Meso-meso linked corroles

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Supporting information

Experimental part

All chemicals were used as received unless otherwise noted. Reagent grade solvents (CH_2Cl_2, hexanes, cyclohexane, toluene) were distilled prior to use. All reported ^1H NMR spectra were recorded on Bruker AM 500 MHz or Varian 200 MHz spectrometer. Chemical shifts (δ ppm) were determined with TMS as the internal reference; *J* values are given in Hz. VT-NMR of corrole **4** was performed in DMSO-d_6, temperature range 303-363 K (in 10 K increments) on Bruker AM 500 MHz. UV-Vis spectra were recorded in toluene (Cary). Chromatography was performed on silica (Kieselgel 60, 200-400 mesh). 5-Mesityldipyrromethane and 5-(2,6-dichlorophenyl)dipyrromethane were prepared as described in literature.[1]

***Meso-meso* linked dimer 2.** 5-Mesityldipyrromethane (157 mg, 0.6 mmol) was dissolved in 3 mL of the pre-prepared solution of TFA (10 μL, 0.13 mmol) in CH_2Cl_2 (100 mL) and formaldehyde (36% solution in water, 16 μL, 0.2 mmol) was added. After 5h at room temperature, the reaction mixture was diluted with THF (2 mL) and added to vigorously stirred THF (30 mL) simultaneously with the solution of DDQ (118 mg, 0.52 mmol) in THF (5 mL) over 15 min. The reaction was stirred at room temperature for a further 15 min. Then solvents were removed on the rotary evaporator and the residue was dissolved in toluene and purified by chromatography [silica, toluene/hexanes (2:3)] to obtain product which was crystallized from CH_2Cl_2/hexane (3.5 mg, 3.3%). R_f = 0.51 [silica, toluene/hexane (1:1)]. ^1H NMR (200 MHz, $CDCl_3$) δ = -1.41 (br s, 6H, NH), 1.97 (s, 24H, CH_3-Ar), 2.52 (s, 12H, CH_3-Ar), 7.19 (br s, 8H, Ar-H), 7.80 (d, *J*=4.6 Hz, 4H, *β*-H), 8.21 (d, *J*=4.6 Hz, 4H, *β*-H), 8.35 (d, *J*=4.0 Hz, 4H, *β*-H), 8.91 (d, *J*=4.0 Hz, 4H, *β*-H); ESI-MS (LR) obsd 1067.6 ($M+H^+$). λ_{abs} (toluene, $\varepsilon \times 10^{-3}$) 408 (120), 448 (71), 569 (24), 604 (15), 637 (7.5).

5,15-Bis-(2,6-dichlorophenyl)corrole (3). 5-(2,6-Dichlorophenyl)dipyrromethane (1.74 g, 6.0 mmol) was dissolved in 30 mL of the pre-prepared solution of TFA (10 μL, 0.13 mmol) in CH_2Cl_2 (100 mL) and formaldehyde (36% solution in water, 155 μL, 2 mmol) was added. After 5h at room temperature, the reaction mixture was added to vigorously stirred CH_2Cl_2 (300 mL) simultaneously with the solution of DDQ (1.18 g, 5.2 mmol) in THF (30 mL) over 10 min. Then the reaction was stirred at room temperature for a further 15 min. Then solvents were removed by the rotary evaporation and the residue was purified by chromatography [silica, CH_2Cl_2/hexane (3:2)]. Subsequent chromatography [silica, CH_2Cl_2/hexane (2:3) then (3:2)] afforded product which was crystallized from CH_2Cl_2/hexane (28 mg, 2.4%). R_f = 0.53 [silica, toluene/hexane (2:3)]. ^1H NMR (500 MHz, $CDCl_3$) δ = -2.53 (br s, 3H, NH), 7.65 (dd, J_1=8.7 Hz, J_2=7.7 Hz, 2H, Ar-H), 7.77 (d, *J*=8.1 Hz, 4H, Ar-H), 8.41 (d, *J*=2.7 Hz, 2H, *β*-H), 8.63 (d, *J*=4.5 Hz, 2H, *β*-H), 8.98 (d, *J*=3.4 Hz, 2H, *β*-H), 8.99 (d, *J*=4.3 Hz, 2H, *β*-H), 9.56 (s, 1H, *meso*); EI-MS obsd 586.0272, calcd 586.0286 ($C_{31}H_{18}N_4Cl_4$); λ_{abs} (toluene, $\varepsilon \times 10^{-3}$) 403 (101), 418 (82), 563 (20), 603 (13), 628 (5.2).

***Meso-meso* linked dimer 4.** 5-(2,6-Dichlorophenyl)dipyrromethane (522 mg, 1.8 mmol) was dissolved in 9 mL of the solution of TFA in CH_2Cl_2 [prepared from TFA (10 μL, 0.13 mmol) and CH_2Cl_2 (100 mL)] and formaldehyde (36% solution in water, 48 μL, 0.6 mmol) was added. After 5h at room temperature, the reaction mixture was diluted with THF (6 mL) and added to vigorously stirred THF (90 mL) simultaneously with the solution of DDQ (354 mg, 1.56 mmol) in THF (10 mL), over 15 min. Then the reaction was stirred at room temperature for a 15 min. and hydrazine (anh., THF solution, 0.2 mL) was added followed by stirred for a further 15 min. Subsequently solvents were removed by the rotary evaporation and the residue was dissolved in toluene and purified by chromatography [silica, toluene/hexanes (2:3) then (3:2)] to obtain product which was crystallized from CH_3OH (22.5 mg, 6.1%). R_f = 0.40 [silica, toluene/hexane (2:3)]. ^1H NMR (200 MHz, THF-d_8) δ = -2.10 (br s, 6H, NH), 7.77 (m, 16H, Ar-H + *β*-H), 8.18 (d, *J*=4.4 Hz, 4H, *β*-H),

Table ESI- S1. Optimization of conditions for the transformation of dipyrromethane **1** into corrole **2**[a]

Entry	TFA (mM)	Time of reaction (h)	**1** (mM)/ CH_2O (mM)	Solvent in the second step	Yield of **2** (%)[b]
1	13	0.17	2/1	CH_2Cl_2	0.5
2	13	0.5	2/1	CH_2Cl_2	0.8
3	13	0.5	2/1	THF	0.9
4[c]	1.3	5	2/1	CH_3CN	1.0
5	1.3	5	2/1	CH_2Cl_2	1.2
6	13	0.5	3/1	CH_2Cl_2	2.2
7	1.3	5	3/1	CH_2Cl_2	2.6
8	1.3	5	3/1	CH_2Cl_2/THF	3.3

[a] All reactions were performed under the following constant conditions: 1st step: CH_2Cl_2, RT; 2nd step: RT, 2.6 eq of DDQ *versus* aldehyde; [b] Isolated yields; [c] CH_3CN was used as a solvent in the first step.

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8.34 (br s, 4H, β-H), 8.98 (d, *J*=2.6 Hz, 4H, β-H); ESI-MS (LR) obsd 1171.1 ($M+H^+$). Anal. Calcd for $C_{62}H_{34}N_8Cl_8 + CH_3OH$: C, 62.71; H, 3.17; N, 9.29. Found: C, 63.01; H, 3.22; N, 9.04; λ_{abs} (toluene, $\varepsilon \times 10^{-3}$) 408 (124), 450 (89), 575 (32), 616 (25).

[1] J. K. Laha, S. Dhanalekshmi, M. Taniguchi, A. Ambroise and J. S. Lindsey, *Org. Proc. Res. Dev.*, 2003, **7**, 799-812.

Spectroscopy

Spectrophotometric grade solvents were used without further purification. Electronic absorption spectra were measured on a Perkin-Elmer Lambda 5 UV/Vis spectrophotometer. Stationary fluorescence spectra were recorded and corrected for instrumental response using a Hitashi 7000 spectrofluorometer. Emission quantum yields were determined after correction for the photomultiplier response, with reference to air-equilibrated toluene solutions of TPP with a $\Phi_{fl} = 0.11$. All samples were excited at 413 nm.

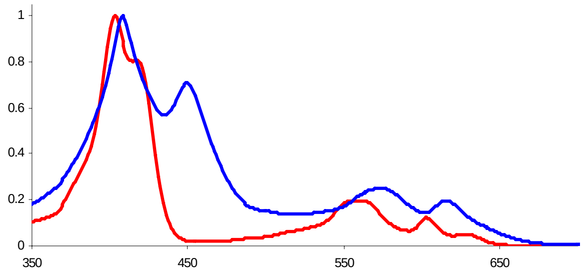

Fig. ESI-1 Normalized absorption spectra of corrole **3** (red line) and corrole **4** (blue line) in toluene.

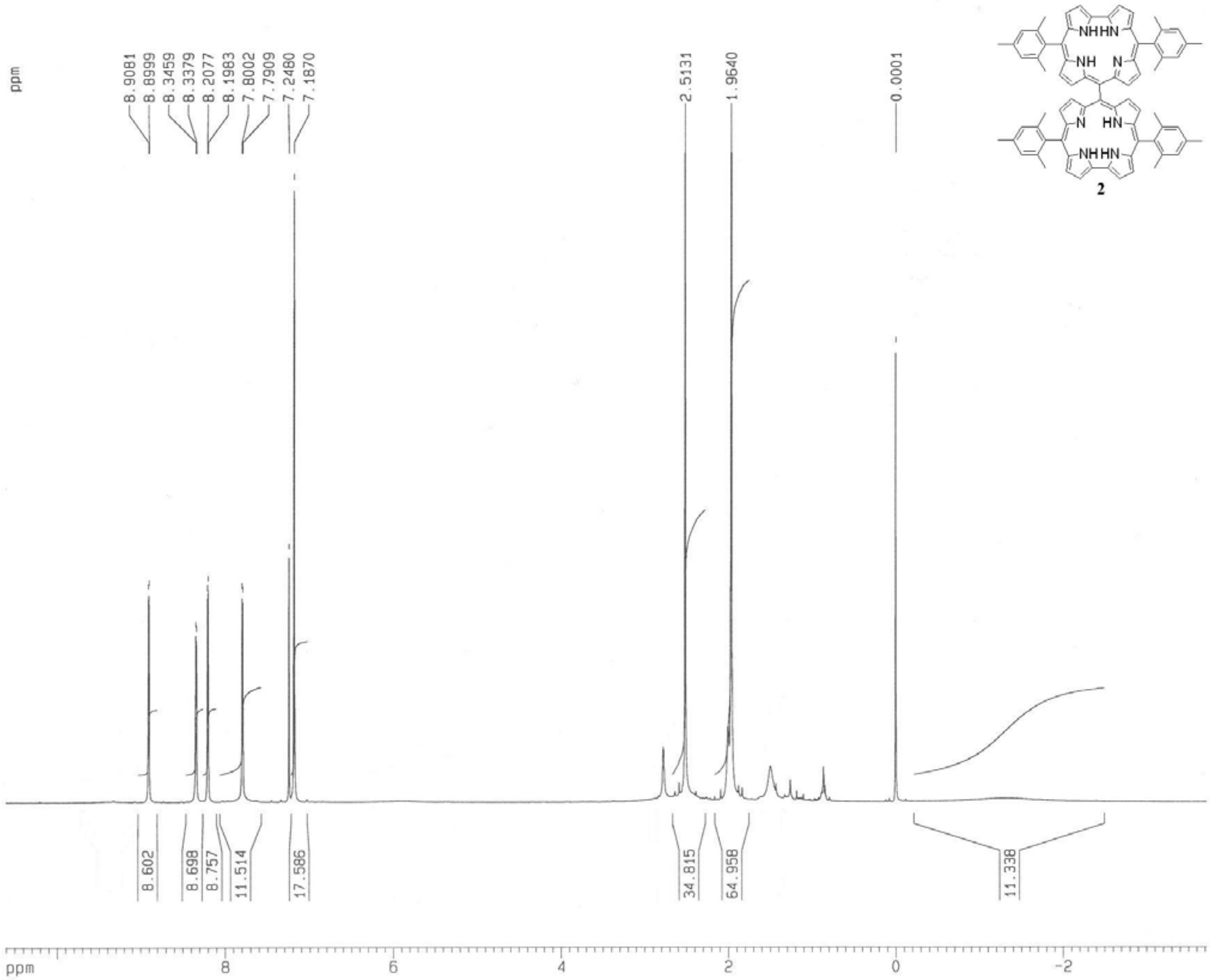

Fig. ESI-2 ^{1}H NMR spectrum of corrole **2**.

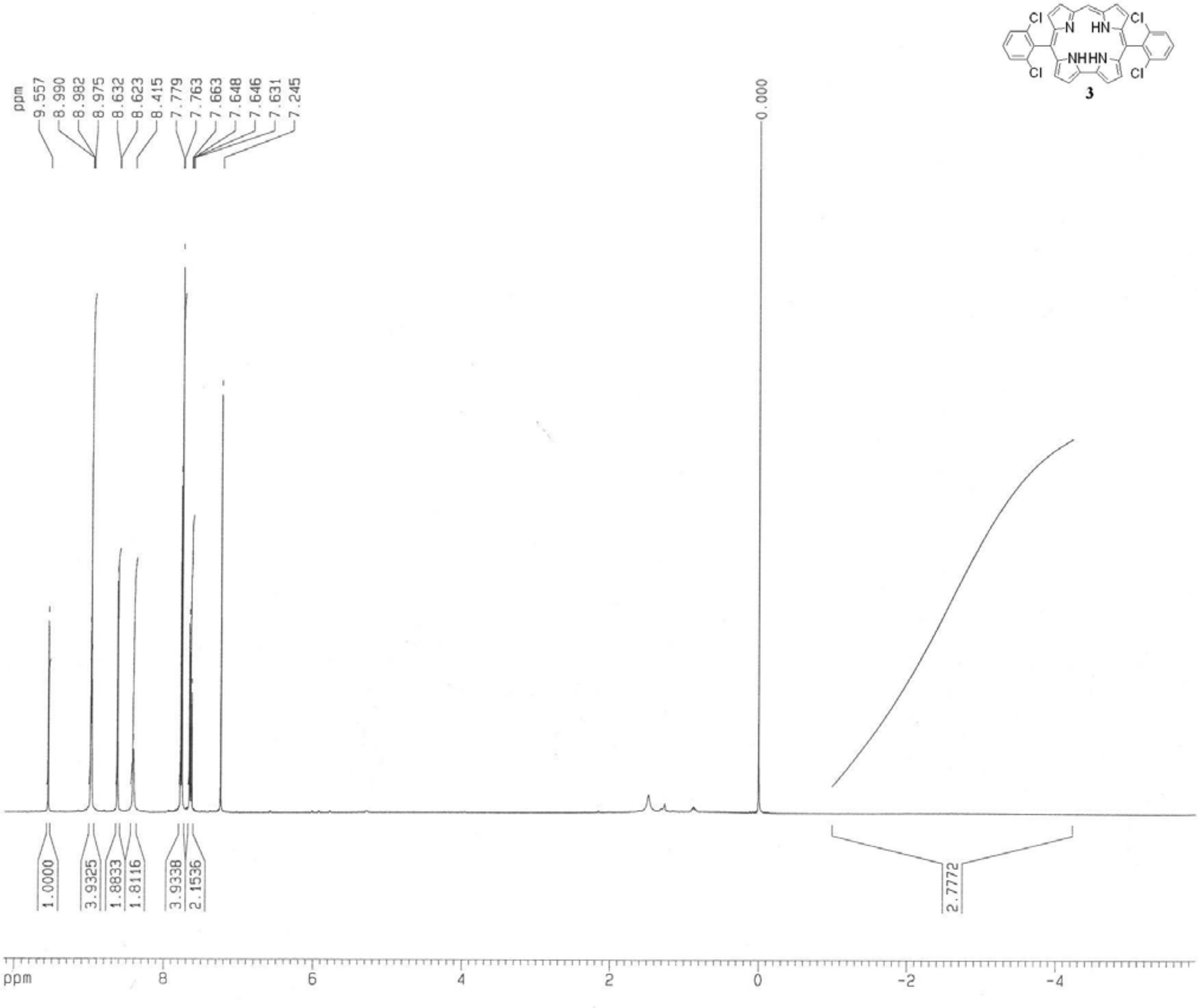

Fig. ESI-3 ^{1}H NMR spectrum of corrole **3**.

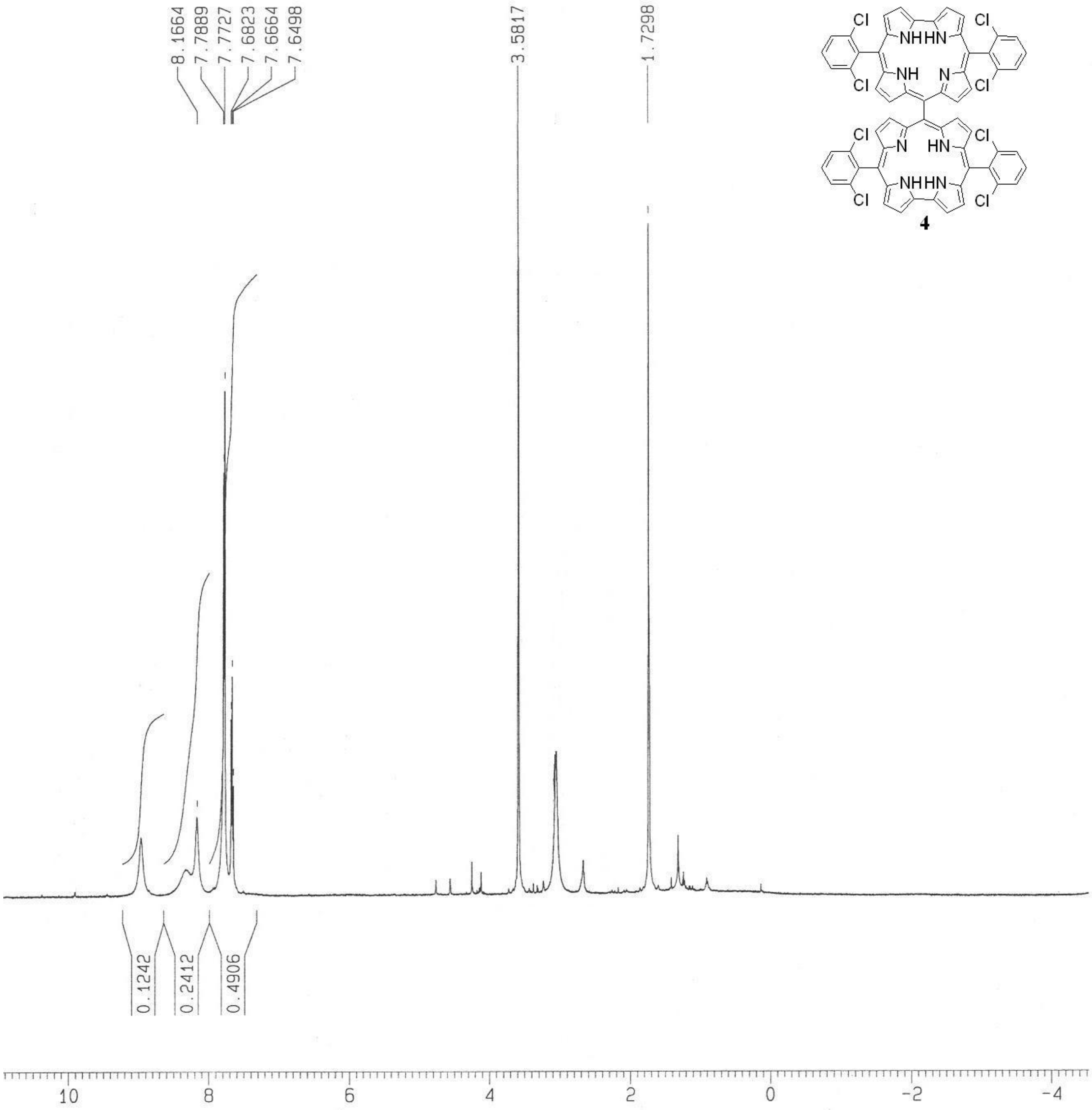

Fig. ESI-4 ^{1}H NMR spectrum of corrole **4** (in THF-d8).