Supplementary data

“Mulliken-Hush analysis of a bis(triarylamine) mixed-valence system with a *N*··*N* distance of 28.7 Å”

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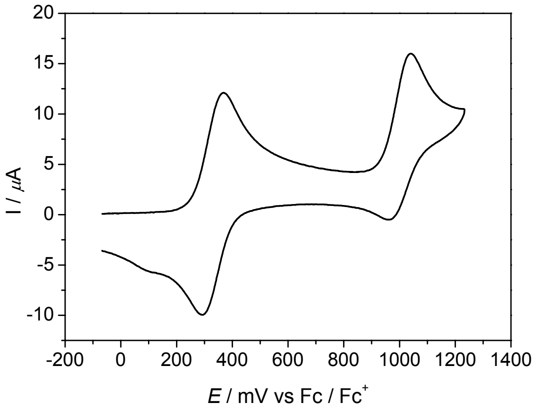
General. All reagents were obtained from commercial suppliers and were uesd without further purification. Diethylamine was freshly destilled and stored under nitrogen atmosphere. Thin-layer chromatography was carried out on Merck silica gel plates (60 F$_{254}$). Merck silica gel 32-63 μm was used for flash chromatography. The NMR spectra were recorded on Bruker AVANCE DMX 600 FT-NMR (600MHz) instrument in acetone-d$_6$ (calibrated at 2.05 and 29.8 ppm for ^{1}H and ^{13}C experiments, respectively). Mass spectra (MS) were determined on a Finnigan MAT 90 mass spectrometer at 70eV ionising voltage (EI), ESI pos and APCI pos high resolution measurements were determined on a Bruker Daltonik micrOTOF focus spectrometer. The melting points were measured with a melting apparatus by Dr. Tottoli from Büchi and are not corrected.

Synthesis of 1,4-Bis{4-[2-(4-bis(4-methoxyphenyl)amino)phenyl)ethynyl]phenyl}buta-1,3-diyne (1a): Silane **4a** (160 mg, 200 μmol, 1.00 equiv.) and Cu(I)Cl (23.7 mg, 240 μmol, 1.20 equiv.) were dissolved in 4 ml of dry dimethylformamide and the solution was stirred vigorously at 60 °C for 3 days. Water (30ml) was added and the mixture was extracted with dichloromethane (3 x 100 ml). The organic layer was washed with water (2 x 50 ml), dried over MgSO$_4$ and the solvent was removed in vacuo. The crude product was further purified by flash chromatography on silica gel (petroleum ether / dichloromethane (1 / 1)) to obtain a red-brown solid (115 mg, 134 μmol, 67 %), m.p. 102 °C. ^{1}H-NMR (600 MHz, acetone-d$_6$, 299 K): δ / ppm = 7.60 (AA′, 4H, CCCCCC*H*CHC or CCCCCHC*H*C), 7.54 (BB`, 4H, CCCCCC*H*CHC or CCCCCHC*H*C), 7.35 (AA′, NCC*H*CHC or NCCHC*H*C), 7.12 (AA`, 8H, NCC*H*CHCOCH$_3$ or NCCHC*H*COCH$_3$), 6.95 (BB`, 8H, NCC*H*CHCOCH$_3$ or NCCHC*H*COCH$_3$), 6.78 (BB`, 4H, NCC*H*CHC or NCCHC*H*C), 3.81 (s, 12H, OC*H$_3$*). ^{13}C-NMR (101 MHz, acetone-d$_6$, 299 K): δ / ppm = 158.0 (quart), 150.6 (quart), 140.6 (quart), 133.49 (CCCCC*C*HCHC or CCCCCH*C*HC), 133.46 (NC*C*HCHC or NCCH*C*HC), 132.3 (CCCCC*C*HCHC or CCCCCH*C*HC), 128.6 (NC*C*HCHCOCH$_3$ or NCCH*C*HCOCH$_3$), 126.1 (quart), 121.3 (quart), 118.9 (NC*C*HCHC or NCCH*C*HC), 115.9 (NC*C*HCHC or NCCH*C*HC), 113.5 (quart), 94.3 (quart), 88.3 (quart), 82.9 (quart), 75.9 (quart), 55.7 (O*C*H$_3$). IR (KBr): $\tilde{\nu}$ = 3036 (w), 2996 (w), 2950 (w), 2929 (vw), 2900 (vw), 2832 (w), 1592 (m), 1505 (vs), 1463 (w), 1440 (w), 1405 (vw), 1323 (m), 1285 (w), 1241 (s), 1188 (w), 1178 (w), 1134 (w), 1104 (w), 1035 (m), 827 (s), 721 (w), 577 (w) cm^{-1}. MS (ESI pos, high resolution): *m*/*z* found: 856.33020, calculated for $C_{60}H_{44}N_2O_4$: 856.33011 (Δppm = 0.11).

Synthesis of 2-{4-[Bis-(4-methoxyphenyl)amino]phenylethynyl}-5-trimethylsilanylethynylbenzonitrile (4b): (4-Ethynylphenyl)-bis(4-methoxyphenyl)amine **(2)** (2.00g, 6.07 mmol, 1.00 equiv.), 2-iodo-5-trimethylsilanylethynylbenzonitrile **(3)** (2.72 g, 8.36 mmol, 1.38 equiv.), CuI (135 mg, 0.71 mmol, 0.12 equiv.) and Pd(PPh$_3$)$_2$Cl$_2$ (480 mg, 0.68 mmol, 0.11 equiv.) were dissolved in dry diethylamine and the mixture was stirred under a nitrogen atmosphere at room temperature for 24 h. The solvent was removed in vacuo and the residue was redissolved in dichloromethane and washed with water. The organic layer was dried over MgSO$_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography over silica gel eluting with ethyl acetate / petroleum ether (2 / 98) to obtain a yellow solid (2.00 g, 3.80 mmol, 63 %), m.p. 52-53 °C. ^{1}H-NMR (600 MHz, acetone-d$_6$, 299 K): δ / ppm = 7.88 (dd, $^4J_{HH}$ = 1.7 Hz, $^5J_{HH}$ = 0.6 Hz, 1H, CC*H*CCN), 7.73 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, SiCCCC*H*CH), 7.66 (dd, $^3J_{HH}$ = 8.2 Hz, $^5J_{HH}$ = 0.6 Hz, 1H, SiCCCCHC*H*C), 7.40 (AA′, 2H, NCC*H*CHCC or NCCHC*H*CC), 7.15 (AA′, 4H, OCC*H*CHC or OCCHC*H*C), 6.96 (BB′, 4H, OCC*H*CHC or OCCHC*H*C), 6.80 (BB′, 2H, NCC*H*CHCC or NCCHC*H*CC), 3.81 (s, 6H, OC*H*$_3$), 0.25 (s, 9H, Si(C*H*$_3$)$_3$). ^{13}C-NMR (101 MHz, acetone-d$_6$, 299 K): δ / ppm = 157.3 (quart), 150.4 (quart), 140.0 (quart), 136.5 (C*C*HCCN), 136.4 (SiCCC*C*HCH), 133.5 (NC*C*HCHCC or NCCH*C*HCC), 132.6 (SiCCCCH*C*HC), 128.5 (OC*C*HCHC or OCCH*C*HC), 127.6 (quart), 123.3 (quart), 118.3 (NC*C*HCHCC or NCCH*C*HCC), 117.3 (quart), 115.3 (quart). 115.2 (OC*C*HCHC or OCCH*C*HC), 111.9 (quart), 102.6 (quart), 99.4 (quart), 99.0 (quart), 85.1 (quart), 55.5 (O*C*H$_3$), -0.2 (Si*C*H$_3$). IR (KBr): $\tilde{\nu}$ = 3039 (vw), 2999 (vw), 2955 (m), 2834 (w), 2201 (s), 2147 (m), 1591 (s), 1505 (vs), 1463 (w), 1441 (w), 1328 (m), 1280 (m), 1242 (vs), 1189 (w), 1152 (m), 1105 (w), 1034 (m), 935 (w), 858 (s), 827 (s), 760 (m), 731 (m), 640 (m), 607 (w), 577 (m) cm^{-1}. MS (EI, 70 eV) [*m*/*z*, %]: 526 (100, M$^+$), 511 (20, M$^+$-CH$_3$). MS (APCI pos, high resolution): *m*/*z* found: 527.21596, calculated for $C_{34}H_{31}N_2O_2Si^+$: 527.21548 (Δppm = 0.91).

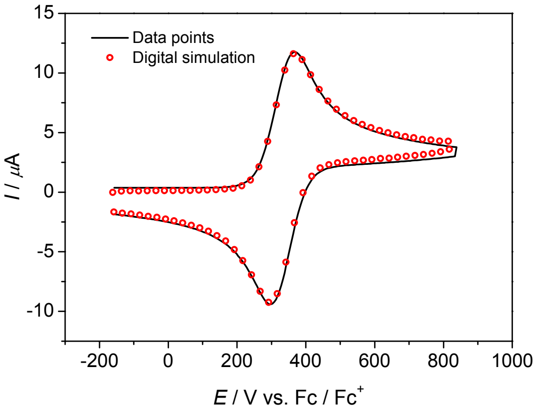
Synthesis of 1,4-Bis{4-[2-(4-bis(4-methoxyphenyl)amino)phenyl)ethynyl]-3-cyanophenyl}buta-1,3-diyne (1b): Silane **4b** (250 mg, 475 μmol, 1.00 equiv.) and Cu(I)Cl (56,4 mg, 570 μmol, 1.20 equiv.) were dissolved in 5 ml of dry dimethylformamide and the solution was stirred vigorously at 60 °C for 3 days. Water (50ml) was added and the mixture was extracted with dichloromethane (3 x 100 ml). The organic layer was washed with water (2 x 100 ml), dried over MgSO$_4$ and the solvent was removed in vacuo. The crude product was further purified by flash chromatography on silica gel (petroleum ether / dichloromethane (1 /1 > 1 / 99) to obtain a deep red solid (170 mg, 187 μmol, 78 %), m.p. 85 °C. ^{1}H-NMR (600 MHz, acetone-d$_6$, 299 K): δ / ppm = 8.07 (dd, $^4J_{HH}$ = 1.8 Hz, $^5J_{HH}$ = 0.5 Hz, 2H, NCCC*H*C), 7.88 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.8 Hz, 2H, NCCCHCC*H*CH), 7.73 (dd, $^3J_{HH}$ = 8.2 Hz, $^5J_{HH}$ = 0.5 Hz, 2H, NCCC*H*CH), 7.41 (AA`, 4H, NCC*H*CHCC or NCCHC*H*CC), 7.16 (AA`, 8H, OCC*H*CHCN or OCCHC*H*CN), 6.97 (BB`, 8H, OCC*H*CHCN or OCCHC*H*CN), 6.80 (BB`, 4H, NCC*H*CHCC or NCCHC*H*CC), 3.81 (s, 12H, OC*H*$_3$). ^{13}C-NMR (151 MHz, acetone-d$_6$, 299 K): δ / ppm = 158.2 (quart), 151.4 (quart), 140.2 (quart), 137.4 (NCC*C*HC), 137.2 (NCCCHC*C*HCH), 133.9 (NC*C*HCHCC or NCCH*C*HCC), 133.0 (NCC*C*HCH), 129.1 (quart), 128.8 (OC*C*HCHCN or OCCH*C*HCN), 121.6 (quart), 118.4 (NC*C*HCHCC or NCCH*C*HCC), 117.2 (quart), 116.0 (quart), 115.9 (OC*C*HCHCN or OCCH*C*HCN), 111.9 (quart), 101.1 (quart), 85.6 (quart), 81.7 (quart), 76.8 (quart), 55.5 (O*C*H$_3$). IR (KBr): $\tilde{\nu}$ = 3039 (vw), 2954 (w), 2927 (w), 2830 (w), 2200 (m), 1587 (s), 1504 (vs), 1461 (w), 1439 (w), 1319 (m), 1287 (m), 1240 (s), 1188 (w), 1150 (m), 1090 (w), 1032 (m), 826 (s), 727 (m), 575 (m), 526 (w), 504 (w) cm^{-1}. MS (APCI pos, high resolution): *m*/*z* found: 907.32957, calculated for $C_{62}H_{43}N_4O_4^+$: 907.32843 (Δppm = 1.26).

CV of compound 1b:



CV of compound **1b** in a dichloromethane / 0.1 M tetrabutylammonium hexafluorophosphate solution, scan rate 250 mV/s. The signal observed at ca. 100 mV is due to the irreversible oxidation processes of the dication to higher oxidised species at ca. 1100 mV. This irreversibility is also confirmed by thin layer measurements.

Digital simulation of the CV of 1b:



The digital simulation of the first two unresolved oxidation processes yields: E^1_{Ox} = 330 mV and E^2_{Ox} = 385 mV versus Fc / Fc$^+$. From the separation of the half wave potentials the disproportination coefficient K_c for the equilibrum (1) can be determined with eqn. 1.

$$\mathrm{M} + \mathrm{M}^{2+} \rightleftharpoons 2\mathrm{M}^{+} \tag{1}$$

$$K_\mathrm{c} = e^{\frac{(E_\mathrm{Ox}^2 - E_\mathrm{Ox}^1)\mathrm{F}}{\mathrm{R}T}} \qquad \text{(eqn. 1)}$$

From the disproportination coefficient K_c the real concentration of the monocation can be calculated. Owing to the uncertainty of the redox potential difference, K_c also has a large error and cannot be used to calculate the real concentration of $\mathbf{1b}^{+}$ in solution.

AM1 Calculations: The semiempirical calculations were done using the AM1 parametrisation implemented in the MOPAC 2002 program. The optimisation of the structures were performed without symmetry restrictions in Cartesian coordinates by the eigenvector following (EF) method. Self consistent field (SCF) convergence was achieved by Pulay`s method. The configuration interactions included singles and doubles excitations (CISD) within an active orbital window comprising the four highest doubly occupied, one single occupied, and two lowest unoccupied orbitals. The solvent influence on the optical properties was modeled by the COSMO method for a solvent with $\varepsilon = 2.0$ and a solvent radius of 2.5 Å at the CISD optimised gas phase structures.