6.359 Å. The two alkynyl cyclopentadienyl rings C(21)−C(25) and C(31)−C(35) are slightly tilted with respect to the benzene ring ($\phi = 15.3$ and 3.6°, respectively). Both ferrocenyl groups deviate significantly from the eclipsed conformation by an average of 20.6 and 16.0°. These structural features are in contrast to those of 1,2-

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[20] Molecular aggregation is a well-known phenomenon of phthalocyanines and 2,3-naphthalocyanines which usually hinders the purification and characterization of these functional dyes if they are not appropriately substituted. See, for example: (a) Isago, H.; Leznoff, C. C.; Ryan, M. F.; Metcalfe, R. A.; Davids, R.; Lever, A. B. P. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1039 and references therein. (b) Choi, M. T. M.; Li, P. P. S.; Ng, D. K. P. *Tetrahedron* **2000**, *56*, 3881 and references therein.

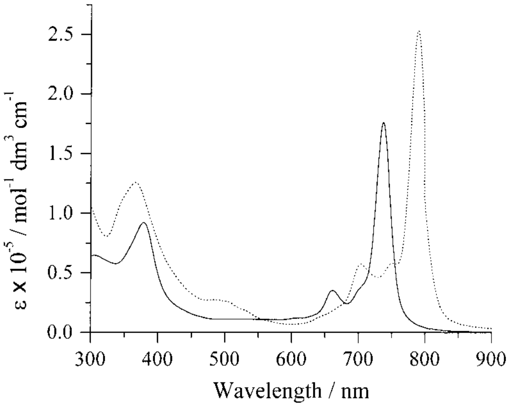

Figure 2. UV−vis spectra of **4** (—) and **7** (- - -) in THF.

diferrocenylbenzene and 5-chloro- or cyano-1,3-diferrocenylbenzene.[21] Due to the steric constraints between the two ferrocenyl groups in the former complex, they are significantly tilted ($\phi = 68.6$ and 32.5°). For the latter two complexes, the cyclopentadienyl rings are nearly parallel to the benzene mean planes ($\phi = 10.0-14.7°$), but the two ferrocenyl units are located at opposite sides of the benzene ring.

Compound **4** was characterized with a range of spectroscopic methods. The MALDI-TOF mass spectrum of **4** displayed an intense isotopic cluster peaking at m/z 2242.6 assignable to the molecular ion. The relative abundance of the isotopic cluster was in good agreement with the simulated spectrum of M^+. The UV−vis spectrum of **4** in THF is shown in Figure 2, which is typical for nonaggregated phthalocyanines. Due to the eight ferrocenylethynyl moieties, both the B band (378 nm) and the Q-band (737 nm) are substantially red-shifted by comparing with those of unsubstituted zinc(II) phthalocyanine ($\lambda_{max} = 340$ and 666 nm in THF) and even the octaalkynyl analogues ($\lambda_{max} = 368-370$ and 706−714 nm in THF).[18a] Thus, each ferrocenylethynyl unit causes the Q-band to red-shift by ca. 9 nm, which is over the range (4−6 nm) normally observed for alkynyl-substituted phthalocyanines.[18b] This may arise from the additional conjugation effect due to the ferrocenyl moiety. The molar absorptivities of the B and Q-bands of **4** were found to be essentially unchanged in the concentration range of 3.2×10^{-7} to 1.4×10^{-5} mol dm^{-3}. The values decreased in higher concentrations, showing that the aggregation of this species became significant under these conditions.

The ^{1}H NMR spectrum of **4** in CDCl$_3$ showed only broad signals at δ 4.0−4.7 due to the ferrocenyl moieties; the signal attributable to the aromatic protons was not observed. As the concentration for NMR measurements is usually much higher (about 2 orders of magnitude) than that for UV−vis studies, the absence of this signal may be due to the aggregation effects as suggested previously.[22] The problem, however, could be remedied by using THF-d_8 as the solvent. The spectrum showed a new broad signal at δ 9.4, which can be assigned to the phthalocyanine ring protons, together with two singlets at δ 4.92 and 4.48 (two overlapping signals) for the ferrocenyl ring protons.

The 2,3-naphthalocyanine analogue **7** was prepared in a similar manner as shown in Scheme 2. Treatment of **5** with ferrocenylethyne (**2**), under standard Sonogashira reaction conditions, afforded the dinitrile **6**, which underwent a typical cyclization to give the octasubstituted naphthalocyanine **7**. It is worth noting that naphthalocyanines with ferrocenyl or alkynyl substituents have not been reported so far and compound **7** represents the first example containing both of these functionalities. Apart from this symmetrical macrocycle, we also prepared the unsymmetrical tribenzophthalocyanine **9**, which contains six ferrocenylethynyl groups on the periphery, using a mixed cyclization of the dinitriles **6** and **8**[15] (15:1) (Scheme 2). The reaction also afforded **7** as a side product, which could be separated from **9** readily by column chromatography. Having three long dodecyloxy side chains, **9** has an enhanced solubility in organic solvents and a higher mobility in silica gel columns.

The spectral properties of **7** and **9** resembled those of the phthalocyanine analogue **4**. As shown in Figure 2, the UV−vis spectrum of **7** shows an intense Q-band at 789 nm, which as expected is significantly red-shifted by comparing with that of the phthalocyanine **4** (737 nm in THF). The UV−vis spectrum of **9** was similar to that of **7**, but due to the shortage of one fused benzene ring and two ferrocenylethynyl units, the Q-band appeared at shorter wavelength (763 nm). The ^{1}H NMR spectra of **7** and **9** were also recorded in CDCl$_3$ and THF-d_8. Similar to the case of **4**, the macrocyclic ring protons' signals, which could not be observed in CDCl$_3$, emerged as two broad signals in THF-d_8. The spectra also showed characteristic resonances arising from the ferrocenyl and tris(dodecyloxy)benzyloxy (for **9** only) substituents. The presence of dodecyloxy side chains in **9** was also confirmed by IR spectroscopy which showed very intense aliphatic C−H stretching at 2923 and 2853 cm^{-1}.

Apart from these tetrapyrrole derivatives, the porphyrin analogue **11** was also prepared by treating the *meso*-dibromoporphyrin **10** with ferrocenylethyne (**2**), using a modified Sonogashira coupling reaction in which THF was used as the solvent (Scheme 3).[23] The UV−vis spectrum of **11** showed the expected Soret band at 433 nm (red-shifted by ca. 30 nm relative to that of nickel(II) *meso*-diphenylporphyrin)[24] along with two Q-bands at 564 and 624 nm. No fluorescence emission was observed for all the ferrocenylethynyl tetrapyrroles **4**, **7**, **9**, and **11**, which could be rationalized by the efficient quenching due to electron transfer from ferrocene to the excited tetrapyrroles.[8,11a,25]

The electrochemistry of the dinitriles **3** and **6**, and the tetrapyrrole derivatives **4**, **7**, and **11** was studied by cyclic voltammetry and the data are summarized in Table 1. As shown in Figure 3 (a), the voltammogram of **3** displays a couple centered at 0.39 V assignable to the oxidation of ferrocenyl units and a couple at −1.63 V due to the reduction of dicyanobenzene ring to the corresponding radical anion. By comparing with the respective values for phthalonitriles substituted with 2-ferrocenylethoxy moieties (ca. 0 and −2 V),[8] it is clear that the unsaturated ethynyl linkers greatly facilitate the addition of an electron to the benzene ring, but hinder the removal of

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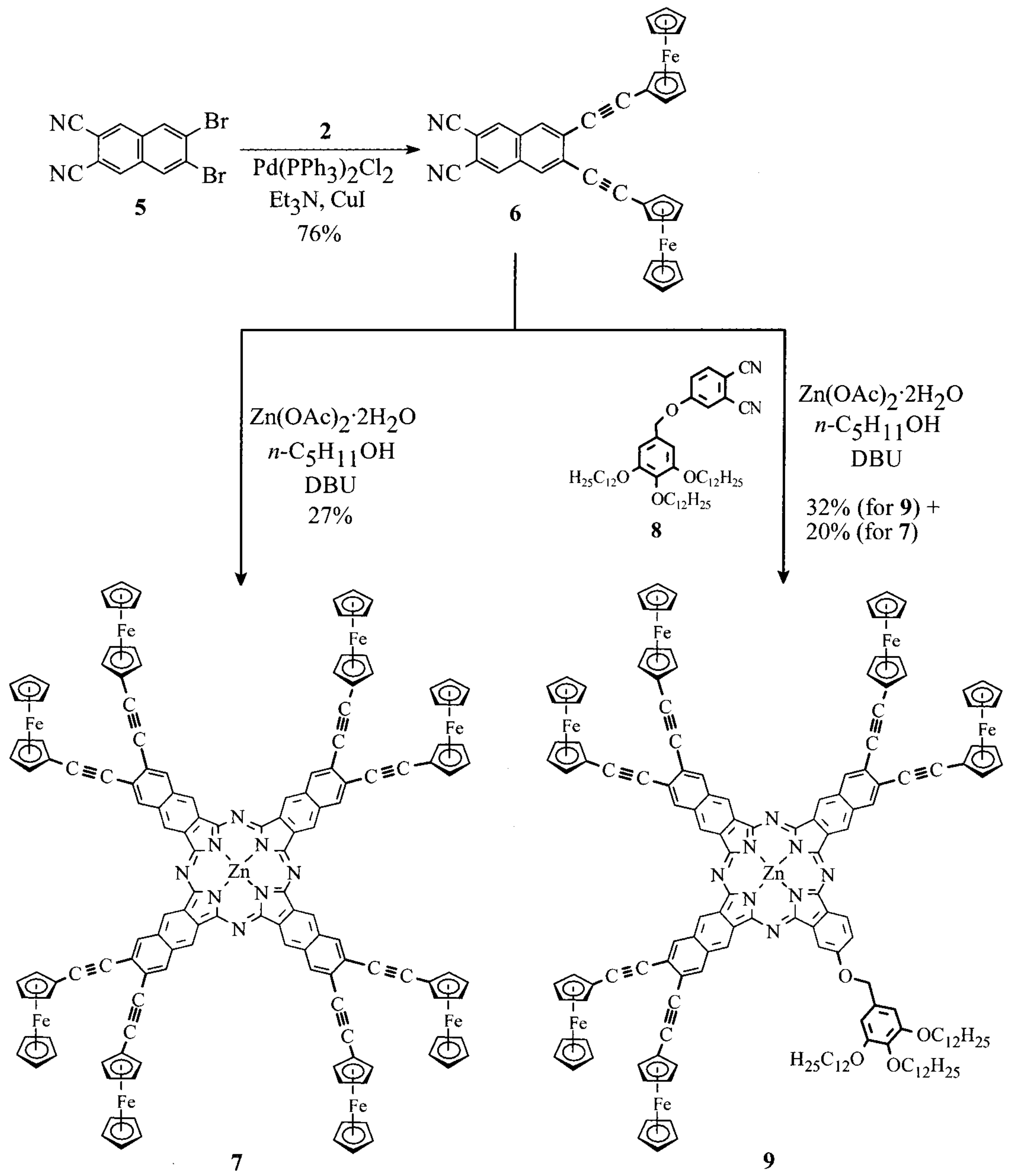
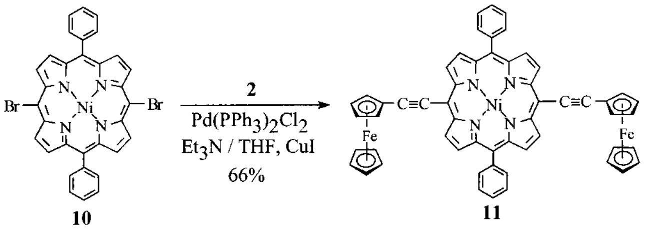
Scheme 2



Scheme 3



electrons from the ferrocenyl moieties. On the basis of the separation between the anodic and cathodic potential (ΔE), both couples could be regarded as a quasi-reversible process. The naphthalene analogue **6** behaved similarly, but the two processes were less well-defined and the waveform depended on the electrolyte used. By changing the electrolyte from $[Bu_4N][ClO_4]$ to $[Bu_4N][PF_6]$, the quasi-reversible naphthalonitrile couple was clearly shown and the cathodic peak for the ferrocene couple became much more intense (Figure 3b,c). This sharp cathodic stripping peak suggested that adsorption of the oxidized product onto the electrode may occur which in fact is rather common for multi-ferrocenyl systems.[8,27]

The cyclic voltammogram of **7** showed the ferrocene couple at 0.23 V together with two quasi-reversible couples at −1.30 and −1.71 V, which could be ascribed to naphthalocyanine-centered reductions (Figure 4a).[28] The peak current ratio $|i_{pa}/i_{pc}|$ for the ferrocene couple (0.58) again was much smaller than unity, showing that the adsorption of the oxidized product on the electrode

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(26) By using ferrocene as an internal standard, it was found that this reference potential was +0.31 V vs the saturated calomel electrode. 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.

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Table 1. Electrochemical Data for Ferrocenyl Dinitriles and Tetrapyrroles[a]

	ferrocene			dinitrile/tetrapyrrole			
compd	$E_{1/2}$ (ox)	ΔE^b	$\lvert i_{pa}/i_{pc}\rvert$	$E_{1/2}$ (red1)	ΔE^b	$\lvert i_{pa}/i_{pc}\rvert$	other processes
3	393	98	0.80	−1630	100	0.72	
6[c]	303	214	0.35	−1786	88	0.59	
4[d,e]	250	124	0.74				
7[d]	230	100	0.58	−1300	100	0.87	$E_{1/2}$ (red2) = -1707, ΔE = 55, $\lvert i_{pa}/i_{pc}\rvert$ = 0.46
11	314	108	0.52	−1424	104	0.66	$E_{1/2}$ (ox1)[f] = 917, ΔE = 190, $\lvert i_{pa}/i_{pc}\rvert$ = 1.08 $E_{1/2}$ (ox2)[f] = 841, ΔE = 239, $\lvert i_{pa}/i_{pc}\rvert$ = 2.30

[a] Recorded with $[Bu_4N][ClO_4]$ as electrolyte in CH_2Cl_2 (0.1 mol dm^{-3}) containing 0.2−0.4 mmol dm^{-3} of sample and using a Pt-microsphere working electrode 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.[26] [b] $\Delta E = |E_{pc} - E_{pa}|$. [c] With $[Bu_4N][PF_6]$ as electrolyte. [d] In THF with a Pt-disk working electrode, scan rate = 20 mV s^{-1}. [e] The couples due to the phthalocyanine core were too weak to be observed. [f] Assignable to the porphyrin or Ni center.

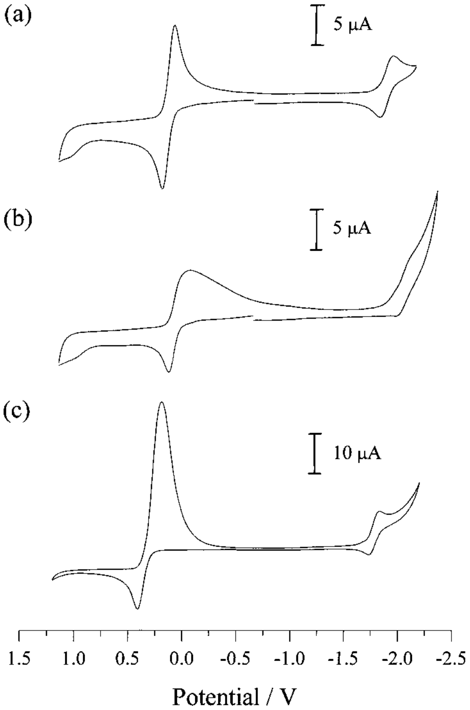

Figure 3. Cyclic voltammograms of (a) **3** in CH_2Cl_2 containing 0.1 mol dm^{-3} $[Bu_4N][ClO_4]$ and **6** in CH_2Cl_2 containing 0.1 mol dm^{-3} (b) $[Bu_4N][ClO_4]$ or (c) $[Bu_4N][PF_6]$. Scan rate = 100 mV s^{-1}.

surface was significant. The waveform of this couple was found to be dependent on the geometry of the working electrode and the scan rate. When the platinum-disk electrode was replaced with a platinum-microsphere electrode and at a sufficiently slow scan rate (below 50 mV s^{-1}), the couple became split as shown in Figure 4b. This peculiar waveform could also be attributed to an adsorption phenomenon. Attempts to solve the problem of adsorption by using other solvents such as CH_2Cl_2, MeCN, and PhCN were not successful as the compound is not stable in CH_2Cl_2 and its solubility in the latter two solvents is very low. As only one couple was observed for the ferrocenyl units, metal−metal interactions among these redox-active centers appear to be insignificant. Similar results were obtained for the phthalocyanine counterpart **4**, except that the two ring-based reduction couples were rather weak and poorly resolved.

Figure 5 shows the cyclic voltammogram of porphyrin **11**. Apart from the ferrocene/ferrocenium couple at 0.31 V, the voltammogram displays two partially overlapping oxidations centered at 0.84 and 0.92 V, and a reduction at −1.42 V, which are characteristic of nickel(II) tetraarylporphyrins.[29] The two oxidations are due to the porphyrin ring and the nickel(II) center, while the reduction is a porphyrin-centered process. No splitting was observed for the ferrocene couple even at a scan rate of 10 mV s^{-1} showing that the two ferrocenyl moieties also behave independently and are oxidized at the same potential. This is in contrast to the β-alkyl *meso*-bis(ferrocenyl)porphyrins reported by Burrell et al. in which

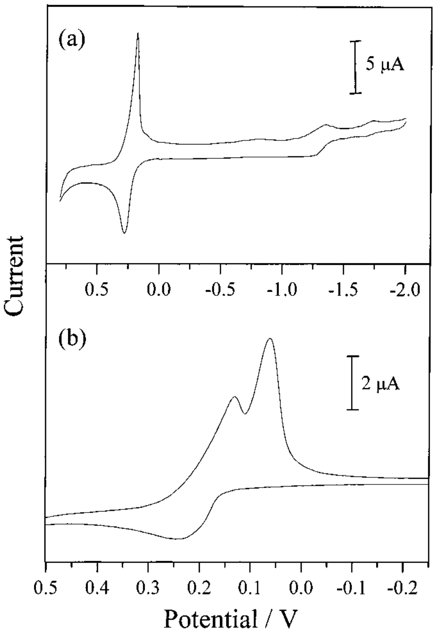

Figure 4. Cyclic voltammograms of **7** in THF containing 0.1 mol dm^{-3} $[Bu_4N][ClO_4]$ at a scan rate of 20 mV s^{-1}, using (a) a platinum-disk or (b) a platinum-microsphere working electrode.

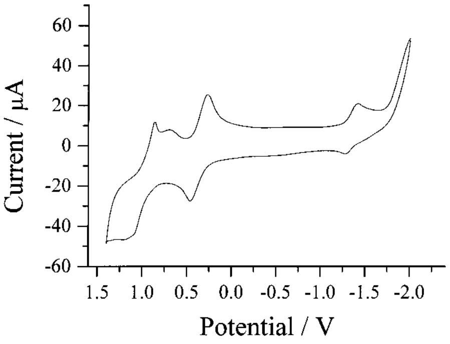

Figure 5. Cyclic voltammogram of **11** in CH_2Cl_2 containing 0.1 mol dm^{-3} $[Bu_4N][ClO_4]$ at a scan rate of 100 mV s^{-1}.

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the two opposite ferrocenyl units are strongly coupled.[5] According to the single-crystal X-ray analyses, the porphyrin core of these compounds is ruffled which shortens the ferrocene-ferrocene distance. However, because of the ethynyl linkers and the absence of β-substituents, compound **11** exhibits a relatively planar structure and the two iron(II) centers are separated by ca. 19 Å as revealed by a molecular modeling study.[30] The difference in ferrocene-ferrocene separation may account for the different behavior of these compounds.

In summary, we have prepared a series of tetrapyrrole derivatives substituted with up to eight ferrocenylethynyl moieties. Even though the ferrocenyl groups are connected to the macrocyclic cores with unsaturated ethynyl bridges, electrochemical studies show that these redox-active centers are basically independent, undergoing an electrochemical oxidation at the same potential.

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Supporting Information Available: Crystallographic data for dinitrile **3** (tables of crystallographic details, non-hydrogen coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates and isotropic thermal parameters). This material is available free of charge via the Internet at http://pubs.acs.org.

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[30] PCMODEL version 6.0, Serena Software, 1996.