

The First Electron-Donor-Acceptor Paracyclophanes with Ferrocene NLO-Phores: Synthesis, Absorption and Electrochemical Properties

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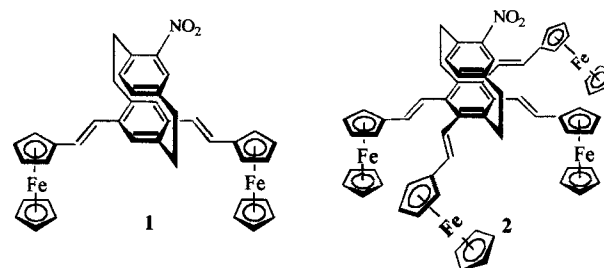
As potential nonlinear optical materials, 12-nitro-4,7-bis(2-ferrocenylvinyl)[2.2]paracyclophane (**1**) and 12-nitro-4,5,7,8-tetrakis(2-ferrocenylvinyl)[2.2]paracyclophane (**2**) have been synthesized by Pd-catalyzed coupling reactions of vinylferro-

cene with the precursor cyclophanes **9** and **13**, respectively. The absorption and electrochemical properties of **1** and **2** are also described.

Recent advances in the chemistry of both electron-donor-acceptor (EDA) cyclophanes^[1–3] and nonlinear optical (NLO) materials^[4,5] have renewed interest in the potential use of EDA cyclophanes as novel NLO materials. In general, second harmonic generation (SHG) requires materials with hyperpolarizability and a non-centrosymmetric structure, i.e. properties which give rise to a large, second-order, nonlinear optical susceptibility. Consequently, most studies have focused on dipolar molecular systems in which the optical nonlinearities arise from intramolecular charge transfer^[6,7]. These criteria for SHG could also be satisfied by EDA cyclophanes with suitably oriented electron-donating and -withdrawing groups, especially when efficient NLO chromophores such as organometallic ferrocene^[4,8–11] are incorporated as π -electron donors to the donor ring of the cyclophane molecule.

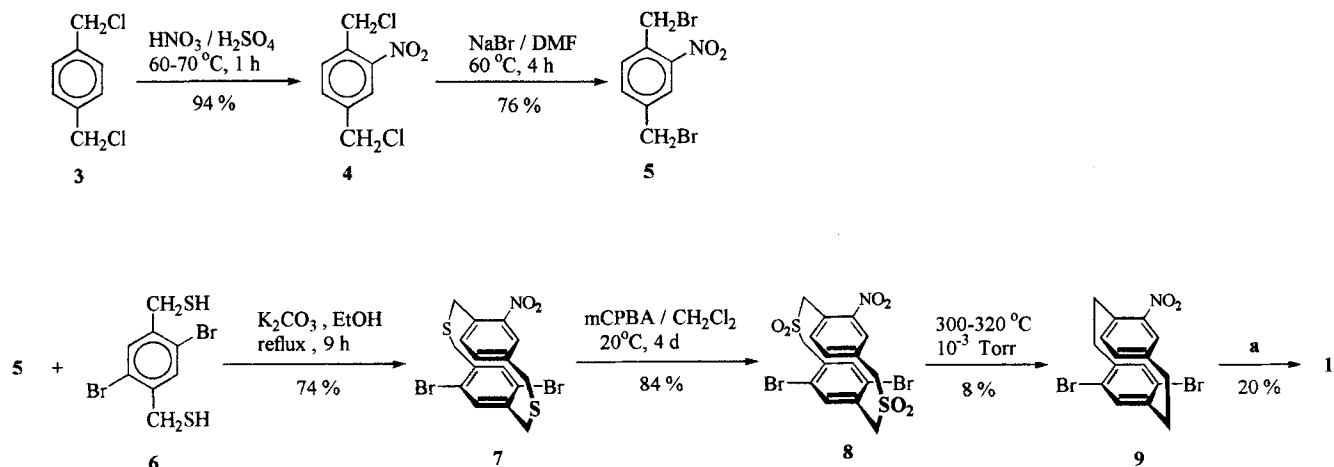
With these ideas in mind, our recent results^[12] on the Pd-catalyzed coupling of vinylferrocenes with [2.2]paracyclophanes prompted us to synthesize the novel vinylferrocene-substituted EDA-paracyclophanes **1** and **2** as potential NLO materials. Both compounds **1** and **2** contain a nitrobenzene subunit as a common acceptor. This choice of acceptor is based mainly on the grounds that most NLO standard materials with which comparisons can be made, such as 2-methylnitroaniline (MNA)^[4] and *para*-nitroaniline (PNA)^[4], also contain the electron-withdrawing nitro group.

For the synthesis of **1** (Scheme 1) it was first necessary to synthesize the precursor cyclophane **9**. This was achieved using a typical method of cyclophane synthesis^[12,13] involving cyclization, oxidation and pyrolysis. In order to prepare the cyclization component, commercially available 1,4-bis(chloromethyl)benzene (**3**) was nitrated to give 1,4-bis(chloromethyl)-2-nitrobenzene (**4**) and then its chloromethyl groups were converted to bromomethyl groups by treatment

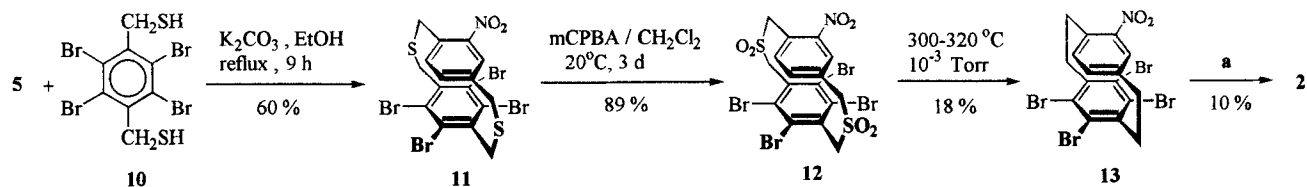


with NaBr in DMF, affording **5** in good yields. Subsequently, dropwise addition of a dilute methanolic solution of **5** and **6**^[14] to hot alcoholic K₂CO₃ under dilute conditions afforded **7** in 74% yield as a major fraction after column chromatography. Oxidation of **7** with *m*CPBA provided the disulfone **8** in a yield of 84%, pyrolysis of which at 300 °C and 10^{–3} Torr gave **9** (8%) as a cold-trap condensate. From ¹H- and ¹³C-NMR data, it is evident that compound **9** exists in the *pseudo-ortho* form, which is less symmetrical than the alternative *pseudo-geminal* form (<2%); the chemical shift and splitting patterns of the cyclophane ring protons are diagnostic of this. Compound **9** thus obtained was finally coupled with vinylferrocene units by Pd-catalyzed Heck reaction^[15] under phase-transfer conditions^[16] to yield **1** (20%) as a brownish-red crystalline solid. Thermogravimetric analysis (TGA) of **1** showed that no significant weight loss occurred until a temperature of 114.4 °C was reached.

In an analogous fashion, cyclization of **3** and **10**^[12] gave **11** (60%), subsequent oxidation of which produced the disulfone **12** (89%). Pyrolysis of **12** afforded **13** in 18% yield. The Pd-catalyzed fourfold coupling step of **13** with vinylferrocene proceeded smoothly and efficiently to give **2** in a yield of 10%. The deep brownish-red crystalline product

Scheme 1. Synthesis of **1**

a: 3.0 equiv. of vinylferrocene, Pd(OAc)₂ [10 mol %], DMF, K₂CO₃, Bu₄NBr, 80 °C, 3 d.

Scheme 2. Synthesis of **2**

a: 6.0 equiv. of vinylferrocene, Pd(OAc)₂ [10 mol %], DMF, K₂CO₃, Bu₄NBr, 80 °C, 3 d.

melted at 146–148 °C and its TGA curve showed stepwise weight losses at 198, 302 and 431 °C, respectively.

Both cyclophanes **1** and **2** are highly colored: solutions in CH₃CN are intensely purple-red and crystals are brownish-red. The electronic absorption data of **1** and **2** are shown in Table 1, together with the absorption data of the acceptor component **14** and of the donor components **15** and **16**, which are also novel. The longest wavelength absorption band of **1** appears at 481.5 nm with an intensity of log ϵ = 3.65 and thus shows a bathochromic shift of 33.5 nm from the longest wavelength absorption band of the acceptor **14** and the donor **15** (located at 457 nm), as well as a significant increase in the extinction coefficient. Similarly, the longest wavelength absorption band of **2** appears at λ_{\max} = 483 nm with an intensity of log ϵ = 3.95, i.e. at a slightly longer wavelength and with a higher intensity compared to **1**. It is most likely that the bathochromic shifts and the increased intensities of absorption bands are caused by strong transannular charge-transfer interactions between the acceptor ring and the vinylferrocene-substituted donor ring in molecules **1** and **2**.

The electrochemical properties of **1** and **2** were examined by cyclic voltammetry. The voltammograms of **1** and **2** exhibited an electrochemically irreversible oxidation peak and a reduction wave, respectively (Table 1). A comparison of the oxidation and reduction potentials of **1** with those of **2** indicates that tetrakisvinylferrocene-substituted **2** is easier to oxidize, but more difficult to reduce than compound **1**. The molecular and crystal structures of **1** and **2** have not been

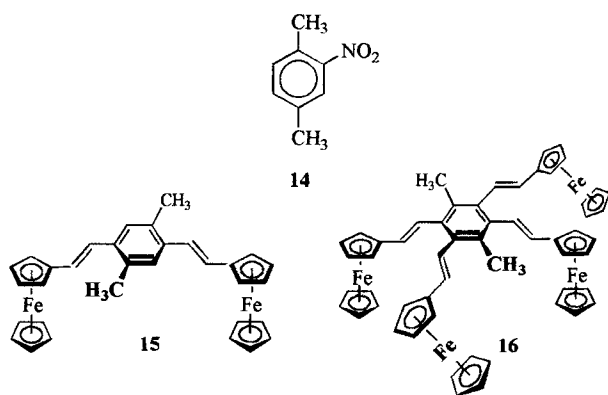
Table 1. Results of UV/Vis and cyclic voltammetric studies

Compound	UV/Vis λ_{max} (lg ϵ)	E_{ox} [a, b]	E_{re} [b, c]
	in CH ₃ CN		
1	211 (4.50), 362.5 (4.30)	0.7260	0.3847
	381 (sh, 4.28), 481.5 (3.65)		
2	319 (4.66), 384 (sh, 4.45)	0.5640	0.4400
	483 (3.95)		
14	208.5 (4.63), 263 (4.18)	–	–
	316 (3.71)		
15	268 (3.75), 349.5 (4.11)	–	–
	457 (3.29)		
16	205 (5.14), 307.5 (4.55)	–	–
	457 (3.56)		

[a] For the measurement of **1** (5.94×10^{-5} M in CH₃CN), tetrabutylammonium perchlorate (1.17×10^{-5} M) as a supporting electrolyte.

– [b] Scan rate 20 mV/sec, 25 °C, potential in V vs. Ag/Ag⁺ with Pt working electrode in CH₃CN. – [c] For the measurement of **2** (7.32×10^{-6} M in CH₃CN), tetrabutylammonium perchlorate (1.17×10^{-5} M) as a supporting electrolyte.

determined due to the inadequacy of the crystal quality. We are currently studying the NLO properties of **1** and **2**, and future research will be directed at the synthesis of ferrocene-substituted EDA cyclophanes with further enhanced acceptor strength.



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Experimental Section

^1H NMR: Varian Gemini-200; $\delta = 0$ for tetramethylsilane as internal standard, $\delta = 7.26$ for chloroform. – IR: Nicolet 550 FT IR. – UV/Vis: Jasco V-550. – Elemental analysis: Fisons instruments EA 1108 (C, H, N, S/O). – Melting points: Electrothermal melting point apparatus, not corrected. – Column chromatography (CC): Merck silica gel 60, 70–230 mesh. – TLC: Merck silica gel (60 F₂₅₄).

General Procedure (GP) for the Palladium-Catalyzed Coupling of Vinylferrocene: A mixture of 1.00 mmol of **2**, 10.0 mmol of potassium carbonate, 4.00 mmol of tetrabutylammonium bromide, the given amount of appropriate bromine-substituted paracyclophane, and 23 mg (0.100 mmol) of $\text{Pd}(\text{OAc})_2$ in 30 ml of dimethylformamide (DMF) was heated under nitrogen for the time stated. The cooled reaction mixture was filtered, diluted with 100 ml of dichloromethane and washed with six 50 ml portions of water. The organic phase was dried with Na_2SO_4 , filtered, and the solvent was removed from the filtrate in vacuo. The crude products were purified by CC on silica gel and subsequent recrystallization.

1,4-Bis(chloromethyl)-2-nitrobenzene (4): 15.0 g (85.7 mmol) of 1,4-bis(chloromethyl)benzene (**3**) was dissolved in 10 ml of 60% nitric acid at 0°C , and 15 ml of 95% sulfuric acid was added with stirring. After heating for 2 h at 60°C , the yellow reaction mixture was poured onto 500 ml of ice/water. The precipitate was filtered, washed with water, dried in vacuo, and recrystallized from ethanol: 17.8 g (94.4%) of **4**, m.p. $39\text{--}40^\circ\text{C}$. – TLC: $R_f = 0.21$ ($\text{CH}_2\text{Cl}_2/\text{hexane}$, 1:2). – ^1H NMR (CDCl_3): $\delta = 4.63$ (s, 2H), 4.97 (s, 2H), 7.69 (s, 2H), 8.08 (s, 1H). – IR (KBr): $\tilde{\nu} = 1530\text{ cm}^{-1}$, 1357, 690. – $\text{C}_8\text{H}_7\text{Cl}_2\text{NO}_2$ (220.05): calcd. C 43.67, H 3.21, N 6.37; found C 43.56, H 3.30, N 6.57.

1,4-Bis(bromomethyl)-2-nitrobenzene (5): 32.0 g (0.145 mol) of **4** was converted to the bromomethyl derivative by treatment with 60.0 g of pulverized sodium bromide in 150 ml of DMF at 60°C for 4 h. This solution was then diluted with 800 ml ice/water, the precipitate was filtered off, washed with water, dried in vacuo, and recrystallized from ethanol: 34.0 g (75.7%) of **5**, m.p. $90\text{--}91^\circ\text{C}$. – TLC: $R_f = 0.45$ (EA/hexane, 1:2). – ^1H NMR (CDCl_3): $\delta = 4.50$ (s, 2H), 4.82 (s, 2H), 7.56 and 7.65 (AB, $J = 7.96$ Hz, 2H), 8.08 (s, 1H). – IR (KBr): $\tilde{\nu} = 1525\text{ cm}^{-1}$, 1362. – $\text{C}_8\text{H}_7\text{Br}_2\text{NO}_2$ (308.96): calcd. C 31.10, H 2.28, N 4.53; found C 31.51, H 2.41, N 4.87.

5,8-Dibromo-14-nitro-2,11-dithia[3.3]paracyclophane (7): A solution of 3.09 g (10.0 mmol) of **5** and 3.28 g (10.0 mmol) of 2,5-

dibromo-1,4-bis(mercaptomethyl)benzene (**6**)^[14] in 500 ml of THF was added dropwise over a period of 8 h to a refluxing solution of 4.50 g (32.6 mmol) of K_2CO_3 in 2 l of EtOH under nitrogen. After an additional 1 h at the reflux temperature, the mixture was cooled, the solvents were removed under reduced pressure and the resulting residue was taken up in dichloromethane. The organic solution was washed with water, the solvent was removed, and the resulting solid was chromatographed on silica gel ($\text{CH}_2\text{Cl}_2/\text{hexane}$, 1:1) to yield 3.50 g (73.6%) of **7** as a pale-yellow solid ($R_f = 0.25$), m.p. $214\text{--}216^\circ\text{C}$. – ^1H NMR (CDCl_3): 3.40–4.30 (m, 7H), 4.50–4.80 (m, 1H), 7.14–7.40 (m, 4H), 7.90 (s, 1H). – IR (KBr): $\tilde{\nu} = 3068\text{ cm}^{-1}$, 2961, 2926, 2859, 1525, 1357, 1062. – $\text{C}_{16}\text{H}_{13}\text{Br}_2\text{NO}_2\text{S}_2$ (475.23): calcd. C 40.44, H 2.76, N 2.91, S 13.49; found C 39.93, H 2.73, N 2.79, S 13.47.

5,8-Dibromo-14-nitro-2,11-dithia[3.3]paracyclophane 2,2,11,11-tetraoxide (8): A mixture of 3.50 g (7.36 mmol) of **7** and 6.40 g (37.1 mmol) of *m*CPBA in 500 ml of dichloromethane was stirred for 4 d at 20°C . The reaction mixture was then concentrated to a volume of 150 ml, the precipitated disulfone was filtered off, washed with cold MeOH, and dried in vacuo: 3.35 g (84.4%) of **8**, colorless powder (dec. $>320^\circ\text{C}$), practically insoluble in all conventional solvents. The product was therefore used for the following reaction without purification. – IR (KBr): $\tilde{\nu} = 3104\text{ cm}^{-1}$, 2992, 2915, 1541, 1362, 1332, 1133, 1067. – $\text{C}_{16}\text{H}_{13}\text{Br}_2\text{NO}_6\text{S}_2$ (539.22): calcd. C 35.64, H 2.43, N 2.60, S 11.89; found C 36.11, H 2.56, N 2.72, S 12.29.

pseudo-ortho-4,7-Dibromo-12-nitro[2.2]paracyclophane (9): 3.20 g (5.93 mmol) of **8** was pyrolyzed in 200-mg portions at $300\text{--}320^\circ\text{C}/10^{-3}$ Torr. The collected sublimates were chromatographed on silica gel ($\text{CH}_2\text{Cl}_2/\text{hexane}$, 1:5) to give 190 mg (7.79%) of **9** as a yellow solid ($R_f = 0.24$), m.p. $176\text{--}178^\circ\text{C}$. – IR (KBr): $\tilde{\nu} = 3063\text{ cm}^{-1}$, 2946, 2854, 1520, 1342, 1047. – ^1H NMR (CDCl_3): $\delta = 2.70\text{--}2.88$ (m, 1H), 2.90–3.55 (m, 6H), 3.80–3.96 (m, 1H), 6.63 (s, 1H), 6.68 (s, 1H), 6.75 and 7.30 (AB, $J = 7.50$ Hz, 2H), 7.86 (s, 1H). – ^{13}C NMR (50.29 MHz, CDCl_3): $\delta = 149.11$, 141.32, 141.18, 140.87, 138.29, 137.43, 135.29, 133.19, 125.78, 125.59, 125.34, 125.26, 34.82, 34.33, 32.93, 32.10. – UV/Vis (CHCl_3): λ_{max} (lg ϵ) = 243.5 nm (4.59), 309 (4.31), 310.5 (4.31), 311.5 (4.31), 314 (4.31) at 9.73×10^{-5} M. – $\text{C}_{16}\text{H}_{13}\text{Br}_2\text{NO}_2$ (411.09): calcd. C 46.75, H 3.19, N 3.41; found C 46.82, H 3.22, N 3.58.

pseudo-geminal Form: m.p. $226\text{--}228^\circ\text{C}$. – ^1H NMR (CDCl_3): $\delta = 2.74\text{--}3.02$ (m, 2H), 3.02–3.70 (m, 5H), 4.17–4.49 (m, 1H), 6.63 (s, 1H), 6.69 (s, 1H), 6.64 and 7.40 (AB, $J = 7.67$ Hz, 2H), 7.55 (s, 1H). – UV/Vis (CH_3CN): λ_{max} (lg ϵ) = 243.5 nm (4.13), 262.5 (4.00), 313 (sh, 3.50), 350 (sh, 3.23) at 1.07×10^{-4} M.

12-Nitro-4,7-bis(2-ferrocenylvinyl)[2.2]paracyclophane (1): 300 mg (0.730 mmol) of **9** and 371 mg (1.75 mmol) of vinylferrocene were heated for 3 d at 80°C according to the GP. The crude product was chromatographed on silica gel ($\text{CH}_2\text{Cl}_2/\text{hexane}$, 1:1) to yield 100 mg (20.3%) of **1** ($R_f = 0.39$) as a reddish-brown solid, m.p. $220\text{--}222^\circ\text{C}$. – IR (KBr): $\tilde{\nu} = 3091.8\text{ cm}^{-1}$, 3039.1, 2927.2, 2861.4, 1630.7, 1518.8, 1341.1, 1110.8, 814.6. – ^1H NMR (CDCl_3): $\delta = 2.72\text{--}3.73$ (m, 8H), 3.98–4.72 (m, 18H), 6.52–7.04 (m, 8H), 7.62 (s, 1H). – ^{13}C NMR (50.29 MHz, CDCl_3): $\delta = 148.98$, 141.54, 137.56, 137.29, 137.16, 136.99, 136.92, 136.10, 133.74, 130.78, 128.61, 127.53, 127.46, 126.53, 123.09, 122.73, 83.93, 83.80, 69.19, 68.89, 67.63, 67.12, 66.84, 66.19, 35.27, 33.68, 32.53. – UV/Vis (CH_3CN): λ_{max} (lg ϵ) = 211 nm (4.50), 362.5 (4.30), 381 (sh, 4.28), 481.5 (3.65), at 3.86×10^{-5} M. – $\text{C}_{40}\text{H}_{35}\text{Fe}_2\text{NO}_2$ (673.42): calcd. C 71.34, H 5.24, N 2.08; found C 71.16, H 5.51, N 2.12.

5,6,8,9-Tetrabromo-14-nitro-2,11-dithia[3.3]paracyclophane (11): A solution of 4.86 g (10.0 mmol) of **10** and 3.09 g (10.0 mmol) of 2,5-

5 in 500 ml of THF was added dropwise over 8 h to a boiling solution of 4.50 g (32.6 mmol) of potassium carbonate in 2 l EtOH. The solvent was distilled off in vacuo and the residue was chromatographed on silica gel ($\text{CH}_2\text{Cl}_2/\text{hexane}$, 1:1) to yield 3.80 g (60.0%) of **11** as a pale-yellow solid, m.p. 266–268 °C. – TLC: R_f = 0.31 ($\text{CH}_2\text{Cl}_2/\text{hexane}$, 1:1). – IR (KBr): $\tilde{\nu}$ = 1530 cm^{-1} , 1352, 1098. – ^1H NMR (CDCl_3): δ = 3.80–4.15 (m, 3H), 4.15–4.40 (m, 2H), 4.45–4.75 (m, 3H), 7.51 and 7.60 (AB, J = 8.0 Hz, 2H), 7.96 (s, 1H). – $\text{C}_{16}\text{H}_{11}\text{Br}_4\text{NO}_2\text{S}_2$ (633.02): calcd. C 30.36, H 1.75, N 2.21, S 10.13; found C 30.55, H 1.85, N 2.21, S 10.30.

5,6,8,9-Tetrabromo-14-nitro-2,11-dithia[3.3]paracyclophane-2,2,11,11-tetraoxide (12): A mixture of 3.50 g (5.53 mmol) of **11** and 5.00 g (29.0 mmol) of *m*CPBA in 400 ml of dichloromethane was stirred at room temperature for 3 d. The precipitate was filtered off, washed with cold MeOH, and dried in vacuo: 3.41 g (88.5%) of **12** as a colorless powder (dec. >310 °C), practically insoluble in all conventional solvents. The product was therefore used for the following reaction without purification. – IR (KBr): $\tilde{\nu}$ = 1541 cm^{-1} , 1333, 1332, 1128. – $\text{C}_{16}\text{H}_{11}\text{Br}_4\text{NO}_6\text{S}_2$ (697.02): calcd. C 27.57, H 1.59, N 2.01, S 9.20; found C 27.82, H 1.66, N 2.10, S 9.45.

4,5,7,8-Tetrabromo-12-nitro[2.2]paracyclophane (13): 3.20 g (4.59 mmol) of **12** was pyrolyzed in 200 mg portions at 300–320 °C/10^{−3} Torr. The collected condensates were chromatographed on silica gel ($\text{CH}_2\text{Cl}_2/\text{hexane}$, 1:5) to yield 464 mg (17.8%) of **13** as a pale-yellow solid, m.p. 186–188 °C. – IR (KBr): $\tilde{\nu}$ = 1525 cm^{-1} , 1342, 1087. – ^1H NMR (CDCl_3): δ = 3.07–3.38 (m, 3H), 3.49–3.77 (m, 3H), 3.82–4.06 (m, 1H), 4.12–4.35 (m, 1H), 7.13 and 7.19 (AB, J = 7.76 Hz, 2H), 7.98 (s, 1H). – ^{13}C NMR (50.29 MHz, CDCl_3): δ = 147.23, 142.51, 141.91, 140.41, 135.52, 133.72, 132.90, 129.55, 129.03, 128.85, 128.75, 125.80, 39.00, 38.75, 32.29, 31.23. – UV/Vis (CHCl_3): λ_{max} (lg ϵ) = 244.5 nm (4.15), 262 (4.10), 300 (3.61), 350 (3.11) at 9.84×10^{-5} M. – $\text{C}_{16}\text{H}_{11}\text{Br}_4\text{NO}_2$ (568.89): calcd. C 33.78, H 1.95, N 2.46; found C 33.80, H 1.98, N 2.49.

12-Nitro-4,5,7,8-tetrakis(2-ferrocenylvinyl)[2.2]paracyclophane (2): 200 mg (0.352 mmol) of **13** and 373 mg (1.76 mmol) of vinylferrocene were heated for 5 d at 80 °C according to the GP. The crude product was chromatographed on silica gel ($\text{CH}_2\text{Cl}_2/\text{hexane}$, 1:1) to give 40 mg (10.4%) of **2** (R_f = 0.42) as a dark, reddish-brown solid, m.p. 146–148 °C. – IR (KBr): $\tilde{\nu}$ = 3091.7 cm^{-1} , 3039.1, 2933.7, 2861.3, 1630.3, 1525, 1327.5, 820.6. – ^1H NMR (CDCl_3): δ = 2.71–3.07 (m, 3H), 3.09–3.33 (m, 2H), 3.34–3.71 (m, 3H), 4.00–4.80 (m, 36H), 6.33–7.23 (m, 11H). – UV/Vis (CH_3CN): λ_{max} (lg ϵ) = 319 nm (4.66), 384 (sh, 4.45), 483 (3.95) at 1.10×10^{-5} M. – $\text{C}_{64}\text{H}_{55}\text{Fe}_4\text{NO}_2$ (1093.54): calcd. C 70.30, H 5.07, N 1.28; found C 70.26, H 5.03, N 1.27.

2-Nitro-*p*-xylene (14)^[17]: 47.6 g (0.448 mol) of commercially available *p*-xylene was dissolved in 35 ml of 60% nitric acid at 0 °C, and 40 ml of 95% sulfuric acid was added with stirring. After heating at 60 °C for 2 h, the yellow reaction mixture was poured onto 500 ml of ice/water. The resulting organic phase was decanted off and the solution was extracted with EA. The combined organic extracts were washed with water, dried over Na_2SO_4 , and evaporated. The yellow liquid was then vacuum distilled, and the fraction boiling at 145–150 °C/20 Torr was collected. The yellow distillate was chromatographed on silica gel (hexane) to yield 60.0 g (88.6%) of **14** as a yellow liquid. – TLC: R_f = 0.56 (EA/hexane, 1:2). – ^1H NMR (CDCl_3): δ = 2.40 (s, 3H), 2.55 (s, 3H), 7.21 and 7.31

(AB, J = 7.15 Hz, 2H), 7.78 (s, 1H). – IR (neat): $\tilde{\nu}$ = 3072.0 cm^{-1} , 2986.5, 2933.8, 2874.6, 1538.6, 1354.3. – UV/Vis (CH_3CN): λ_{max} (lg ϵ) = 208.5 nm (4.63), 263 (4.18), 316 (3.71) at 5.96×10^{-5} M. – $\text{C}_8\text{H}_9\text{NO}_2$ (151.17): calcd. C 63.56, H 6.00, N 9.27; found C 63.50, H 5.97, N 9.29.

2,5-Bis(2-ferrocenylvinyl)-*p*-xylene (15): 100 mg (0.379 mmol) of 2,5-dibromo-*p*-xylene^[14] and 241 mg (1.14 mmol) of vinylferrocene were heated for 3 d at 100 °C according to the GP. The crude product was chromatographed on silica gel (hexane) to give 125 mg (62.8%) of **15** (R_f = 0.50, $\text{CH}_2\text{Cl}_2/\text{hexane}$, 2:1) as a red solid, m.p. >220 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 3098.4 cm^{-1} , 3039.1, 2927.2, 1630.7, 1110.8, 959.4, 814.6. – ^1H NMR (CDCl_3): δ = 2.40 (s, 6H), 4.15 (s, 10H), 4.29 (s, 4H), 4.48 (s, 4H), 6.76 and 6.89 (AB, J = 16.1 Hz, 4H), 7.35 (s, 2H). – ^{13}C NMR (CDCl_3): δ = 135.30, 132.60, 127.37, 126.69, 123.58, 83.94, 69.25, 68.99, 66.86, 19.62. – UV/Vis (CH_3CN): λ_{max} (lg ϵ) = 457 nm (3.29), 349.5 (4.11), 268 (3.75) at 7.60×10^{-5} M. – $\text{C}_{32}\text{H}_{30}\text{Fe}_2$ (526.28): calcd. C 73.03, H 5.75; found C 72.98, H 5.76.

2,3,5,6-Tetrakis(2-ferrocenylvinyl)-*p*-xylene (16): 100 mg (0.237 mmol) of commercially available 2,3,5,6-tetrabromo-*p*-xylene and 301 mg (1.42 mmol) of vinylferrocene were heated for 5 d at 100 °C according to the GP. The crude product was chromatographed on silica gel ($\text{CH}_2\text{Cl}_2/\text{hexane}$, 1:1) to give 83 mg (37.1%) of **16** (R_f = 0.50) as a red solid, m.p. >88 °C (dec.). – ^1H NMR (CDCl_3): δ = 2.46 (s, 6H), 3.81–4.51 (m, 36H), 5.87–6.90 (m, 8H). – IR (KBr): $\tilde{\nu}$ = 3094.7 cm^{-1} , 2926.3, 2849.1, 1642.1, 821.1. – UV/Vis (CH_3CN): λ_{max} (lg ϵ) = 457 nm (3.56), 307.5 (4.55), 205 (5.14) at 2.11×10^{-5} M. – $\text{C}_{56}\text{H}_{50}\text{Fe}_4$ (946.40): calcd. C 71.07, H 5.33; found C 71.02, H 5.35.

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