25,27-Dithiasapphyrin and Pyrrole-Inverted Isomer of 21,23-Dithiaporphyrin from Condensation of Pyrrole and 2,5-Bis(*p*-tolylhydroxy-methyl)thiophene

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Supplementary materials

Experimental

Preparation of precursors. 2,5-Bis(*p*-tolyhydroxymethyl)thiophene was synthesized according to the known procedure.[1e]

Condensation. 2,5-Bis(*p*-tolyhydroxymethyl)thiophene, (1.21 g, 3.7 mmol) and pyrrole (255 μl, 3.7 mmol) were added to freshly distilled dichloromethane (500 ml). The solution was deoxygenated by bubbling N_2 for 20 minutes and CH_3SO_3H (191 μl, 2.9 mmol) was added. After 1 h of stirring in the absence of light, to the reaction mixture *p*-chloranil (2.7 g, 11 mmol) was added and the solution was refluxed (1.5 h). Then the solvent was evaporated under reduced pressure. The dry residue was dissolved in dichloromethane and chromatographed on a basic alumina column. The first orange fraction containing 5,10,15,20-tetra-(*p*-tolyl)-21,23-dithiaporphyrin was removed and the fractions, eluted with $CHCl_3$ or MeOH/$CHCl_3$ (20/80 v/v), were subjected to further chromatography on basic alumina. The fractions were eluted with dichloromethane with increasing concentration of chloroform. The chromatography was monitored by UV-vis electronic spectroscopy. 5,10,15,20-tetraphenyl-25,27-dithiasapphy-rin 25,27-S_2TPSH (pink-orange) was eluted with dichloromethane. This fraction is followed by yellow-green 5,10,15,20-tetraaryl-2-aza-21-carba-22,24-di-thiaporphyrin S_2CTTP, eluted with chloroform and by 5,10,15,20-tetraphenyl-26,28-dithiasapphyrin 26,28-S_2TPSH. The procedure gave S_2CTTP with 4.7 % yield, and ca. 1% of 25,27-S_2TPSH.

S$_2$CTTP UV-Vis (λ_{max}[nm] (log ε)): 352 (4.40); 461 (5.16), 548 (4.05), 592 (4.23); 800 (4.07);

HRMS (EI, 70eV): *m/z* = 705.2363; (found for $[M+H]^+$), $m/z_{calcd.}$ = 705.2393 for $C_{48}H_{37}N_2S_2$.

S$_2$CTTP, ^{1}H NMR (500 MHz, 298 K, chloroform-*d*): δ = 9.53, 9.27 (AB, $^3J_{AB}$ = 5.1 Hz, 7,8-H, th.); 9.51, 9.26 (AB, $^3J_{AB}$ = 4.9 Hz, 17,18-H, th.); 8.40, 8.36 (AB, $^3J_{AB}$ = 4.6 Hz; 12,13-H, pyrr.); 7.96 (s, 3-H, inv. pyrr.); 8.25 (d, ^3J = 7.8 Hz, 5-*o*-Tol); 8.19 (d, ^3J = 7.8 Hz, 20-*o*-Tol); 8.00 (d, ^3J = 7.8 Hz, 15-*o*-Tol.); 7.97 (d, ^3J = 7.8 Hz, 10-*o*-Tol); 7.64 (d, ^3J = 7.1 Hz, 5-*m*-Tol); 7.63 (d, ^3J = 7.1 Hz, 20-*m*-Tol); 7.56 (d, ^3J = 7.8 Hz, 15-*m*-Tol); 7.55 (d, ^3J = 7.8 Hz, 15-*m*-Tol); 2.66 (CH_3, 5,10,15-*p*-Tol); 2.63 (s, CH_3, 20-*p*-Tol); –1.64 (s, 21-H, inv. pyrr.)

S$_2$CTTPH$^+$, ^{1}H NMR (500 MHz, 228 K, dichloromethane-d_2, 5% TFA): δ = 16.57 (s, 2-NH), 9.59, 9.28 (AB, $^3J_{AB}$ = 4.6 Hz, 7,8-H, th.); 9.55, 9.28 (AB, $^3J_{AB}$ = 4.6 Hz, 17,18-H, th.); 8.37, 8.35 (AB, $^3J_{AB}$ = 4.6 Hz; 12,13-H, pyrr.); 7.96-7.92 (m, *o*-Tol); 7.75 (s, 3-H, inv. pyrr.) 7.74, (d, ^3J = 7.3 Hz, *m*-Tol); 7.70 (d, ^3J = 7.3 Hz, *m*-Tol); 7.58 (d, ^3J = 7.8 Hz, *m*-Tol); 2.65, 2.66, 2.67 (CH_3, *p*-Tol); –1.19 (s, 21-H, inv. pyrr.)

S$_2$CTTPH$_3$$^{2+}$, ^{1}H NMR (500 MHz, 298 K, dichloromethane-d_2, 5% TFA): δ = 9.51, 9.40, 9.16, 9.13 (AB, $^3J_{AB}$ = 5.0 Hz, 7,8-H,17,18-H, th.) 8.40, 8.36 (AB, $^3J_{AB}$ = 4.5 Hz; 12,13-H, pyrr.); 8.27,8,25 (d, ^3J = 7.3 Hz *o*-Tol); 8.06,8,05 (d, ^3J = 7.7 Hz *o*-Tol); 7.84, 7.88 (d, ^3J = 7.7 Hz, *m*-Tol) 7.75 (s, 3-H, inv. pyrr.); 7.69,7.68 (d, ^3J = 7.7 Hz, *m*-Tol); 2.74, 2.70, 2.69 (CH_3, *p*-Tol); –0.48 (s, 21-H, inv. pyrr.)

S$_2$TTSH UV-Vis (λ_{max}[nm] (log ε)): 321 (3.72); 503 (4.51), 634 (3.43), 695 (3.56); 756 (3.23); 837 (3.23);

S$_2$TTSH, ^{1}H NMR (500 MHz, 193 K, dichloromethane-d_2): δ = 10.65, 10.06 (AB, $^3J_{AB}$ = 4.6 Hz, 2,3-H, th.); 9.80, 9.03 (AB, $^3J_{AB}$ = 4.1 Hz, 22,23-H, pyrr.); 9.42 (d, ^3J = 7.8 Hz, 10-*o*-Tol), 9.38 (d, ^3J = 7.8 Hz, 15-*o*-Tol); 8.97, 8.80 (AB, $^3J_{AB}$ = 3.9 Hz; 17,18-H, pyrr.); 8.75, 8.68 (AB, $^3J_{AB}$ = 3.9 Hz; 7,8-H, pyrr.) 8.25, 8.15 (m, 5-*o*-Tol, 20-*o*-Tol, 20-*o'*-Tol); 7.82 (d, ^3J = 7.8 Hz, 15-*m'*-Tol.); 7.79 (d, ^3J = 7.8 Hz, 10-*m'*-Tol); 7.75-7.63 (m, 5-*o'*-Tol, 5-*m*-Tol, 5-*m'*-Tol, 20-*m*-Tol, 20-*m'*-Tol) 7.47 (d, ^3J = 7.1 Hz, 10-*o'*-Tol); 7.37 (d, ^3J = 7.1 Hz, 15-*o'*-Tol); 7.24 (d, ^3J = 7.8 Hz, 10-*m'*-Tol); 7.01 (d, ^3J = 7.8 Hz, 15-*m'*-Tol); 2.70, 2.68, 2,57 (CH_3, 5,10,15,20-*p*-Tol); –1.17 (s, NH), –1.32, –1.73 (12,13-H, th.)

HRMS (EI, 70eV): *m/z* = 770.2629 (found for $[M+H]^+$), $m/z_{calcd.}$ = 770.2658 for $C_{52}H_{40}N_3S_2$.

Instrumentation. NMR spectral data were recorded on a Bruker AVANCE 500 spectrometer. Absorption spectra were recorded on a diode array Hewlett Packard 8453 spectrometer.

Mass spectra were recorded on an AD-604 spectrometer using the electron impact and liquid matrix secondary ion mass spectrometry technique.

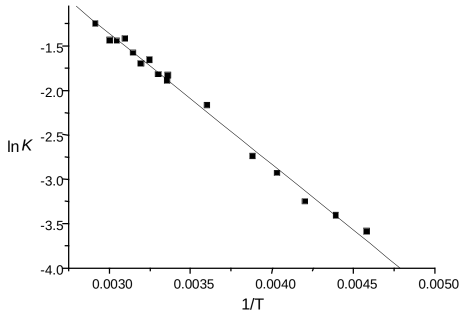

Figure 1. Plot of ln$K$ = –ΔH°/RT + ΔS°/R
K = [**3-*P***]/[**3-*I***]