Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

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1. Methods and materials

THF was dried in Puresolv™ micro solvent purification system. All commercial chemicals and solvents were purchased from suppliers such as Sigma Aldrich, Acros and TCI at reagent grade and were used as obtained. All reaction were carried out in flame-dried flasks under argon. Thin-layer chromatography (TLC) was conducted on aluminum sheets coated with silica gel 60 F254 with visualization by a UV lamp (254 or 365 nm). ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, with a Bruker AVANCE 400 instrument. Chemical shifts in ^{1}H, ^{13}C spectra are reported in ppm relative to the signal of Me_4Si. The residual solvent signal in the ^{1}H and ^{13}C-NMR spectra was used as an internal reference ($CDCl_3$ 7.25 and 77.23 ppm, CD_2Cl_2 5.32 and 54.00 ppm and *d*^{6}-DMSO 2.55 and 39.51). Apparent resonance multiplicities are described as s (singlet), d (doublet), and m (multiplet), apparent coupling constants of multiplets (^{3}J or ^{4}J) are given in Hz. IR spectra were recorded as neat using HATR adapter on a Perkin-Elmer FTIR Spectrum BX spectrometer. EI-MS spectra were measured on a GC/MS configuration comprised of an Agilent Technologies 6890N gas chromatograph equipped with a 5973 Network MS detector (EI 70 eV, mass range 33–550 Da). High resolution MALDI MS spectra were measured on a MALDI mass spectrometer LTQ Orbitrap XL (Thermo Fisher Scientific, Bremen, Germany) equipped with nitrogen UV laser (337 nm, 60 Hz). The LTQ Orbitrap instrument was operated in positive- or negative-ion mode over a normal mass range (*m/z* 50 – 2000) with resolution 100,000 at *m/z* = 400. The survey crystal positioning system (survey CPS) was set for the random choice of shot position by automatic crystal recognition. The used matrices were 2,5-dihydroxybenzoic acid (DHB), 2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) or 9-aminoacridine (9-AA). Mass spectra were averaged over the whole MS record for all measured samples. Thermal properties of target molecules were measured by DSC with a Mettler-Toledo STARe System DSC 2/700 equipped with FRS 6 ceramic sensor and cooling system HUBERT TC100-MT RC 23. Melting points of intermediates were measured in open capillaries and were uncorrected. The two-photon absorption properties of the dyes were studied by means of a two-photon excited fluorescence (TPEF) technique in which a mode-locked Ti:sapphire laser emitting 80 fs pulses tunable from 750 to 850 nm was used as the excitation source.[1] The laser beam passed through a beam expander and then was focused on the samples by a 0.32 NA objective lens. The 2PA induced fluorescence of the samples was collected backward by the same objective lens and

it was separated from the excitation beam by using a dichroic mirror and a series of short-pass filters. A photomultiplier connected to photon-counting electronics was used to detect the emitted fluorescence. In all cases, the fluorescence intensity was measured as a function of the excitation power and the quadratic law was verified, ensuring that the observed fluorescence was only due to two-photon absorption. The samples were 10^{-4} M solutions of the dyes in THF. Finally, the calculation of the two-photon absorption cross sections, δ_{TPA}, was made by using Rhodamine B (10^{-4} M in methanol), having a well-known 2PA spectrum, as reference.

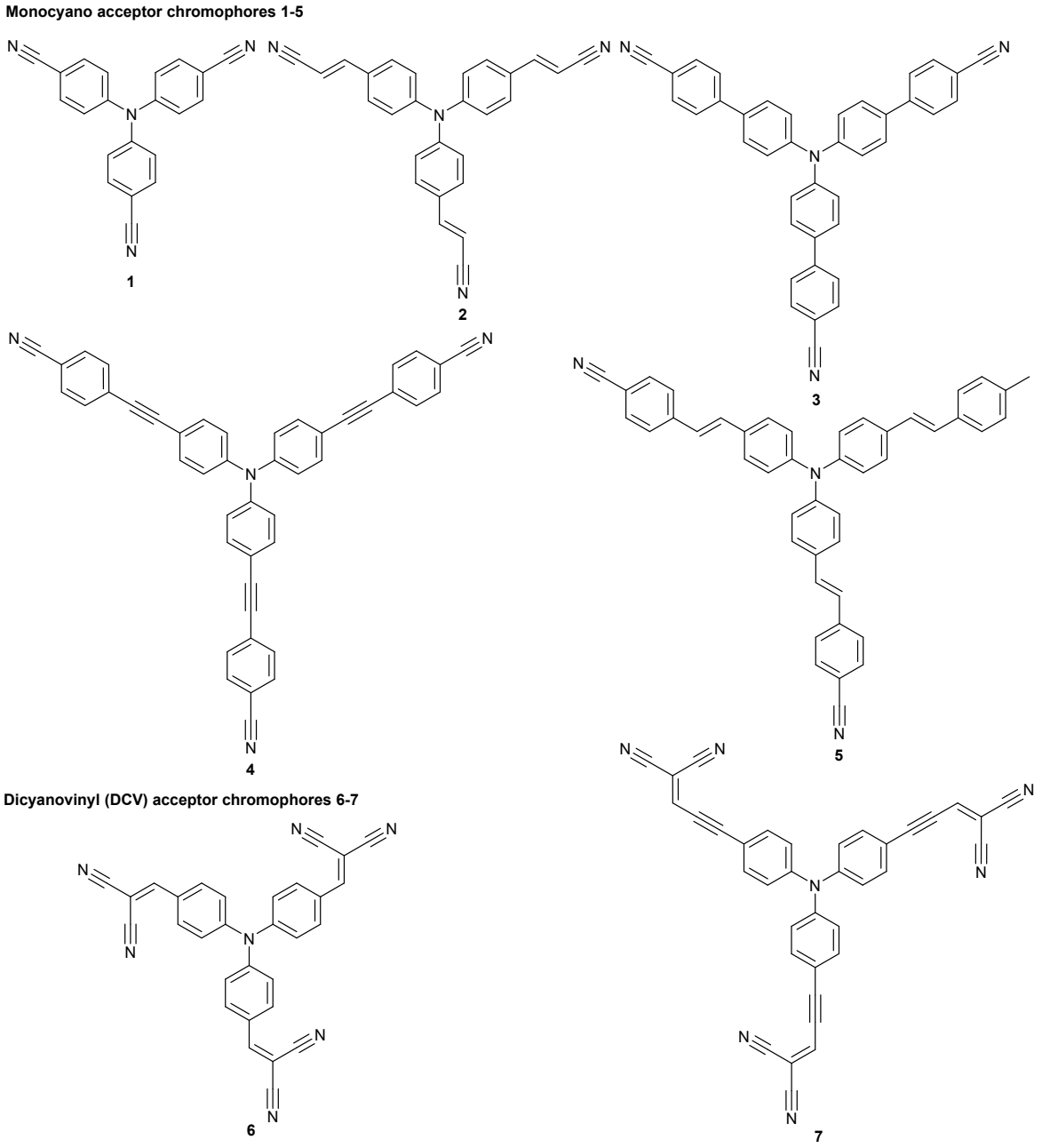


Figure S1. Molecular structures of chromophores **1**-**5** and **7**-**9** with monocyano and DCV acceptors.

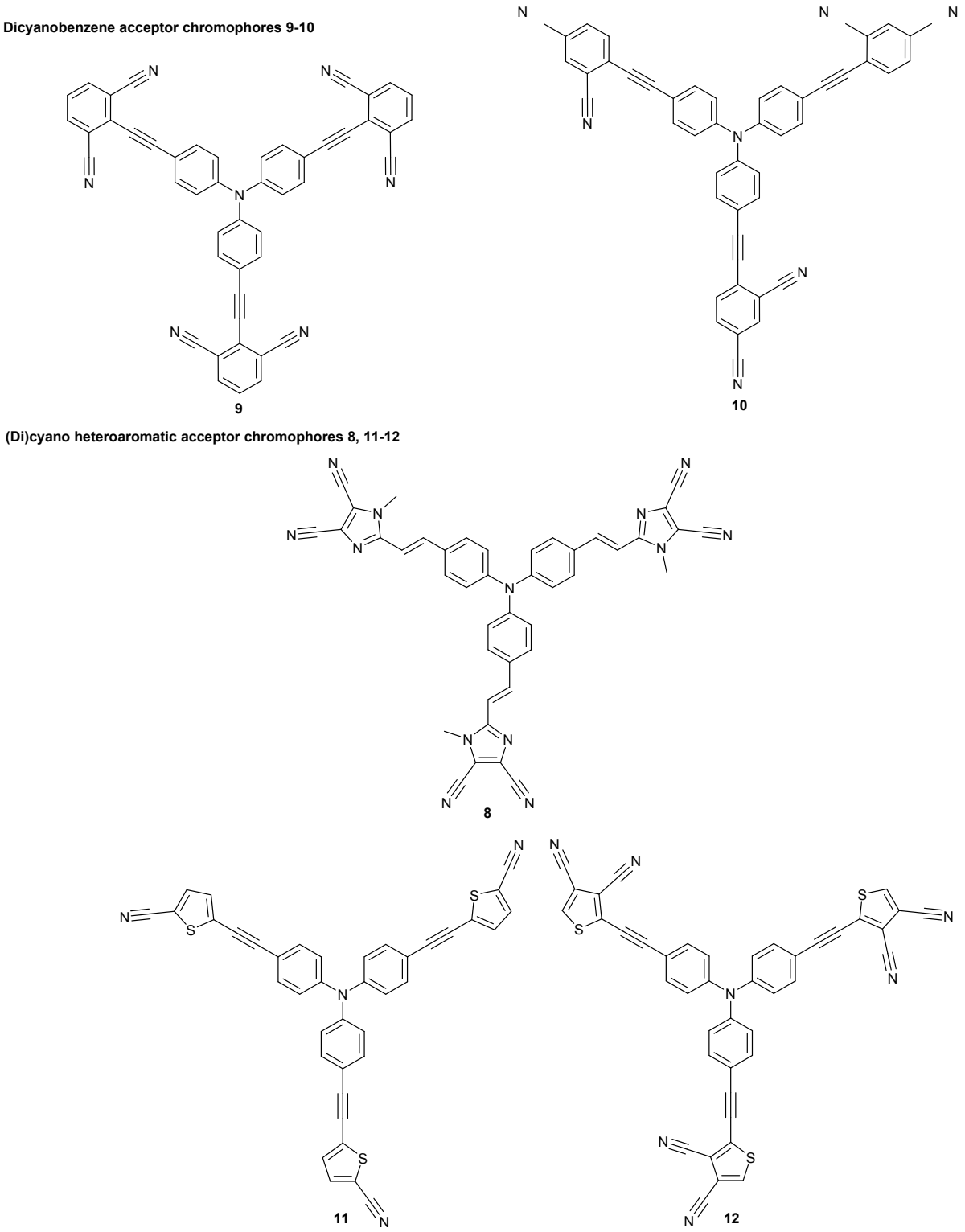


Figure S2. Molecular structures of chromophores **9**-**10** and **8**, **11**-**12** with (di)cyano benzene and heteroaromatic acceptors.

2. Synthesis of chromophores 1–5

Chromophore 1

Triphenylamine 4,4',4''-triscarboxaldehyde (200 mg, 0.61 mmol) was heated to reflux with $NH_3OH^+Cl^-$ (212 mg, 3.04 mmol) in 25 ml of DMF. After gaining the boiling point of the mixture, TFAA (384 mg, 1.83 mmol) was added dropwise and the resulting mixture was refluxed for 6 h. The reaction mixture was poured over ice/water and was extracted with DCM (3 × 100 ml). The combined organic extracts were washed with water (100 ml) and brine (2 × 100 ml), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. Column chromatography (SiO_2; DCM/hexane 1:1) afforded **1** as off-white solid (90 mg, 46 %). R_f 0.75 (DCM/Hexane 1:1). Mp 343 °C (lit.[2] 340–342 °C). IR (HATR), ν_{max}/cm^{-1} 2921, 2214 (CN), 1589, 1496, 1270, 1177, 836. ^{1}H-NMR: δ_H (400 MHz; CD_2Cl_2) 7.15 (6 H, d, ^3J 8.8, CH_{Ar}), 7.61 (6 H, d, ^3J 8.8, CH_{Ar},). ^{13}C-NMR: δ_C (100 MHz; CD_2Cl_2) 108.3, 119.0, 125.5, 134.5, 149.9. HR-MALDI-MS (DHB): calcd for $C_{21}H_{12}N_4$ (M^+) 320.1057; found 320.1059.

Chromophore 2

Compound **2** was prepared according to the literature[3] starting from **13** (243 mg, 0.39 mmol). Purification by column chromatography afforded **2** as greenish-yellow solid (115 mg, 74 %). R_f 0.6 (SiO_2; EtOAc/Hexane 1:3). Mp 275 °C. IR (HATR), ν_{max}/cm^{-1} 2892, 2212 (CN), 1589, 1497, 1264, 1178, 964, 947, 808. ^{1}H-NMR: δ_H (400 MHz; CD_2Cl_2) 5.81 (3H, d, ^3J 16.8, CH=), 7.09 (6 H, d, ^3J 8.4, CH_{Ar}), 7.35 (3 H, d, ^3J 16.8, =CH), 7.40 (6 H, d, ^3J 8.4, CH_{Ar}). ^{13}C-NMR: δ_C (100 MHz; CD_2Cl_2) 95.3, 118.5, 124.7, 129.1, 129.5, 148.8, 149.4. HR-MALDI-MS (DCTB): calcd for $C_{27}H_{18}N_4$ (M^+) 398.1526 found 390.1528.

Chromophore 3

Triiodotriphenylamine **13** (150 mg, 0.24 mmol) and 4-cyanophenylboronic acid **27** (123 mg, 0.84 mmol) were dissolved in a mixture of THF and water (30 ml, 4:1). Argon was bubbled through the mixture for 10 min, whereupon Na_2CO_3 (106 mg, 1 mmol) and $PdCl_2(PPh_3)_2$ (17 mg, 0.024 mmol) were added and the mixture was refluxed for 8 h. The reaction was quenched with saturated NH_4Cl aq. solution and was extracted with DCM (3 × 100 ml). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. Purification of the crude product by column chromatography (SiO_2; EtOAc/hexane 1:3) afforded **3** as yellowish solid (100 mg, 76

%). R_f 0.35 (SiO_2; EtOAc/hexane 1:3). Mp 329 °C. IR (HATR): ν_{max}/cm^{-1} 3034, 2220 (CN), 1589, 1488, 1272, 1182, 820. ^{1}H-NMR: δ_H (400 MHz; CD_2Cl_2) 7.26 (6 H, d, ^3J 8.8, CH_{Ar}), 7.59 (6 H, d, ^3J 8.8, CH_{Ar}), 7.70-7.75 (12 H, m, CH_{Ar}). ^{13}C-NMR: δ_C (100 MHz; CD_2Cl_2) 111.1, 119.5, 125.2, 127.7, 128.8, 133.2, 134.5, 145.2 148.1. HR-MALDI-MS (DCTB): calcd for $C_{21}H_{12}N_4$ (M^+) 320.1057 found 320.1059.

Chromophore 4

Triiodotriphenylamine **13** (146 mg, 0.23 mmol) and 4-ethynylbenzonitrile (**28**, 115 mg, 0.91 mmol) were dissolved in dry THF (15 ml) and TEA (5 ml, 36 mmol). Argon was bubbled through the mixture for 10 min, whereupon $PdCl_2(PPh_3)_2$ (16 mg, 0.023 mmol) and CuI (13 mg, 0.069 mmol) were added and the reaction was heated to 70 °C for 8 h. The reaction mixture was poured into the saturated NH_4Cl solution (100 ml) and was extracted with DCM (3 × 100 ml). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by column chromatography (SiO_2, Hexane/EtOAc 4:1). Yield (98 mg, 69 %), R_f 0.25 (SiO_2; EtOAc/hexane 1:4), mp 217 °C (lit.[4] 234–236 °C). IR (HATR), ν_{max}/cm^{-1} 2921, 2216 (CN), 1587, 1486, 1260, 1067, 1021, 806. ^{1}H-NMR: δ_H (400 MHz; $CDCl_3$) 7.09 (6 H, d, ^3J 8.8, CH_{Ar}), 7.45 (6 H, d, ^3J 8.8, CH_{Ar}), 7.57 (6 H, d, ^3J 8.4, CH_{Ar}), 7.62 (6 H, d, ^3J 8.4, CH_{Ar}). ^{13}C-NMR: δ_C (100 MHz; $CDCl_3$) 88.1, 93.8, 111.5, 117.4, 118.7, 124.3, 128.4, 132.1, 132.2, 133.3, 147.3. HR-MALDI-MS (DHB): calcd for $C_{45}H_{24}N_4$ (M^+) 620.1996 found 620.2003.

Chromophore 5

Triiodotriphenylamine **13** (212 mg, 0.34 mmol) and pinacol 2-(4-cyanophenyl)vinylboronate **29** (280 mg, 1.10 mmol) were dissolved in 50 ml of 4:1 dioxane/water mixture. Argon was bubbled through the mixture for 10 min, whereupon Na_2CO_3 (127 mg, 1.20 mmol) and $PdCl_2(PPh_3)_2$ (24 mg, 0.034 mmol) were added and the mixture was heated to 90 °C for 8h. The reaction mixture was poured into the saturated NH_4Cl solution (100 ml) and was extracted with DCM (3×100 ml). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by column chromatography (SiO_2, EtOAc/Hexane 1:4) to afford **5** as yellow solid. Yield (100 mg, 76 %). R_f 0.4 (SiO_2; EtOAc/Hexane 1:4). Mp 291 °C. IR (HATR), ν_{max}/cm^{-1} 2920, 2219 (CN), 1589, 1505, 1277, 1172, 960, 831. ^{1}H-NMR: δ_H (400 MHz; CD_2Cl_2) 7.05 (3 H, d, ^3J 16.4, CH=CH), 7.13 (6 H, d, ^3J 8.4, CH_{Ar}), 7.22 (3 H, d, ^3J 16.4, CH=CH), 7.48 (6 H, d, ^3J 8.8, CH_{Ar}),

7.61 (12 H, q, ^3J 8.8, CH_{Ar}). ^{13}C-NMR: δ_C (100 MHz; CD_2Cl_2) 88.1, 93.8, 111.5, 117.4, 118.7, 124.3, 128.4, 132.1, 132.2, 133.3, 147.3. HR-MALDI-MS (DHB): calcd for $C_{45}H_{30}N_4$ (M^+) 626.2471 found 626.2474.

3. Synthesis of TPA precursors 13–16

Precursor 13

Triphenylamine (3.0 g, 12 mmol), HgO (red, 12.2 g, 56 mmol) and I_2 (15.2 g, 60 mmol) in ethanol (60 mL) were stirred 12 h at 20 °C. The reaction mixture was concentrated *in vacuo* and extracted with boiling toluene. The combined extracts were filtered through a plug (Al_2O_3, toluene) and concentrated to 50 mL. The resulting solution was precipitated with methanol to afford 6.7 g (88%) of desired product as a white solid. Yield (6.7 g, 88%). R_f 0.47 (SiO_2, hexane), M.p. 168–169 °C (lit.[3] 169 °C). IR (HATR): ν_{max}/cm^{-1} 1576, 1480, 1311, 1268, 1176, 1059, 1002, 806, 708. ^{1}H NMR: δ_H ($CDCl_3$, 400 MHz) 6.81 (6 H, d, ^3J 9.0, CH_{Ar}), 7.53 (6 H, d, J 9.0, CH_{Ar}). ^{13}C NMR δ_C ($CDCl_3$, 100 MHz) 86.6, 126.0, 138.4, 146.5; HR-EI-MS *m/z* for $C_{18}H_{12}I_3N$ (M^+) calcld 622.8099 found 622.8104.

Precursor 14

Starting from **13** (1.0 g, 1.6 mmol), precursor **14** was prepared via threefold Sonogashira cross-coupling and subsequent TMS group removal according to literature.[1] Yield (385 mg, 76 %). R_f 0.55 (Al_2O_3, ether), M.p. 110–112 °C (lit.[1] 113–114 °C). ^{1}H NMR: δ_H ($CDCl_3$, 300 MHz) 3.05 (3 H, s, CH), 7.00 (6 H, d, ^3J 8.4, CH_{Ar}), 7.37 (6 H, d, ^3J 8.4, CH_{Ar}). ^{13}C NMR δ_C ($CDCl_3$, 75 MHz) 77.2, 83.6, 117.0, 124.1, 133.6, 147.2. HR-MALDI-MS (DHB): calcd for $C_{24}H_{15}N$ (M^+) 317.1199 found 317.1201.

Precursor 15

To the degassed solution of **13** (820 mg, 1.31 mmol), propargyl alcohol (0.31 mL, 5.23 mmol) in THF (10 mL), $PdCl_2(PPh_3)_2$ (92 mg, 0.13 mmol), CuI (25 mg, 0.13 mmol) and triethylamine (3 ml, 21.5 mmol) were added and the reaction mixture was stirred 12 h at 20 °C. Evaporation of the solvents and subsequent column chormatography (SiO_2; hexane/EtOAc 1:1) afforded desired product as a yellow solid.

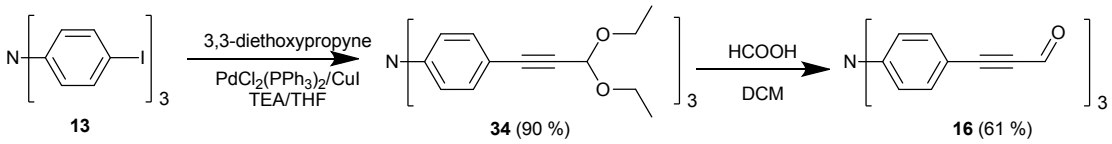
Yield 0.49 g (91%). M.p. 166–167 °C; IR (neat): ν_{max}/cm^{-1} 3269, 2237, 1595, 1496, 1316, 1288, 1268, 1011, 950, 832, 678. ^{1}H NMR: δ_H (DMSO, 400 MHz) 4.28 (6 H, d, ^3J 6.0, CH_2), 5.30 (3 H, t, ^3J 6.0, OH), 6.98 (6 H, d, ^3J 9.0, CH_{Ar}), 7.36 (6 H, d, ^3J 9.0,

CH_{Ar}). ^{13}C NMR δ_C (DMSO, 100 MHz) 49.5, 83.3, 89.5, 117.3, 123.9, 132.8, 146.2. HR-MALDI-MS (DHB): calcd for $C_{27}H_{21}NO_3$ (M^+) 407.1516 found 407.1509.

Precursor 16

To a suspension of triole **15** (100 mg, 0.25 mmol) in DCM (40 mL) Dess-Martin periodinane (3.0 g, 1.06 mmol) was added and the reaction mixture was stirred 3 hours at 20 °C, poured on saturated aqueous solution of $NaHCO_3$ (30 mL) and extracted with DCM (2 × 50 ml). The combined organic extracts were washed with water (2 × 50 ml), dried (Na_2SO_4) and concentrated *in vacuo*. The crude product was purified by column chromatography (SiO_2; hexane/EtOAc 1:2). Reddish solid. Yield 80 mg (81%). M.p. ~ 101 °C (dec.). IR (HATR), ν_{max}/cm^{-1} 2170, 1643, 1583, 1493, 1318, 1261, 1177, 973, 831, 749. ^1H NMR: δ_H ($CDCl_3$, 400 MHz) 7.10 (6 H, d, ^3J 9.0, CH_{Ar}), 7.55 (6 H, d, ^3J 9.0, CH_{Ar}), 9.41 (3 H, s, CH=O). ^{13}C NMR δ_C ($CDCl_3$, 100 MHz) 89.1, 94.8, 114.7, 124.3, 135.0, 148.3, 176.5. HR-MALDI-MS (DHB): calcd for $C_{27}H_{15}NO_3$ (M^+) 401.1046 found 401.1053.

Another synthetic path leading to precursor 16



13 **34** (90 %) **16** (61 %)

To the degassed solution of **13** (150 mg, 0.24 mmol) and 3,3-diethoxypropyne (110 mg, 0,87 mmol) in THF (10 mL), $PdCl_2(PPh_3)_2$ (14 mg, 0.02 mmol), CuI (8 mg, 0.04 mmol) and triethylamine (1 ml) were added and the reaction mixture was stirred 12 h at 20 °C. The reaction mixture was quenched with saturated NH_4Cl solution (50 ml) and extracted with DCM (2 × 50 ml). Combined organic extracts were dried over anhydrous Na_2SO_4 and the solvents were evaporated *in vacuo*. Subsequent column chromatography (SiO_2; hexane/EtOAc 1:1) afforded **34** as a reddish oil. Yield 135 mg (90 %). R_f 0.65 (SiO_2; EtOAc/Hexane 1:1). ^1H NMR: δ_H ($CDCl_3$, 400 MHz) 1.26 (18 H, t, ^3J 7.2, CH_2CH_3), 3.61–3.82 (12 H, m, CH_2CH_3), 5.48 (3 H, s, $CH(OEt)_2$), 7.05 (6 H, d, ^3J 8.8, CH_{Ar}), 7.43 (6 H, d, ^3J 8.8, CH_{Ar}). ^{13}C NMR δ_C ($CDCl_3$, 100 MHz) 15.4, 61.2, 84.6, 85.4, 92.0, 119.0, 120.8, 125.7, 146.0. HR-MALDI-MS (DHB): calcd for $C_{39}H_{45}NO_6$ (M^+) 623.3241 found 623.3241.

Compound **34** (50 mg, 0.08 mmol) was dissolved in 3 ml of DCM. Formic acid (20 mg, 0,44 mmol) was added dropwise and the solution was stirred for 1 h at 20 °C. The reaction mixture was subsequently filtered through a short plug (SiO_2, DCM). The combined organic fractions were dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to afford **16** (20 mg, 61 %) as a red solid. The spectral data were consistent with those obtained above.

4. Synthesis of acceptor intermediates 17–25

General procedure for preparation of carboxylic acids 17–19

Oxidation of bromoxylenes and bromomesitilene was carried out according to modified literature procedure.[5] The appropriate commercial bromoxylene or bromomesitylene (20 mmol) was dissolved in ^{t}BuOH (15 ml) and water (15 ml) and the mixture was heated to 117 °C. Solid $KMnO_4$ (40 mmol per each methyl group + 40 mmol excess) was added portion wise into the hot mixture during 2 h. The reaction mixture was heated to reflux for 10 h, cooled to 25 °C, whereupon formaldehyde (50 ml, 40% aq. solution) was added and the mixture was boiled again to degrade the residual $KMnO_4$. Hot reaction mixture was filtered through a 5 cm plug of Celite and the plug was subsequently washed with boiling water (3 × 100 ml). The combined opalescent filtrates were concentrated to one third of the original volume *in vacuo*. The pH was adjusted to 1-2 with HCl (35 %). The white precipitate formed was filtered off and the crude product was recrystallized from water to afford **17**–**19** as white solids.

2-Bromoisophtalic acid 17

Yield (3.5 g, 71 %). Mp 220–221 °C (lit[6] 213-214 °C). ^{1}H-NMR: δ_H (400 MHz; d_6-DMSO) 5.04 (2 H, br s, COOH), 7.56 (1 H, t, ^3J 7.6, CH_{Ar}), 7.74 (2 H, d, ^3J 7.6, CH_{Ar}). ^{13}C-NMR: δ_C (100 MHz; d_6-DMSO) 116.4, 128.1, 131.0, 137.0, 168.1. HR-MALDI-MS (9-AA): calcd for $C_8H_5BrO_4$ ($[M-H]^-$) 242.9298/244.9278 found 242.9304/244.9283.

4-Bromoisophtalic acid 18

Yield (3.2 g, 65 %). Mp 283–284 °C (lit[7] 291-292 °C). ^{1}H-NMR: δ_H (400 MHz; d_6-DMSO) 4.46 (2 H, br s, COOH), 7.86 (1 H, d, ^3J 8.3, CH_{Ar}), 7.95 (1 H, dd, ^3J 8.3, ^4J 2.0, CH_{Ar}). ^{13}C-NMR: δ_C (100 MHz; d_6-DMSO) 125.6, 129.8, 131.6, 132.9, 133.2, 134.1,

166.5, 167.1. HR-MALDI-MS (9-AA): calcd for $C_8H_5BrO_4$ ([M-H]$^-$) 242.9298/244.9278 found 242.9304/244.9284.

2-Bromotrimesilic acid 19

Yield (3.4 g, 59 %). Mp 285–286 °C (lit.[8] 291–294 °C) ^{1}H-NMR: δ_H (400 MHz; d_6-DMSO) 5.99 (3 H, br s, COOH), 8.19 (2 H, s, CH_{Ar}), ^{13}C-NMR: δ_C (100 MHz; d_6-DMSO) 121.9, 130.6, 131.3, 137.4, 165.7, 167.4. HR-MALDI-MS (9-AA): calcd for $C_8H_5BrO_4$ ([M-H]$^-$) 286.9197/288.9176 found 286.9202/288.9182.

General procedure of preparation of amides 20–22

Amides **20**-**22** were prepared according to modified literature procedure.[9] Well dried compounds **17**–**19** (10 mmol) were suspended in $SOCl_2$ (40 ml, 206 mmol) and DMF (2 ml, 26 mmol) was added. The reaction mixture was heated to reflux for 4 h. $SOCl_2$ was distilled off and the residue was dissolved in dry DCM (200 ml). Gaseous NH_3 was bubbled through the solution for 2 h (apparent and spontaneous cooling of the reaction mixture usually indicated end of the reaction). DCM was evaporated *in vacuo* and the crude product was recrystallized two or three times from water to afford **20**–**22** as white solids.

2-Bromoisophtalic acid diamide 20

Yield (1.7 g, 70 %). Mp. 249–250 °C. ^{1}H-NMR: δ_H (400 MHz; d_6-DMSO) 7.40–7.42 (2 H, m, CH_{Ar}), 7.45–7.49 (1 H, m, CH_{Ar}). ^{13}C-NMR: δ_C (100 MHz; d_6-DMSO) 115.3, 127.4, 128.3, 140.5, 169.1. HR-MALDI-MS (DHB): calcd for $C_8H_7BrN_2O_2$ ([M+H]$^+$) 242.9764/244.9743 found 242.9767/244.9746.

4-Bromoisophtalic acid diamide 21

Yield (1.85 g, 76 %). Mp 242–243 °C (lit[10] 248–249 °C). ^{1}H-NMR: δ_H (400 MHz; d_6-DMSO) 7.59 (1 H, s, NH_2), 7.72 (1 H, s, NH_2), 7.78 (1 H, d, ^3J 8.0, CH_{Ar}), 7.85 (1 H, dd, ^3J 8.0, ^4J 2.0, CH_{Ar}), 7.95 (1 H, d, ^4J 2.0, CH_{Ar}), 8.01 (1 H, s, NH_2), 8.17 (1 H, s, NH_2). ^{13}C-NMR: δ_C (100 MHz; d_6-DMSO) 121.9, 127.4, 129.5, 132.8, 133.3, 139.2, 166.4, 168.7. HR-MALDI-MS (DHB): calcd for $C_8H_7BrN_2O_2$ ([M+H]$^+$) 242.9764/ 244.9743 found 242.9760/244.9747.

2-Chlorotrimesylic acid triamide 22

Yield (1.35 g, 56 %). Mp 290–292 °C. ^{1}H-NMR: δ_H (400 MHz; d_6-DMSO) 7.64 (1 H, s, NH_2), 7.77 (2 H, s, NH_2), 7.99 (2 H, s, NH_2), 8.06 (2 H, s, CH_{Ar}), 8.22 (1 H, s, NH_2). ^{13}C-

NMR: δ_C (100 MHz; d_6-DMSO) 127.5, 129.05, 132.32, 138.1, 165.8, 167.7. HR-MALDI-MS (DHB): calcd for $C_9H_8ClN_3O_3$ (M^+) 241.0249 found 241.0249.

General procedure of preparation of nitriles 23–25

Dehydratation of amides was carried out via a standard literature procedure.[11] Amide **20**-**22** (3 mmol) was suspended in 1,4-dioxane (30 ml). Pyridine (3 ml, 37 mmol) was added and the reaction mixture was cooled to 0 °C. TFAA (6 mmol per each amide group) was added dropwise with cooling during 30 min and the mixture was allowed to reach 25 ° where was stirred for additional 2 h. The reaction pH was adjusted to 7-8 with saturated $NaHCO_3$ solution and then extracted with DCM (3 × 50 ml). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude product was recrystallized from the mixture of diethyether and pet-ether to afford **23**–**25** as off white solid.

2-Bromobenzene-1,3-dicabronitirle 23

Yield (590 mg, 95 %). Mp. 191–192 °C (lit.[11] 190–190.5). ^{1}H-NMR: δ_H (400 MHz; $CDCl_3$) 7.59 (1 H, t, ^3J 7.8, CH_{Ar}), 7.87 (2 H, d, ^3J 7.8, CH_{Ar}). ^{13}C-NMR: δ_C (100 MHz; $CDCl_3$) 115.8, 118.3, 128.6, 128.9, 137.8. EI-MS (70 eV) *m/z* (rel. int.): 206/208 (M^+, 100 %), 127 (40), 100 (30), 75 (20).

4-Bromobenzene-1,3-dicarbonitrile 24

Yield (602 mg, 97 %). Mp 191–193 °C (lit.[11]193–193.5 °C). ^{1}H-NMR: δ_H (400 MHz; $CDCl_3$) 7.70 (1 H, dd, ^3J 8.4, ^4J 2.0, CH_{Ar}), 7.86 (1 H, d, ^3J 8.4, CH_{Ar}), 7.93 (1 H, d, ^4J 2.0, CH_{Ar}). ^{13}C-NMR: δ_C (100 MHz; $CDCl_3$) 112.9, 115.5, 116.3, 118.0, 131.1, 134.8, 136.7, 137.5. EI-MS (70 eV) *m/z* (rel. int.): 206/208 (M^+, 100 %), 127 (45), 100 (35), 75 (25).

2-Chlorobenzene-1,3,5-tricarbonitrile 25

Yield (482 mg, 86 %). Mp 167-168 °C (lit[10] 167–168 °C). ^{1}H-NMR: δ_H (400 MHz; $CDCl_3$) 8.17 (2 H, s, CH_{Ar}), ^{13}C-NMR: δ_C (100 MHz; $CDCl_3$) 112.7, 113.5, 114.3, 117.3, 140.2, 144.4. EI-MS (70 eV) *m/z* (rel. int.): 187 (M^+, 100 %), 152 (10), 125 (14), 100 (12), 75 (18).

5. Electrochemistry

Electrochemical measurements were carried out in acetonitrile containing 0.1 M Bu_4NPF_6 in a three electrode cell by cyclic voltammetry (CV) and rotating disk voltammetry (RDV). The working electrode was platinum disk (2 mm in diameter) for CV and RDV experiments. As the reference and auxiliary electrodes were used saturated calomel electrode (SCE) separated by a bridge filled with supporting electrolyte and Pt wire, respectively. All potentials are given *vs.* SCE. Voltammetric measurements were performed using a potentiostat PGSTAT 128N (AUTOLAB, Metrohm Autolab B.V., Utrecht, The Netherlands) operated via NOVA 1.10 software.

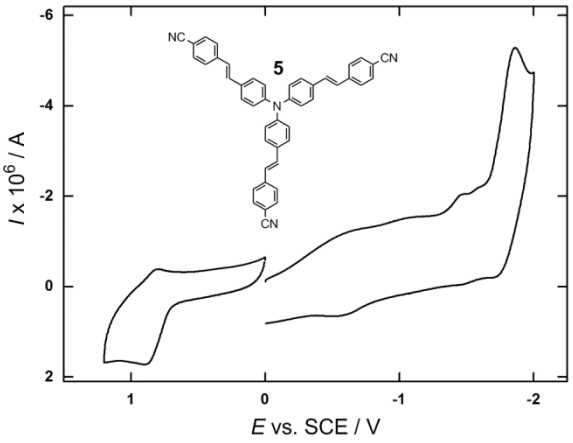


Figure S3. Representative CV curve of the oxidation and reduction of chromophore **5** at Pt electrode in acetonitrile containing 0.1 M Bu_4NPF_6.

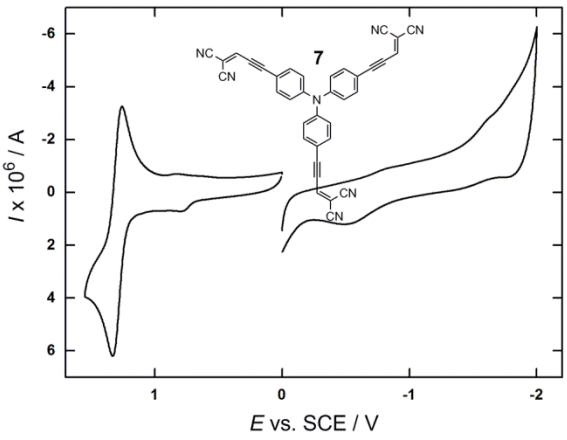


Figure S4. Representative CV curve of the oxidation and reduction of chromophore **7** at Pt electrode in acetonitrile containing 0.1 M Bu_4NPF_6.

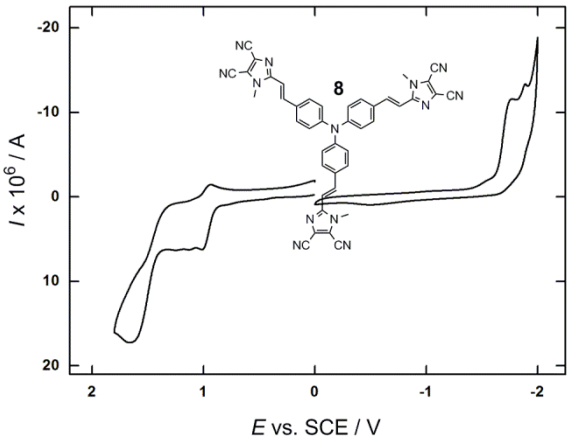


Figure S5. Representative CV curve of the oxidation and reduction of chromophore **8** at Pt electrode in acetonitrile containing 0.1 M Bu_4NPF_6.

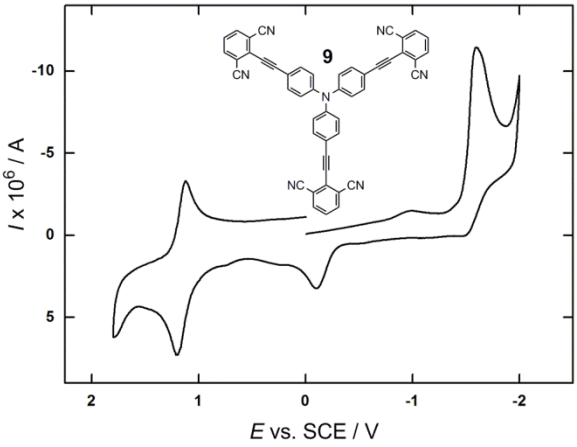


Figure S6. Representative CV curve of the oxidation and reduction of chromophore **9** at Pt electrode in acetonitrile containing 0.1 M Bu_4NPF_6.

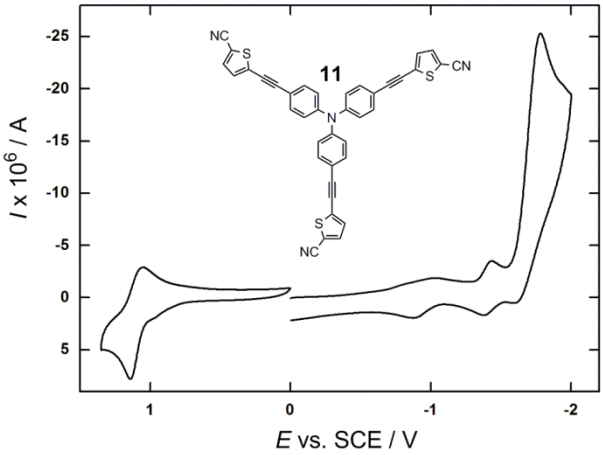


Figure S7. Representative CV curve of the oxidation and reduction of chromophore **11** at Pt electrode in acetonitrile containing 0.1 M Bu_4NPF_6.

6. Optical properties

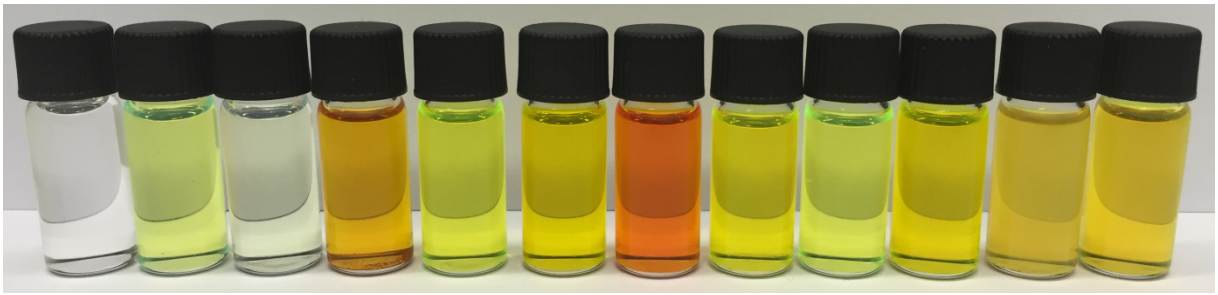


Figure S8. Colors of chromophores **1**-**12** (from left to right, DCM).

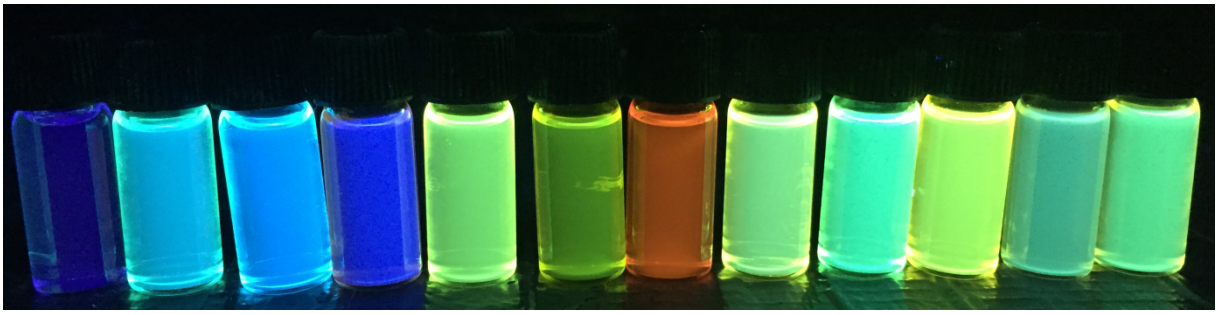


Figure S9. Colors of chromophores **1**-**12** (from left to right, DCM) under irradiation with handheld UV-lamp (365 nm).

7. Data correlations

$$1240/\lambda_{max} = (1.25\pm0.24) + (6.79\pm0.86)\ 10^{-1}\ \Delta E$$

$$n = 10,\ s = 7.62\ 10^{-2},\ r = 0.941$$

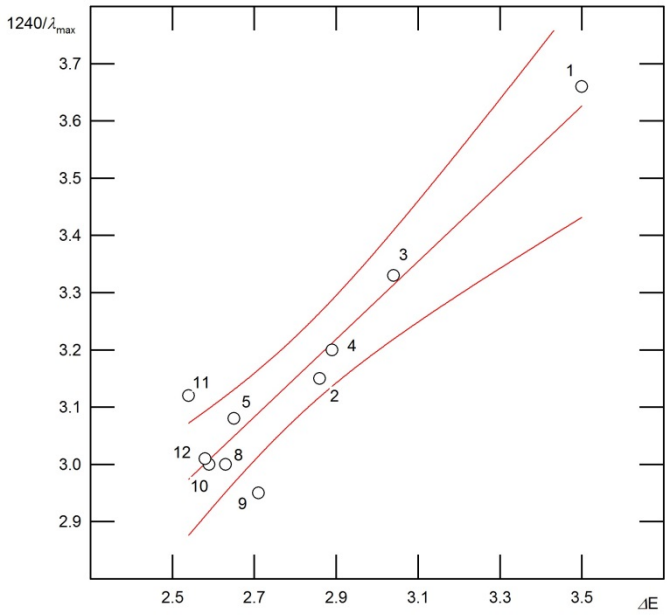


Figure S10. Correlation of the energy of the longest-wavelength absorption maxima and the electrochemical gap.

$$1240/\lambda_{max,F} = -(1.05\pm0.25) + (1.17\pm0.08)\ 1240/\lambda_{max,A}$$

$$n = 12,\ s = 7.16\ 10^{-2},\ r = 0.976$$

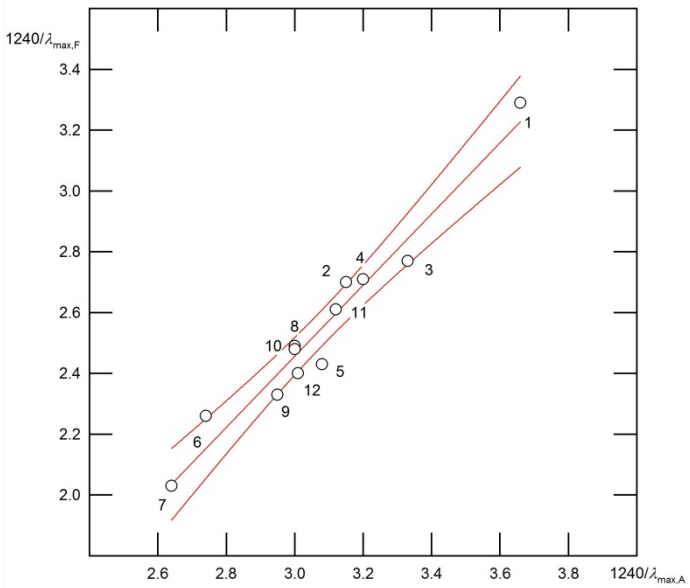


Figure S11. Correlation of the energies of the longest-wavelength fluorescent and absorption maxima.

E_{HOMO} = -(2.89±0.43) + (4.44±0.07) 10^{-1} $E_{HOMO,DFT}$

n = 12, s = 8.15 10^{-2}, r = 0.903

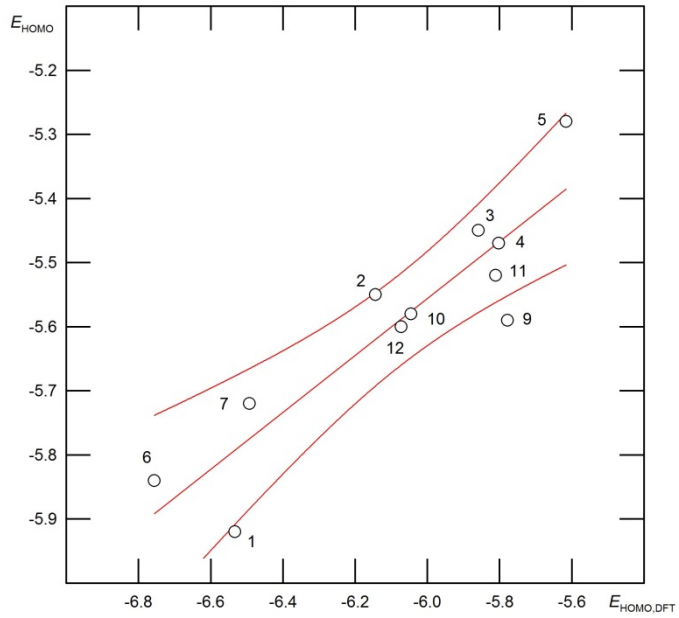


Figure S12. Correlation of the electrochemically- and DFT-derived energies of the HOMO (**8** as an outlier).

E_{LUMO} = -(9.17±1.65) 10^{-1} + (6.15±0.60) 10^{-1} $E_{LUMO,DFT}$

n = 6, s = 3.15 10^{-2}, r = 0.981

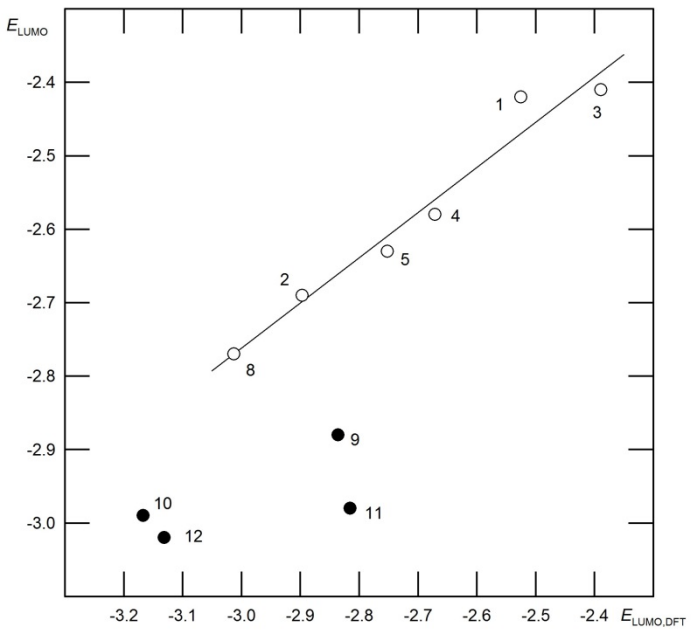


Figure S13. Correlation of the electrochemically- and DFT-derived energies of the LUMO (excluding **9**-**12**).

$$\Delta E = (3.65 \pm 3.64)\ 10^{-1} + (7.66 \pm 1.14)\ 10^{-1}\ \Delta E_{DFT}$$

$$n = 12,\ s = 1.21\ 10^{-1},\ r = 0.922$$

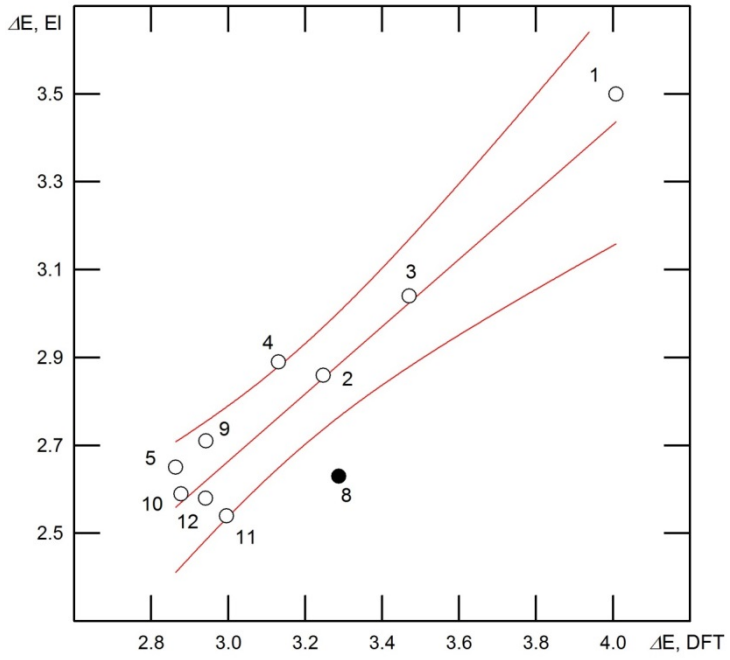


Figure S14. Correlation of the electrochemically- and DFT-derived HOMO-LUMO gaps.

8. HOMO and LUMO localizations in TPA and 1–12

The following HOMO and LUMO localizations in TPA and molecules **1**-**12** were derived from the calculations using PM7 method implemented in MOPAC2012 program (lit.[12]) . The visualizations have been performed in program OPchem.[13]

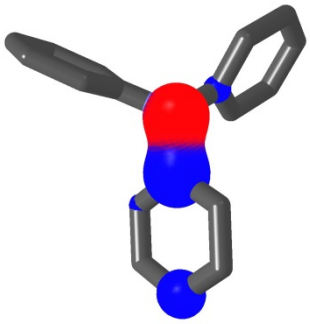


Figure S15. HOMO (red) and LUMO (blue) localizations in TPA.

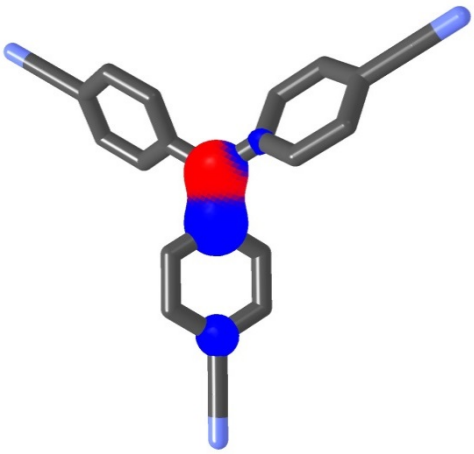


Figure S16. HOMO (red) and LUMO (blue) localizations in chromophore **1**.

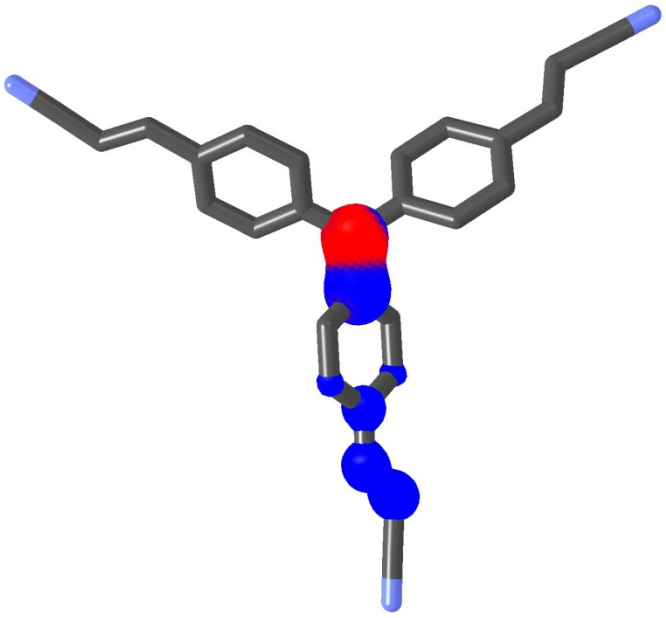


Figure S17. HOMO (red) and LUMO (blue) localizations in chromophore **2**.

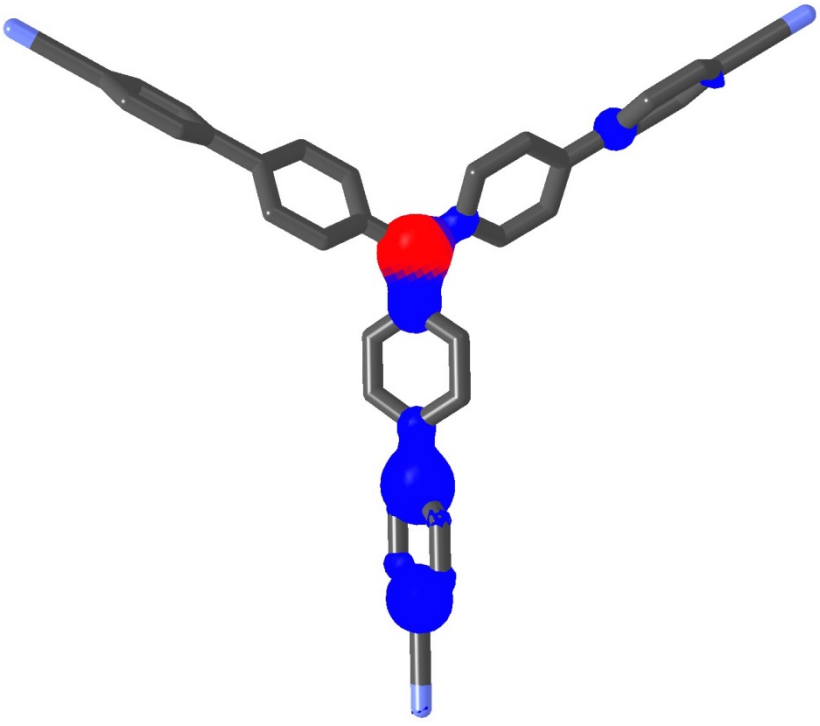


Figure S18. HOMO (red) and LUMO (blue) localizations in chromophore **3**.

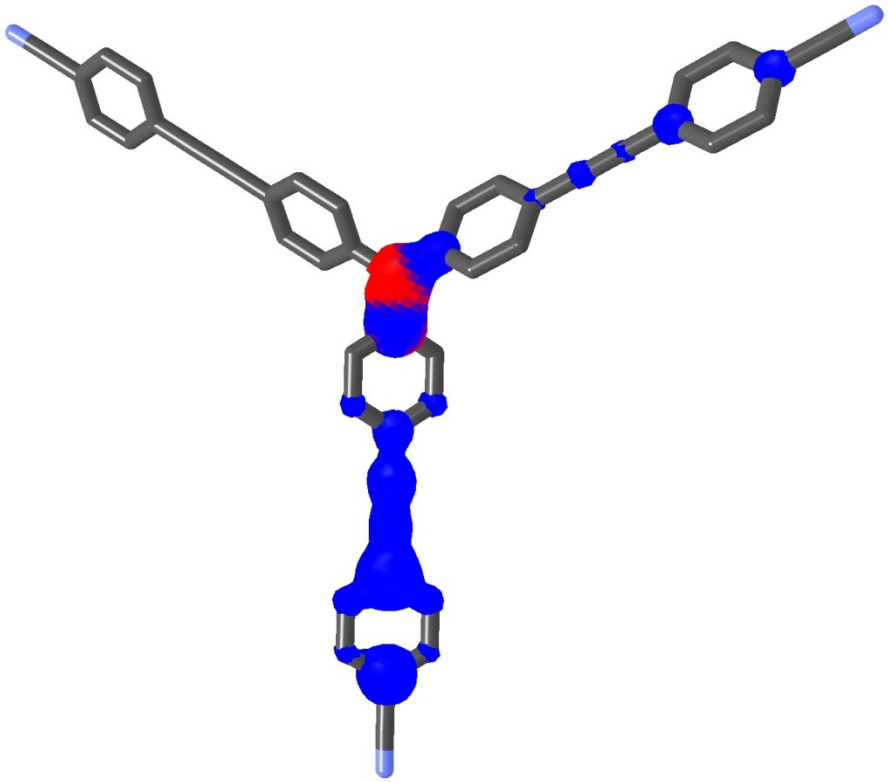


Figure S19. HOMO (red) and LUMO (blue) localizations in chromophore **4**.

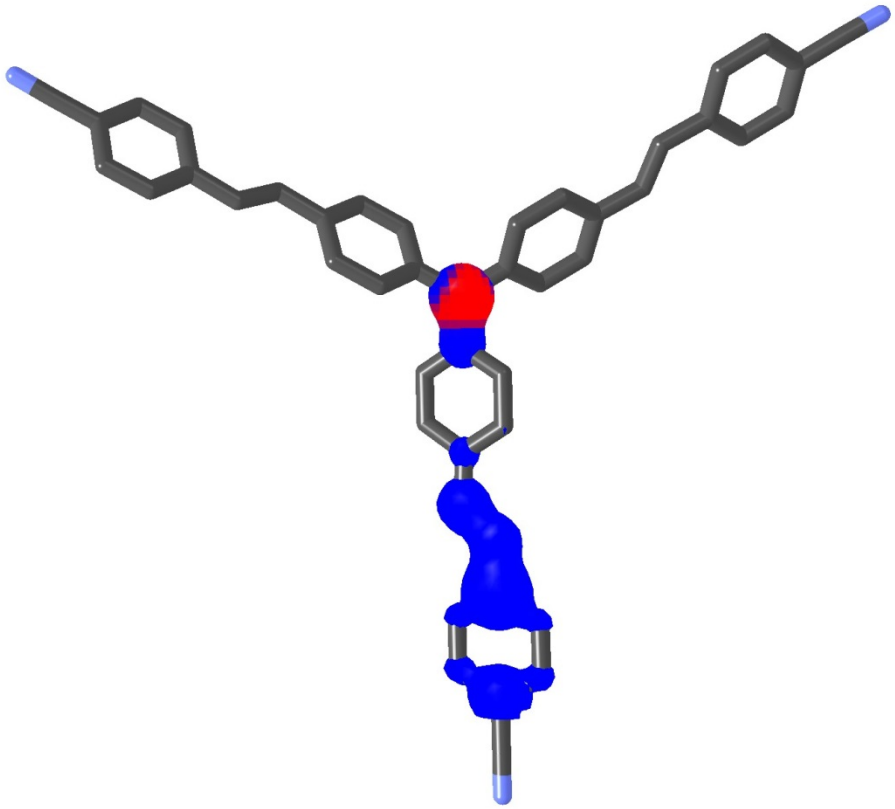


Figure S20. HOMO (red) and LUMO (blue) localizations in chromophore **5**.

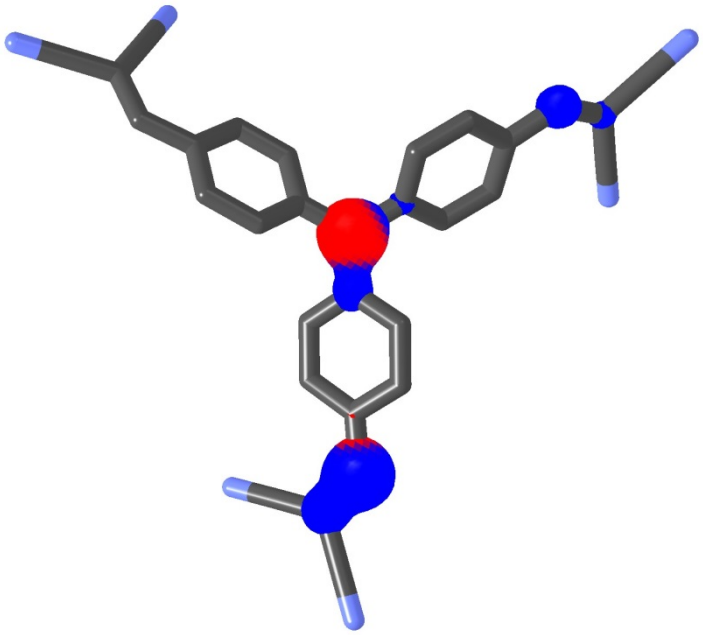


Figure S21. HOMO (red) and LUMO (blue) localizations in chromophore **6**.

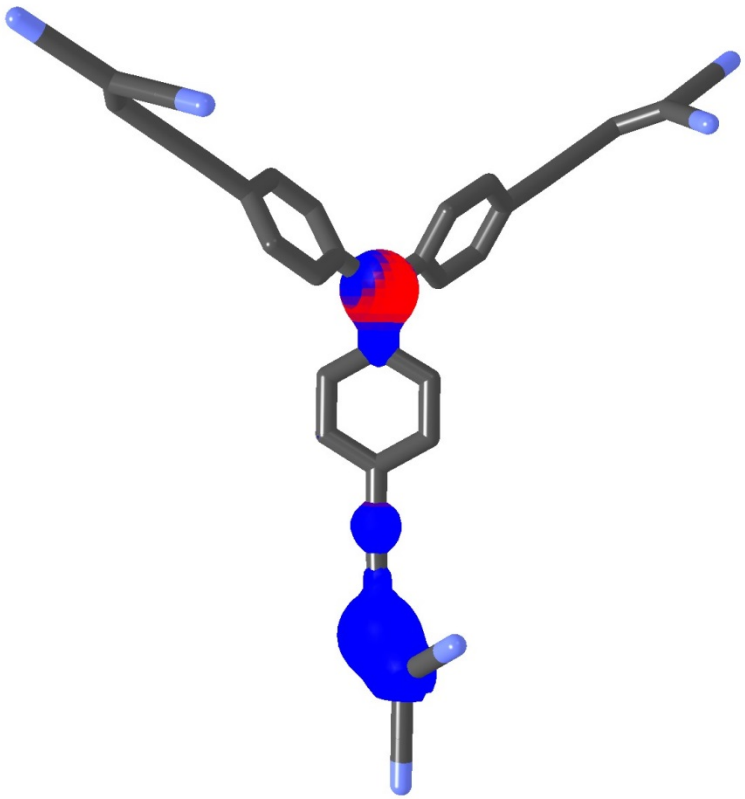


Figure S22. HOMO (red) and LUMO (blue) localizations in chromophore **7**.

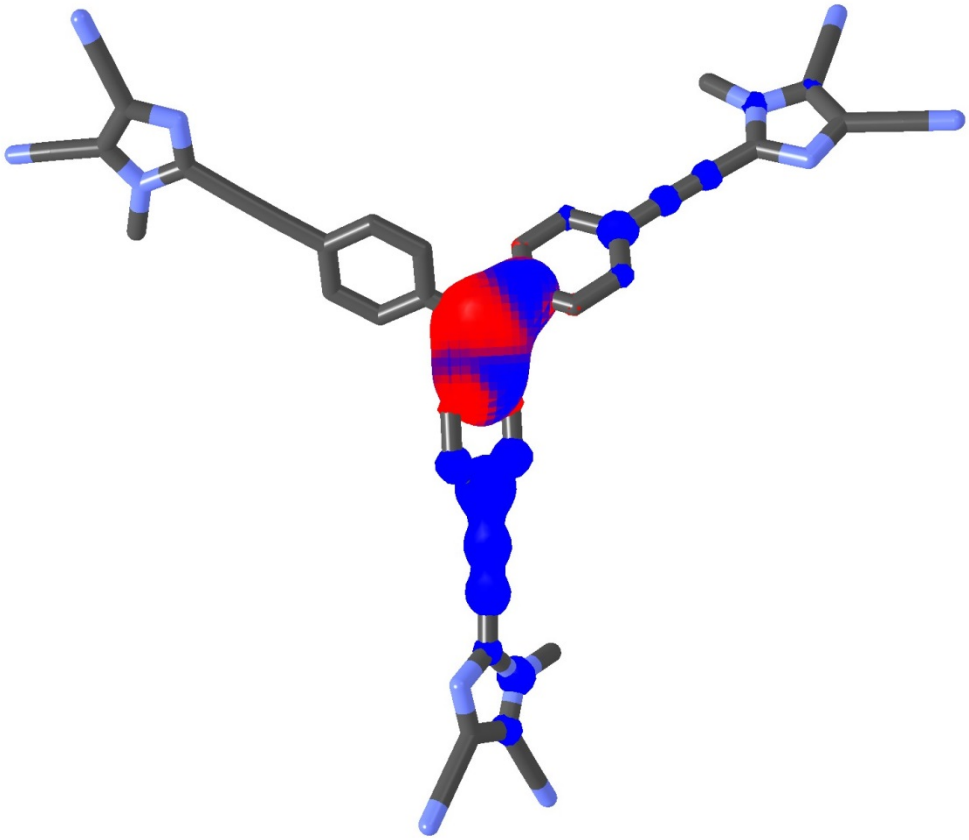


Figure S23. HOMO (red) and LUMO (blue) localizations in chromophore **8**.

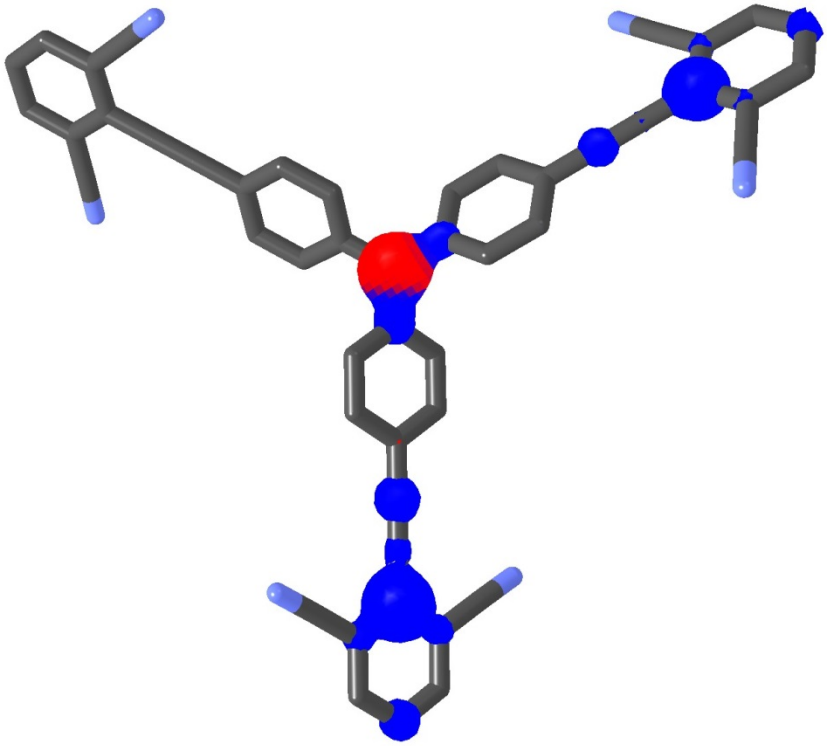


Figure S24. HOMO (red) and LUMO (blue) localizations in chromophore **9**.

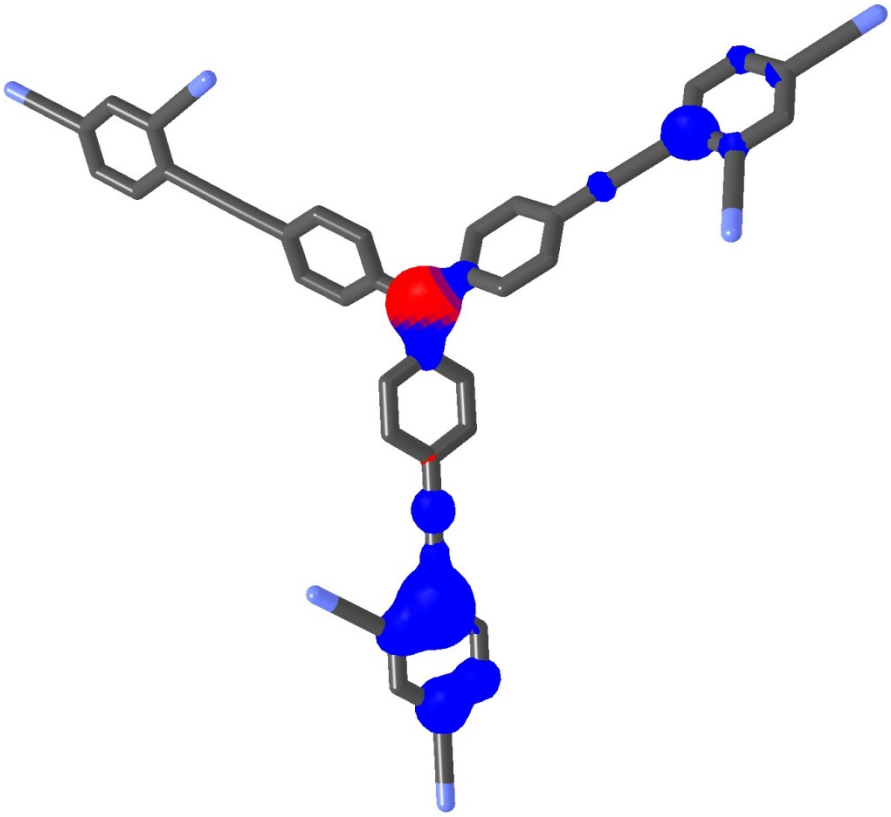


Figure S25. HOMO (red) and LUMO (blue) localizations in chromophore **10**.

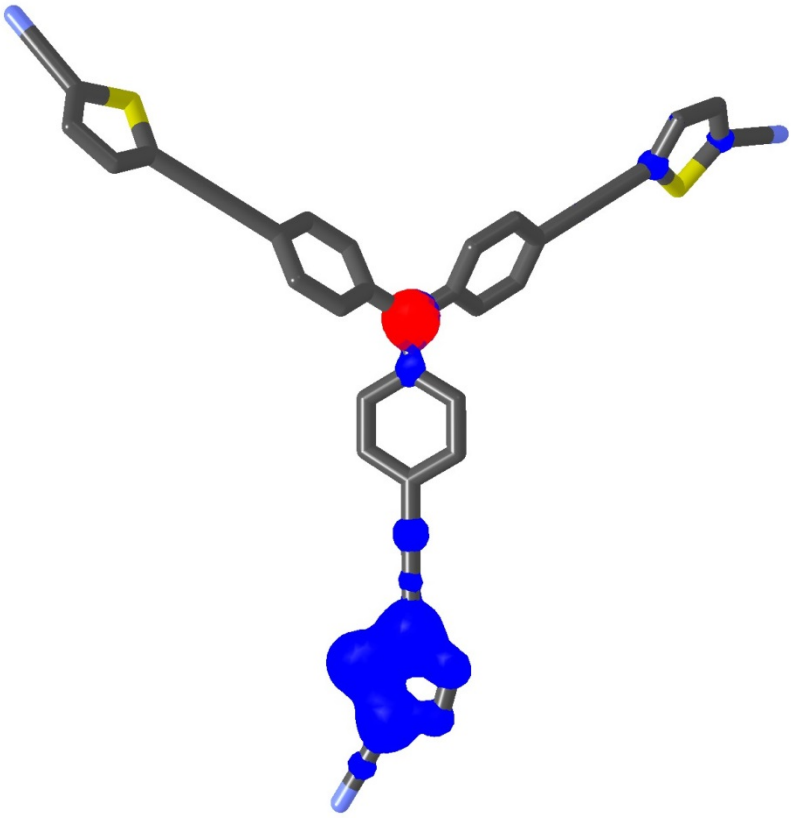


Figure S26. HOMO (red) and LUMO (blue) localizations in chromophore **11**.

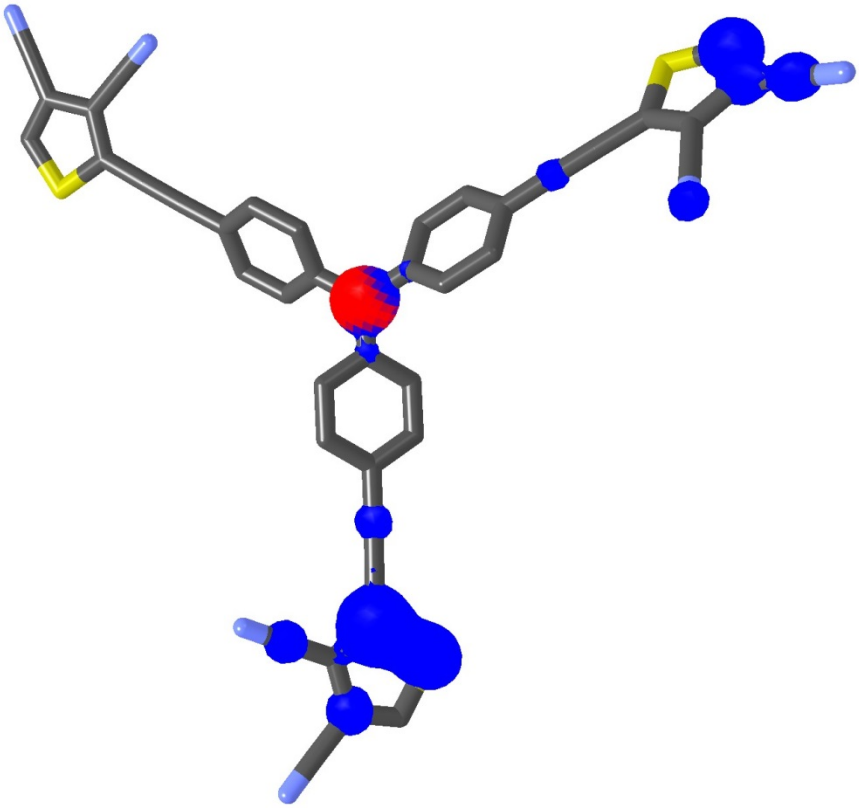


Figure S27. HOMO (red) and LUMO (blue) localizations in chromophore **12**.

9. NMR Spectra of 1–12

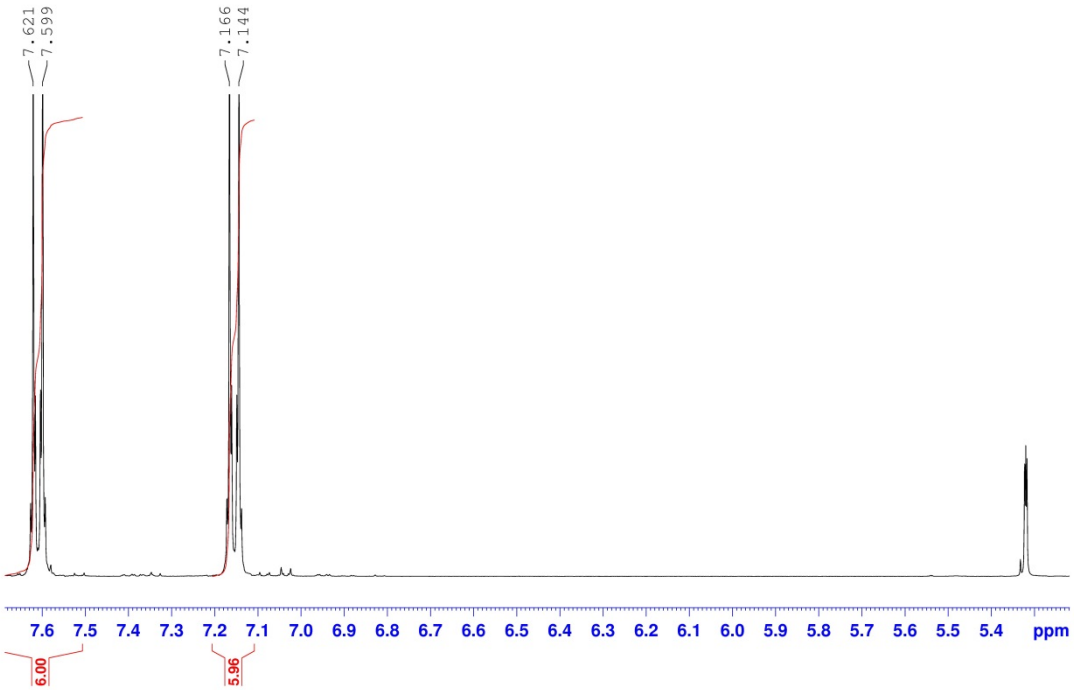


Figure S28. ^{1}H-NMR spectrum of chromophore **1** (400 MHz, CD_2Cl_2).

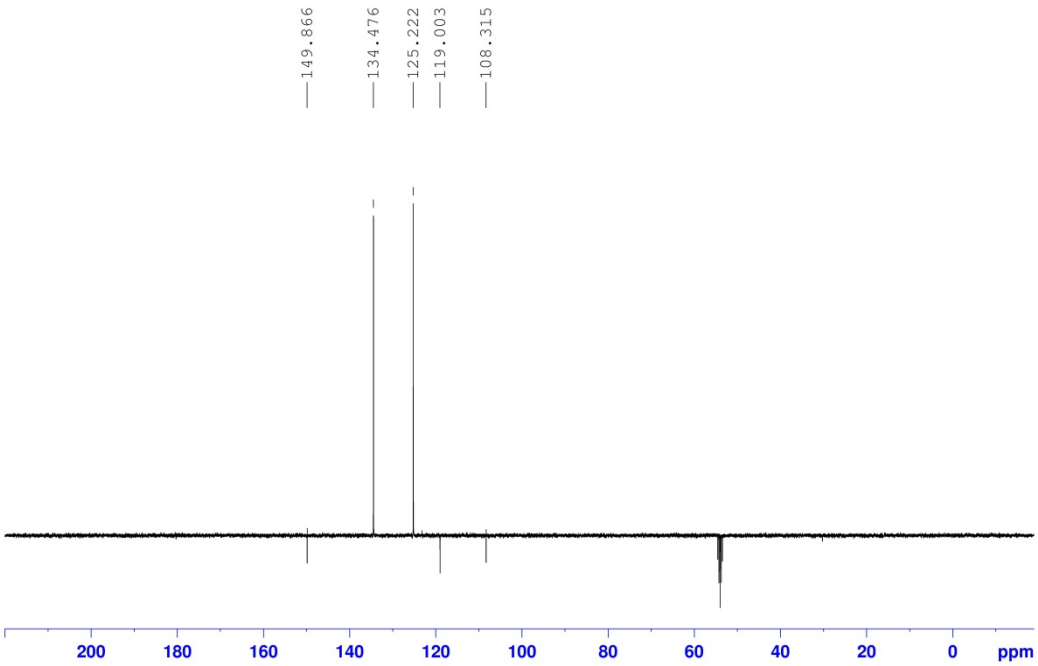


Figure S29. ^{13}C-NMR spectrum of chromophore **1** (100 MHz, CD_2Cl_2).

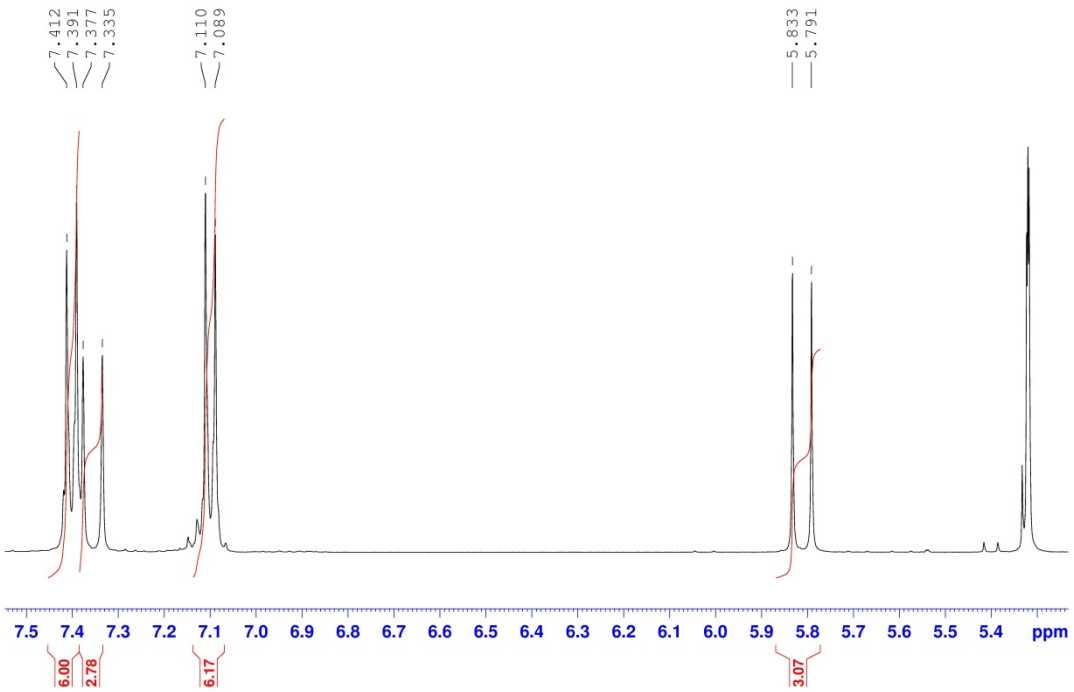


Figure S30. ^{1}H-NMR spectrum of chromophore **2** (400 MHz, CD_2Cl_2).

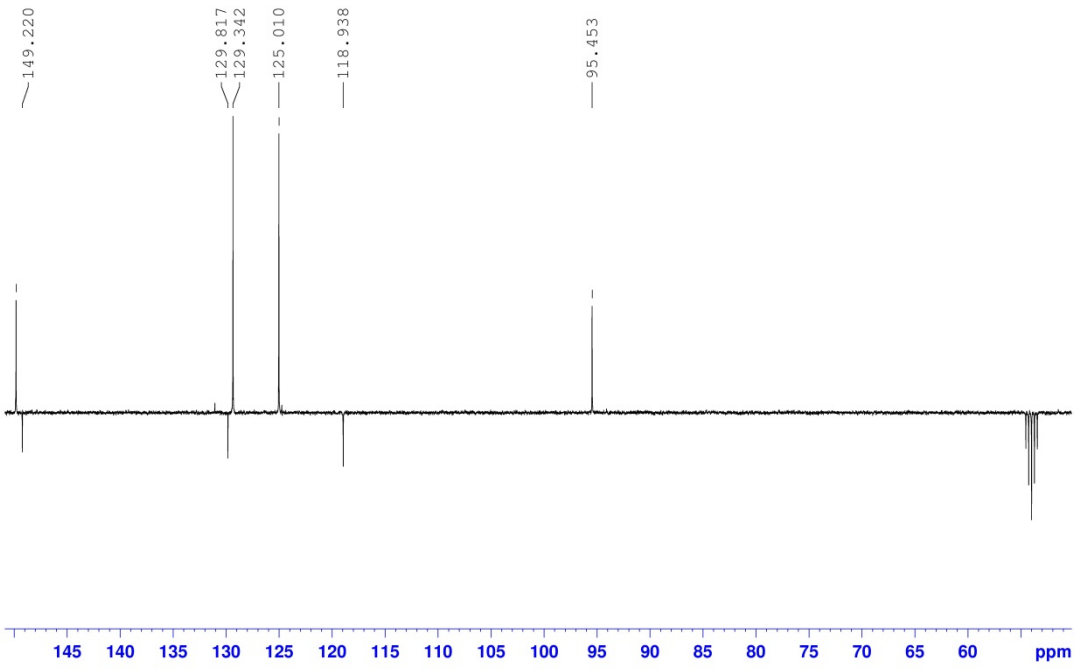


Figure S31. ^{13}C-NMR spectrum of chromophore **2** (100 MHz, CD_2Cl_2).

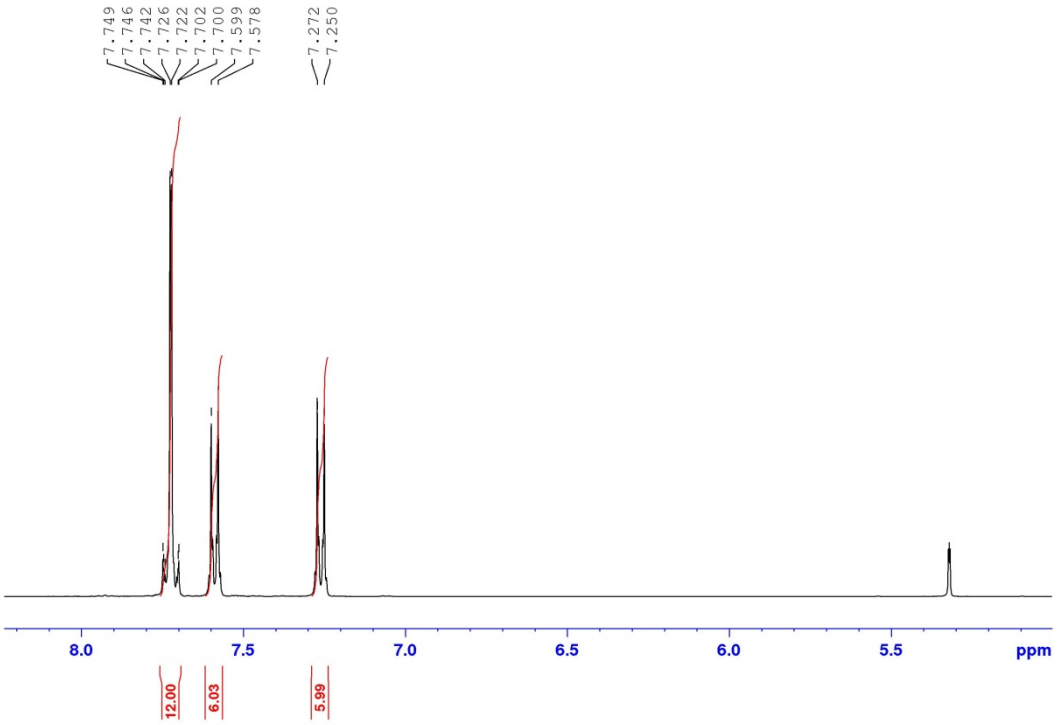


Figure S32. ^{1}H-NMR spectrum of chromophore **3** (400 MHz, CD_2Cl_2).

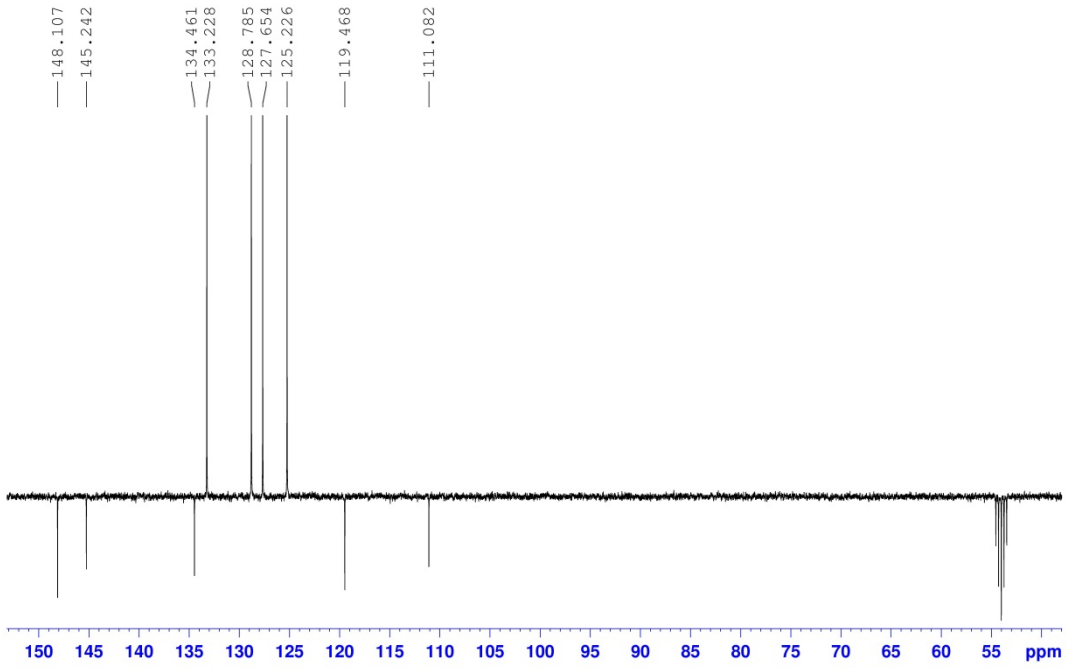


Figure S33. ^{13}C-NMR spectrum of chromophore **3** (100 MHz, CD_2Cl_2).

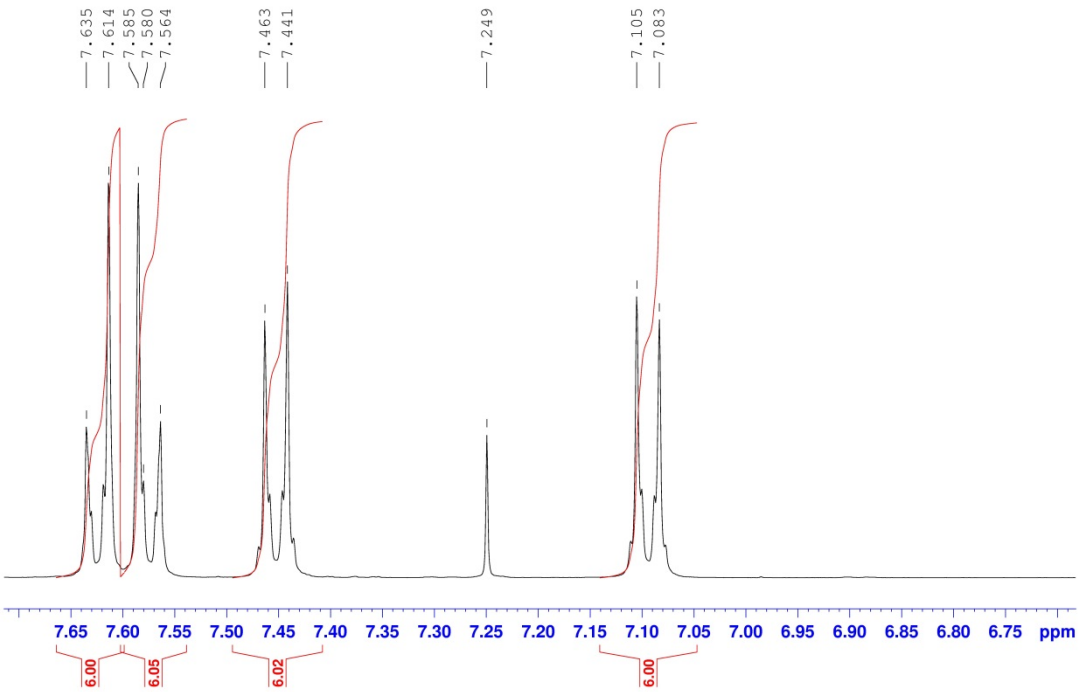


Figure S34. ^{1}H-NMR spectrum of chromophore **4** (400 MHz, $CDCl_3$).

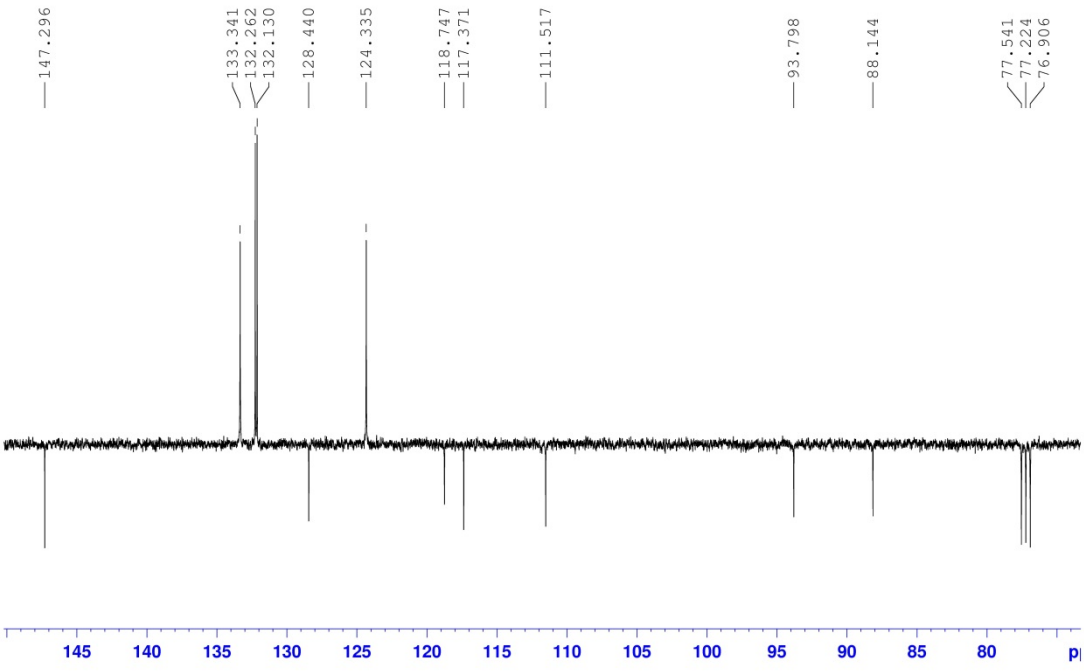


Figure S35. ^{13}C-NMR spectrum of chromophore **4** (100 MHz, $CDCl_3$).

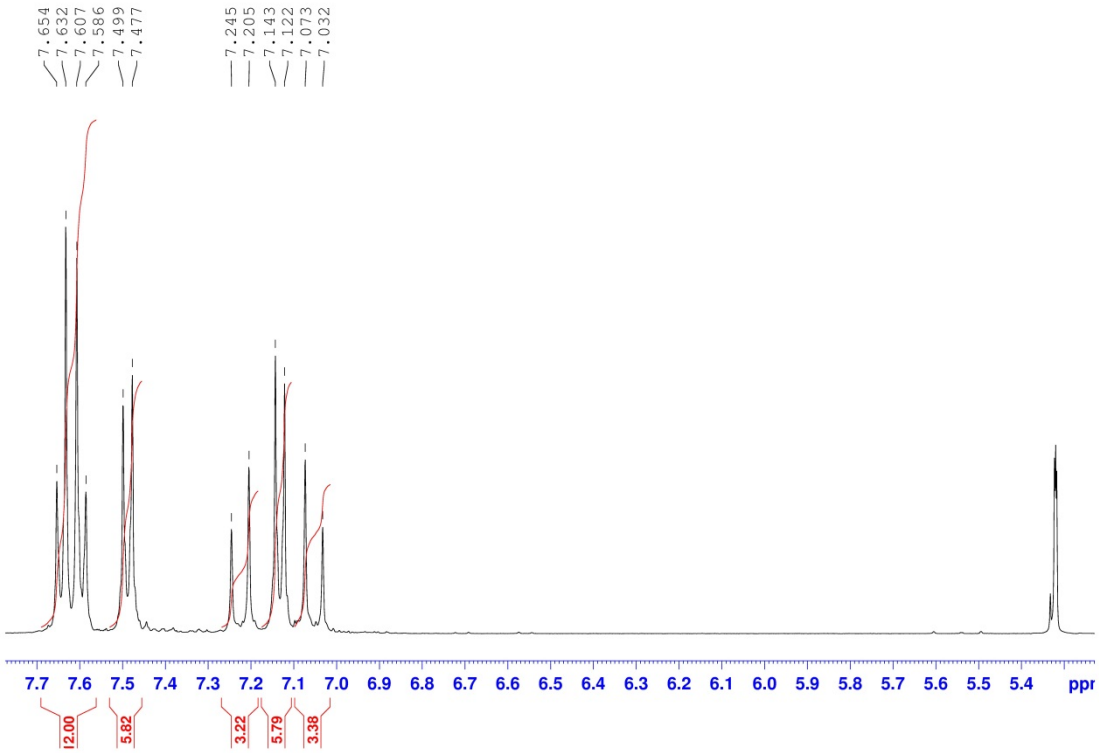


Figure S36. ^{1}H-NMR spectrum of chromophore **5** (400 MHz, CD_2Cl_2).

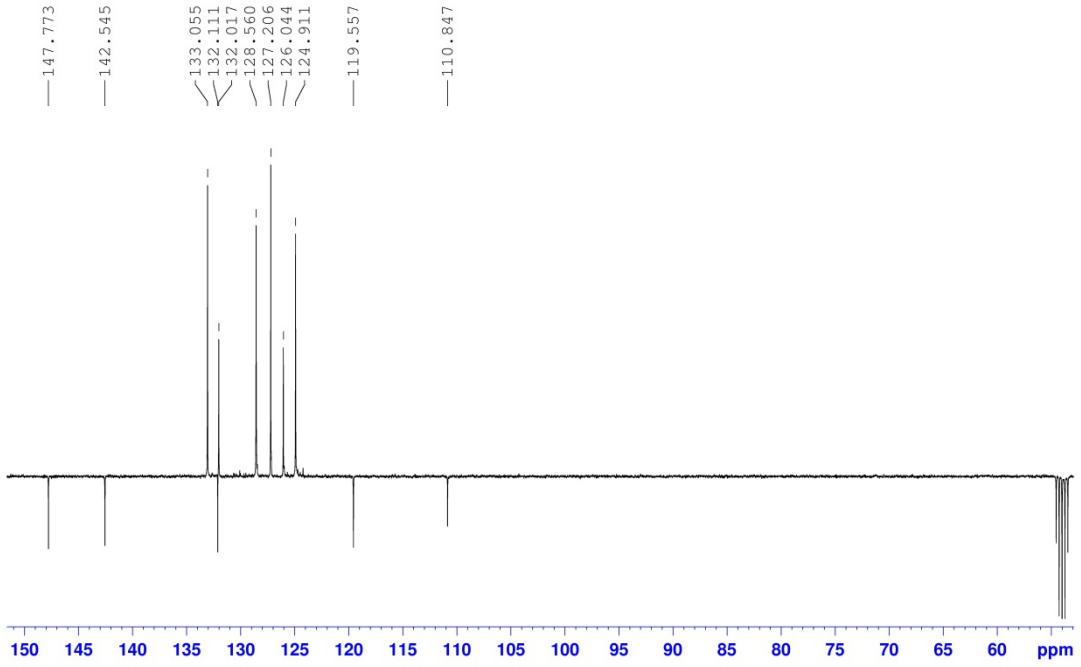


Figure S37. ^{13}C-NMR spectrum of chromophore **5** (100 MHz, CD_2Cl_2).

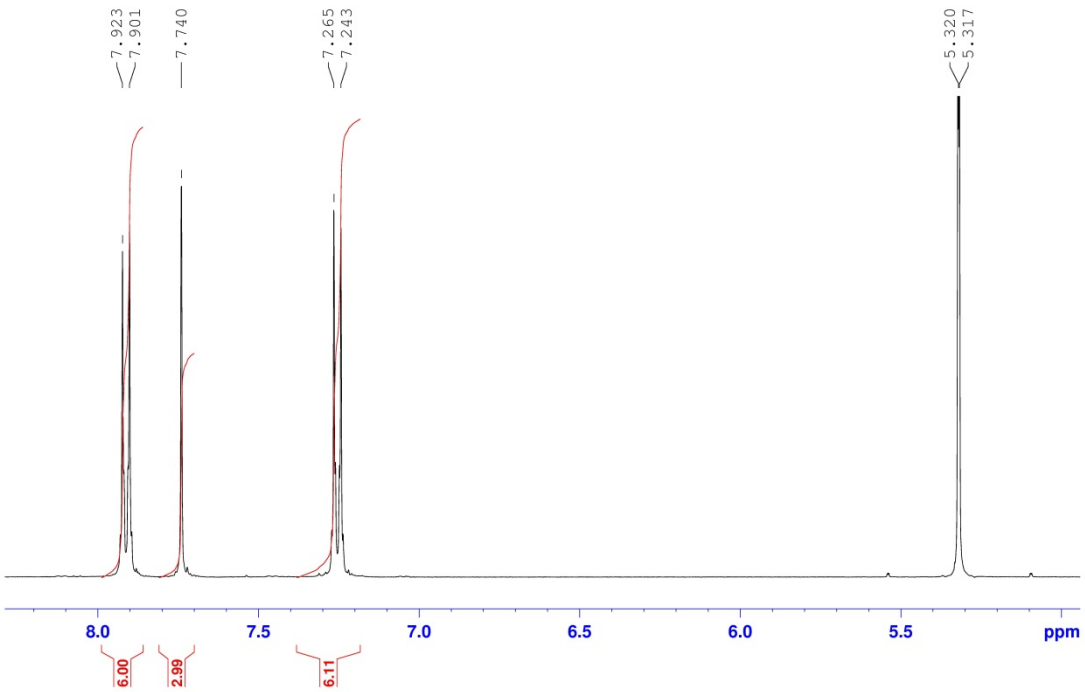


Figure S38. ^{1}H-NMR spectrum of chromophore **6** (400 MHz, CD_2Cl_2).

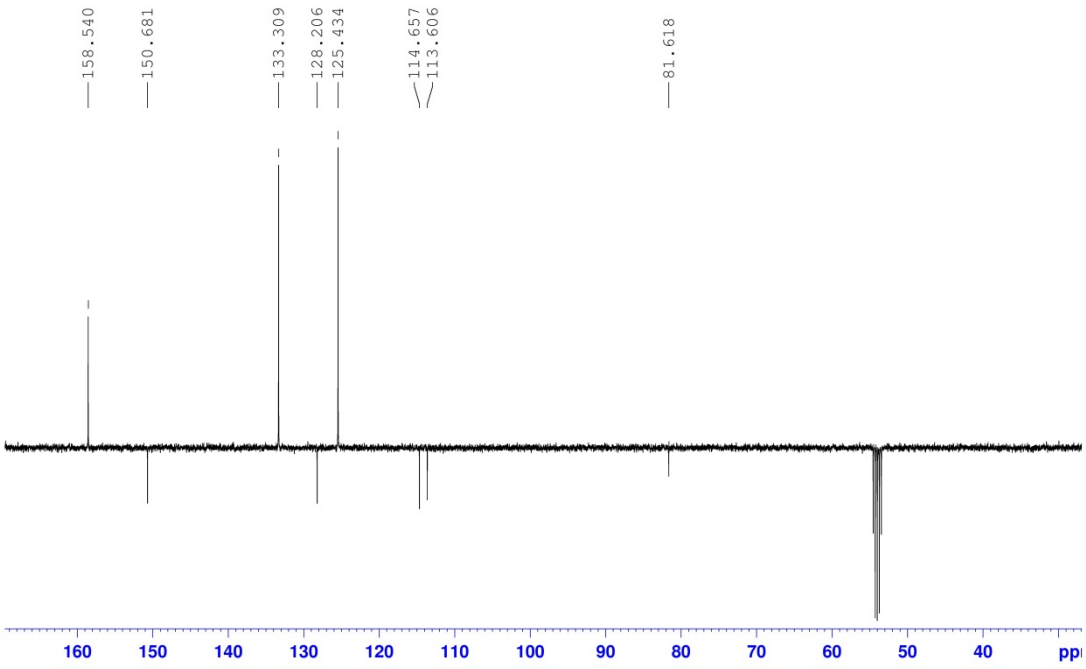


Figure S39. ^{13}C-NMR spectrum of chromophore **6** (100 MHz, CD_2Cl_2).

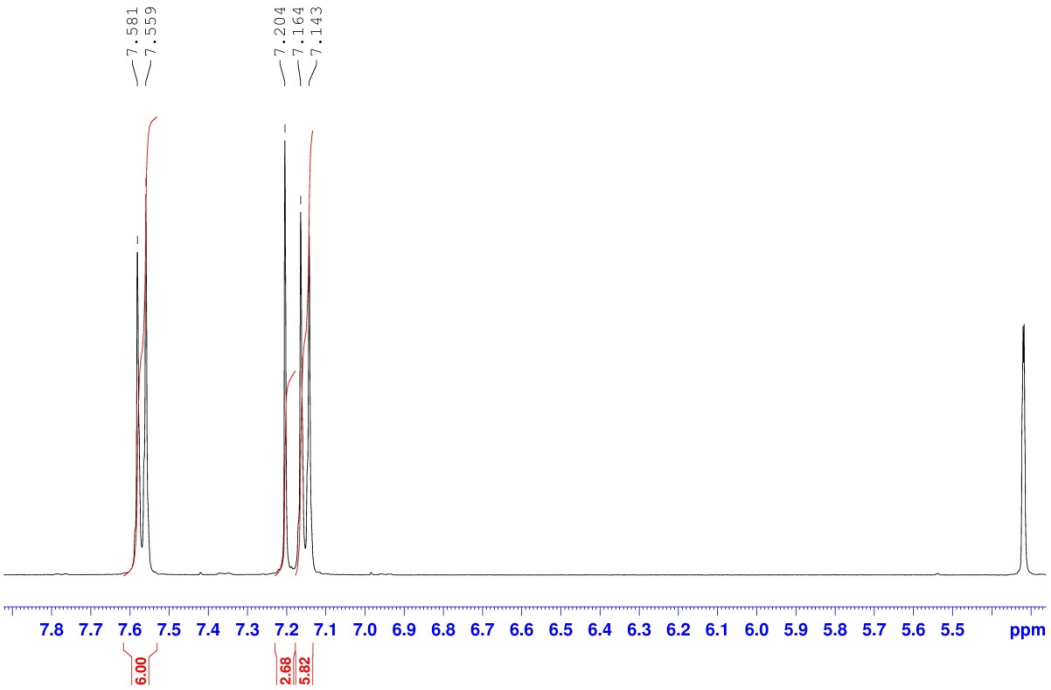


Figure S40. ^{1}H-NMR spectrum of chromophore **7** (400 MHz, CD_2Cl_2).

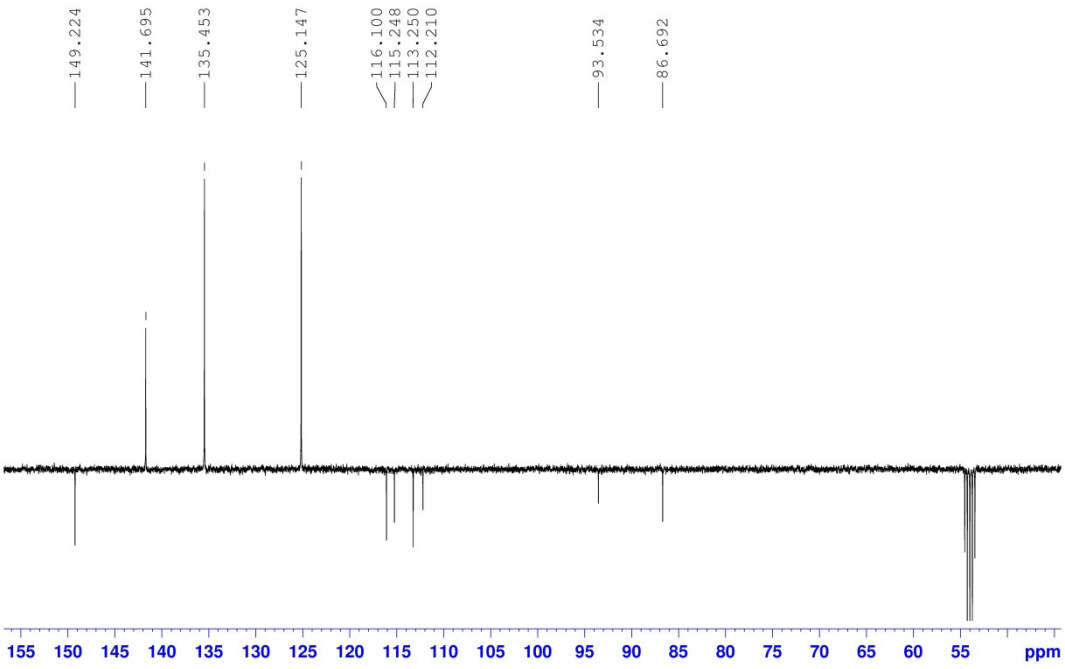


Figure S41. ^{13}C-NMR spectrum of chromophore **7** (100 MHz, CD_2Cl_2).

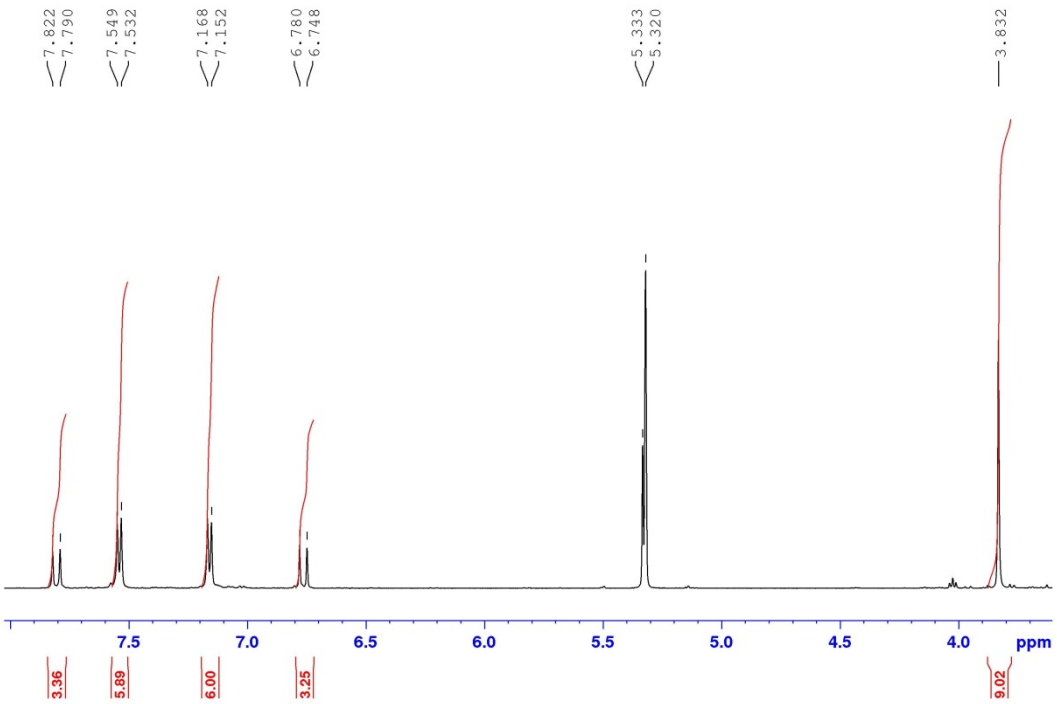


Figure S42. ^{1}H-NMR spectrum of chromophore **8** (400 MHz, CD_2Cl_2).

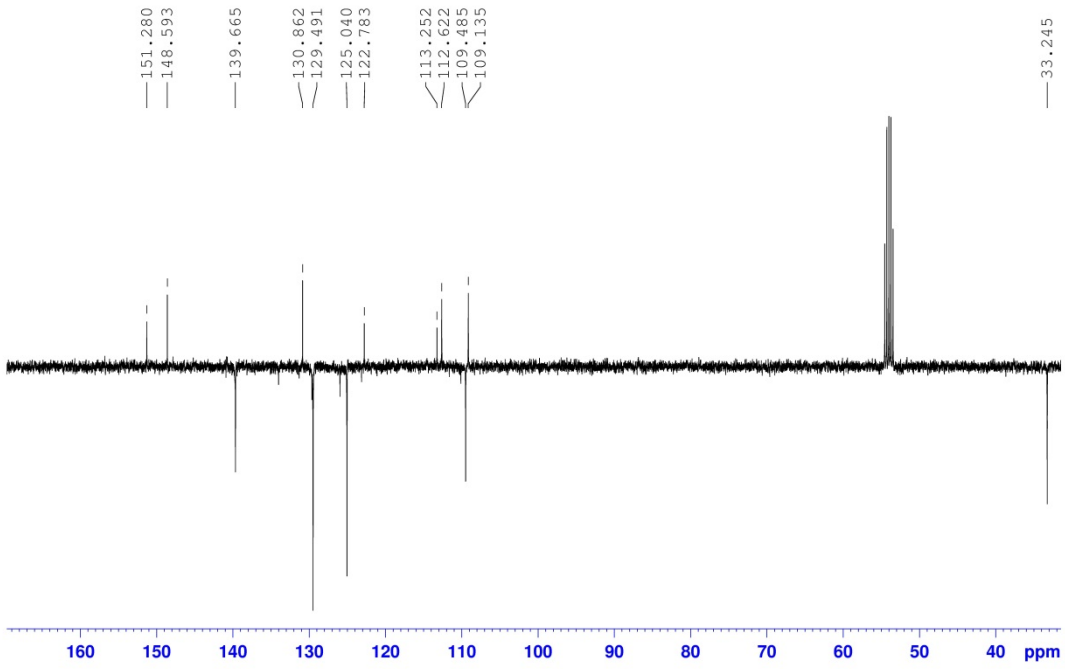


Figure S43. ^{13}C-NMR spectrum of chromophore **8** (100 MHz, CD_2Cl_2).

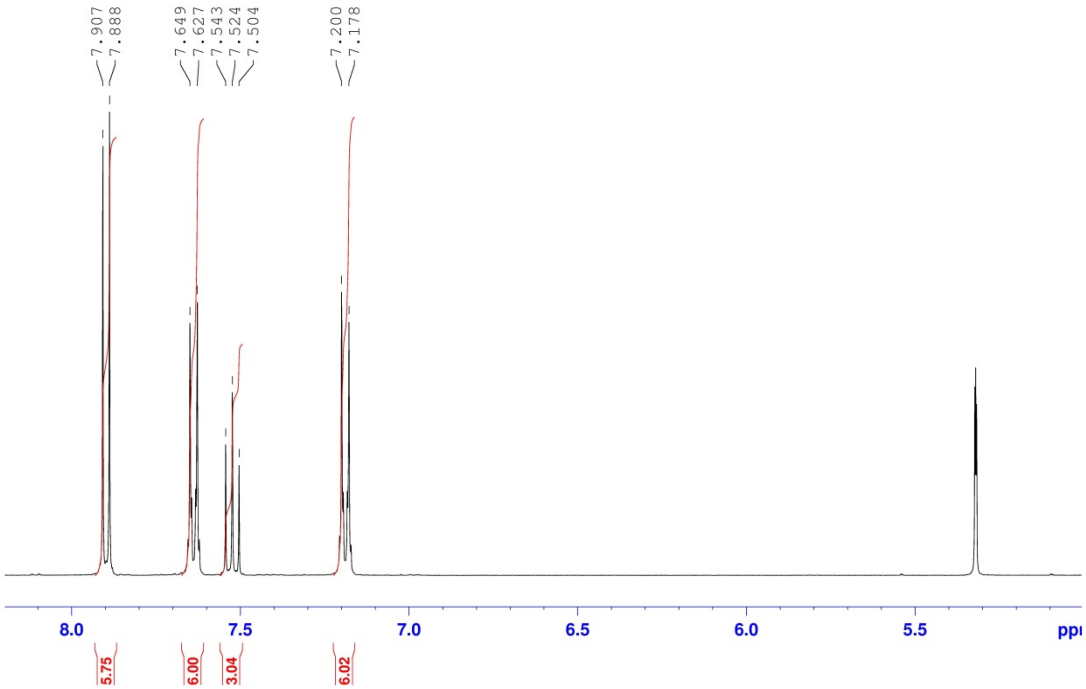


Figure S44. ^{1}H-NMR spectrum of chromophore **9** (400 MHz, CD_2Cl_2).

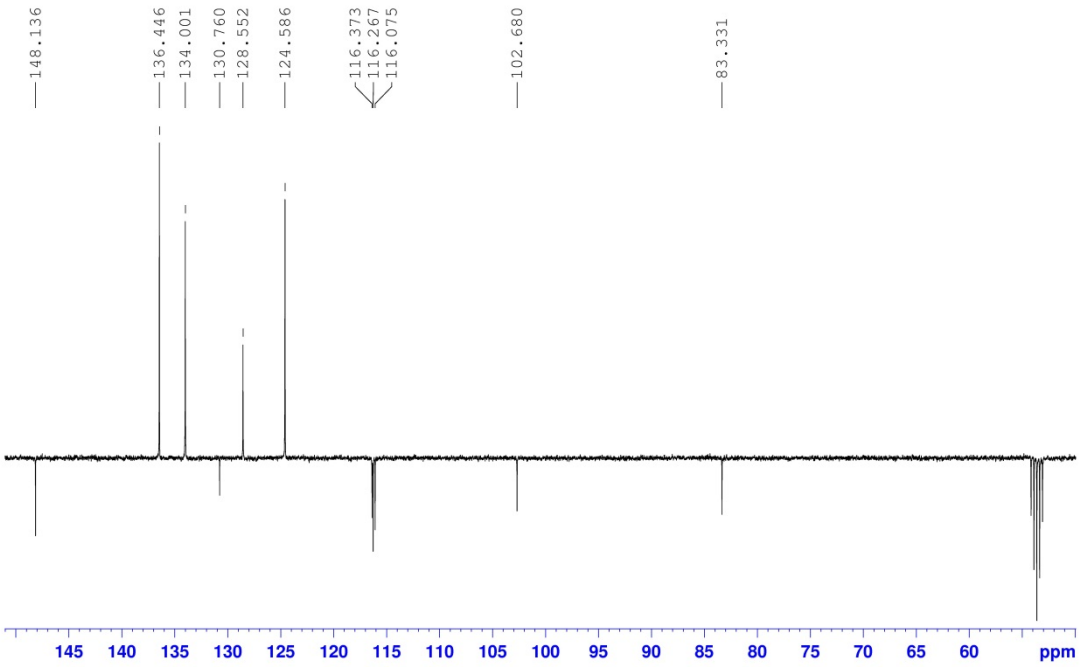


Figure S45. ^{13}C-NMR spectrum of chromophore **9** (100 MHz, CD_2Cl_2).

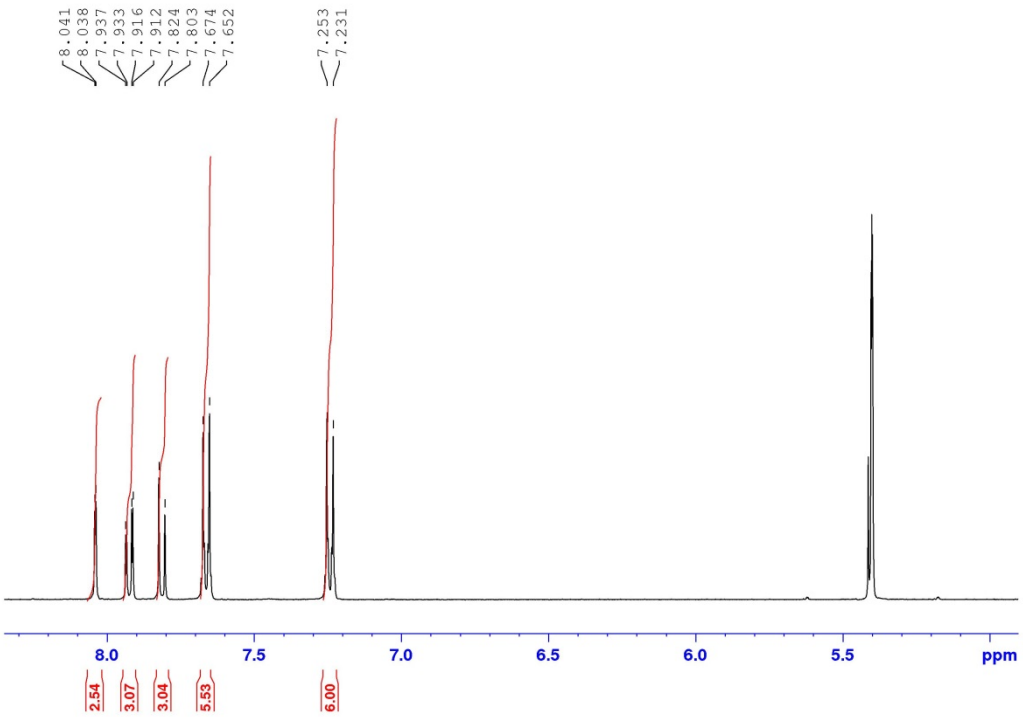


Figure S46. ^{1}H-NMR spectrum of chromophore **10** (400 MHz, CD_2Cl_2).

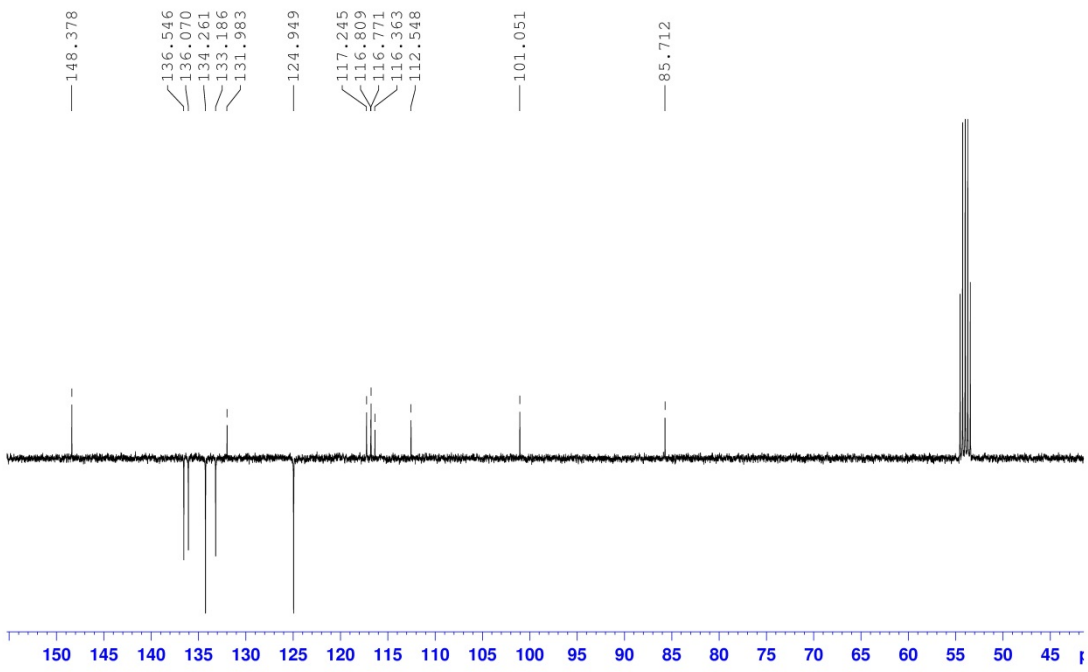


Figure S47. ^{13}C-NMR spectrum of chromophore **10** (100 MHz, CD_2Cl_2).

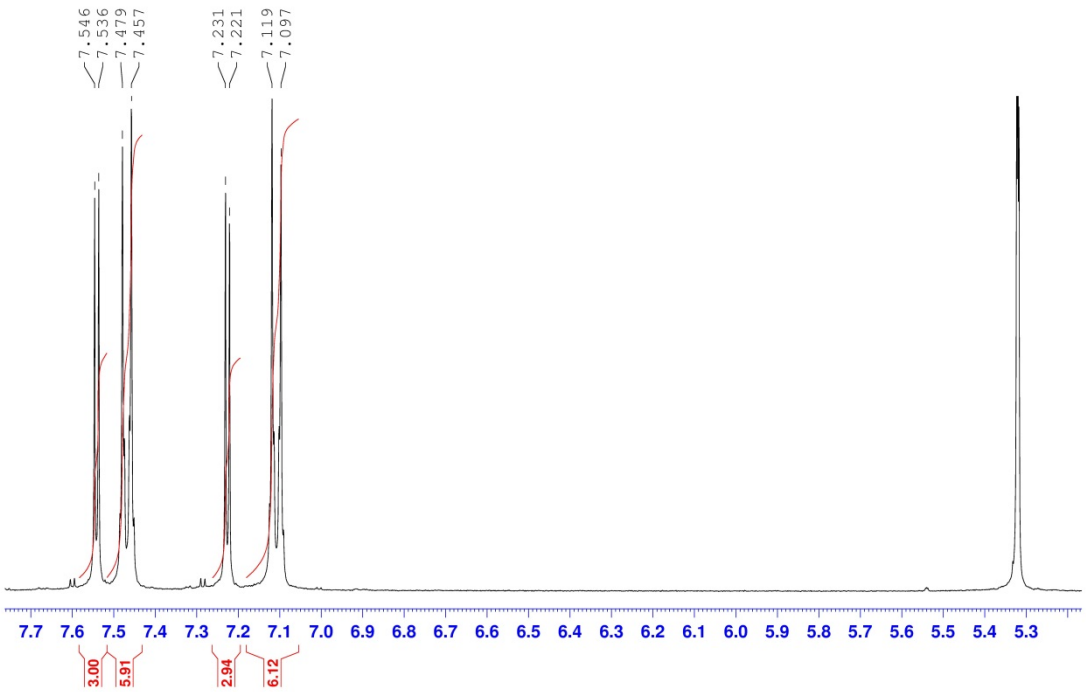


Figure S48. ^{1}H-NMR spectrum of chromophore **11** (400 MHz, CD_2Cl_2).

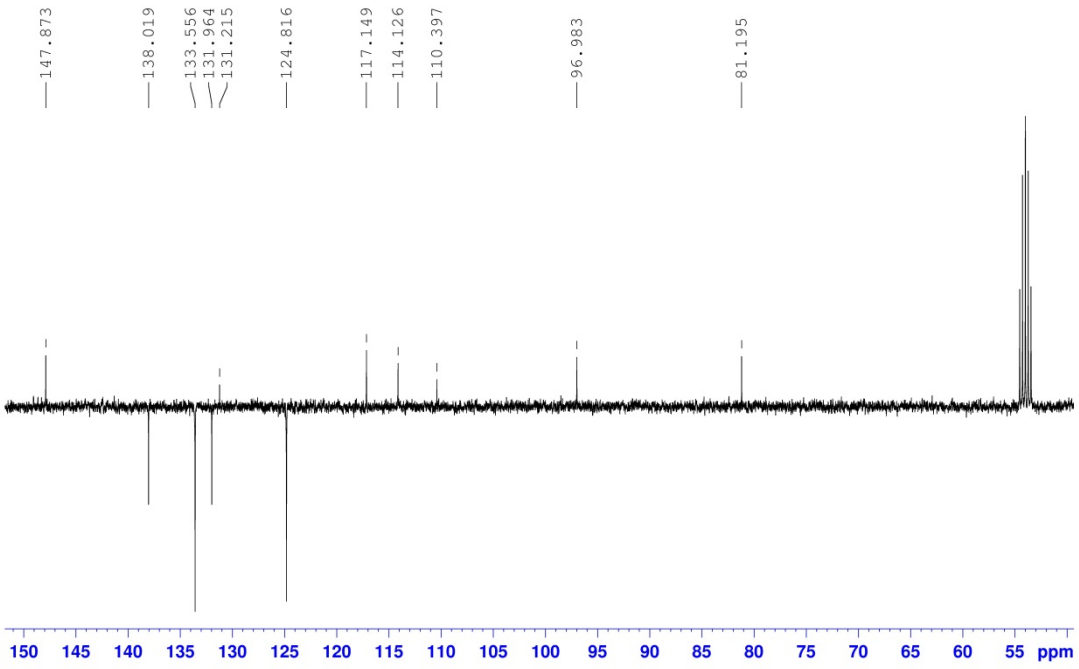


Figure S49. ^{13}C-NMR spectrum of chromophore **11** (100 MHz, CD_2Cl_2).

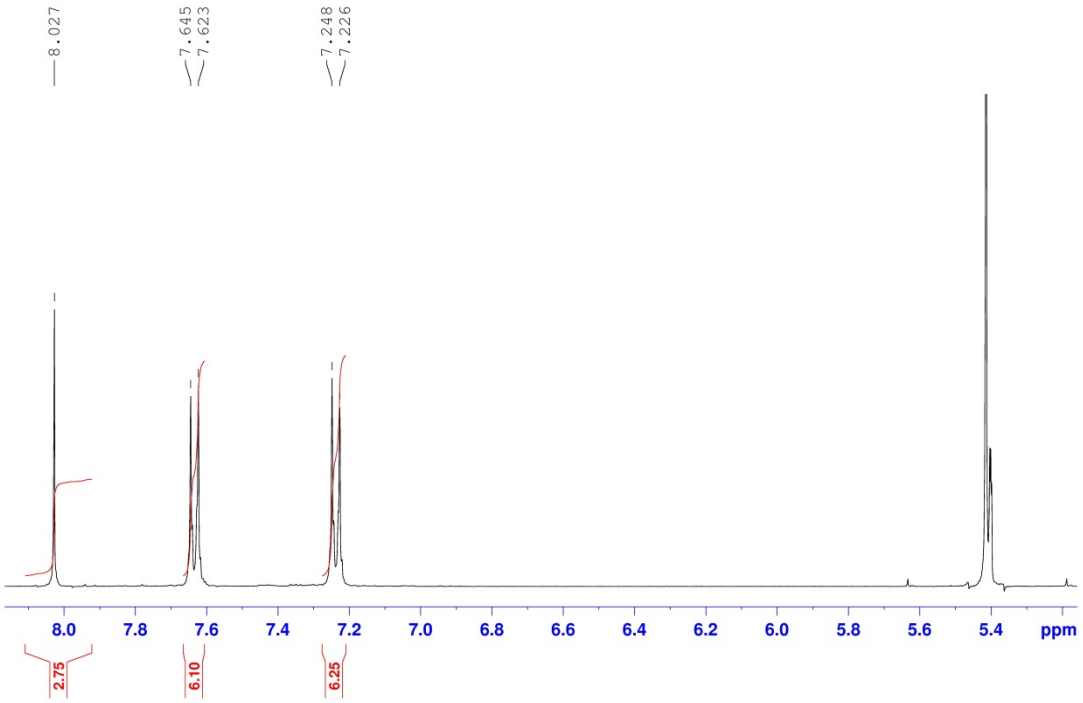


Figure S50. ^{1}H-NMR spectrum of chromophore **12** (400 MHz, CD_2Cl_2).

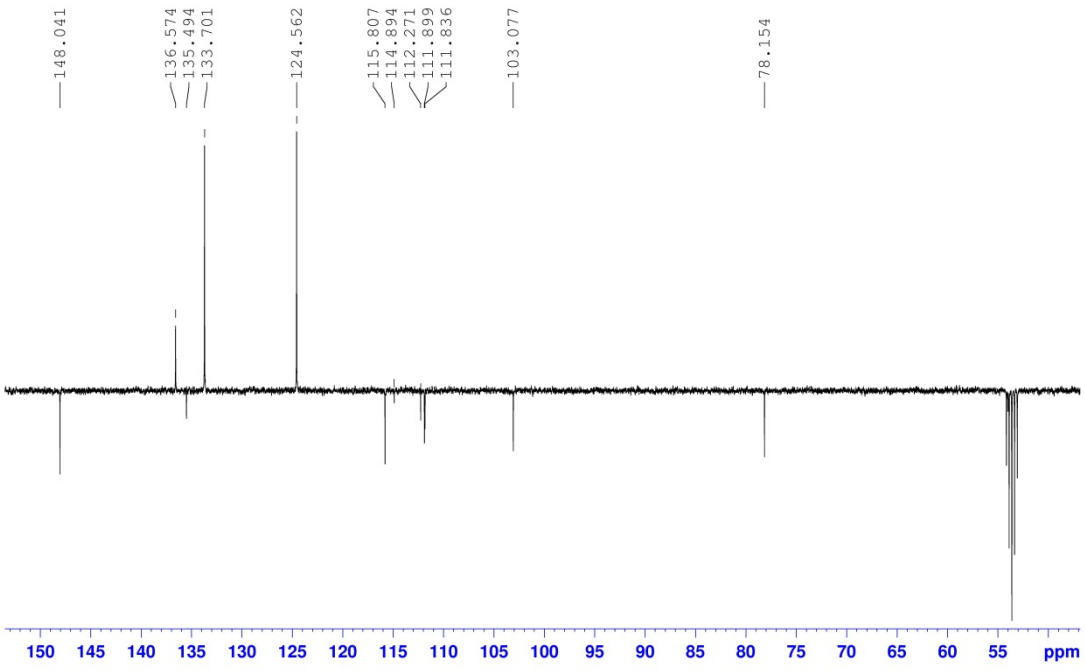


Figure S51. ^{13}C-NMR spectrum of chromophore **12** (100 MHz, CD_2Cl_2).

10. References

[1] P. Hrobarik, V. Hrobarikova, I. Sigmundova, P. Zahradnik, M. Fakis, I. Polyzos and P. Persephonis, *J. Org. Chem.*, 2011, **76**, 8726.

[2] G. A. Pearson, M. Rocek and R. I. Walter, *J. Phys. Chem.*, 1978, **82**, 1185.

[3] Y.-P. Tian, L. Li, J.-Z. Zhang, J.-X. Yang, H. Zhou, J. Wu, P. Sun, L. Tao, Y. Guo, C.-K. Wang, H. Xing, W. Huang, X.-T. Tao and M.-H. Jiang, *J. Mater. Chem.*, 2007, **17**, 3646.

[4] S. P. McIlroy, E. Clo, L. Nikolajsen, P. K. Frederiksen, C. B. Nielsen, K. V. Mikkelsen, K. V. Gothel and P. R. Ogilby, *J. Org. Chem.*, 2005, **70**, 1134.

[5] F. C. Courchay, J. C. Sworen, I. Ghiviriga, K. A. Abboud and K. B. Wagener; *Organometallics*, 2006, **25**, 6074.

[6] A. Padwa, K. E. Krumpe and J. M. Kassir *J. Org. Chem.*, 1992, **57**, 4940.

[7] E. W. Crandall, R. Beasley, L. L. Lambing and R. Moriconi, *J. Org. Chem.*, 1967, **32**, 134.

[8] P. Holý**,** J. Závada, J. Zezula, I. Císařová and J. Podlaha, *Collect. Czech. Chem. Commun.*, 2001, **66**, 820.

[9] K. Wallenfels, F. Witzler and K.Friedrich, *Tetrahedron*, 1967, **23**, 1353.

[10] E. J. Fendler , J. H. Fendler , C. E. Griffin and J. W. Larsen, *J. Org. Chem.*, 1970, **35**, 287.

[11] C. C. Leznoff, Z. Li, H. Isago, A. M. D'Ascanio and D. S. Terekhov*, J. Porphyrins Phthalocyanines*, 1999, **3**, 406.

[12] MOPAC2012, J. J. P. Stewart, Stewart Computational Chemistry, version 13.084W, webpage: http://OpenMOPAC.net.

[13] OPchem, O. Pytela, version 7.6, webpage: http://pytela.upce.cz/OPgm.