Supplementary Material (ESI) for Chemical Communications

Supporting information for:

Molecular Diabolos: Synthesis of subphthalocyanine-based diboranes†

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Synthesis of Subphthalocyanine Diboranes 3a,b.

General. UV/Vis spectra were recorded with a Hewlett-Packard 8453 instrument. FAB-MS spectra were determined on a VG AutoSpec instrument. MALDI-TOF MS and HRMS spectra were recorded with a Bruker Reflex III spectrometer. NMR spectra were recorded with a Bruker AC-300 and a Bruker DRX-500 instruments. Chemicals were purchased from Aldrich Chemical Co. and used as received without further purification. Solvents were dried by standard methods and freshly distilled prior to use. All manipulations were performed under an atmosphere of dry argon using Schlenk techniques. Chlorosubphthalocyanines **1a,b** were prepared using reported procedures.[8a]

Chlorosubphthalocyanine 1a.

^{1}H NMR (300 MHz, CS_2 + 10% $CDCl_3$, 25°C, TMS): δ= 8.84 - 8.81 (m, 6 H, $H^{3,6}$ benzene), 7.94 - 7.91 ppm (m, 6 H, $H^{4,5}$ benzene); UV/Vis (toluene): λ_{max}(log ε) = 303 (4.7), 538 (sh), 557 nm (4.9).

Chlorosubphthalocyanine 1b.

^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ= 8.87 - 8.80 (m, 6 H, $H^{3,6}$ benzene), 8.00 (m, 3 H, $H^{4(5)}$ benzene), 1.57 ppm (s, 27 H, *t*-Bu); UV/Vis ($CHCl_3$): λ_{max}(log ε)= 309 (4.4), 527 (4.1), 551 (4.3), 567 nm (4.6).

General procedure for the synthesis of 3a,b.

A mixture of the corresponding chlorosubphthalocyanine **1a,b** (0.047 mmol) and $NaK_{2,8}$ alloy (2 ml) in *n*-hexane (50 ml) were stirred at room temperature and protected from light for 12 h. After filtration and extraction of the residue with *n*-heptane/toluene, a solution of the diborane **3a,b** was obtained. The solvents were removed under reduced pressure and the resulting solid was repeatedly washed with *n*-hexane.

Subphthalocyanine diborane 3a:

Dark violet solid (26% yield). ^{1}H NMR (300 MHz, CS_2 + 10% $CDCl_3$, 25°C, TMS): δ= 8.61 - 8.57 (m, 12 H, $H^{3,6}$ benzene), 7.78 - 7.72 ppm (m, 12 H, $H^{4,5}$ benzene); ^{11}B NMR (96 MHz, CS_2 + 10% $CDCl_3$, 25°C, $BF_3{\cdot}OEt_2$): δ= –1.1 ppm (broad); UV/Vis (*n*-heptane): λ_{max}(log ε) = 302 (5.1), 540 (sh), 557 nm (5.2); MS (MALDI-TOF, TCNQ): *m/z*= 395 $[M/2]^+$.

Subphthalocyanine diborane 3b:

Violet solid (57% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ= 8.0 - 7.5 (m, 12 H, $H^{3,6}$ benzene), 7.1 - 6.9 (m, 6 H, $H^{4(5)}$ benzene) 1.6 - 1.3 ppm (4s, 54 H, *t*-Bu); ^{11}B NMR (96 MHz, $CDCl_3$, 25°C, $BF_3{\cdot}OEt_2$): δ= –0.56 ppm (broad); UV/Vis ($CHCl_3$): λ_{max}(log ε)= 310 (4.5), 527 (4.4), 549 (4.6), 566 nm (4.9); MS (FAB, NBA/TFA): *m/z*= 1125-1131 $[M^+]$ + $[M + H]^+$ + $[M + 2H]^+$, 562-566 $[M/2]^+$ + $[M/2 + H]^+$; HRMS (FAB, NBA/TFA): calcd. for $C_{72}H_{72}B_2N_{12}$, 1126.619; found 1126.625.

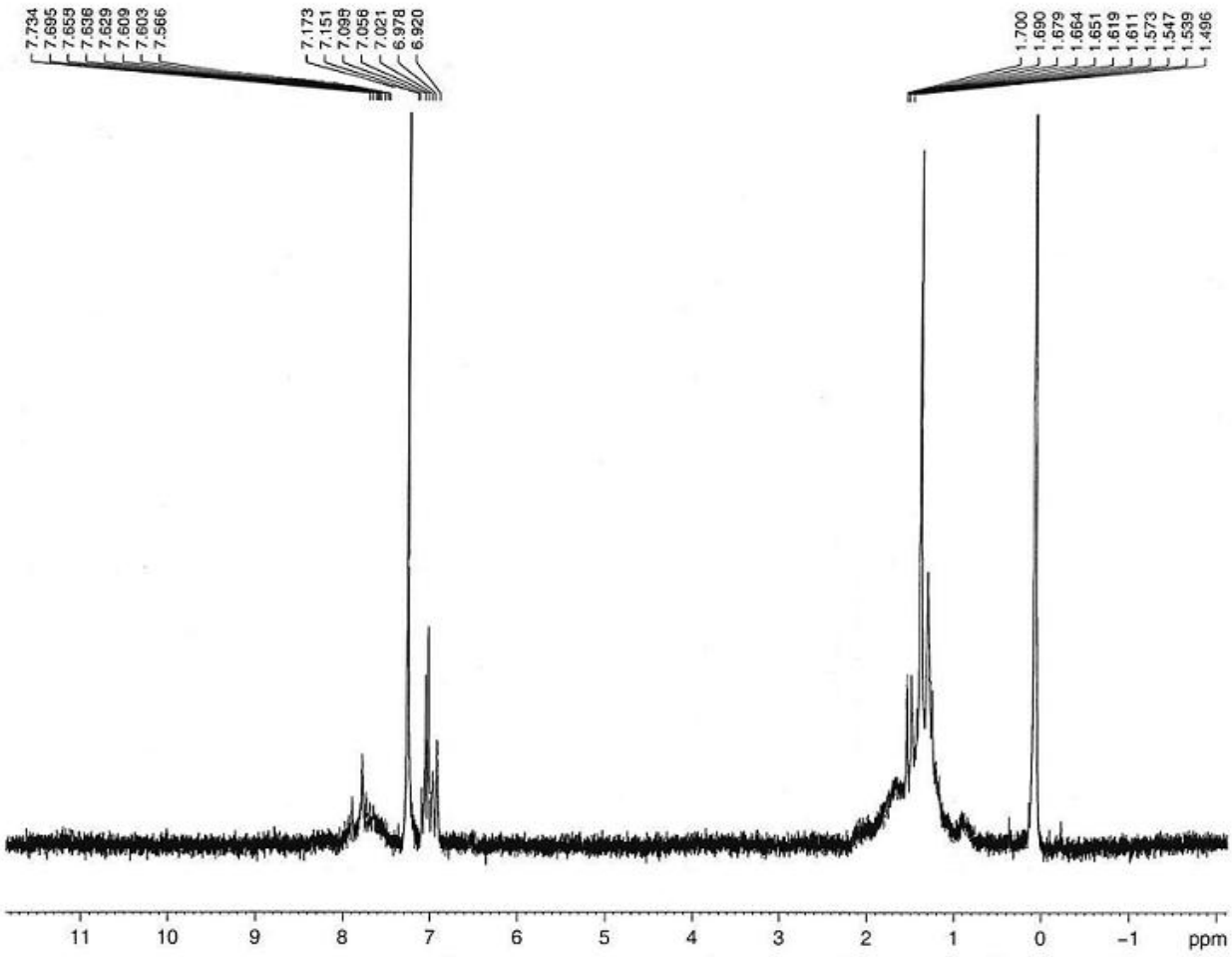

Figure S-1. ^{1}H NMR spectrum of **3b** (300 MHz, $CDCl_3$).

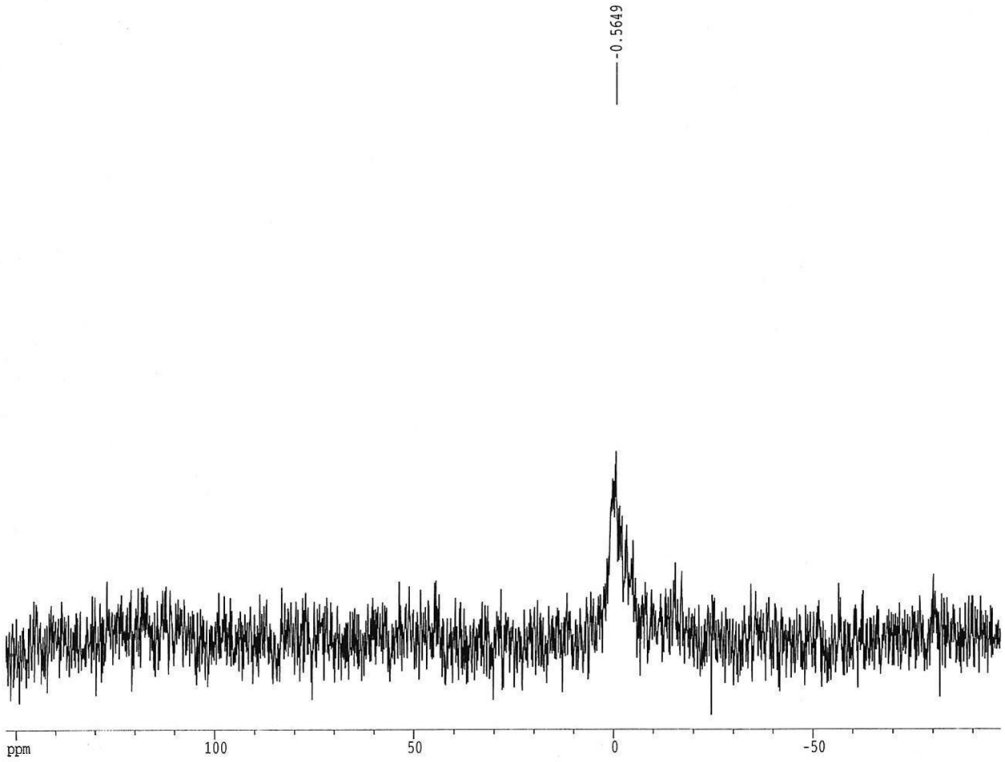

Figure S-2. ^{11}B NMR spectrum of **3b** (96 MHz, $CDCl_3$)

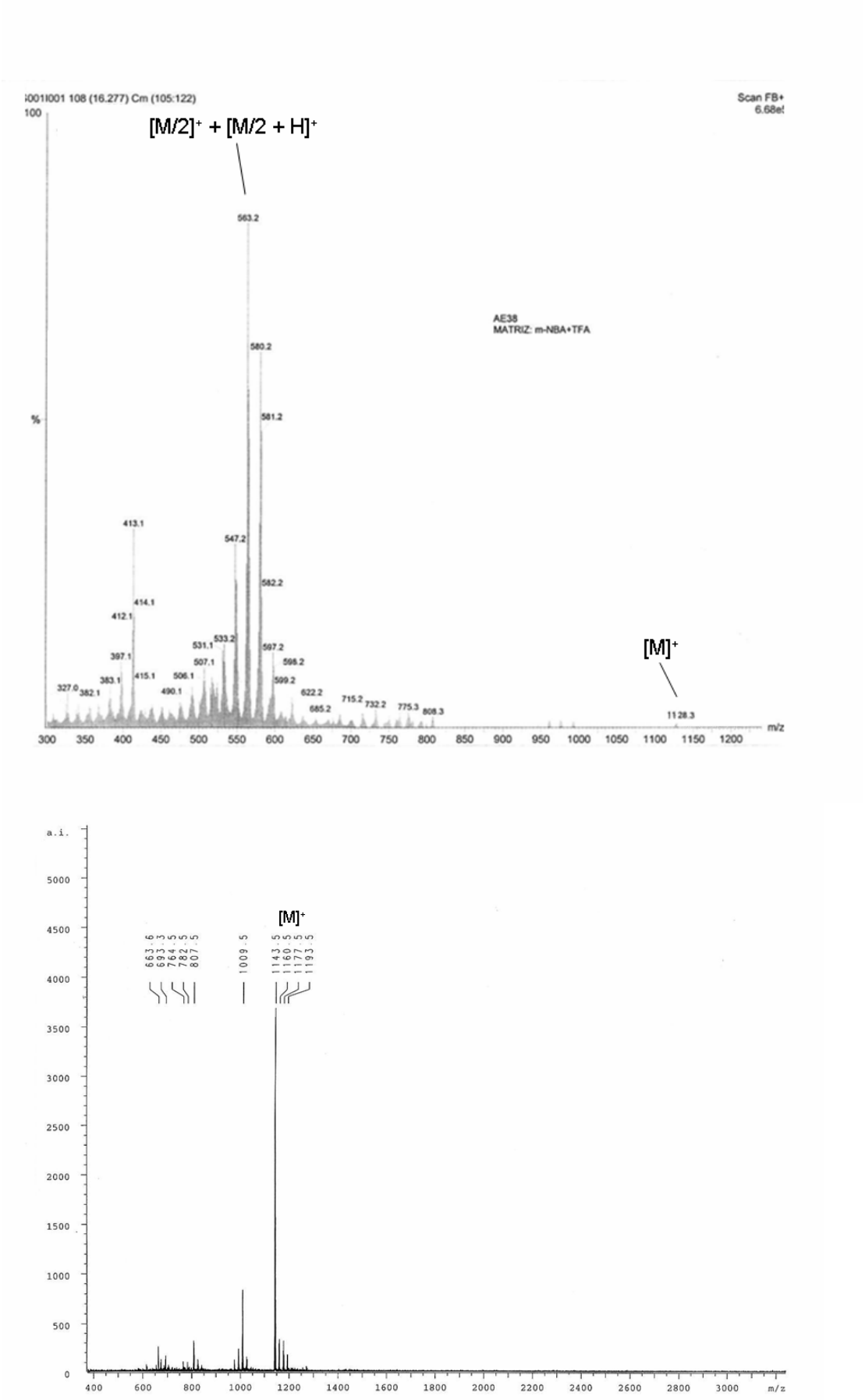

Figure S-3. Upper part: MS (FAB, *m*-NBA + TFA) spectrum of diborane **3b** and lower part: MS (MALDI-TOF, aminonitropyridine) spectrum of μ-oxodimer **2b**, for comparison.

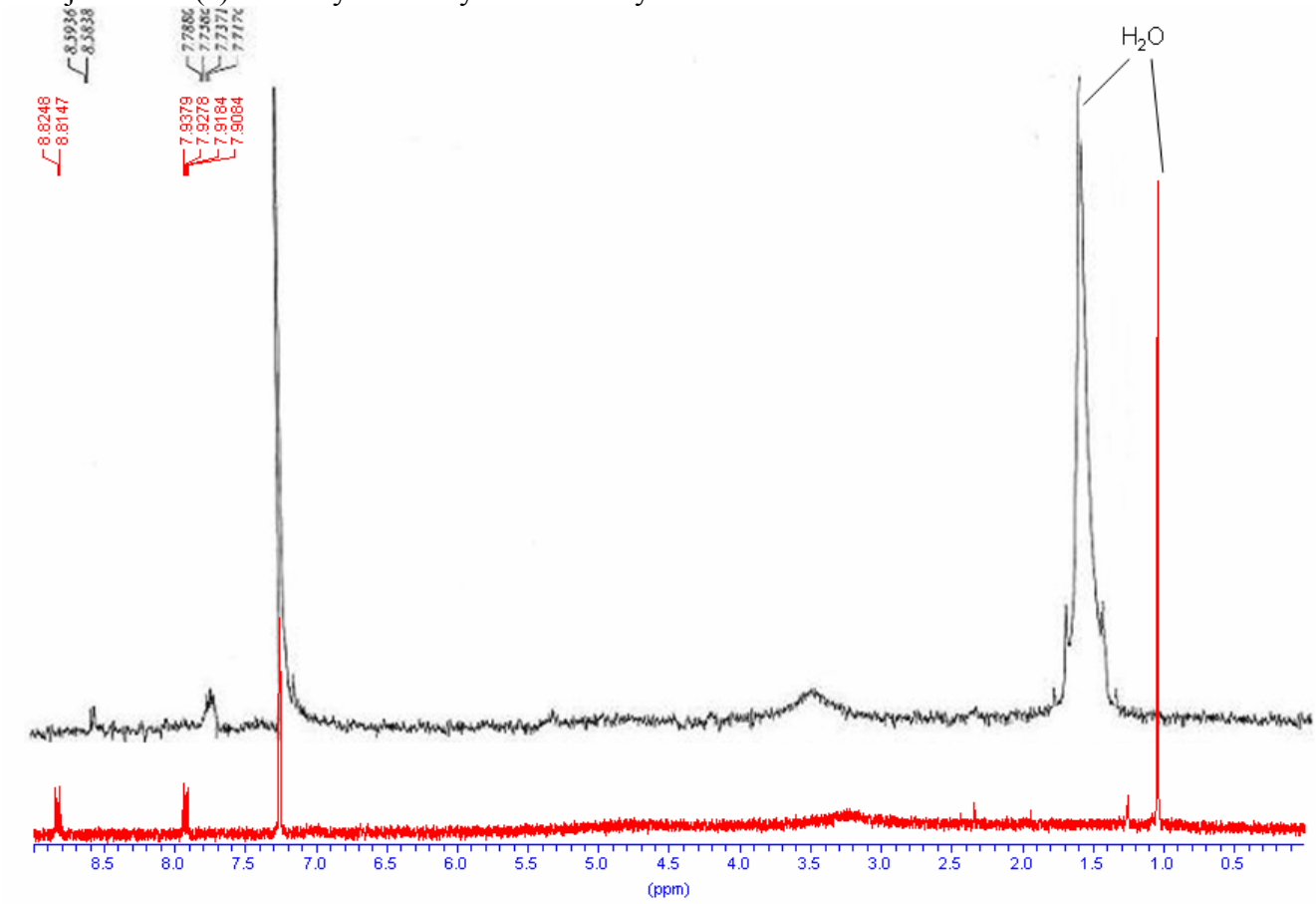

Figure S-4. ^{1}H NMR spectrum of precursor **1a** (red line) compared to ^{1}H NMR spectrum of diborane **3a** (black line) (300 MHz, CS_2 + 10% $CDCl_3$).

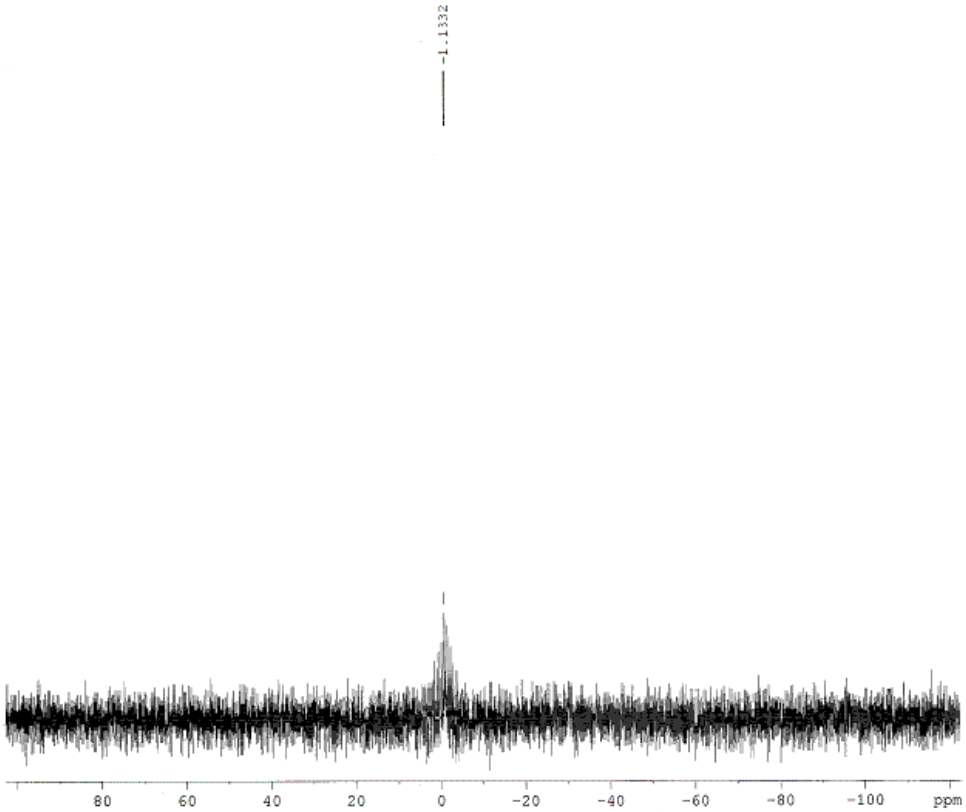

Figure S-5. ^{11}B NMR spectrum of **3a** (96 MHz, CS_2 + 10% $CHCl_3$).

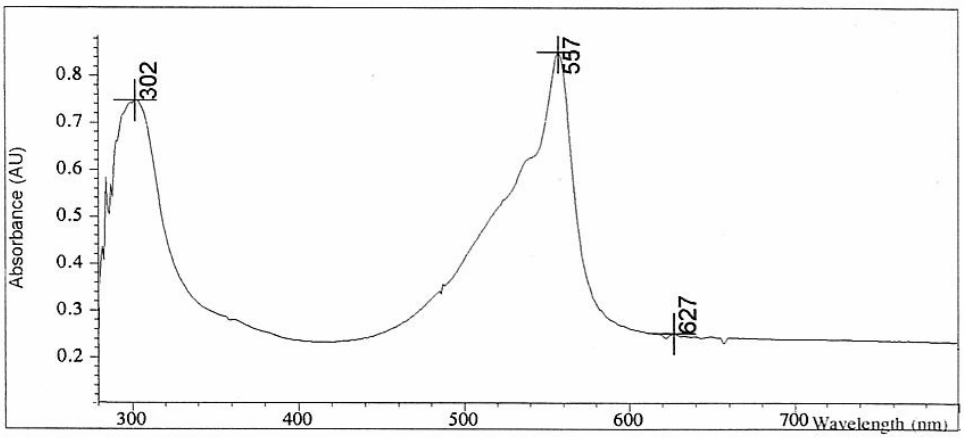

Figure S-6. UV/Vis spectrum of **3a** (*n*-heptane, c= 5×10^{-6}).

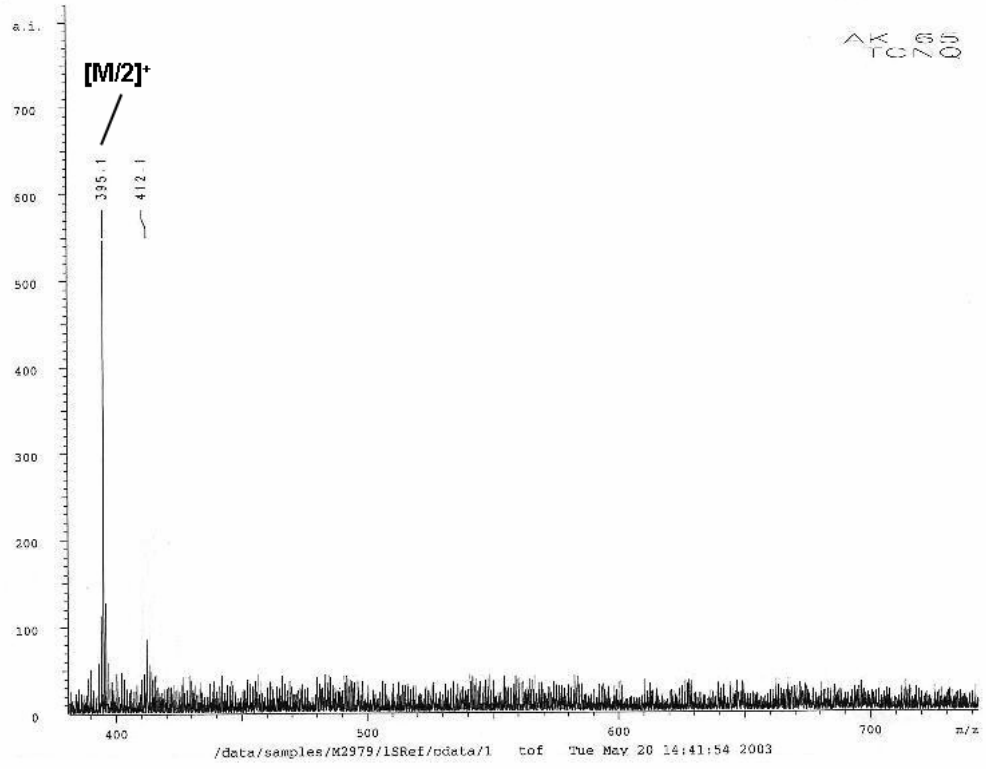

Figure S-7. MS (MALDI-TOF, TCNQ) spectrum of dimer **3a**.

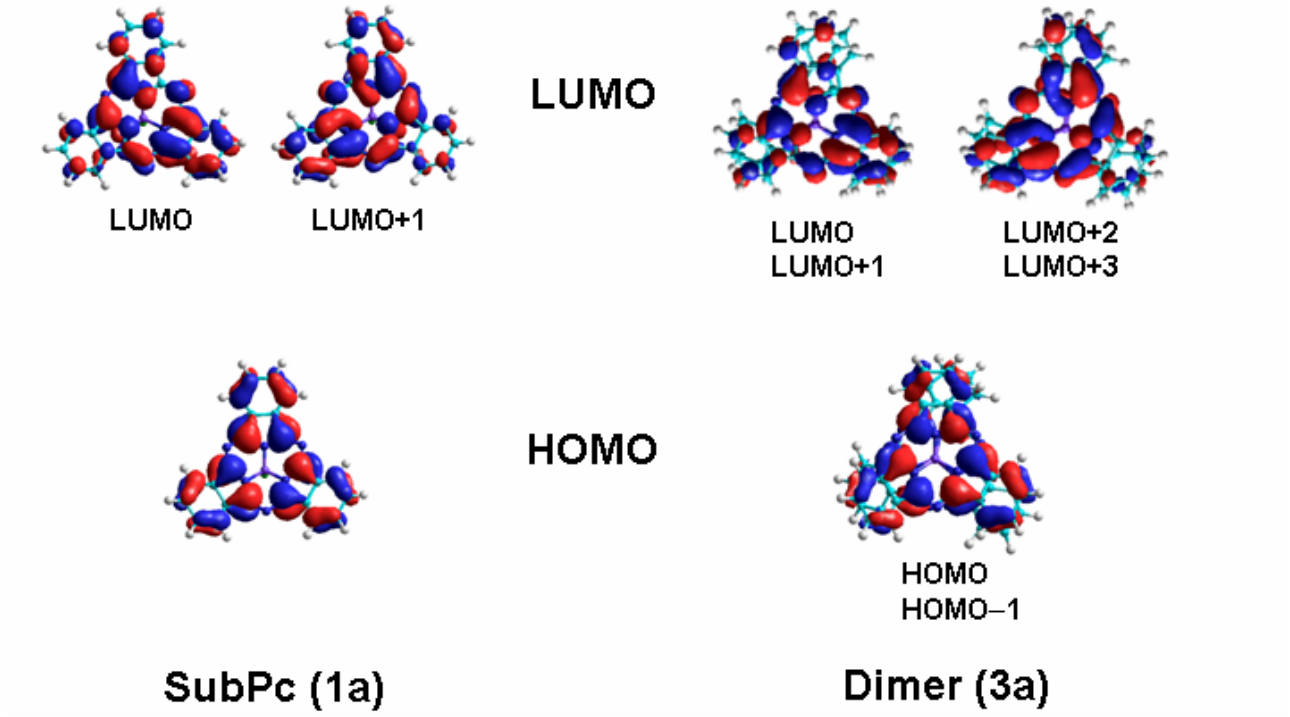

Figure S-8. Frontier orbitals of SubPc **1a** and diborane **3a** obtained by AM1 semiempirical calculations.