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Property Tuning in Charge-Transfer Chromophores by Systematic Modulation of the Spacer Between Donor and Acceptor

Filip Bureš, W. Bernd Schweizer, Joshua C. May, Corinne Boudon, Jean-Paul Gisselbrecht,
Maurice Gross, Ivan Biaggio, and François Diederich*

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4-(tert-Butyldimethylsilyloxy)but-2-ynal (13). To *t*BuMe₂Si-protected propargyl alcohol (5.0 g, 29.35 mmol) in anhydrous THF (100 mL), MeLi·LiBr (14.1 mL, 31.0 mmol, 2.2 M solution in Et₂O) was added slowly at 0 °C under N₂. The solution was stirred for 15 min at 0 °C, DMF (3.5 mL, 45.0 mmol) added, and stirring continued for 1 h at 20 °C. The mixture was poured into a vigorously stirred bi-phasic system of saturated aqueous KH₂PO₄ and Et₂O at 5 °C (50/50 mL). The organic layer was separated and the aqueous layer extracted with Et₂O (2 × 50 mL). The combined organic layers were dried (MgSO₄), the solvents evaporated in vacuo, and the residue filtered through a plug (SiO₂; CH₂Cl₂) to afford pure **13** (5.2 g, 89%) as an orange oil. R_f = 0.81 (SiO₂; CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃, 20 °C, TMS): **d** = 0.13 (s, 6H; SiCH₃), 0.91 (s, 9H; CCH₃), 4.50 (d, ⁵J(H,H) = 0.6 Hz, 2H; CH₂), 9.23 ppm (t, ⁵J(H,H) = 0.6 Hz, 1H; CHO); ¹³C NMR (75 MHz, CDCl₃, 20 °C, TMS): **d** = -5.37, 18.12, 25.58, 51.42, 84.08, 94.77, 176.34 ppm; IR (neat): **n** = 2930, 2858, 2188, 1674, 1472, 1363, 1255, 1121, 1088, 831, 777,

668 cm^{-1} ; elemental analysis calcd (%) for $\text{C}_{10}\text{H}_{18}\text{O}_2\text{Si}$ (198.33): C 60.56, H 9.15; found C 60.46, H 9.19.

1,7-Bis(*tert*-butyldimethylsilyloxy)hepta-2,5-diyne-4-one (14).

*t*BuMe₂Si-protected propargyl alcohol (2.0 g, 11.74 mmol) in anhydrous THF (50 mL) at $-20\text{ }^{\circ}\text{C}$ under N_2 was treated with *n*BuLi (7.35 mL, 11.74 mmol, 1.6 M solution in hexane) for 15 min. A solution of **13** (2.3 g, 11.5 mmol) in THF (10 mL) was added and the resulting mixture stirred for 1 h, then quenched with saturated aqueous NH_4Cl . The crude mixture was extracted with CH_2Cl_2 (50 mL) and the combined organic layers dried (MgSO_4) and concentrated in vacuo to afford pure 1,7-bis(*tert*-butyldimethylsilyloxy)hepta-2,5-diyne-4-ol (4.0 g, 94%) as an oil. ^1H NMR (300 MHz, CDCl_3 , $20\text{ }^{\circ}\text{C}$, TMS): **d** = 0.12 (s, 12H; SiCH₃), 0.91 (s, 18H; CCH₃), 2.25 (d, $^3J(\text{H},\text{H}) = 6.9\text{ Hz}$, 1H; OH), 4.35 (d, $^5J(\text{H},\text{H}) = 1.8\text{ Hz}$, 4H; CH₂), 5.16 ppm (m, 1H; CH); ^{13}C NMR (75 MHz, CDCl_3 , $20\text{ }^{\circ}\text{C}$, TMS): **d** = -4.98, 18.46, 25.98, 51.80, 52.50, 81.77, 83.50 ppm; IR (neat): **n** = 2930, 1463, 1362, 1254, 1112, 1081, 1004, 831, 775 cm^{-1} ; HR-EI-MS: *m/z*: calcd for $\text{C}_{15}\text{H}_{27}\text{O}_3\text{Si}_2^+$: 311.1494; found 311.1496 ($[\text{M}-\text{C}_4\text{H}_9]^+$). This alcohol (2.0 g, 5.43 mmol) was taken up in CH_2Cl_2 (50 mL) and oxidized by MnO_2 (1.0 g, 11.5 mmol). The suspension was stirred for an hour and then filtered through a plug (SiO_2 ; CH_2Cl_2) to afford desired product **14** as oil. Yield 1.9 g (97%). $R_f = 0.80$ (SiO_2 ; CH_2Cl_2); ^1H NMR (300 MHz, CDCl_3 , $20\text{ }^{\circ}\text{C}$, TMS): **d** = 0.13 (s, 12H; SiCH₃), 0.91 (s, 18H, CCH₃), 4.48 ppm (s, 4H; CH₂); ^{13}C NMR (75 MHz, CDCl_3 , $20\text{ }^{\circ}\text{C}$, TMS): **d** = -5.06, 18.39, 25.92, 51.71, 84.66, 91.71, 160.20 ppm; IR (neat): **n** = 2930, 2856, 2206, 1636, 1472, 1363, 1254, 1226, 1096, 830, 776, 712 cm^{-1} ; UV/Vis (CH_2Cl_2): **I**_{max} (**e**) = 241 nm (8700 $\text{mol}^{-1}\text{ dm}^3\text{ cm}^{-1}$); HR-EI-MS *m/z*: calcd for $\text{C}_{15}\text{H}_{25}\text{O}_3\text{Si}_2^+$: 309.1337; found 309.1336 ($[\text{M}-\text{C}_4\text{H}_9]^+$).

Corey-Fuch's dibromoolefination - general method. A slurry of CBr₄ (8.1 g, 24.4 mmol), PPh₃ (6.4 g, 24.4 mmol), and Zn dust (1.6 g, 24.4 mmol) in CH₂Cl₂ (50 mL) was stirred for 1 h at -40 °C under N₂. A solution of aldehyde or ketone (5 mmol) in CH₂Cl₂ (20 mL) was added dropwise and the mixture stirred for the indicated time, then diluted with hexane. The formed precipitate was filtered off on a short plug (SiO₂; hexane) and washed properly with hexane. The hexane filtrates were concentrated in vacuo and subjected to CC.

1,1-Dibromo-4-trimethylsilylbut-1-en-3-yn (9). To a suspension of 3-(trimethylsilyl)propargyl alcohol (2.04 g, 15.94 mmol), Celite (7 g), and molecular sieves (6 g, 4Å) in CH₂Cl₂ (60 mL), PCC (6.2 g, 28.8 mmol) was added and the mixture stirred for 2.5 hours at 20 °C. Filtration through a plug (SiO₂; CH₂Cl₂) and evaporation afforded unstable 3-(trimethylsilyl)propynal (2.0 g, 15.9 mmol). Dibromoolefination was carried out following the general method, stirring for 14 h at 20 °C. Product **9** (3.1 g, 69%) was obtained after CC (SiO₂; hexane) as an oil. R_f = 0.63 (SiO₂; hexane); ¹H NMR (300 MHz, CDCl₃, 20 °C, TMS): **d** = 0.22 (s, 9H; SiCH₃), 6.57 ppm (s, 1H; CH); ¹³C NMR (75 MHz, CDCl₃, 20 °C, TMS): **d** = 0.21, 100.69, 103.12, 103.82, 119.61 ppm; IR (neat): **n** = 2959, 2171, 1782, 1560, 1250, 1074, 838, 758, 700, 641 cm⁻¹; UV/Vis (CH₂Cl₂): I_{max} (**e**) = 254 nm (sh, 14300 mol⁻¹ dm³ cm⁻¹); EI-MS (70 eV) m/z (%): 73 (100); elemental analysis calcd (%) for C₇H₁₀Br₂Si (282.05): C 29.81, H 3.57, Br 56.66; found C 29.89, H 3.49, Br 56.69.

O-(tert-Butyldimethylsilyl)-1,1-dibromopent-1-en-3-yn-5-ol (15). The title compound was prepared from aldehyde **13** (1.7 g, 8.57 mmol) following the general method. The mixture was stirred for 2 h at 20 °C, and CC (SiO₂; hexane → hexane/CH₂Cl₂ 1:1) afforded **15** (1.35 g, 46%) as an oil. R_f = 0.2 (SiO₂; hexane); ¹H NMR (300 MHz, CDCl₃, 20 °C, TMS): **d** = 0.14 (s, 6H;

SiCH₃), 0.91 (s, 9H; CCH₃), 4.43 (d, ⁵J(H,H) = 2.4 Hz, 2H; CH₂), 6.59 ppm (t, ⁵J(H,H) = 2.4 Hz, 1H; CH); ¹³C NMR (75 MHz, CDCl₃, 20 °C, TMS): **d** = -4.93, 18.43, 25.91, 52.33, 81.35, 95.95, 101.90, 119.23 ppm; IR (neat): **n** = 2954, 2929, 2857, 1472, 1252, 1048, 1004, 833, 776, 670 cm⁻¹; UV/Vis (CH₂Cl₂): **I**_{max} (**e**) = 247 nm (sh, 13300 mol⁻¹ dm³ cm⁻¹); HR-EI-MS *m/z*: calcd for C₁₁H₁₈Br₂OSi⁺: 351.9489; found 351.9489 (*M*⁺).

O-(tert-Butyldimethylsilyl)-1,1-dibromo-2-[3-(tert-butyldimethylsilyloxy)prop-1-ynyl]pent-1-en-3-yn-5-ol (16).

The title compound was synthesized from ketone **14** (1.8 g, 4.91 mmol) following the general method. The mixture was stirred for 24 h at 20 °C, and CC (SiO₂; hexane/CH₂Cl₂ 1:1) afforded **16** (290 mg, 11%) as an oil. *R*_f = 0.5 (SiO₂; hexane/CH₂Cl₂ 1:1); ¹H NMR (300 MHz, CDCl₃, 20 °C, TMS): **d** = 0.14 (s, 12H; SiCH₃), 0.91 (s, 18H; CCH₃), 4.44 ppm (s, 4H; CH₂); ¹³C NMR (75 MHz, CDCl₃, 20 °C, TMS): **d** = -4.90, 18.44, 25.97, 52.34, 81.34, 94.88, 108.22, 113.70 ppm; IR (neat): **n** = 2929, 2857, 1471, 1362, 1253, 1089, 920, 830, 776, 663 cm⁻¹; UV/Vis (CH₂Cl₂): **I**_{max} (**e**) = 272 nm (sh, 10300 mol⁻¹ dm³ cm⁻¹); EI-MS (70 eV): *m/z* (%): 294 (100), 75 (25); elemental analysis calcd (%) for C₂₀H₃₄Br₂O₂Si₂ (522.46): C 45.98, H 6.56, Br 30.59; found C 46.04, H 6.60, Br 30.62.

Suzuki cross-coupling reaction on dibromoolefines - general method.^[1] To a degassed solution of dibromoolefin (7.31 mmol) and 4-(dimethylamino)phenylboronic acid (3.0 g, 18.3 mmol) in THF/H₂O (150 mL, 4:1), [PdCl₂(PPh₃)₂] (513 mg, 0.73 mmol) and Na₂CO₃ (1.94 g, 18.23 mmol) were added. The mixture was stirred for 14 h under N₂ at 70 °C, diluted with water, and extracted with CH₂Cl₂ (3 × 50 mL). The combined organic layers were dried (MgSO₄) and concentrated in vacuo, and CC afforded pure product.

4,4'-[4-(Trimethylsilyl)but-1-en-3-yne-1,1-diyl]bis(*N,N*-dimethylaniline) (10a). The title compound was synthesized from dibromoolefin **9** (2.0 g, 7.1 mmol) following the general method. Final purification by CC (SiO₂; hexane/CH₂Cl₂ 1:1) afforded **10a** (1.7 g, 67%) as a brown solid. *R*_f = 0.5 (SiO₂; hexane/CH₂Cl₂ 1:1); M.p. 124–125 °C; ¹H NMR (300 MHz, CDCl₃, 20 °C, TMS): **d** = 0.16 (s, 9H; SiCH₃), 2.97 (s, 6H; NCH₃), 3.00 (s, 6H; NCH₃), 5.73 (s, 1H; CH), 6.66 (t, ³*J*(H,H) = 9.0 Hz, 4H; Ar), 7.20 (d, ³*J*(H,H) = 9.0 Hz, 2H; Ar), 7.48 ppm (d, ³*J*(H,H) = 9.0 Hz, 2H; Ar); ¹³C NMR (75 MHz, CDCl₃, 20 °C, TMS): **d** = -0.10, 40.29, 40.35, 96.60, 100.94, 106.35, 110.90, 111.56, 126.98, 129.37, 129.99, 131.40, 150.19, 150.37, 154.18 ppm; IR (neat): **n** = 2892, 2112, 1606, 1520, 1358, 1233, 1193, 1154, 1066, 951, 835, 806, 753, 646 cm⁻¹; UV/Vis (CH₂Cl₂): **I**_{max} (**e**) = 243 (sh, 16500), 335 nm (28800 mol⁻¹ dm³ cm⁻¹); HR-FT-MALDI-MS (3-HPA) *m/z*: calcd for C₂₃H₃₁N₂Si⁺: 363.2251; found 363.2246 (MH⁺).

4,4'-[5-(*tert*-Butyldimethylsilyloxy)pent-1-en-3-yne-1,1-diyl]bis(*N,N*-dimethylaniline) (17a). The title compound was synthesized from dibromoolefin **15** (1.25 g, 3.65 mmol) following the general method. Purification by CC (SiO₂; hexane/CH₂Cl₂ 1:1 → CH₂Cl₂) afforded **17a** (0.96 g, 61%) as a brown solid. *R*_f = 0.6 (SiO₂; CH₂Cl₂); M.p. 83–85 °C; ¹H NMR (300 MHz, CDCl₃, 20 °C, TMS): **d** = 0.10 (s, 6H, SiCH₃), 0.91 (s, 9H, CCH₃), 2.97 (s, 6H; NCH₃), 2.99 (s, 6H; NCH₃), 4.42 (d, ⁵*J*(H,H) = 2.4 Hz, 2H; CH₂), 5.77 (t, ⁵*J*(H,H) = 2.4 Hz, 1H; CH), 6.64 (d, ³*J*(H,H) = 9.0 Hz, 2H; Ar), 6.69 (d, ³*J*(H,H) = 9.0 Hz, 2H; Ar), 7.20 (d, ³*J*(H,H) = 9.0 Hz, 2H; Ar), 7.41 ppm (d, ³*J*(H,H) = 9.0 Hz, 2H; Ar); ¹³C NMR (75 MHz, CDCl₃, 20 °C, TMS): **d** = -5.21, 18.24, 25.81, 40.31, 52.56, 85.13, 89.62, 101.05, 111.23, 111.61, 127.31, 129.17, 130.07, 121.11, 150.01, 150.31, 152.70 ppm; IR (neat): **n** = 2929, 2854, 2202, 1605, 1519, 1356, 1251, 1166, 1059, 995, 946, 832, 813, 772, 724 cm⁻¹; UV/Vis (CH₂Cl₂): **I**_{max} (**e**) = 327 nm

(32000 mol⁻¹ dm³ cm⁻¹); HR-FT-MALDI-MS (3-HPA) *m/z*: calcd for C₂₇H₃₉N₂OSi⁺: 435.2826; found 435.2819 (MH⁺).

4,4'-{5-(tert-Butyldimethylsilyloxy)-2-[3-(tert-butyldimethylsilyloxy)prop-1-ynyl]pent-1-en-3-yne-1,1-diyl}bis(*N,N*-dimethylaniline) (18a). The title compound was synthesized from dibromoolefin **16** (1.3 g, 2.49 mmol) following the general method. Purification by CC (SiO₂; hexane/CH₂Cl₂ 1:2) afforded **18a** (0.81 g, 54%) as a brown solid. *R*_f = 0.6 (SiO₂; CH₂Cl₂); M.p. 87–89 °C; ¹H NMR (300 MHz, CDCl₃, 20 °C, TMS): *d* = 0.09 (s, 12H; SiCH₃), 0.81 (s, 18H; CCH₃), 2.98 (s, 12H; NCH₃), 4.40 (s, 4H; CH₂), 6.62 (d, ³*J*(H,H) = 9.0 Hz, 4H; Ar), 7.33 ppm (d, ³*J*(H,H) = 9.0 Hz, 4H; Ar); ¹³C NMR (75 MHz, CDCl₃, 20 °C, TMS): *d* = -4.96, 18.37, 25.97, 40.31, 52.53, 85.03, 88.24, 95.19, 110.75, 128.31, 131.78, 150.13, 156.59 ppm; IR (neat): *n* = 2928, 2855, 2209, 1604, 1521, 1444, 1357, 1252, 1193, 1166, 1092, 1052, 946, 832, 818, 776 cm⁻¹; UV/Vis (CH₂Cl₂): *I*_{max} (*e*) = 364 nm (sh, 25700 mol⁻¹ dm³ cm⁻¹); HR-FT-MALDI-MS (3-HPA) *m/z*: calcd for C₃₆H₅₅N₂O₂Si₂⁺: 603.3797; found 603.3788 (MH⁺).

Sonogashira cross-coupling reaction on dibromoolefines - general method. To a degassed solution of dibromoolefin (7.1 mmol), 4-ethynyl-*N,N*-dimethylaniline (2.18 g, 15.0 mmol) in Et₃N (150 mL), [PdCl₂(PPh₃)₂] (121 mg, 0.17 mmol) and CuI (60 mg, 0.32 mmol) were added. The mixture was stirred for 14 h under N₂ at 20 °C. The solvent was evaporated in vacuo and the residue purified by CC.

4,4'-[3-(3-(Trimethylsilyl)prop-2-ynylidene]penta-1,4-diyne-1,5-diyl}bis(*N,N*-dimethylaniline) (10b). The title compound was synthesized from dibromoolefin **9** (2.0 g, 7.1 mmol) following the general method. Purification by CC (SiO₂; hexane/CH₂Cl₂ 2:1 → 1:1) afforded **10b** (2.3 g, 79%) as an orange solid. *R*_f = 0.45 (SiO₂; hexane/CH₂Cl₂ 1:1); M.p. 61–64 °C; ¹H

NMR (300 MHz, CDCl₃, 20 °C, TMS): **d** = 0.28 (s, 9H; SiCH₃), 2.99 (s, 6H; NCH₃), 3.01 (s, 6H; NCH₃), 6.06 (s, 1H; CH), 6.62–6.66 (m, 4H; Ar), 7.37–7.44 ppm (m, 4H; Ar); ¹³C NMR (75 MHz, CDCl₃, 20 °C, TMS): **d** = -0.05, 40.04, 85.33, 86.01, 93.76, 96.97, 103.32, 105.95, 108.96, 109.26, 111.52, 111.56, 117.52, 118.73, 132.95, 133.17, 133.53, 150.27, 150.31 ppm; IR (neat): **n** = 2895, 2178, 2114, 1602, 1520, 1443, 1353, 1227, 1186, 1078, 945, 839, 811, 757, 702, 639 cm⁻¹; UV/Vis (CH₂Cl₂): **I**_{max} (**e**) = 295 (sh, 37000), 384 nm (46300 mol⁻¹ dm³ cm⁻¹); HR-FT-MALDI-MS (3-HPA) *m/z*: calcd for C₂₇H₃₀N₂Si⁺: 410.2173; found 410.2181 (*M*⁺).

4,4'-{3-[4-(*tert*-butyldimethylsilyloxy)but-2-ynylidene]penta-1,4-diyne-1,5-diyl}bis(*N,N*-dimethylaniline) (17b). The title compound was synthesized from dibromoolefin **15** (1.08 g, 3.16 mmol) following the general method. Purification by CC (SiO₂; hexane/CH₂Cl₂ 1:1 → CH₂Cl₂) afforded **17b** (1.26 g, 83%) as a moderate stable dark solid, stored as a CH₂Cl₂ solution). *R*_f = 0.84 (SiO₂; CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃, 20 °C, TMS): **d** = 0.16 (s, 6H; SiCH₃), 0.93 (s, 9H; CCH₃), 2.99 (s, 6H; NCH₃), 3.00 (s, 6H; NCH₃), 4.60 (d, ⁵*J*(H,H) = 2.4 Hz, 2H; CH₂), 6.09 (t, ⁵*J*(H,H) = 2.4 Hz, 1H; CH), 6.60–6.65 (m, 4H; Ar), 7.36–7.43 ppm (m, 4H; Ar); ¹³C NMR (75 MHz, CDCl₃, 20 °C, TMS): **d** = -5.12, 18.25, 25.78, 40.04, 52.52, 83.25, 85.02, 86.04, 93.09, 96.40, 98.59, 109.03, 109.32, 111.50, 111.56, 116.41, 118.86, 132.88, 133.19, 133.53, 150.23, 150.24 ppm; IR (neat): **n** = 2926, 2854, 2178, 1604, 1520, 1444, 1354, 1252, 1164, 1102, 1074, 944, 833, 812, 776, 736 cm⁻¹; UV/Vis (CH₂Cl₂): **I**_{max} (**e**) = 294 (37300), 382 nm (37000 mol⁻¹ dm³ cm⁻¹); HR-FT-MALDI-MS (3-HPA) *m/z*: calcd for C₃₁H₃₈N₂OSi⁺: 482.2748; found 482.2736 (*M*⁺).

4,4'-[3-(2,2,3,3,13,13,14,14-Octamethyl-4,12-dioxa-3,13-disilapentadeca-6,9-diyne-8-ylidene)penta-1,4-diyne-1,5-diyl]bis(*N,N*-dimethylaniline) (18b). The title compound was

synthesized from dibromoolefin **16** (290 mg, 0.56 mmol) following the general method. Purification by CC (SiO₂; hexane/CH₂Cl₂ 1:1) afforded **18b** (267 mg, 74%) as brown solid. $R_f = 0.88$ (SiO₂; CH₂Cl₂); M.p. 98–100 °C (dec.); ¹H NMR (300 MHz, CDCl₃, 20 °C, TMS): **d** = 0.17 (s, 12H; SiCH₃), 0.94 (s, 18H; CCH₃), 3.00 (s, 12H; NCH₃), 4.61 (s, 4H; CH₂), 6.63 (d, ³J(H,H) = 9.0 Hz, 4H; Ar), 7.42 ppm (d, ³J(H,H) = 9.0 Hz, 4H; Ar); ¹³C NMR (75 MHz, CDCl₃, 20 °C, TMS): **d** = -5.08, 18.24, 25.80, 40.01, 52.40, 82.78, 86.17, 95.83, 100.23, 109.15, 111.50, 111.63, 119.46, 133.24, 150.40 ppm; IR (neat): **n** = 2927, 2854, 2172, 1604, 1522, 1355, 1252, 1115, 1073, 945, 832, 813, 776 cm⁻¹; UV/Vis (CH₂Cl₂): **I**_{max} (**e**) = 297 (30000), 422 nm (27000 mol⁻¹ dm³ cm⁻¹); HR-FT-MALDI-MS (3-HPA) *m/z*: calcd for C₄₀H₅₅N₂O₂Si₂⁺: 651.3797; found 651.3785 (*M*⁺).

9-[4-(Dimethylamino)phenyl]-7-[(4-(dimethylamino)phenylethynyl]nona-6-en-2,4,8-triyn-1-ol (12).
To a solution of **10b** (100 mg, 0.24 mmol) in THF (30 mL) *n*Bu₄NF (0.5 mL, 0.5 mmol, 1 M THF solution) was added. The solution was stirred for 1 h, then CH₂Cl₂ (30 mL) and water (50 mL) were added. The organic layer was separated and the water layer extracted with CH₂Cl₂ (2 × 30 mL). The combined organic layers were dried (MgSO₄) and concentrated to 5 mL. CH₂Cl₂ (30 mL), propargyl alcohol (56 mg, 1.0 mmol), and Hay catalyst (2 mL) were added and the mixture stirred for 14 h in an open flask. Evaporation of the solvent and CC (SiO₂; CH₂Cl₂) afforded **12** (78 mg, 81%) as a moderate stable brown oil. $R_f = 0.38$ (SiO₂; CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃, 20 °C, TMS): **d** = 1.80 (br s, 1H; OH), 3.00 (s, 6H; NCH₃), 3.01 (s, 6H; NCH₃), 4.45 (d, ⁷J(H,H) = 1.2 Hz, 2H; CH₂), 6.04 (t, ⁷J(H,H) = 1.2 Hz, 1H; CH), 6.62–6.66 (m, 4H; Ar), 7.38 (d, ³J(H,H) = 9.0 Hz, 2H; Ar), 7.44 ppm (d, ³J(H,H) = 9.0 Hz, 2H; Ar); ¹³C NMR (75 MHz, CDCl₃, 20 °C, TMS): **d** = 40.03, 51.79, 70.94, 77.62, 83.23, 84.26, 85.47, 86.27, 95.59, 98.13, 108.62, 108.76, 111.56, 116.56, 120.28,

133.05, 133.39, 150.41, 150.50 ppm; IR (neat): ν = 3286, 2863, 2174, 1601, 1522, 1444, 1356, 1186, 1103, 1023, 944, 816, 636 cm^{-1} ; UV/Vis (CH_2Cl_2): I_{max} (ϵ) = 298 (sh, 24500), 418 nm (30500 $\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$); HR-FT-MALDI-MS (3-HPA) m/z : calcd for $\text{C}_{27}\text{H}_{24}\text{N}_2\text{O}^+$: 392.1883; found 392.1882 (M^+).

X-ray analysis: All X-ray measurements were carried out on a Bruker Kappa CCD diffractometer equipped with graphite monochromator (MoK_α radiation, $\lambda = 0.71073 \text{ \AA}$) and an Oxford Cryostream low-temperature device. Unit cell dimensions were obtained by least-squares refinement of all measured reflexions (HKL, Scalepack^[2]). All structures were solved by direct methods (SIR97^[3], SHELX-97^[4]). Non-hydrogen atoms were refined anisotropically (**1b** isotropically because of poorly diffracting crystals) by full-matrix least-squares analysis. Hydrogen positions have been calculated and included in the final structure factor calculation. All ellipsoids in the ORTEP^[5] plots are at the 50% level.

Table S11. Summary of the X-ray data for chromophores **1a–6b**.

	1a	1b	2a	2b	3b	5b	6b
Formula	$\text{C}_{20}\text{H}_{20}\text{N}_4$, CH_2Cl_2	$\text{C}_{24}\text{H}_{20}\text{N}_4$	$\text{C}_{22}\text{H}_{22}\text{N}_4$	$\text{C}_{26}\text{H}_{22}\text{N}_4$	$\text{C}_{31}\text{H}_{30}\text{N}_4\text{Si}$, CH_2Cl_2	$\text{C}_{30}\text{H}_{22}\text{N}_4$	$\text{C}_{34}\text{H}_{22}\text{N}_6$
Crystal size [mm]	0.44×0.40×0.01	0.66×0.06×0.03	0.60×0.32×0.10	0.24×0.12×0.02	0.46×0.46×0.22	0.56×0.40×0.04	0.40×0.10×0.04

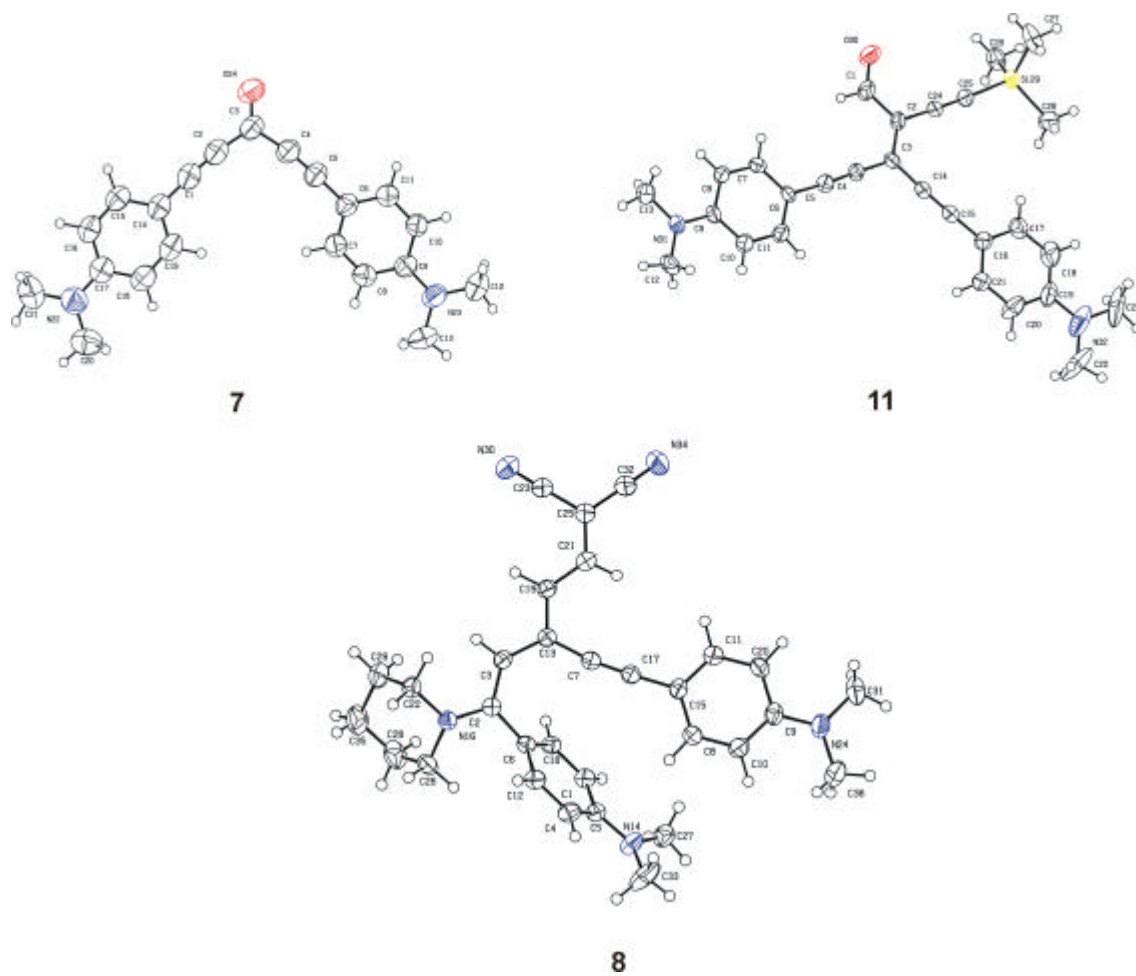
M_r	401.34	364.45	342.44	390.49	571.63	438.53	514.59
T [K]	153	173	298	113	173	173	203
Crystal syst.	monoclinic	triclinic	monoclinic	triclinic	triclinic	triclinic	triclinic
Spacegroup	$P2_1/a$	$P1$	$P2_1/n$	$P1$	$P1$	$P1$	$P1$
a [Å]	7.5614(1)	4.6906(8)	7.3186 (1)	10.1031 (5)	10.7790 (2)	7.5688 (2)	7.5895 (4)
b [Å]	22.2803(2)	9.334(2)	8.1826(2)	10.4905(5)	12.9601(2)	12.6740(3)	13.5378(5)
c [Å]	12.5439(4)	23.08(7)	32.2784(7)	22.419(1)	13.3166(2)	12.9566(4)	15.1111(7)
α [°]	-	92.75(2)	-	99.589(2)	111.932(1)	86.460(1)	112.991(3)
β [°]	105.225(1)	93.49(2)	93.320(2)	93.863(2)	97.901(1)	89.971(1)	91.743(2)
γ [°]	-	100.92(1)	-	114.646(2)	108.4793(7)	81.222(1)	99.044(2)
V [Å ³]	2039.09(7)	988.5(4)	1929.75(7)	2104.5(2)	1565.95(4)	1225.94(6)	1404.3(1)
Z	4	2	4	4	2	2	2
Unique refl.	4685	2199	4207	5467	7152	5581	6383
Observed refl. ($I > 2\sigma$)	3589	939	2963	3887	5667	3835	3550
parameters	332	113	323	541	352	395	449
$R(\text{obs})$	0.066	(isotropic) 0.285	0.056	0.272 ^[a]	0.055	0.076	0.071

[a] Very badly diffracting crystal. Hardly any reflection above theta 22°. Refinement in $P1$ with $z'=4$ shows high correlation between the almost centrosymmetric molecule pairs.

Table SI2. Summary of the X-ray data of intermediates **7** and **11** and side product **8**.

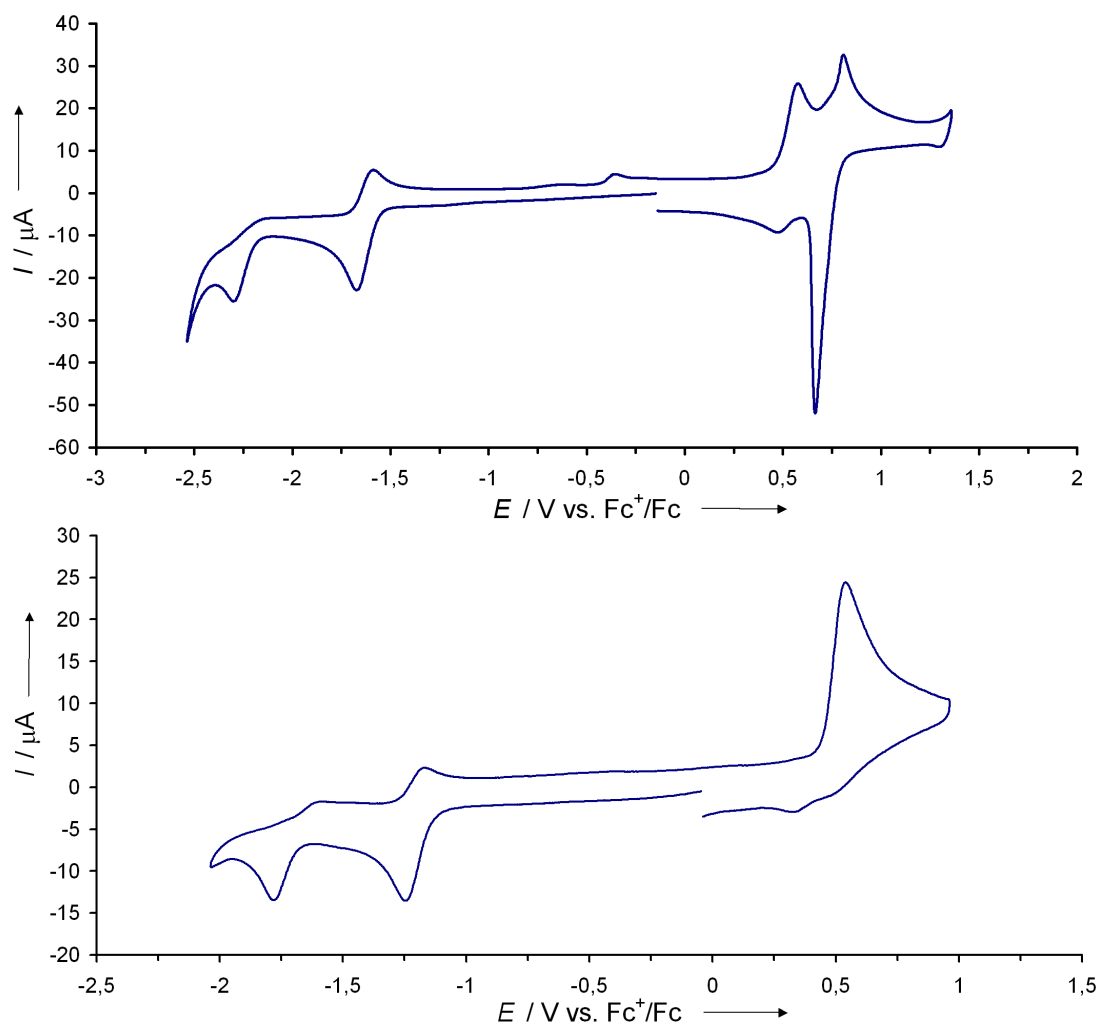
	7	8	11
Formula	C ₂₁ H ₂₀ N ₂ O	C ₃₁ H ₃₃ N ₅	C ₂₈ H ₃₀ N ₂ OSi
Crystal size [mm]	0.60×0.40×0.16	0.60×0.40×0.30	0.44×0.30×0.16
M_r	316.40	475.64	438.65
T [K]	298	173	153
Crystal syst.	monoclinic	monoclinic	orthorhombic
Spacegroup	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>a</i>	<i>P</i> na2 ₁
a [Å]	7.6559(2)	10.5451(2)	19.6024 (5)
b [Å]	18.0757(5)	17.8462(4)	18.4942(4)
c [Å]	12.8204(3)	14.5745(3)	7.0238(1)
a [°]	-	-	-
b [°]	95.710(2)	102.145(1)	-
g [°]	-	-	-
V[Å³]	1765.36(8)	2681.4(1)	2546.34(9)
Z	4	4	4
Unique refl.	3939	6120	5540
Observed refl.	2975	4662	4525
(I>2σ) parameters	218	457	289
R(obs)	0.062	0.062	0.055

Figure 1SI. ORTEP plots of intermediates **7** and **11** and side product **8**.



Electrochemistry:

Figure 2SI. Representative cyclic voltammetry ($v = 0.1 \text{ V}\cdot\text{s}^{-1}$) of chromophores **2a** (top) and **2b** (bottom) in $\text{CH}_2\text{Cl}_2 + 0.1 \text{ M } n\text{Bu}_4\text{NPF}_6$.



Optical spectroscopy:

Figure 3SI. Protonation/deprotonation experiment for **6a** in CH_2Cl_2 .

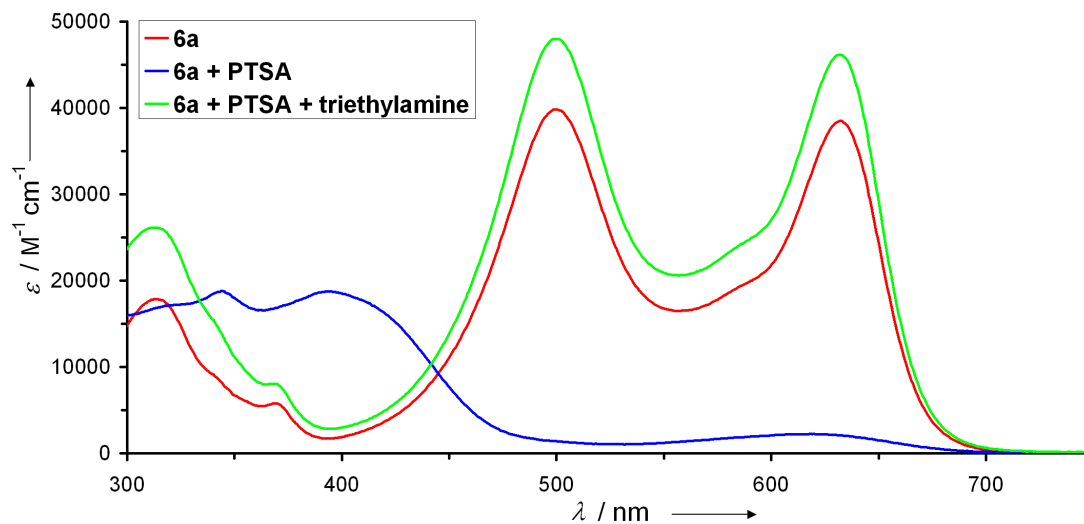


Figure 4SI. Linear correlation between the optical gap E_{gap} determined from I_{max} (○) and I_{end} (■) for **1a**, **1b**, **2a**, **2b**, **3b**, **4b**, and **5b**, and $\Delta(E_{\text{ox},1} - E_{\text{red},1})$.

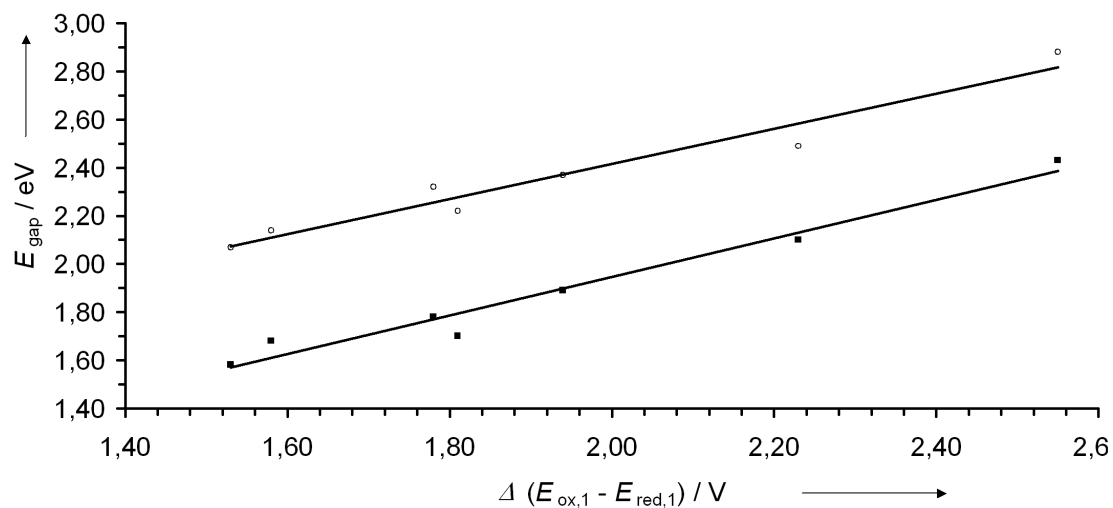
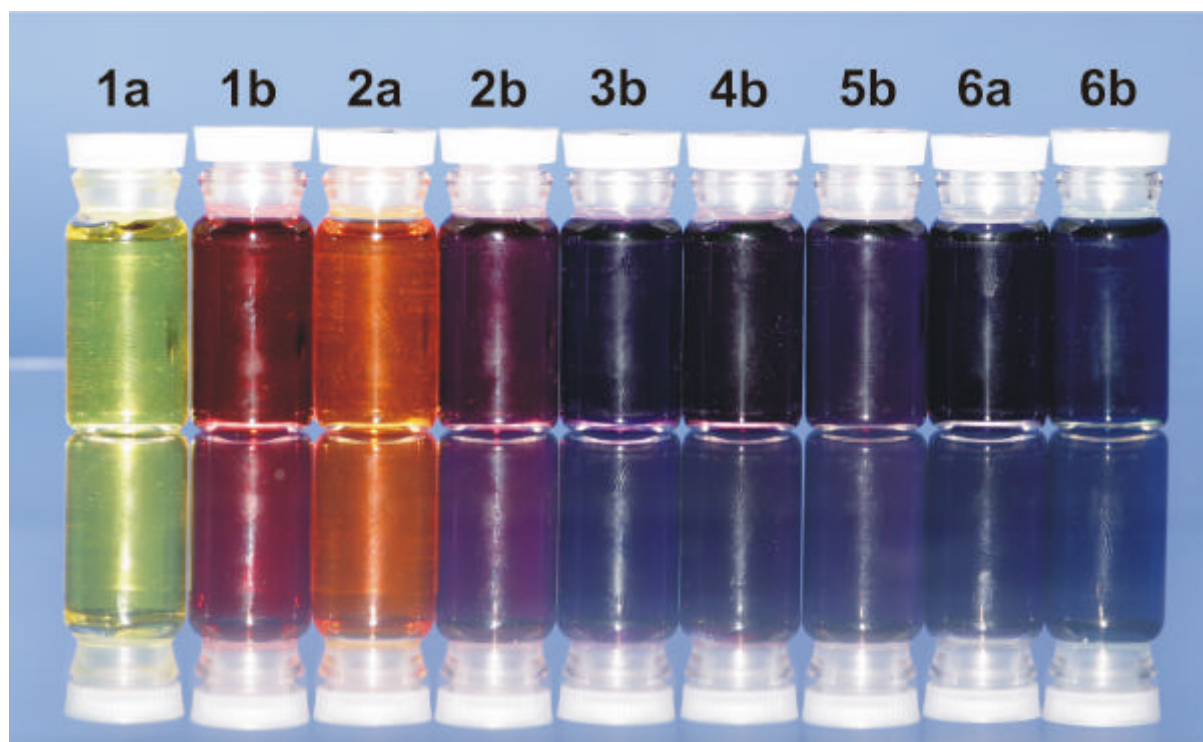


Figure 5SI. Solutions of the synthesized chromophores in CH_2Cl_2 .



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