Chemical Communications

Electronic Supplementary Information

A Novel Reaction of 7,7,8,8-Tetracyanoquinodimethane (TCNQ): Charge-Transfer Chromophores by [2+2] Cycloaddition with Alkynes

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Experimental

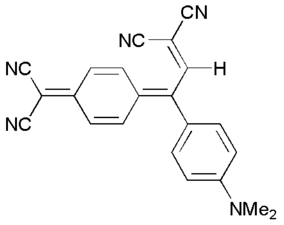
Experimental Section

Materials and general methods: Reagents and solvents were purchased at reagent grade from Acros, Aldrich and Fluka, and used as received. Tetrahydrofuran (THF) was freshly distilled from Na/benzophenone and CH_2Cl_2 from CaH_2 under N_2. Hay catalyst refers to a freshly prepared solution of CuCl (100 mg, 1.0 mmol) and *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA; 0.15 cm^3, 1.0 mmol) in acetone (25 cm^3). All reactions, except Hay couplings, were performed under an inert atmosphere by applying a positive presure of N_2 or Ar. (4-Ethynylphenyl)dimethylamine (**10**) was prepared from (4-iodophenyl)dimethylamine and ethynyltrimethylsilane by Sonogashira cross-coupling reaction, followed by desilylation of Me_3Si protected **11** (K_2CO_3, MeOH/THF 1:1) in 90% overall yield. Compounds **13**,[1] **14**,[2] **15**, **17**, as well as oligoalkynes[3] for the synthesis of **8** and **9** were prepared according to literature procedures. Column chromatography (CC) and plug filtrations were carried out with SiO_2 60 (particle size 0.040–0.063 mm, 230–400 mesh; Fluka) and distilled technical solvents. Thin-layer chromatography (TLC) was conducted on aluminum sheets coated with SiO_2 60 F_{254} obtained from Macherey-Nagel; visualisation with a UV lamp (254 or 366 nm). Melting points (mp) were measured on a Büchi B-540 melting-point apparatus in open capillaries and are uncorrected. "Decomp" refers to decomposition. ^1H NMR and ^{13}C NMR spectra were measured on a Varian Gemini 300 or on a Bruker DRX500 spectrometer at 298 K unless otherwise stated. Chemical shifts (δ) are reported in ppm relative to the signal of tetramethylsilane (TMS). Residual solvent signals in the ^1H and ^{13}C NMR spectra were used as an internal reference. Coupling constants (J) are given in Hz. The apparent resonance multiplicity is described as s (singlet), br s (broad singlet), d (doublet), t (triplet), q (quartet), sept (septuplet), and m (multiplet). Infrared spectra (IR) were recorded on a Perkin-Elmer FT1600; signal designations: s (strong), m (medium), w (weak). UV/Vis spectra were recorded on a Varian Cary-5 spectrophotometer. The spectra were measured in CH_2Cl_2 in a quartz cuvette (1 cm) at 298 K. The absorption maxima (λ_{max}) are reported in nm with the extinction coefficient (ε) M^{-1} cm^{-1} in brackets; shoulders are indicated as sh. High-resolution (HR) EI-MS spectra were measured on a Hitachi-Perkin-Elmer VG-Tribrid spectrometer. HR FT-ICR-MALDI spectra were measured on an IonSpec Ultima Fourier transform (FT) instrument with [(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB), or 3-hydroxypicolinic acid (3-HPA) as matrix. The most important peaks are reported in *m*/*z* units with *M* as the molecular ion. MALDI-TOF spectra were recorded on a Bruker Daltonics Ultraflex mass spectrometer using DCTB as matrix. Elemental analyses were performed by the Mikrolabor at the Laboratorium für Organische Chemie, ETH Zürich, with a LECO CHN/900 instrument.

Electrochemistry: The electrochemical measurements were carried out at 20 °C in CH_2Cl_2, containing 0.1 M nBu$_4$NPF$_6$ in a classical three-electrode cell. CH_2Cl_2 was purchased in spectroscopic grade from Merck, dried over molecular sieves (4 Å) and stored under Ar prior to use. nBu$_4$NPF$_6$ was purchased in electrochemical grade from Fluka and used as received. The working electrode was a glassy carbon disk electrode (3 mm in diameter) used either motionless for cyclic voltammetry (0.1 to 10 V s^{-1}) or as rotating-disk electrode for rotating disk voltammetry (RDV). The auxiliary electrode was a Pt wire, and a Pt wire was used as the pseudo-reference electrode. All potentials are referenced to the ferricinium/ferrocene (Fc^+/Fc) couple, used as an internal standard, and are uncorrected from ohmic drop. The cell was connected to Autolab PGSTAT20 potentiostat (Eco Chemie BV, Utrecht, The Netherlands) controlled by the GPSE software running on a personal computer.

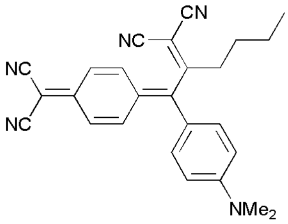
Synthetic Protocols:

(4-{3,3-Dicyano-1-[4-(dimethylamino)phenyl]prop-2-en-1-ylidene}cyclohexa-2,5-dien-1-ylidene)malononitrile (1)



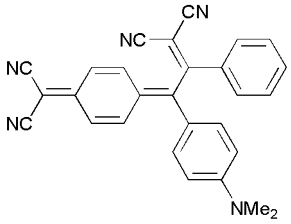
TCNQ (35 mg, 0.172 mmol) was added to a solution of **10** (25 mg, 0.172 mmol) in CH_2Cl_2 (10 cm^3). The mixture was stirred for 6 h at 20 °C. Evaporation of the solvent *in vacuo* and CC (SiO_2; CH_2Cl_2/EtOAc 97:3) afforded **1** (49 mg, 81%). Black metallic solid. $R_f = 0.65$ (SiO_2; CH_2Cl_2/EtOAc 97:3); mp 211 °C; λ_{max}(CH_2Cl_2)/nm 276 (13400), 369 (sh, 19000), 418 (39400), 526 (13700), 759 (27800); ν_{max}(neat)/cm^{-1} 3024, 2910, 2232, 2194, 2170, 1614, 1568, 1523, 1480, 1393, 1367, 1346, 1229, 1207, 1153, 1087, 1062, 922, 839, 821; δ_H(300 MHz; $CDCl_3$) 3.15 (6 H, s), 6.78 (2 H, d, *J* 9.0), 7.15 (2 H, d, *J* 9.0), 7.30 (4 H, br s), 8.18 (1 H, s); δ_C(125 MHz; $CDCl_3$) 40.17, 76.46, 92.58, 110.53, 112.31, 113.78, 114.08, 122.72, 126.39 br s, 134.22, 135.74, 146.45, 152.89, 152.95, 156.63; HR-FT-ICR-MALDI-MS (DCTB) calcd for $C_{22}H_{15}N_5^-$ ([*M*]$^-$): 349.1333; found 349.1341.

(4-{2-Butyl-3,3-dicyano-1-[4-(dimethylamino)phenyl]prop-2-en-1-ylidene}cyclohexa-2,5-dien-1-ylidene)malononitrile (2)



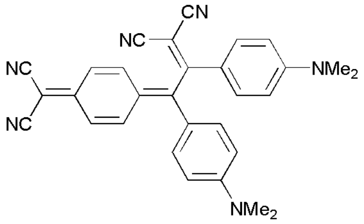
TCNQ (41 mg, 0.199 mmol) was added to a solution of **12** (40 mg, 0.199 mmol) in CH_2Cl_2 (20 cm^3). The mixture was stirred for 13 h at 20 °C. Evaporation of the solvent *in vacuo* and CC (SiO_2; CH_2Cl_2/EtOAc 98:2) afforded **2** (86 mg, 100%). Copper-like metallic solid. $R_f = 0.55$ (SiO_2; CH_2Cl_2/EtOAc 98:2); mp 163–164 °C; λ_{max}(CH_2Cl_2)/nm 259 (17000), 281 (sh, 14600), 339 (20000), 417 (22300), 655 (50300); ν_{max}(neat)/cm^{-1} 2921, 2859, 2635, 2196, 1611, 1573, 1519, 1480, 1339, 1204, 1151, 939, 899, 827, 800; δ_H(300 MHz; $CDCl_3$) 0.87 (3 H, t, *J* 7.1), 1.23–1.47 (4 H, m), 2.61 (1 H, br s), 2.87 (1 H, br s), 3.16 (6 H, s), 6.76 (2 H, d, *J* 9.0), 6.98 (1 H, dd, *J* 9.8 and 2.2), 7.18 (2 H, d, *J* 9.0), 7.24 (2 H, m), 7.37 (1 H, dd, *J* 9.7 and 2.2); δ_C(125 MHz; $CDCl_3$) 13.46, 22.67, 29.74, 38.03, 40.16, 72.36, 90.82, 111.13, 111.33, 112.32, 114.47, 114.52, 121.40, 125.16, 125.37, 131.35, 133.76, 133.79, 135.80, 151.82, 152.87, 154.33, 179.76; HR-FT-ICR-MALDI-MS (DCTB) calcd for $C_{26}H_{23}N_5^-$ ([*M*]$^-$): 405.1953; found 405.1950.

(4-{3,3-Dicyano-1-[4-(dimethylamino)phenyl]-2-phenylprop-2-en-1-ylidene}cyclohexa-2,5-dien-1-ylidene)malononitrile (3)



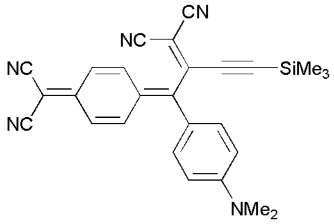
TCNQ (41 mg, 0.200 mmol) was added to a solution of **13** (45 mg, 0.200 mmol) in CH_2Cl_2 (15 cm^3). The mixture was stirred for 14 h at 20 °C. Evaporation of the solvent *in vacuo* and CC (SiO_2; $CH_2Cl_2 \rightarrow CH_2Cl_2$/EtOAc 98:2) afforded **3** (79 mg, 93%). Copper-like metallic solid. $R_f = 0.38$ (SiO_2; CH_2Cl_2); mp 244–245 °C; λ_{max}(CH_2Cl_2)/nm 268 (18500), 291 (sh, 19000), 330 (22000), 459 (16200), 676 (36300); ν_{max}(neat)/cm^{-1} 2917, 2850, 2638, 2228, 2195, 1613, 1573, 1524, 1484, 1393, 1341, 1154, 1072, 939, 906, 877, 837, 823; δ_H(300 MHz; $CDCl_3$) 3.13 (6 H, s), 6.71 (2 H, d, *J* 9.3), 6.99 (1 H, dd, *J* 9.5 and 1.9), 7.14 (1 H, dd, *J* 9.5 and 2.0), 7.24–7.29 (3 H, m), 7.43–7.55 (4 H, m), 7.63–7.66 (2 H, m); δ_C(75 MHz; $CDCl_3$) 40.37, 71.48, 87.71, 112.46, 112.72, 113.17, 114.99, 115.06, 123.65, 125.02, 125.42, 129.77, 129.83, 131.87, 133.78, 134.58, 134.76, 134.97, 136.11, 152.28, 153.14, 154.31, 173.01; HR-FT-ICR-MALDI-MS (DCTB) calcd for $C_{28}H_{19}N_5^-$ ($[M]^-$): 425.1640; found 425.1639.

(4-{3,3-Dicyano-1,2-bis[4-(dimethylamino)phenyl]prop-2-en-1-ylidene}cyclohexa-2,5-dien-1-ylidene)malononitrile (4)



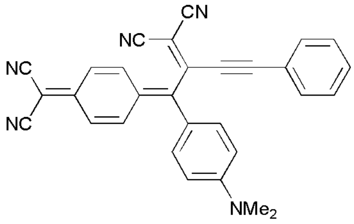
TCNQ (39 mg, 0.189 mmol) was added to a solution of **14** (50 mg, 0.189 mmol) in CH_2Cl_2 (10 cm^3). The mixture was stirred for 17 h at 20 °C. Evaporation of the solvent *in vacuo* and CC (SiO_2; $CH_2Cl_2 \rightarrow CH_2Cl_2$/EtOAc 98:2) afforded **4** (89 mg, 100%). Deep purple metallic solid. $R_f = 0.50$ (SiO_2; CH_2Cl_2/EtOAc 98:2); mp 259–262 °C; λ_{max} (CH_2Cl_2)/nm 333 (18000), 424 (49400), 662 (51900); ν_{max}(neat)/cm^{-1} 2918, 2850, 2627, 2193, 1600, 1571, 1478, 1437, 1402, 1327, 1287, 1212, 1149, 1116, 939, 880, 820; δ_H(300 MHz; $CDCl_3$) 3.10 (6 H, s), 3.13 (6 H, s), 6.64 (2 H, d, *J* 9.3), 6.72 (2 H, d, *J* 9.0), 6.96 (1 H, dd, *J* 9.7 and 1.8), 7.07 (1 H, dd, *J* 9.3 and 1.8), 7.22 (1 H, dd, *J* 9.7 and 1.8), 7.34 (2 H, d, *J* 9.3), 7.55 (1 H, dd, *J* 9.3 and 1.8), 7.72 (2 H, d, *J* 9.0); δ_C(75 MHz; $CDCl_3$) 40.27, 40.37, 69.53, 76.36, 111.96, 112.63, 114.51, 115.40, 115.51, 121.46, 124.26, 124.80, 130.89, 132.99, 134.87, 135.26, 136.16, 153.15, 154.00, 154.80, 155.09, 169.47; HR-FT-ICR-MALDI-MS (DCTB) calcd for $C_{30}H_{24}N_6^-$ ([*M*]$^-$): 468.2068; found 468.2062.

[1-{[4-(Dicyanomethylene)cyclohexa-2,5-dien-1-ylidene][4-(dimethylamino)phenyl]-methyl}-3-(trimethylsilyl)prop-2-yn-1-ylidene]malononitrile (5)



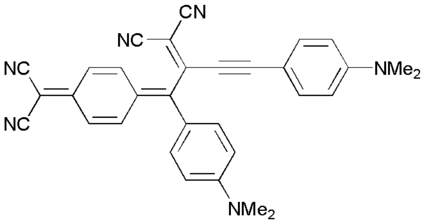
TCNQ (34 mg, 0.165 mmol) was added to a solution of diyne **15** (40 mg, 0.165 mmol) in toluene (25 cm^3). The mixture was stirred for 12 h at 80 °C. Evaporation of the solvent *in vacuo* and CC (SiO_2; $CH_2Cl_2 \rightarrow CH_2Cl_2$/EtOAc 98:2) afforded **3** (24 mg, 33%). Black metallic solid. $R_f = 0.55$ (SiO_2; CH_2Cl_2/EtOAc 98:2); mp 209–211 °C; λ_{max}(CH_2Cl_2)/nm 270 (26300), 307 (26200), 368 (sh, 12000), 480 (26400), 709 (36000); ν_{max}(neat)/cm^{-1} 2918, 2853, 2806, 2635, 2202, 1608, 1582, 1528, 1504, 1439, 1408, 1367, 1344, 1323, 1296, 1249, 1203, 1171, 1125, 1063, 1031, 999, 973, 942, 902, 843, 809; δ_H(300 MHz; $CDCl_3$) 0.24 (9 H, s), 3.17 (6 H, s), 6.76 (2 H, d, *J* 9.3), 7.25–7.34 (6 H, m); δ_C(75 MHz; $CDCl_3$) –0.74, 40.41, 72.45, 96.99, 100.78, 110.94, 112.34, 112.48, 114.92, 123.59, 124.76, 124.96, 125.54, 131.62, 134.46, 135.04, 136.28, 148.60, 153.33, 154.26, 154.43; HR-FT-ICR-MALDI-MS (DCTB) calcd for $C_{27}H_{23}N_5Si^-$ ([*M*]$^-$): 445.1723; found 445.1726.

(1-{[4-(Dicyanomethylene)cyclohexa-2,5-dien-1-ylidene][4-(dimethylamino)phenyl]-methyl}-3-phenylprop-2-yn-1-ylidene)malononitrile (6)



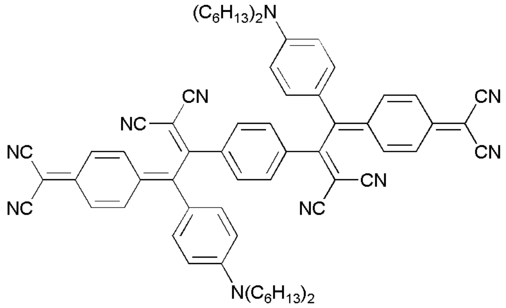
TCNQ (42 mg, 0.204 mmol) was added to a solution of diyne **16** (50 mg, 0.204 mmol) in 1,2-dichloroethane (30 cm^3). The mixture was stirred for 5 h at 80 °C. Evaporation of the solvent *in vacuo* and CC (SiO$_2$; CH$_2$Cl$_2$ → CH$_2$Cl$_2$/EtOAc 98:2) afforded **6** (66 mg, 72%). Deep-purple metallic solid. R$_f$ = 0.57 (SiO$_2$; CH$_2$Cl$_2$/EtOAc 98:2); mp 229–232 °C; λ_{max}(CH$_2$Cl$_2$)/nm 272 (19300), 320 (26400), 340 (sh, 24000), 361 (sh, 21000), 488 (20300), 708 (27300); ν_{max}(neat)/cm^{-1} 3391, 2914, 2852, 2640, 2196, 2171, 1608, 1573, 1519, 1482, 1443, 1394, 1343, 1266, 1205, 1154, 1116, 940, 902, 824; δ_H(300 MHz; CDCl$_3$) 3.18 (6 H, s), 6.78 (2 H, d, *J* 9.0), 7.26–7.43 (8 H, m), 7.49–7.54 (3 H, m); δ_C(75 MHz; CDCl$_3$) 40.33, 72.26, 88.35, 94.49, 111.05, 112.33, 112.56, 114.67, 114.72, 115.35, 119.71, 123.32, 124.66, 125.32, 128.86, 131.28, 132.12, 133.17, 134.15, 134.76, 136.01, 148.60, 153.01, 153.99, 154.43; HR-FT-ICR-MALDI-MS (DCTB) calcd for $C_{30}H_{19}N_5^-$ ([*M*]$^-$): 449.1640; found 449.1639.

(4-{2-(Dicyanomethylene)-1,4-bis[4-(dimethylamino)phenyl]but-3-yn-1-ylidene}-cyclohexa-2,5-dien-1-ylidene)malononitrile (**7**)



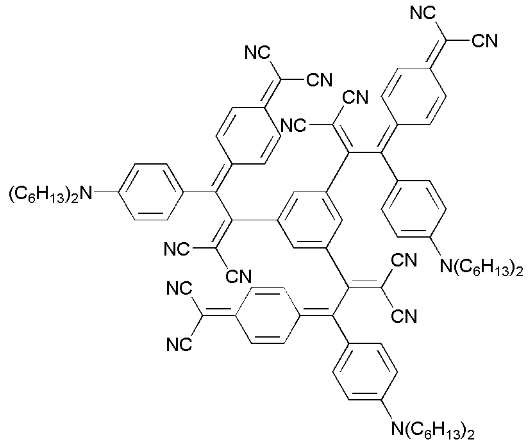
TCNQ (38 mg, 0.184 mmol) was added to a solution of **17** (53 mg, 0.184 mmol) in CH$_2$Cl$_2$ (30 cm^3). The mixture was stirred for 18 h at 20 °C. Evaporation of the solvent *in vacuo* and CC (SiO$_2$; CH$_2$Cl$_2$ → CH$_2$Cl$_2$/EtOAc 98:2) afforded **7** (71 mg, 78%). Black metallic solid. R$_f$ = 0.38 (SiO$_2$; CH$_2$Cl$_2$); mp >300°C (decomp.); λ_{max}(CH$_2$Cl$_2$)/nm 270 (36000), 326 (sh, 29400), 446 (57700), 480 (sh, 50000), 677 (64700); ν_{max}(neat)/cm^{-1} 2906, 2858, 2806, 2628, 2196, 2113, 1597, 1573, 1531, 1439, 1338, 1269, 1230, 1156, 1105, 1015, 939, 901, 806; δ_H(300 MHz; CDCl$_3$) 3.08 (6 H, s), 3.17 (6 H, s), 6.62 (2 H, d, *J* 9.0), 6.76 (2 H, d, *J* 9.0), 7.19–7.26 (2 H, m), 7.35–7.40 (6 H, m); δ_C(75 MHz; $CDCl_3$) 40.27, 40.41, 70.75, 88.66, 92.74, 105.78, 111.94, 112.47, 113.85, 115.27, 123.49, 123.87, 124.36, 125.06, 130.89, 135.00, 135.19, 135.92, 136.57, 150.91, 152.97, 153.32, 154.20, 154.68; HR-FT-ICR-MALDI-MS (DCTB) calcd for $C_{32}H_{24}N_6^-$ ([*M*]$^-$): 492.2068; found 492.2062; EA calcd for $C_{32}H_{24}N_6$ (492.58): C 78.03, H 4.91, N 17.06; found: C 77.80, H 4.79, N 16.54%.

2,2'-[1,4-Phenylenebis({1,1-dicyano-3-[4-(dihexylamino)phenyl]prop-1-en-2-yl-3-ylidene}cyclohexa-2,5-diene-4,1-diylidene)]dimalononitrile (8)



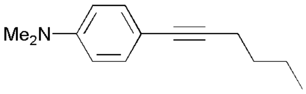
TCNQ (38 mg, 0.186 mmol) was added to a solution of the corresponding dialkyne (60 mg, 0.093 mmol) in 1,2-dichloroethane (30 cm^3). The mixture was stirred for 14 h at 20 °C and 3 h at 80 °C to complete the reaction. Evaporation of the solvent *in vacuo* and CC (SiO_2; $CH_2Cl_2 \rightarrow CH_2Cl_2$/EtOAc 98:2) afforded **8** (91 mg, 93%). Black metallic solid. $R_f = 0.48$ (SiO_2; CH_2Cl_2/EtOAc 98:2); mp 255 °C; λ_{max}(CH_2Cl_2)/nm 275 (sh, 28600), 346 (54800), 685 (68200); ν_{max}(neat)/cm^{-1} 3378, 3062, 2923, 2854, 2650, 2195, 1611, 1573, 1520, 1465, 1383, 1339, 1292, 1210, 1161, 976, 906, 883, 821; δ_H(300 MHz; $C_2D_2Cl_4$) 0.82 (12 H, t, *J* 6.4), 1.21 (24 H, br s), 1.56 (8 H, m), 3.29 (8 H, t, *J* 7.8), 6.62 (4 H, d, *J* 9.3), 6.77 (2 H, d, *J* 9.0), 7.02 (2 H, d, *J* 9.0), 7.18 (6 H, m), 7.44 (2 H, d, *J* 9.0), 7.70 (4 H, s); δ_C(125 MHz; $C_2D_2Cl_4$) 14.42, 22.96, 26.97, 27.68, 31.82, 51.85, 70.09, 89.92, 111.99, 112.67, 113.25, 115.60, 120.60, 122.86, 124.94, 125.35, 130.59, 130.62, 134.00, 135.20, 136.02, 138.66, 150.47, 152.31, 154.15, 171.04; HR-FT-ICR-MALDI-MS (3-HPA) calcd for $C_{70}H_{72}N_{10}^-$ ([*M*]$^-$): 1052.5947; found 1052.5966.

2,2',2''-[Benzene-1,3,5-triyltris({1,1-dicyano-3-[4-(dihexylamino)phenyl]prop-1-en-2-yl-3-ylidene}cyclohexa-2,5-diene-4,1-diylidene)]trimalononitrile (9)



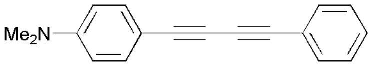
TCNQ (38 mg, 0.186 mmol) was added to a solution of the corresponding trialkyne (57 mg, 0.061 mmol) in 1,2-dichloroethane (30 cm^3). The mixture was stirred for 14 h at 20 °C. Subsequently TCNQ (19 mg, 0.093 mmol) was added, and the mixture was stirred for 2 h at 80 °C to complete the reaction. Evaporation of the solvent *in vacuo* and CC (SiO_2; $CH_2Cl_2 \rightarrow CH_2Cl_2$/EtOAc 98:2) afforded **9** (62 mg, 66%). Black metallic solid. $R_f = 0.63$ (SiO_2; CH_2Cl_2/EtOAc 98:2); mp 229–230 °C; λ_{max}(CH_2Cl_2)/nm 274 (63000), 319 (sh, 63200), 567 (sh, 61000), 709 (87000); ν_{max}(neat)/cm^{-1} 2925, 2855, 2645, 2197, 1609, 1576, 1522, 1388, 1341, 1289, 1261, 1167, 978, 904, 891, 836; δ_H(500 MHz; $C_2D_2Cl_4$) 0.84 (18 H, t, *J* 6.7), 1.27 (36 H, br s), 1.55 (12 H, br s), 3.31 (12 H, br s), 6.59 (6 H, d, *J* 9.1), 6.73 (3 H, br s), 6.91 (3 H, br d, *J* 8.2), 7.06–7.19 (9 H, m), 7.30 (3 H, br d, *J* 8.2), 7.79 (3 H, br s); δ_C(125 MHz; $C_2D_2Cl_4$) 14.42, 22.94, 26.96, 27.64, 31.80, 52.02, 91.95, 111.25, 112.52, 113.57, 115.49, 115.59, 120.60, 123.15 br s, 124.69, 125.19, 130.12 br s, 132.77 br s, 134.06 br s, 135.39, 136.19, 138.10, 149.49 br s, 152.47, 153.57, 170.01; HR-FT-ICR-MALDI-MS (3-HPA) calcd for $C_{102}H_{105}N_{15}^-$ ([*M*]$^-$): 1540.8750; found 1540.8718; EA calcd. for $C_{102}H_{105}N_{15}$ (1541.05): C 79.50, H 6.87, N 13.63; found: C 79.23, H 6.83, N 13.37%.

4-Hex-1-yn-1-yl-*N*,*N*-dimethylaniline (12)



To a degassed solution of (4-iodophenyl)dimethylamine (200 mg, 0.809 mmol) in *i*Pr_2NH (15 cm^3), hex-1-yne (100 mg, 0.14 cm^3, 1.21 mmol), [$PdCl_2(PPh_3)_2$] (28 mg, 0.040 mmol) and CuI (15 mg, 0.081 mmol) were added and the mixture was stirred for 5 h at 20 °C. Removal of the solvent *in vacuo* and CC (SiO_2; CH_2Cl_2/hexanes 1:1) afforded **12** (158 mg, 97%). Brown oil. $R_f = 0.69$ (SiO_2; CH_2Cl_2/hexanes 1:1); λ_{max}(CH_2Cl_2)/nm 289 (51900); ν_{max}(neat)/cm^{-1} 2955, 2929, 2859, 2806, 1608, 1518, 1444, 1352, 1224, 1188, 1166, 1128, 1061, 947, 815; δ_H(300 MHz; $CDCl_3$) 0.97 (3 H, t, *J* 7.1), 1.48–1.61 (4 H, m), 2.42 (2 H, t, *J* 7.0), 2.96 (6 H, s), 6.63 (2 H, dd, *J* 6.9 and 2.2), 7.30 (2 H, dd, *J* 6.9 and 2.2); δ_C(75 MHz; $CDCl_3$) 13.91, 19.42, 22.25, 31.37, 40.50, 81.22, 87.85, 111.46, 112.14, 132.67, 149.84; HR-EI-MS calcd for $C_{14}H_{19}N^+$ ([*M*]$^+$): 201.1517; found 201.1506; EA calcd. for $C_{14}H_{19}N$ (301.21): C 83.53, H 9.51, N 6.96; found: C 83.09, H 9.49, N 6.84%.

N**,*****N*****-Dimethyl-4-(4-phenylbuta-1,3-diyn-1-yl)aniline (16)**



To a mixture of (4-ethynylphenyl)dimethylamine (**10**) (500 mg, 3.44 mmol) and phenylacetylene (1.76 g, 17.2 mmol), Hay catalyst (50 cm^3) was added. The mixture was stirred while exposed to air for 3 h at 20 °C. The solvents were removed *in vacuo*, and the product was purified by CC (SiO_2; CH_2Cl_2/hexanes 1:1) to give **16** (61 mg, 72%). Yellowish solid. $R_f = 0.54$ (SiO_2; CH_2Cl_2/hexanes 1:1); mp 113–114 °C; λ_{max}(CH_2Cl_2)/nm 265 (24000), 284 (24100), 341 (63800), 367 (52600); ν_{max}(neat)/cm^{-1} 2902, 2821, 2620, 2205, 2141, 2122, 1881, 1594, 1522, 1487, 1439, 1369, 1233, 1182, 1168, 1063, 998, 979, 940, 810; δ_H(300 MHz; $CDCl_3$) 3.00 (6 H, s), 6.63 (2 H, d, *J* 9.0), 7.35 (3 H, m), 7.43 (2 H, d, *J* 9.0), 7.54 (2 H, m); δ_C(75 MHz; $CDCl_3$) 40.26, 72.33, 75.00, 81.00, 83.80, 107.95, 111.86, 122.59, 128.62, 128.97, 132.53, 134.04, 150.80; HR-EI-MS calcd for $C_{18}H_{15}N^+$ ([*M*]$^+$): 245.1197; found 245.1204; EA calcd. for $C_{18}H_{15}N$ (245.32): C 88.13, H 6.16, N 5.71; found: C 87.98, H 6.06, N 5.72%.

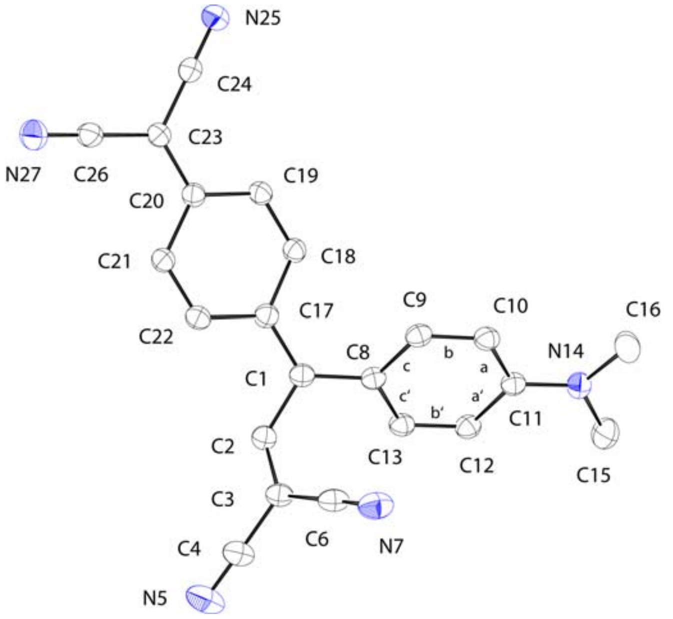


Figure 1(ESI): ORTEP plot of **1**, arbitrary numbering, H-atoms are omitted for clarity. Atomic displacement parameters at 220 K are drawn at the 30% probability level. Selected bond lengths [Å] and bond angles [°]: C1–C2 1.4678(18), C2–C3 1.3409(19), C3–C4 1.438(2), N5–C4 1.145(2), C1–C8 1.4457(18), C8–C9 1.4140(18), C9–C10 1.3697(19), C10–C11 1.4168(19), N14–C11 1.3550(17), C11–C12 1.4158(19), C12–C13 1.3683(18), C8–C13 1.4136(18), C1–C17 1.4021(18), C17–C18 1.4313(18), C18–C19 1.3518(8), C19–C20 1.4307(17), C20–C23 1.3971(18), C23–C24 1.4184(19), N25–C24 1.1448(18), C17-C1-C8 124.05(12), C8-C1-C2 118.07(11), C24-C23-C26 116.06(12), C3-C2-C1 124.56(13). Selected torsion angles [°]: C2-C1-C8-C13 = 33.28(18), C2-C1-C17-C22 = 15.44(19). Quinoid character: $\delta r = (((a+a')/2-(b+b')/2)+((c+c')/2-(b+b')/2))/2$.[4] $\delta r = 0.046$.

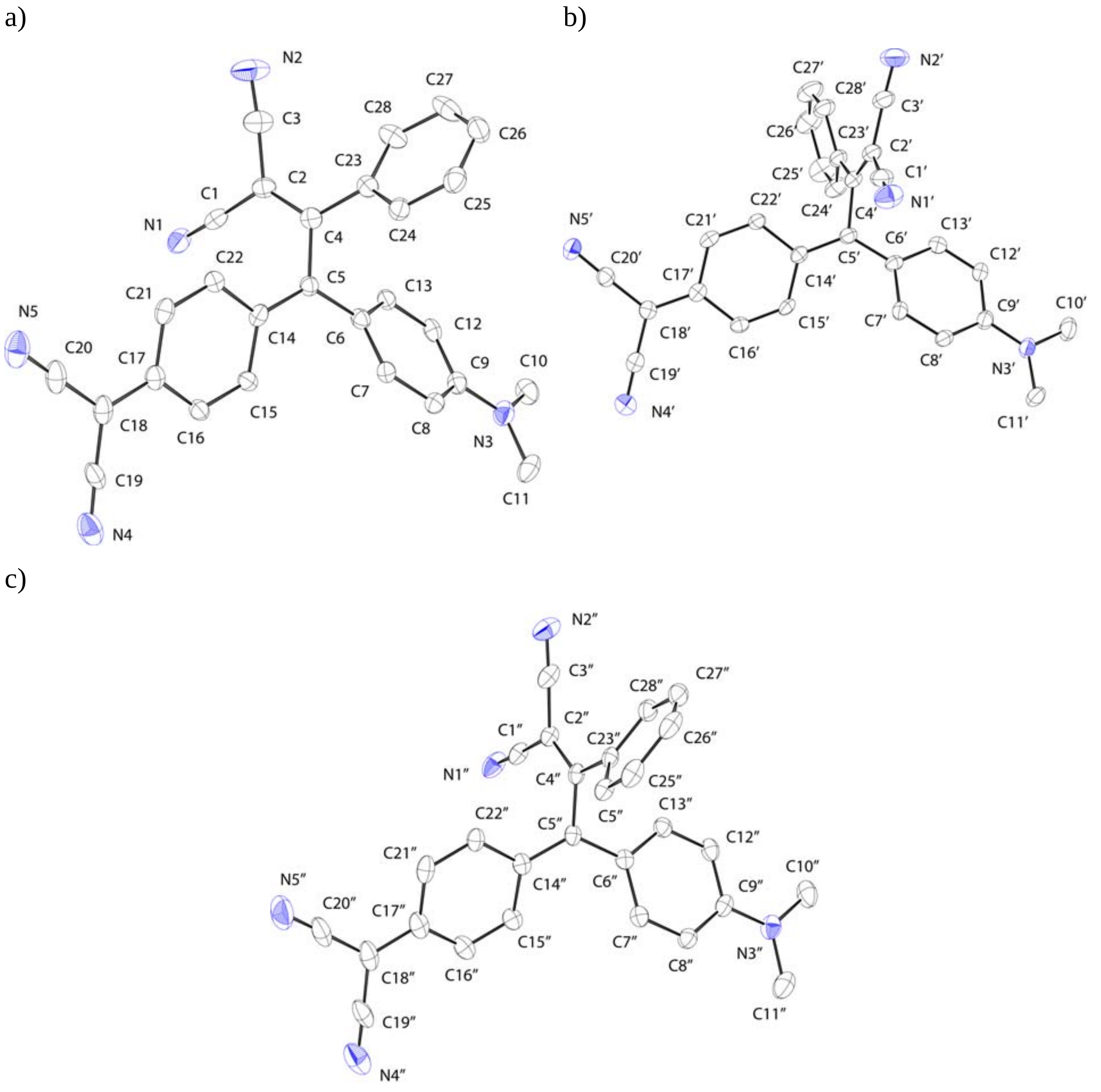


Figure 2(ESI): ORTEP plot of the three independent molecules in the crystal structure of **3**. Atomic displacement parameters obtained at 173 K are shown at the 30 % probability level. Arbitrary numbering, H-atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°] for **3a:** N1–C1 1.144(8), C1–C2 1.440(10), C2–C4 1.358(9), C4–C5 1.469(8), C5–C6 1.447(8), C6–C7 1.405(8), C7–C8 1.385(8), C8–C9 1.397(9), N3–C9 1.380(8), N3–C11 1.455(9), C9–C12 1.414(9), C12–C13 1.372(8), C6–C13 1.408(8), C4–C23 1.482(9), C23–C24 1.404(9), C24–C25 1.382(9), C25–C26 1.383(10), C14–C15 1.445(8), C15–C16 1.335(8), C16–C17 1.418(9), C17–C18 1.412(9), C18–C19 1.400(10), N4–C19 1.143(9), C6-C5-C4 116.5(5), C14-C5-C6 123.5(5), C3-C2-C1 114.9(6), C2-C4-C23 122.4(5), C19-C18-C20 118.1(6). Selected torsion angles [°]: Molecule **3a**: C4-C5-C6-C13 = –40.2(8), C4-C5-C14-C22 = –12.9(9), C4-C5-C14-C15 = 166.3(5), C2-C4-C5-C14 = –55.7(8), C23-C4-C5-C14 = 125.7(6); Molecule **3b**: C4’-C5’-C6’-C13’ = –27.9(9), C4’-C5’-C14’-C22’ = –13.1(8), C4’-C5’-C14’-C15’ = 166.0(5), C2’-C4’-C5’-C14’ = 108.2(7), C23’-C4’-C5’-C14’ = –72.1(7);. Molecule **3c**: C4’’-C5’’-C6’’-C13’’ = –30.3(8), C4’’-C5’’-C14’’-C22’’ = –13.3(8), C4’’-C5’’-C14’’-C15’’ = 167.5(5), C2’’-C4’’-C5’’-C14’’ = –69.5(7), C23’-C4’-C5’-C14’ = 109.8(6). Molecules **3a** and **3c** have approximately the same conformation, while in molecule **3b** the subunit N(1)–C(1)–C(2)–C(3)–N(2) is rotated by ca. 164° with respect to **3a**, and ca. 178° with respect to **3c**.

The crystal structures of **1** and **3** were solved by direct methods (SIRS-97)[5] and refined by full-matrix least-squares analysis (SHELXL-97),[6] using an isotropic extinction correction. All non H-atoms were refined anisotropically; H-atoms were refined isotropically, whereby H-positions are based on stereochemical considerations.

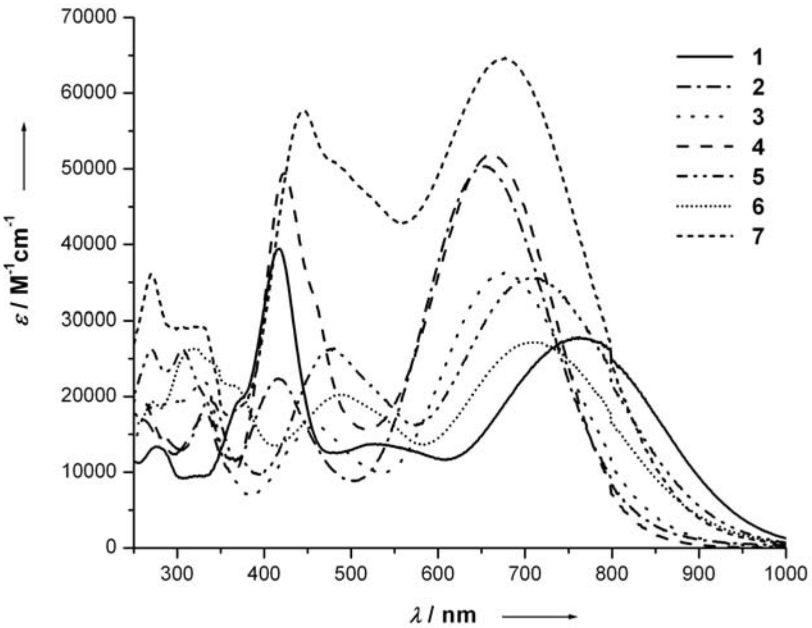


Figure 3(ESI): UV/Vis spectra of chromophores **1–7** in CH_2Cl_2 at 298 K.

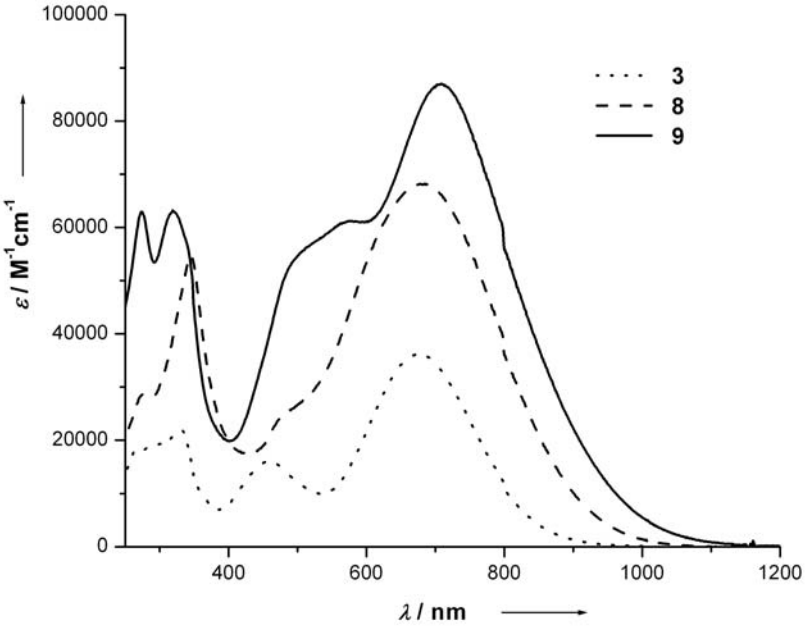


Figure 4(ESI): UV/Vis spectra of oligomeric chromophores **8** and **9** compared to **3** in CH_2Cl_2 at 298 K.

No deviations from the Lambert-Beer law were observed within the studied concentration range (4×10^{-6}–9×10^{-5} M), indicating that chromophores **2** and **7** are unable to undergo any kind of self-aggregation in CH_2Cl_2 solution. It is reasonable to assume the same behaviour of chromophores **1**, **3–6**, and **8–9**. Reduced aggregation tendency and enhanced solubility are some of the distinct advantages of our non-planar CT chromophores.

Table 1(ESI): UV/Vis spectroscopic data for chromophores **1–9** in CH_2Cl_2 at 298 K.

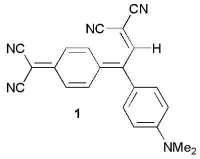
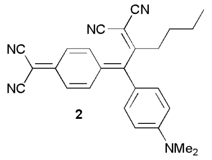
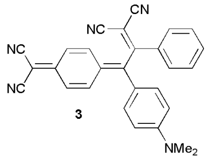
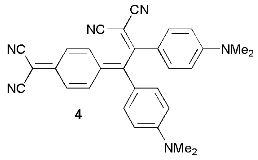
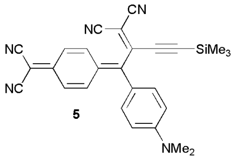
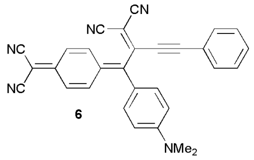
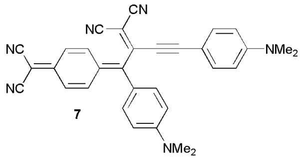
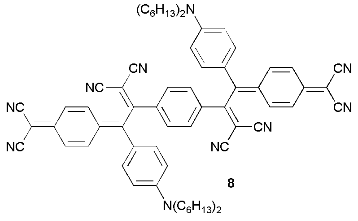
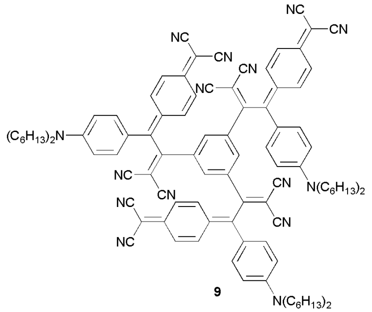
Compound	λ_{max} [nm (eV)]	ε_{max} [$M^{-1}cm^{-1}$]
 **1**	276 (4.50) 418 (2.97) 526 (2.36) 759 (1.63)	13400 39400 13700 27800
 **2**	259 (4.79) 339 (3.66) 417 (2.98) 655 (1.89)	17000 20000 22300 50300
 **3**	268 (4.63) 330 (3.76) 459 (2.70) 676 (1.84)	18500 22000 16200 36300
 **4**	333 (3.73) 424 (2.93) 662 (1.87)	18000 49400 51900
 **5**	270 (4.60) 307 (4.04) 480 (2.58) 709 (1.75)	26300 26200 26400 36000
 **6**	272 (4.56) 320 (3.88) 488 (2.54) 708 (1.75)	19300 26400 20300 27300
 **7**	270 (4.60) 446 (2.78) 677 (1.83)	36000 57700 64700
 **8**	346 (3.59) 685 (1.81)	54800 68200
 **9**	274 (4.53) 709 (1.75)	63000 87000

Table 2(ESI): Solvent effects of chromophores **1–9** in CH_2Cl_2/hexane mixtures at 298 K.

	λ_{max} [nm (eV)][a] in solvent					
Compound	CH_2Cl_2	CH_2Cl_2/hexane 1:1	CH_2Cl_2/hexane 1:3	CH_2Cl_2/hexane 1:9	CH_2Cl_2/hexane 1:19	hexane
1	759 (1.63)	746 (1.66)	727 (1.71)	[b]	[b]	[b]
2	655 (1.89)	625 (1.99)	604 (2.05)	581 (2.14)	574 (2.16)	559 (2.22)
3	676 (1.84)	646 (1.92)	626 (1.98)	600 (2.07)	[b]	[b]
4	665 (1.87)	638 (1.94)	616 (2.01)	596 (2.08)	[b]	[b]
5	709 (1.75)	680 (1.82)	659 (1.88)	635 (1.95)	[b]	[b]
6	708 (1.75)	680 (1.82)	661 (1.88)	630 (1.97)	[b]	[b]
7	677 (1.83)	649 (1.91)	631 (1.97)	607 (2.04)	[b]	[b]
8	685 (1.81)	652 (1.90)	631 (1.97)	[b]	[b]	[b]
9	709 (1.75)	694 (1.79)	677 (1.83)	[b]	[b]	[b]

[a] The charge-transfer (CT) bands were used to observe the solvent effects. [b] Could not be estimated due to low solubility.

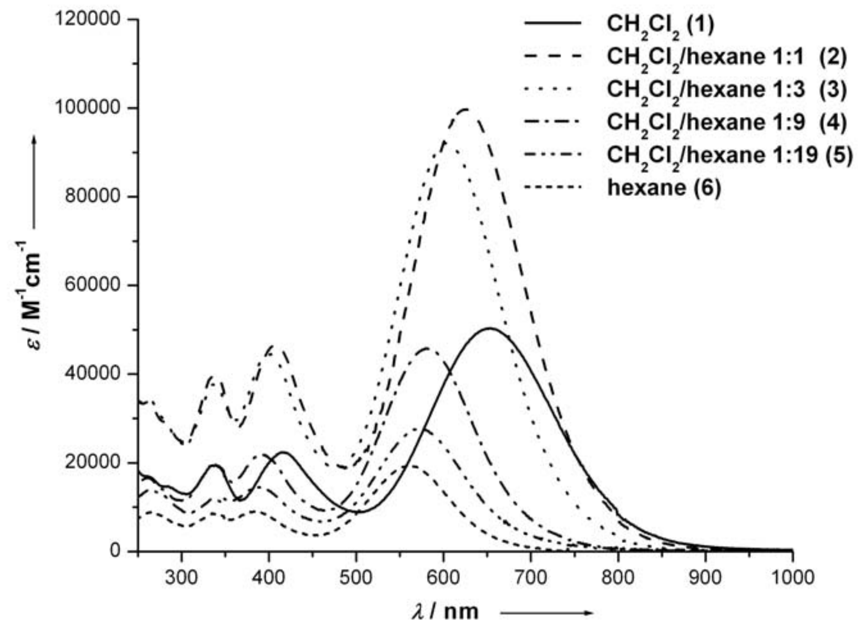


Figure 5(ESI): UV/Vis spectra of **2** in CH_2Cl_2/hexane mixtures at 298 K.

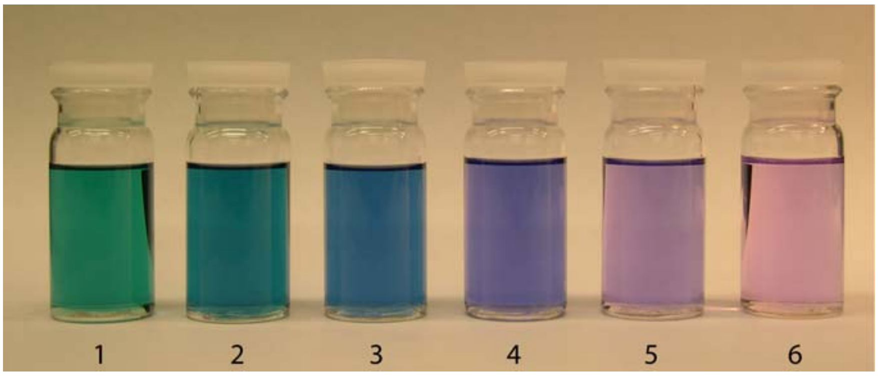


Figure 6(ESI): Solvatochromism of **2** in CH_2Cl_2/hexane mixtures.

Table 3(ESI): Electrochemical data of CT chromophores **1–9** observed by cyclic voltammetry (CV) (scan rate $v = 0.1$ V s^{-1}) and rotating disk voltammetry (RDV) in CH_2Cl_2 (+ 0.1 M *n*Bu_4NPF_6). All potentials are given *vs.* ferricinium/ferrocene (Fc^+/Fc) couple used as internal standard.

		CV		RDV	
	$E°$ [V][a]	ΔE_p [mV][b]	E_p [V][c]	$E_{1/2}$ [V][d]	Slope [mV][e]
1			+0.42	+0.44 (1e$^-$)	60
	–0.50	80		–0.55 (1e$^-$)	70
	–0.76	80		–0.86 (1e$^-$)	70
2			+0.42	+0.42 (1e$^-$)	55
	–0.72	90		–0.71 (1e$^-$)	60
	–0.81	80		–0.84 (1e$^-$)	75
3			+0.42	+0.42 (1e$^-$)	50
	–0.68	70		–0.67 (1e$^-$)	60
	–0.82	70		–0.81 (1e$^-$)	60
4			+0.86		
			+0.39	+0.39 (1e$^-$)	60
	–0.81	60		–0.82 (1e$^-$)	60
	–0.90	60		–0.92 (1e$^-$)	60
5	+0.42	80		+0.43 (1e$^-$)	40
	–0.59	65		–0.58 (1e$^-$)	65
	–0.74	65		–0.75 (1e$^-$)	65
6			+0.45	+0.44 (1e$^-$)	60
	–0.55	90		–0.58 (1e$^-$)	70
	–0.70	90		–0.77 (1e$^-$)	75
7			+0.74	+0.69	[f]
			+0.40	+0.39 (1e$^-$)	55
	–0.64	65		–0.65 (1e$^-$)	60
	–0.75	65		–0.77 (1e$^-$)	60
8			+0.40	+0.39 (1e$^-$)	60
	–0.62	65		–0.63 (1e$^-$)	[g]
	–0.74	70		–0.74 (1e$^-$)	
	–0.85	60		–0.86 (1e$^-$)	
	–0.95	60		–0.97 (1e$^-$)	
9			+0.38	+0.40 (1e$^-$)	[g]
	–0.51	60		–0.50 (1e$^-$)	
	–0.64	55		–0.64 (1e$^-$)	
	–0.76	60		–0.76 (1e$^-$)	
	–0.86	60		–0.84 (1e$^-$)	
	–0.98	60		–0.98 (1e$^-$)	
	–1.14	55		–1.16 (1e$^-$)	

[a] $E° = (E_{pc}+E_{pa})/2$, where E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively. [b] $\Delta E_p = E_{pa}–E_{pc}$. [c] E_p = Irreversible peak potential. [d] $E_{1/2}$ = Half-wave potential. [e] Slope = Slope of the linearized plot of E versus $\log[I/(I_{lim}–I)]$, where I_{lim} is the limiting current and I the current. [f] Bad resolved second oxidation due to strong electrode inhibition. [g] Due to overlapping waves, the slopes for each step could not be determined.

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