Photophysical and redox properties of new donor-acceptor-donor (DAD) compounds containing benzothiadiazole (A) and dimethyldihydroacridine (D) units - a combined experimental and theoretical study

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1. Synthesis

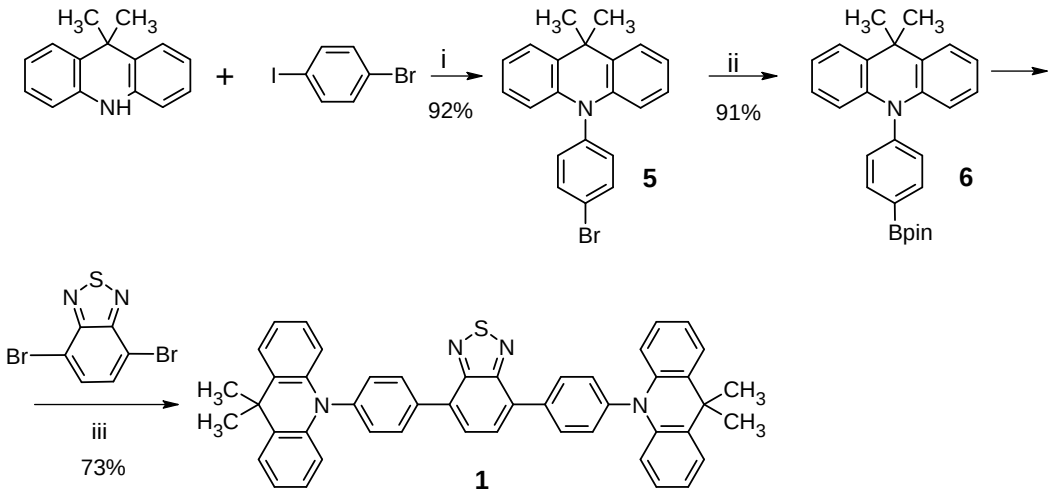
Characterization techniques

^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury (500 and 125 MHz) spectrometer and referenced with respect to TMS and solvents. IR spectra were monitored on Bio-RAD FTS-165 spectrometer using KBr pellets. UV-Vis-NIR spectra were registered using a Cary 5000 (Varian) spectrometer. Mass spectra were measured by ESI method on an AMD 604 mass spectrometer.

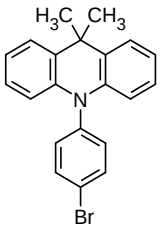
Reagents

9,10-dihydro-9,9-dimethylacridine, 1-bromo-4-iodobenzene, 1-bromo-3,5-diiodobenzene, 4,7-dibromobenzo[c][1,2,5]thiadiazole, bis(pinacolato)diboron, (tribenzylideneacetone) dipalladium(0), $Pd_2(dba)_3$, tetrakis(triphenylphosphine)palladium(0), $Pd(PPh_3)_4$, bis(triphenylphosphine)palladium(II) dichloride, $PdCl_2(PPh_3)_2$, Xantphos, sodium *tert*-butoxide, *t*-BuONa, potassium acetate, KOAc, anhydrous toluene, anhydrous dioxane were purchased from Aldrich.

All glassware was oven dried, assembled hot, and cooled under a dry argon stream before use. All reactions were performed under dry argon.



Scheme S1. Synthetic route to the compound **1** (i) $Pd_2(dba)_3$, Xantphos, *t*-BuONa, toluene, 80 °C, (ii) bis(pinacolato)diboron, AcOK, $PdCl_2(PPh_3)_2$, dioxane, 100 °C, (iii) 4,7-dibromo-2,1,3-benzothiadiazole, $Pd(PPh_3)_4$, 2 M K_2CO_3, toluene, 100 °C.

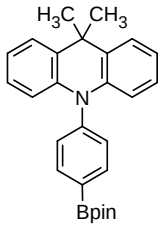


Compound 5

$Pd_2(dba)_3$, 91.1 mg (0.105 mmol) and Xantphos, 243 mg (0.42 mmol) were mixed in 3 mL of dry toluene and stirred under an argon atmosphere for 0.5 h. Then 1-bromo-4-iodobenzene, 1.41

g (5 mmol), 9,10-dihydro-9,9-dimethylacridine, 1.1 g (5.25 mmol), sodium *tert*-butoxide, 0.75 g (7.87 mmol) and *ca.* 12 mL of dry toluene were added to the reaction flask. The mixture was stirred and heated at 80 °C for 20 h. Then the mixture was cooled to room temperature, washed with brine, and extracted with three 10 mL portions of diethyl ether. The combined organic layers were dried over Na_2SO_4. After evaporation of the solvents, the crude product was purified by chromatography on silica gel eluting with CH_2Cl_2/hexanes (1:1) containing 1%$_v$ of Et_3N to give 1.68 g (4.61 mmol, 92% yield) of 9,9-dimethyl-10-(4'-bromophenyl)-9,10-dihydroacridine as a white powder.

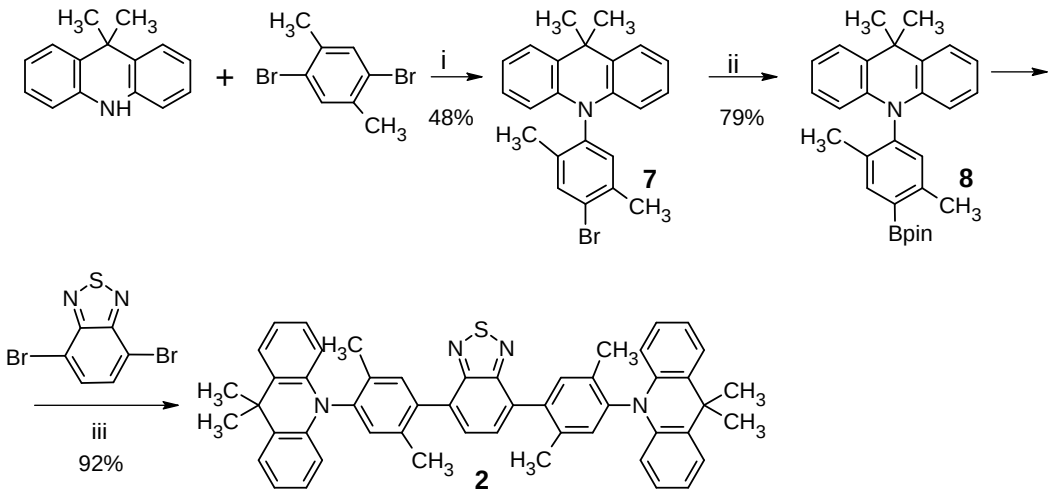
^{1}H NMR (500 MHz, $CDCl_3$) δ, 7.65 (d, *J*=10.5 Hz, 2H), 7.46 (dd, *J*=11, 2.0 Hz, 2H), 7.23 (d, *J*=11 Hz, 2H), 6.99-6.92 (m, 4H), 6.25 (dd, *J*=11, 2 Hz, 2H), 1.69 (s, 6H).



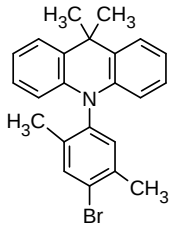
Compound 6

Compound **5**, 0.55 g (1.51 mmol), bis(pinacolato)diboron 0.442 g (1.74 mmol), potassium acetate, 0.444 g (4.53 mmol), $PdCl_2(PPh_3)_2$ 31.8 mg (0.045 mmol) were mixed in 10 ml of dry dioxane under an argon atmosphere and heated at 100 °C for 24 h. Then the mixture was cooled to room temperature, washed with brine, and extracted with dichloromethane. The combined organic layers were dried over Na_2SO_4. After evaporation of the solvents, the crude product was purified by chromatography on silica gel eluting with CH_2Cl_2/hexanes (1:1) to give 0.57 g (1.38 mmol, 91% yield) of 10-[9,9-dimethyl-9,10-dihydroacridine]-phenylboronic acid pinacol ester as a white powder.

^{1}H NMR (500 MHz, $CDCl_3$) δ, 8.06 (d, *J*=10.5 Hz, 2H), 7.44 (d, *J*=11, 2H), 7.34 (d, *J*=10 Hz, 2H), 6.94-6.92 (m, 4H), 6.24 (d, *J*=10.5 Hz, 2H), 1.69 (s, 6H), 1.40 (s, 12H).



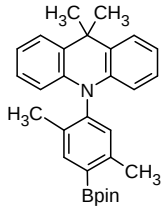
Scheme S2. Synthetic route to the compound **2** (i) $Pd_2(dba)_3$, Xantphos, *t*-BuONa, toluene, 80 °C, (ii) bis(pinacolato)diboron, AcOK, $PdCl_2(PPh_3)_2$, dioxane, 100 °C, (iii) 4,7-dibromo-2,1,3-benzothiadiazole, $Pd(PPh_3)_4$, 2 M K_2CO_3, toluene, 100 °C.



Compound 7

Compound **7** was prepared in the same manner as compound **5**, i.e. $Pd_2(dba)_3$, 54.9 mg (0.06 mmol) and Xantphos, 138.8 mg (0.24 mmol) were mixed in 3 mL of dry toluene and stirred under an argon atmosphere for 0.5 h. Then 1,4-dibromo-2,5-dimethylbenzene, 0.79 g (3 mmol), 9,10-dihydro-9,9-dimethylacridine, 0.63 g (3 mmol), sodium *tert*-butoxide, 0.37 g (3.9 mmol) and *ca.* 7 mL of dry toluene were added to the reaction flask. The mixture was stirred and heated at 100 °C for 20 h. Then the mixture was cooled to room temperature, washed with brine, and extracted with three 10 mL portions of diethyl ether. The combined organic layers were dried over Na_2SO_4. After evaporation of the solvents the crude product was purified by chromatography on silica gel eluting with CH_2Cl_2/hexanes (1:4) containing 1%$_v$ of Et_3N to give 0.57 g (1.45 mmol, 48% yield) of 9,9-dimethyl-10-(4'-bromo-2',5'-dimethylphenyl)-9,10-dihydroacridine as a white powder.

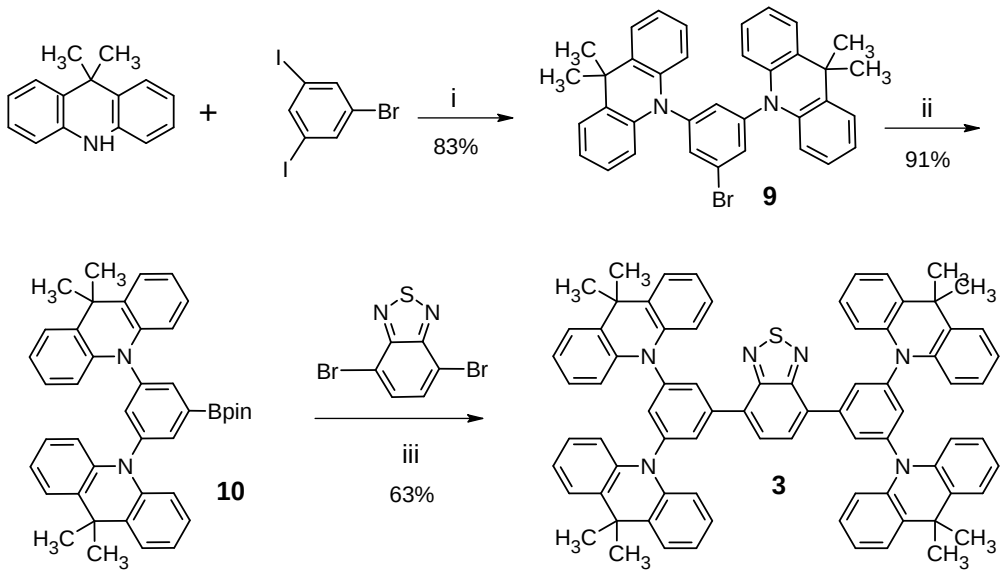
^{1}H NMR (500 MHz, $CDCl_3$) δ, 7.66 (s, 1H), 7.46 (dd, *J*=11.5, 1.5 Hz, 2H), 7.10 (s, 1H), 6.99-6.89 (m, 4H), 6.13 (dd, *J*=11.5, 1.5 Hz, 2H), 2.40 (s, 3H), 2.01 (s, 3H), 1.70 (s, 3H), 1.68 (s, 3H).



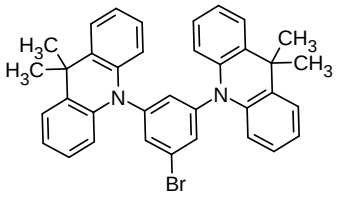
Compound 8

Compound **7**, 0.9 g (2.3 mmol), bis(pinacolato)diboron 0.67 g (2.645 mmol), potassium acetate, 0.68 g (6.9 mmol), $PdCl_2(PPh_3)_2$ 48.4 mg (0.069 mmol) were mixed in 15 ml of dry dioxane under an argon atmosphere and heated at 100 °C for 24 h. Then the mixture was cooled to room temperature, washed with brine, and extracted with dichloromethane. The combined organic layers were dried over Na_2SO_4. After evaporation of the solvents, the crude product was purified by chromatography on silica gel eluting with CH_2Cl_2/hexanes (1:2) to give 0.8 g (1.82 mmol, 79.2% yield) of compound **8** as a white powder.

^{1}H NMR (500 MHz, $CDCl_3$) δ, 7.84 (s, 1H), 7.50 (dd, *J*=11.5, 2.0 Hz, 2H), 7.03 (s, 1H), 6.96-6.87 (m, 4H), 6.13 (dd, *J*=11.5, 2.0 Hz, 2H), 2.53 (s, 3H), 2.02 (s, 3H), 1.70 (s, 3H), 1.68 (s, 3H), 1.40 (s, 12H).



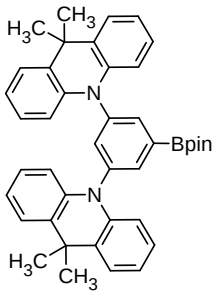
Scheme S3. Synthetic route to the compound **3** (i) $Pd_2(dba)_3$, Xantphos, *t*-BuONa, toluene, 80 °C, (ii) bis(pinacolato)diboron, AcOK, $PdCl_2(PPh_3)_2$, dioxane, 100 °C, (iii) 4,7-dibromo-2,1,3-benzothiadiazole, $Pd(PPh_3)_4$, 2 M K_2CO_3, toluene, 100 °C.



Compound 9

$Pd_2(dba)_3$, 146.5 mg (0.16 mmol) and Xantphos, 370.3 mg (0.64 mmol) were mixed in 5 mL of dry toluene and stirred under an argon atmosphere for 0.5 h. Then 1-bromo-3,5-diiodobenzene, 1.635 g (4 mmol), 9,10-dihydro-9,9-dimethylacridine, 1.67 g (8 mmol), sodium *tert*-butoxide, 1.15 g (12 mmol) and *ca.* 15 mL of dry toluene were added to the reaction flask. The mixture was stirred and heated at 80 °C for 24 h. Then the mixture was cooled to room temperature, washed with brine, and extracted with three 15 mL portions of chloroform. The combined organic layers were dried over Na_2SO_4. After evaporation of the solvents, the crude product was purified by chromatography on silica gel eluting with $CHCl_3$/hexanes (1:1) containing 1%$_v$ of Et_3N to give 1.9 g (3.33 mmol, 83% yield) of compound **9** as a white powder.

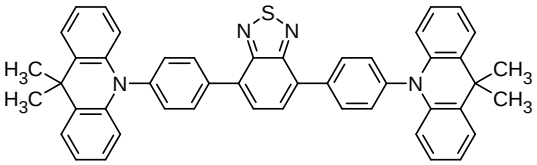
^{1}H NMR (500 MHz, $CDCl_3$) δ, 7.71 (dd, *J*=6.5, 2.5 Hz, 2H), 7.45 (dd, *J*=10.5, 2.5 Hz, 4H), 7.35 (t, *J*=2.5 Hz, 1H), 7.07 (td, *J*=10.5, 2.5 Hz, 4 H), 6.98 (td, *J*=10.5, 2.5 Hz, 4H), 6.45 (d, *J*=2.5 Hz, 2H), 6.43 (d, *J*=2.5 Hz, 2H), 1.68 (s, 12H).



Compound 10

Compound **9**, 1.9 g (3.3 mmol), bis(pinacolato)diboron 0.97 g (3.8 mmol), potassium acetate, 0.97 g (9.9 mmol), $PdCl_2(PPh_3)_2$ 69.5 mg (0.099 mmol) were mixed in 20 ml of dry dioxane under an argon atmosphere and heated at 100 °C for 48 h. Then the mixture was cooled to room temperature, washed with brine, and extracted with dichloromethane. The combined organic layers were dried over Na_2SO_4. After evaporation of the solvents, the crude product was purified by chromatography on silica gel eluting with $CHCl_3$/hexanes (1:2), then $CHCl_3$ to give 1.86 g (3 mmol, 91% yield) of compound **10** as a white powder.

^{1}H NMR (500 MHz, $CDCl_3$) δ, 7.93 (d, *J*=2.5 Hz, 2H), 7.47-7.44 (m, 5H), 7.03 (td, *J*=10.5, 2.0, Hz, 4H), 6.93 (td, *J*=10.5, 2.0 Hz, 4H), 6.41 (dd, *J*=10.5, 2.0 Hz, 4H), 1.68 (s, 12H), 1.35 (s, 12H).



Compound 1

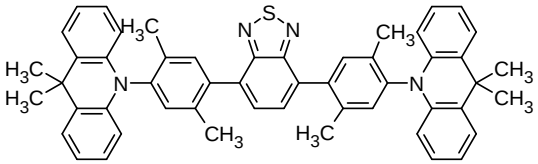
Compound **6**, 0.57 g (1.38 mmol), 4,7-dibromobenzo[c][1,2,5]thiadiazole 176 mg (0.6 mmol) $Pd(PPh_3)_4$ 34.7 mg (0.03 mmol) were dissolved in 10 ml of toluene, then 2.4 ml of 2 M K_2CO_3 aqueous solution and one drop of Aliquat were added. The mixture was heated at 100 °C for 24 h with vigorous stirring. After cooling to room temperature the reaction mixture was extracted with brine and dichloromethane. The organic phases were dried with Na_2SO_4. After evaporation of the solvents, the crude product was purified by chromatography on silica gel eluting with $CHCl_3$/hexanes (3:2) to give 0.31 g (0.44 mmol, 73% yield) of yellow powder.

^{1}H NMR (500 MHz, $CDCl_3$) δ, 8.32 (d, *J*=10.5 Hz, 4H), 8.00 (s, 2H), 7.55 (d, *J*=10.5 Hz, 4H), 7.50 (dd, *J*=11, 1.5 Hz, 4H), 7.05-6.95 (m, 8H), 6.47 (dd, *J*=11, 1.5 Hz, 4H), 1.74 (s, 12H).

^{13}C NMR (125 MHz, $CDCl_3$) δ, 154.2, 141.6, 141.0, 137.2, 132.8, 131.8, 131.7, 130.25, 128.7, 126.6, 125.4, 120.8, 114.4, 36.2, 31.4.

IR (cm^{-1}): 3055, 2964, 2863, 1590, 1516, 1483, 1440, 1340, 1265, 748, 730.

ESI: Calc. Mass for $C_{48}H_{39}N_4S_1$ 703.2895, Found: 703.2897



Compound 2

Compound **8**, 0.44 g (1.0 mmol), 4,7-dibromobenzo[c][1,2,5]thiadiazole 127 mg (0.43 mmol) $Pd(PPh_3)_4$ 28.9 mg (0.025 mmol) were dissolved in 10 ml of toluene, then 2.1 ml of 2 M K_2CO_3 aqueous solution and one drop of Aliquat were added. The mixture was heated at 100 °C for 24 h with vigorous stirring. After cooling to room temperature the reaction mixture was extracted with brine and dichloromethane. The organic phases were dried with Na_2SO_4. After evaporation of the solvents, the crude product was purified by chromatography on silica gel eluting with $CHCl_3$/hexanes (1:1) to give 0.30 g (0.395 mmol, 92% yield) of light yellow powder.

^{1}H NMR (500 MHz, $CDCl_3$) δ, 7.76 (s, 2H), 7.59 (s, 2H), 7.52 (dd, *J*=10.5, 2.0 Hz, 4H), 7.28 (s, 2H), 7.06 (td, *J*=10.5, 2.0 Hz, 4H), 6.96 (td, *J*=10.5, 2.0 Hz, 4H), 6.38 (dd, *J*=10.5, 2.0 Hz, 4H), 2.28 (s, 6H), 2.15 (s, 6H), 1.78 (s, 6H), 1.74 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ, 154.1, 139.7, 139.4, 137.8, 137.1, 136.1, 134.1, 133.05, 129.9, 129.8, 126.8, 125.8, 120.6, 113.7, 36.1, 32.6, 32.2, 31.7, 20.4, 17.4.

IR (cm^{-1}): 3060, 2950, 2852, 1590, 1501, 1474, 1445, 1329, 1273, 746.

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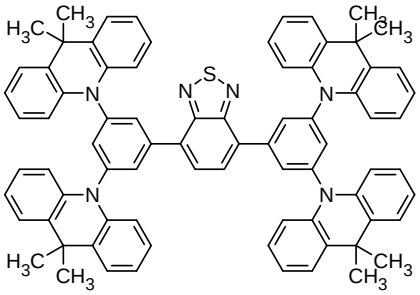


Compound 3

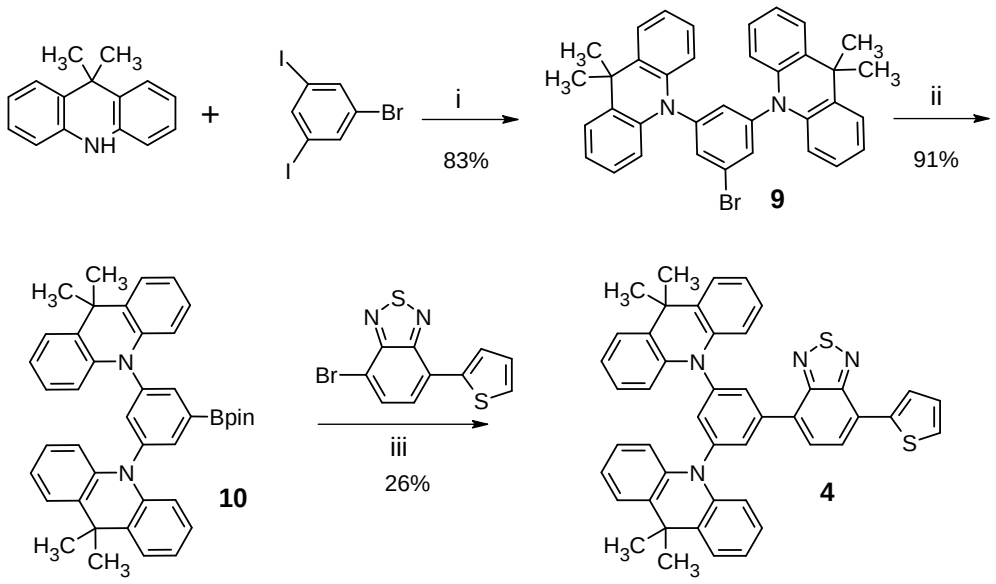
Compound **10**, 742 mg (1.2 mmol), 4,7-dibromobenzo[c][1,2,5]thiadiazole 117.6 mg (0.4 mmol) $Pd_2(dba)_3$ 36.6 mg (0.04 mmol), Sphos 65.7 mg (0.16 mmol) were dissolved in 8 ml of toluene, then 1 ml of 2 M K_2CO_3 aqueous solution and one drop of Aliquat were added. The mixture was heated at 100 °C for 24 h with vigorous stirring. After cooling to room temperature the reaction mixture was extracted with brine and chloroform. The organic phases were dried with Na_2SO_4. After evaporation of the solvents, the crude product was purified by chromatography on silica gel eluting with $CHCl_3$/hexanes (1:9 to 1:1) to give 0.28 g (0.25 mmol, 63% yield) of orange powder.

^{1}H NMR (500 MHz, $CDCl_3$) δ, 8.27 (d, *J*=2.5 Hz, 4H), 7.95 (s, 2H), 7.48 (dd, *J*=10.5, 1.5 Hz, 8H), 7.45 (t, *J*=2.5 Hz, 2 H), 7.10 (td, *J*=10.5, 1.5 Hz, 8 H), 6.98 (td, *J*=10.5, 1.5 Hz, 8 H), 6.63 (dd, *J*=10.5, 1.5 Hz, 8 H), 1.70 (s, 24H).

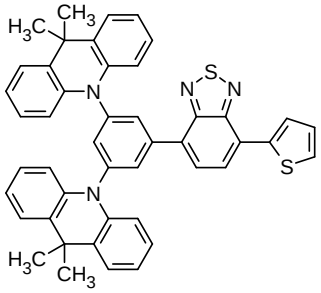
^{13}C NMR (125 MHz, $CDCl_3$) δ, 153.8, 144.2, 142.2, 140.8, 134.4, 132.5, 132.0, 130.4, 128.1, 126.7, 125.5, 121.1, 114.2, 36.2, 31.4.

IR (cm^{-1}): 3030, 2966, 2855, 1590, 1476, 1443, 1332, 1260, 744.

ESI: Calc. Mass for $C_{78}H_{64}N_6S_1$ 1116.4913, Found: 1116.4897



Scheme S4. Synthetic route to the compound **4** (i) $Pd_2(dba)_3$, Xantphos, *t*-BuONa, toluene, 80 °C, (ii) bis(pinacolato)diboron, AcOK, $PdCl_2(PPh_3)_2$, dioxane, 100 °C, (iii) 4-bromo-7-thieno-2,1,3-benzothiadiazole, $Pd(PPh_3)_4$, 2 M K_2CO_3, toluene, 100 °C.



Compound 4

Compound **10**, 0.545 g (0.88 mmol), 4-bromo-7-(thiophen-2-yl)benzo[c][1,2,5]thiadiazole 261.4 mg (0.88 mmol) $Pd(PPh_3)_4$ 101.7 mg (0.088 mmol) were dissolved in 8 ml of toluene, then 1.8 ml of 2 M K_2CO_3 aqueous solution and one drop of Aliquat were added. The mixture was heated at 100 °C for 48 h with vigorous stirring. After cooling to room temperature the reaction mixture was extracted with brine and dichloromethane. The organic phases were dried with Na_2SO_4. After evaporation of the solvents, the crude product was purified by chromatography on silica gel eluting with $CHCl_3$/hexanes (1:3) to give 0.16 g (0.226 mmol, 26% yield) of orange powder.

^{1}H NMR (500 MHz, $CDCl_3$) δ, 8.28 (d, *J*=2.5 Hz, 2H), 8.15 (dd, *J*=6.0 Hz, 1H), 7.94 (d, *J*=9.5 Hz, 1 H), 7.88 (d, *J*=9.5 Hz, 1 H), 7.50-7.48 (m, 5 H), 7.43 (t, *J*=2.5 Hz, 1 H), 7.09-7.08 (m,

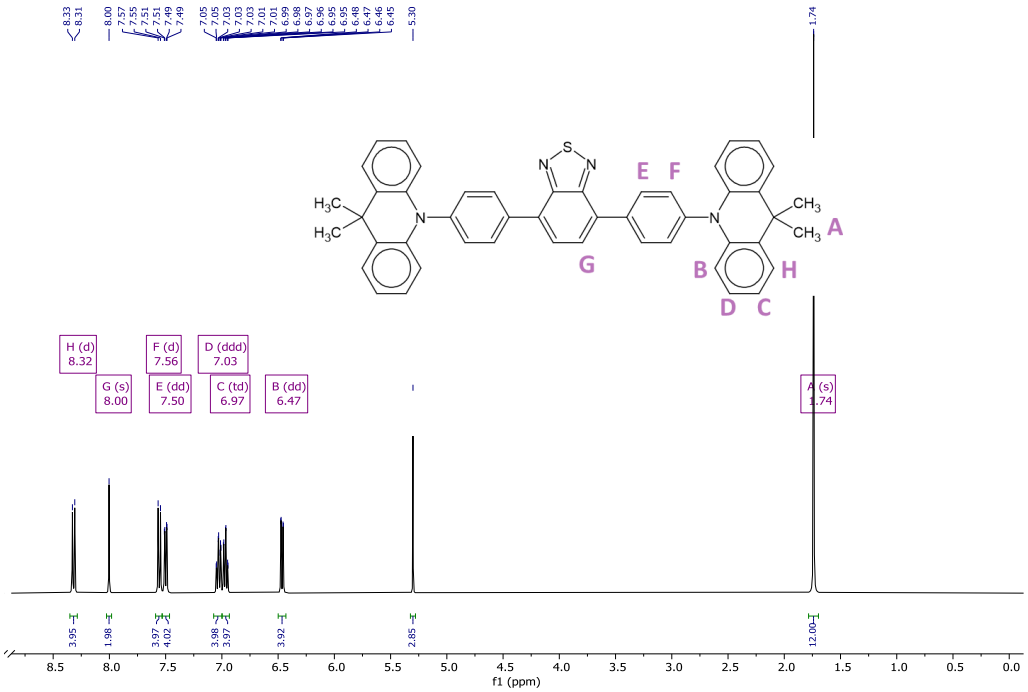
1H), 7.07 (td, *J*=10.5, 2.0 Hz, 4H), 6.98 (td, *J*=10.5, 2.0 Hz, 4H), 6.63 (dd, *J*=10.5, 2.0 Hz, 4 H), 1.70 (12 H).

^{13}C NMR (125 MHz, $CDCl_3$) δ, 153.6, 152.91, 144.2, 142.3, 140.8, 139.2, 134.1, 132.4, 130.4, 130.4, 128.4, 128.2, 128.1, 127.6, 127.4, 126.7, 125.6, 125.5, 36.2, 31.3.

IR (cm^{-1}): 3060, 2955, 2852, 1590, 1473, 1445, 1330, 1259, 834, 745.

ESI: Calc. Mass for $C_{46}H_{37}N_4S_2$ 709.2460, Found: 709.2458

2. NMR spectra



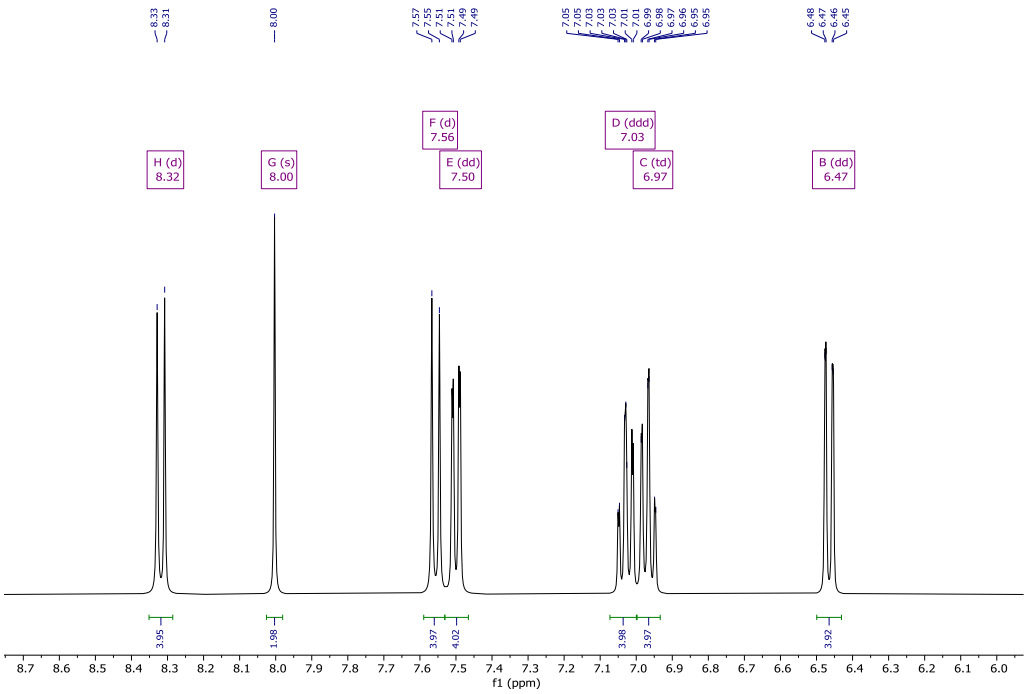


Fig. S1. ^{1}H NMR spectrum of the compound **1** in $CDCl_3$.

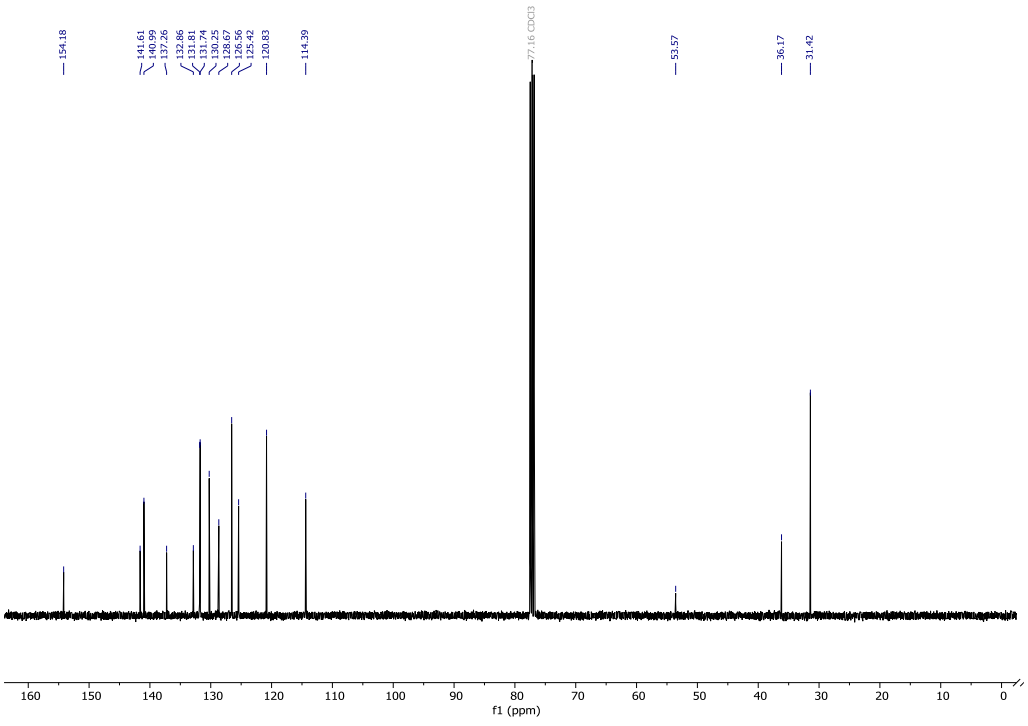


Fig. S2. ^{13}C NMR spectrum of the compound **1** in $CDCl_3$.

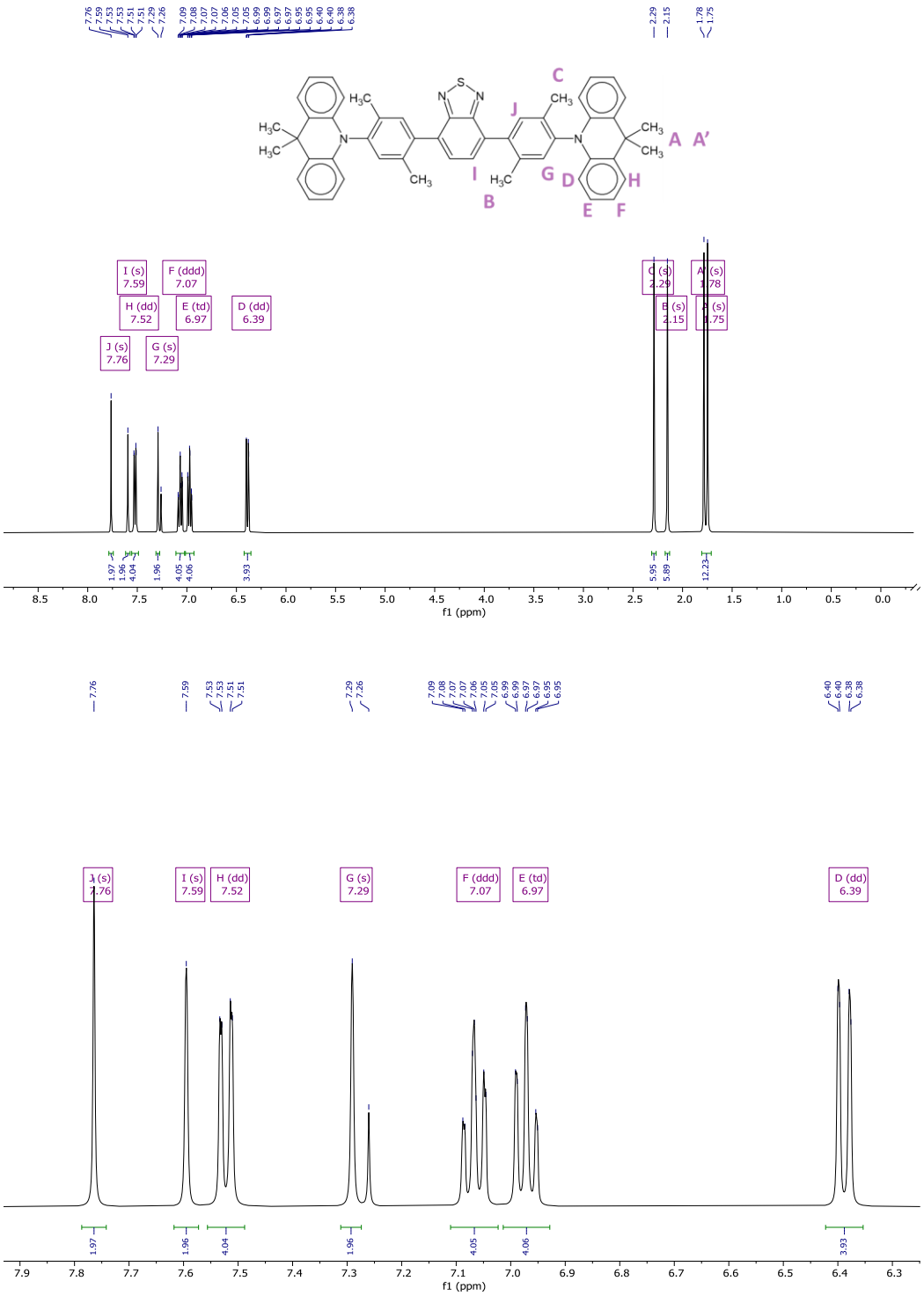


Fig. S3. ^{1}H NMR spectrum of the compound **2** in $CDCl_3$.

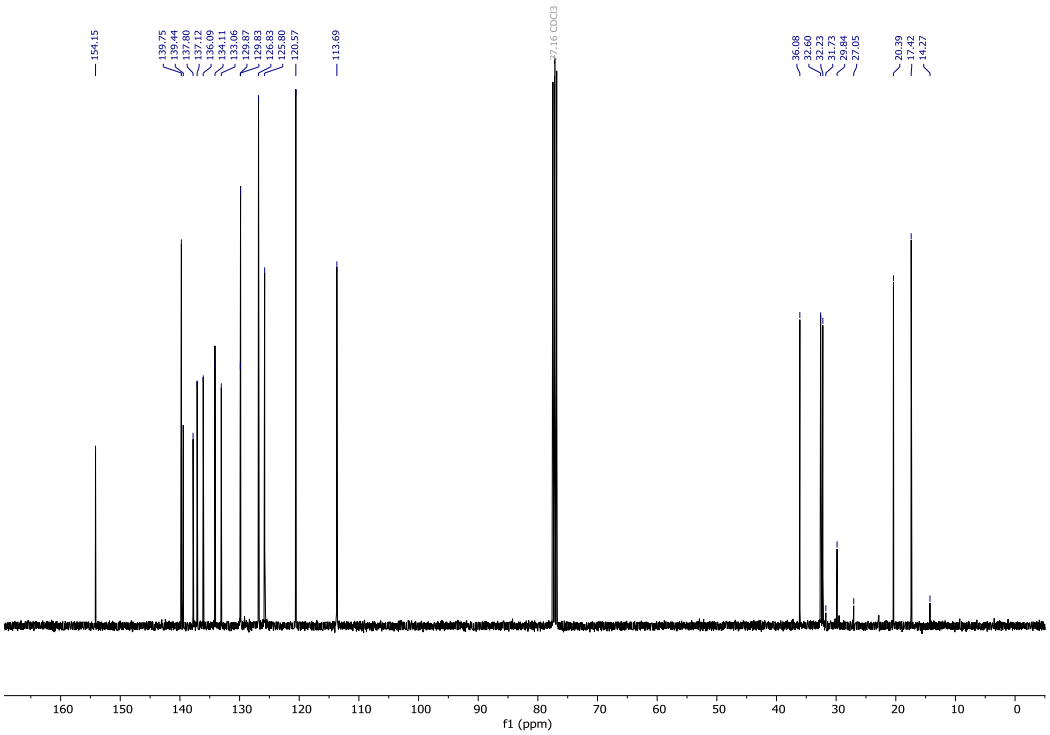


Fig. S4. ^{13}C NMR spectrum of the compound **2** in $CDCl_3$.

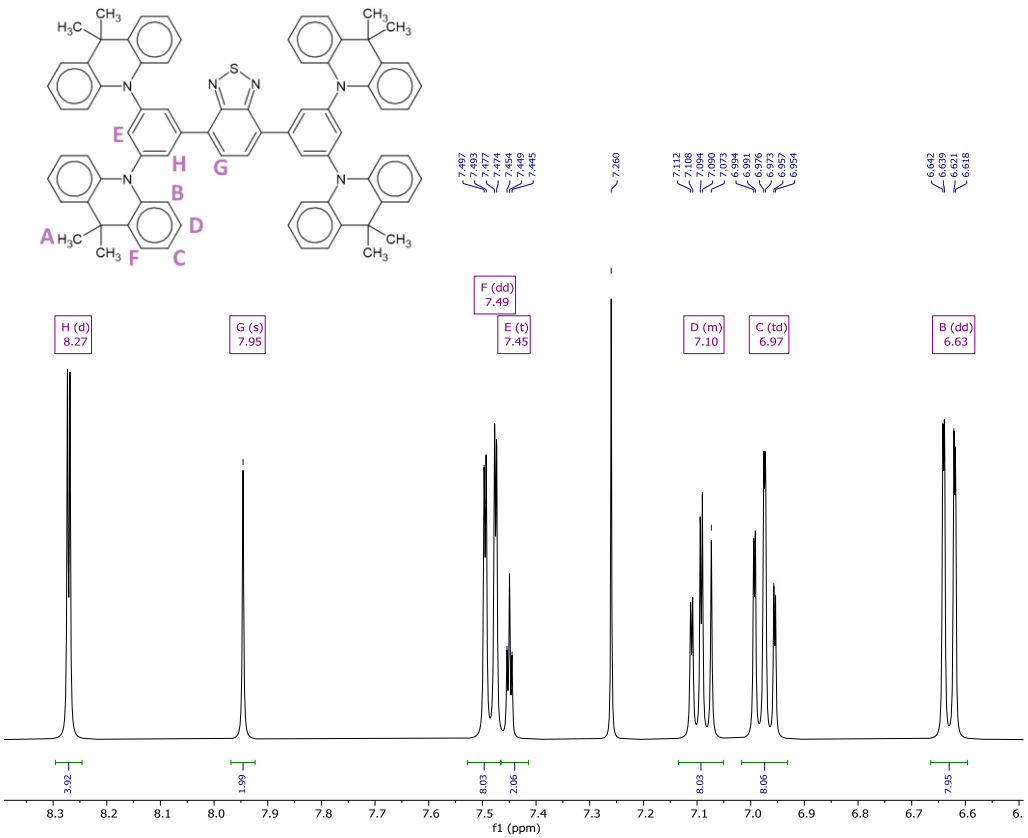


Fig. S5. ^{1}H NMR spectrum of the compound **3** in $CDCl_3$.

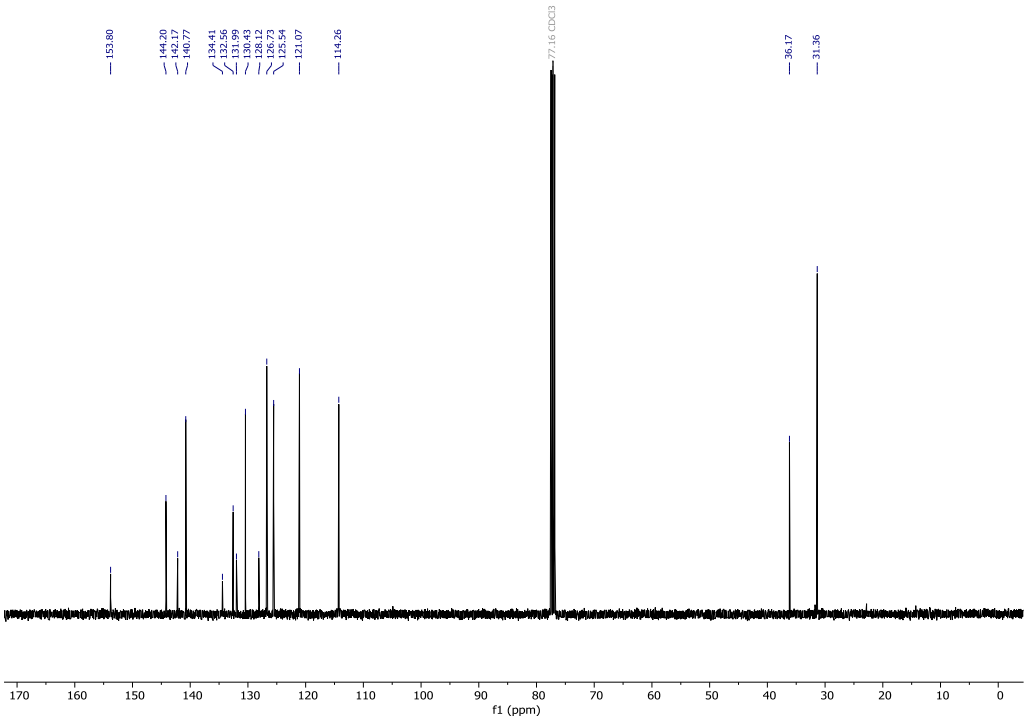


Fig. S6. ^{13}C NMR spectrum of the compound **3** in $CDCl_3$.

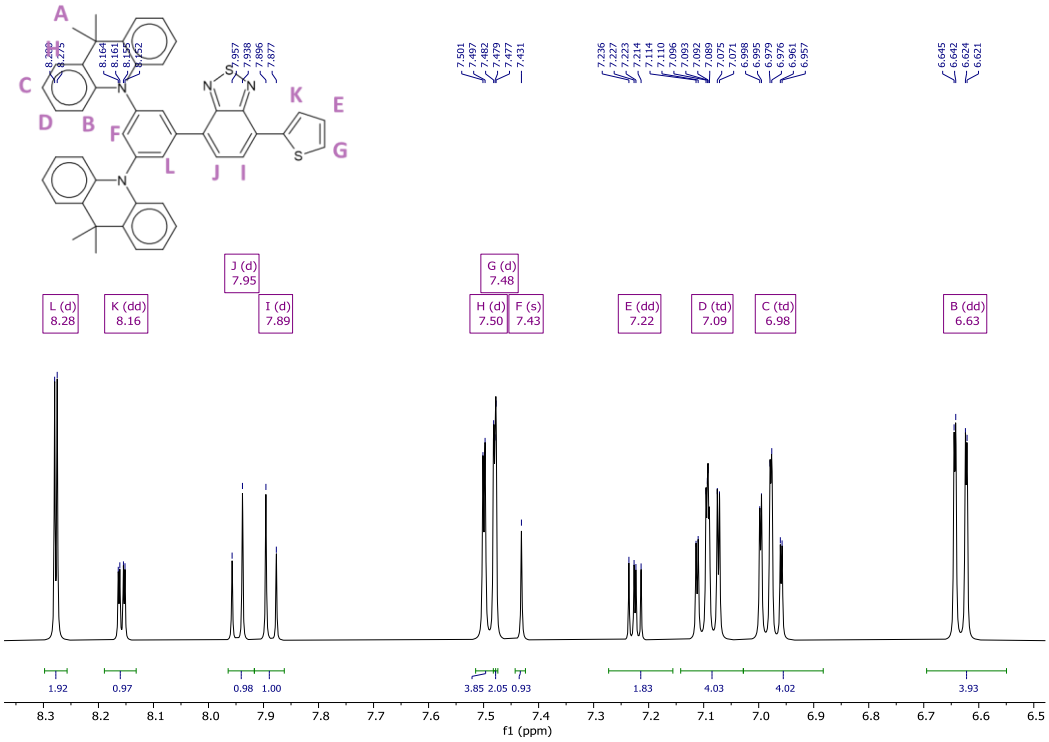


Fig. S7. ^{1}H NMR spectrum of the compound **4** in $CDCl_3$.

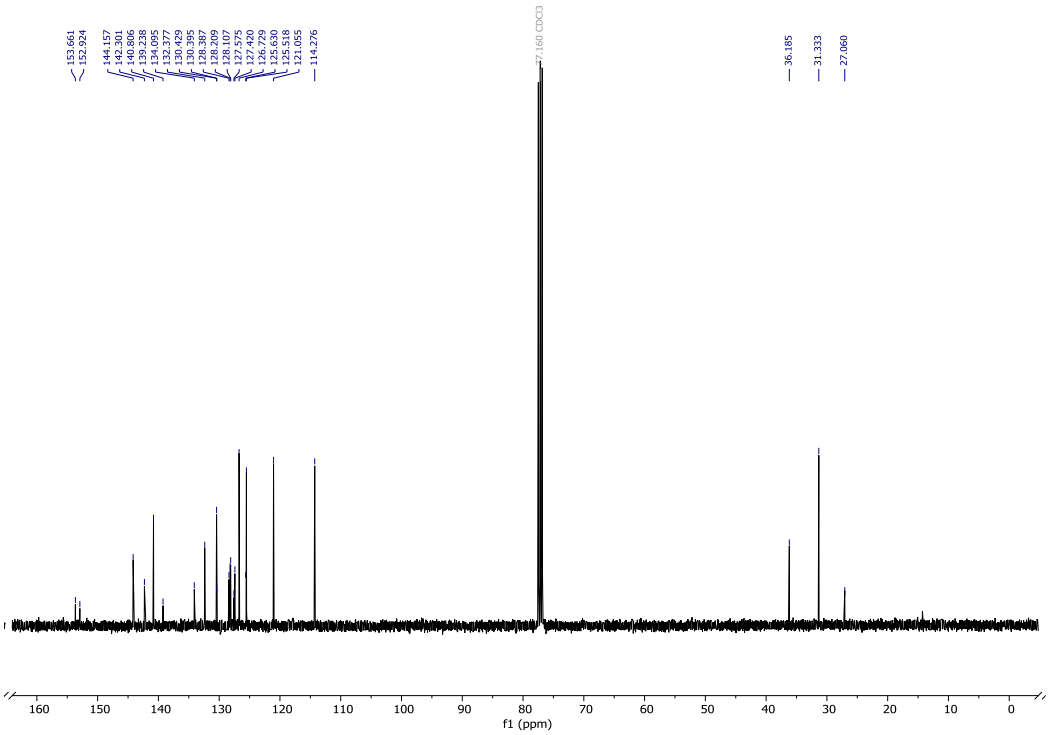
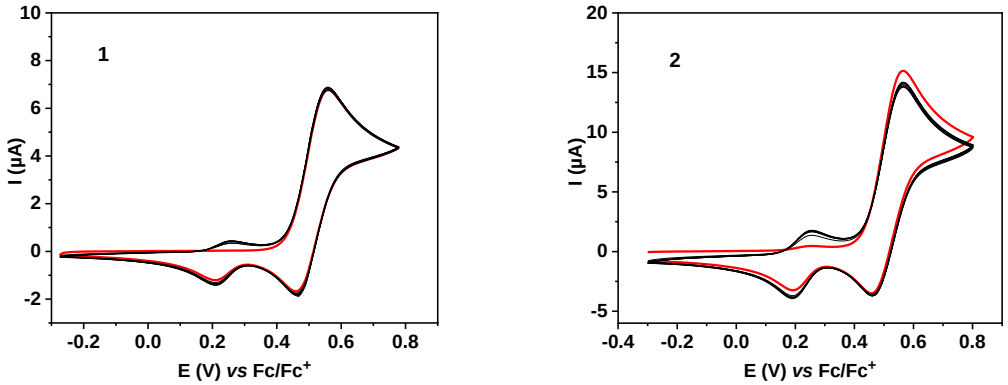


Fig. S8. ^{13}C NMR spectrum of the compound **4** in $CDCl_3$.

3. Electrochemical studies

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) experiments were performed in an one-compartment three-electrode electrochemical cell with a platinum disk (diameter = 2 mm) working electrode, platinum counter electrode, and an Ag/0.1 M $AgNO_3$ /CH_3 CN reference electrode, whose potential was verified at the end of each set of experiments using the ferrocene couple (Fc/Fc^+). The sample concentration was 1×10^{-3} M in an electrolyte consisting of 0.1 M Bu_4NPF_6 (for electrochemical analysis, Sigma-Aldrich) dissolved in anhydrous CH_2Cl_2 (Sigma−Aldrich). For all electrochemical experiments, Autolab PGSTAT 20 (Eco Chemie, Netherlands) was used.



A **B**

Fig. **S9**. 8 consecutive CV oxidation scans registered for **1** (A) and 10 consecutive CV oxidation scans registered for **2** (B). Red line – first oxidation scan. Working electrode: platinum disc; Compound concentration: 1×10^{-3} M; electrolyte: 0.1 M Bu_4NPF_6 solution in DCM; scan rate: 50 mV/s.

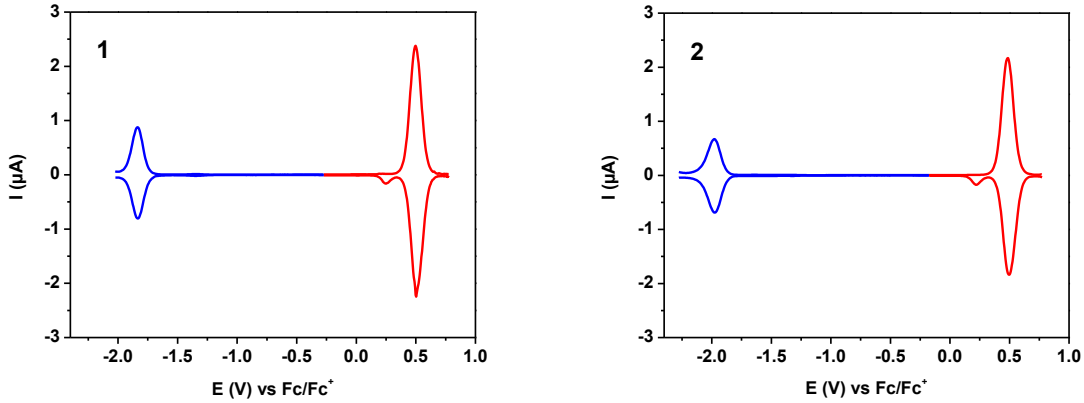


Fig. S10. Differential pulse voltammograms of **1** and **2** recorded on a Pt disk working electrode. Concentration of the studied compounds: 1×10^{-3} M; electrolyte: 0.1 M Bu_4NPF_6 solution in DCM; modulation time 50 ms, modulation amplitude 10 mV, step potential 5 mV.

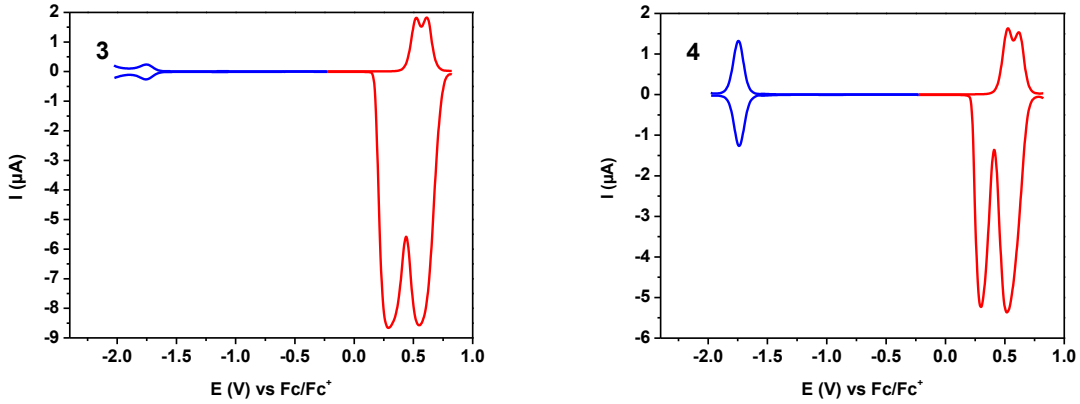


Fig. S11. Differential pulse voltammograms of **3** and **4** recorded on Pt disk working electrode. Concentration of the studied compounds: 1×10^{-3} M; electrolyte: 0.1 M Bu_4NPF_6 solution in DCM; modulation time 50 ms, modulation amplitude 10 mV, step potential 5 mV.

4. X-ray diffraction studies

Single crystal suitable for X-ray diffraction measurements was selected under a polarizing microscope and mounted on nylon loops using Paratone Oil. Diffraction data were collected using Rigaku Oxford Diffraction SuperNova diffractometer equipped with an EOS CCD detector, copper X-ray source (Cu Kα radiation, λ = 1.54184 A) and a low-temperature nitrogen open-gas-flow Oxford Cryosystems device (Oxford Cryostram 700 Series). Data collection and reduction were carried out using the CrysAlisPRO software suite [Rigaku Oxford Diffraction, CRYSALISPRO software system, Rigaku Corporation, Wrocław, Poland.]. The structure was solved using an intrinsic phasing method as implemented in the SHELXT program and refined by least squares minimizations using SHELXL. [1,2] Hydrogens were placed geometrically in the ideal positions. The C−H bond distances were set to 0.95 Å, 0.99 Å or 0.98 Å for $C_{ar}H$, CH_2 and CH_3 groups respectively. The riding model for the hydrogen thermal-motion parameters was applied (Uiso H = x · Ueq C where x = 1.2 for $C_{ar}H$ and CH_2 groups or x = 1.5 for CH_3 groups). [3] Crystal structure of **1** contained two slightly disordered solvent molecules. The disorder on one of the molecules was modelled. THF molecule adopted two conformations – envelope and twist – in 0.3320 : 0.6680 ratio (occupancies refined). Data collection as well as crystal structure refinement details are given in Table S1.

Table S1. Selected X-ray data collection, processing and refinement parameters.

Compound	**1**
Empirical formula	$C_{56}H_{54}N_4O_2S$

Formula weight	847.09
Temperature/K	100.0(1)
Crystal system	triclinic
Space group	P-1
a/Å	12.2872(3)
b/Å	12.8272(3)
c/Å	15.3688(3)
α/°	96.230(2)
β/°	91.199(2)
γ/°	114.121(2)
Volume/Å^3	2192.03(9)
Z	2
ρ_{calc}g/cm^3	1.283
μ/mm^{-1}	1.035
F(000)	900.0
Crystal size/mm^3	0.716 × 0.185 × 0.101
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.8 to 140.128
Index ranges	-14 ≤ h ≤ 14 -15 ≤ k ≤ 14 -18 ≤ l ≤ 18
Reflections collected	41253
Independent reflections	8288 [R_{int} = 0.0216, R_{sigma} = 0.0168]
Data/restraints/parameters	8288/37/595
Goodness-of-fit on F^2	1.021
Final R indexes [I>=2σ (I)]	R_1 = 0.0409, wR_2 = 0.1092
Final R indexes [all data]	R_1 = 0.0423, wR_2 = 0.1098
Largest diff. peak/hole / e Å^{-3}	0.84/-0.65

3. Quantum chemical calculations

Geometries of the molecules **1** - **4** were optimized using the hybrid Density Functional Theory (DFT) method with B3LYP functional augmented by the Grimme empirical dispersion correction with the Becke-Johnson damping (GD3BJ). The dispersion correction was proposed to be used to take into consideration intramolecular dispersion forces acting between conjugated molecular moieties. The quantum chemical calculations were performed using the Gaussian 16 program package applying the 6-311++G(d,p) basis set. Geometries of the molecules 1 - 4 were optimized searching for their total energy minimum in a vacuum as well as in dichloromethane (DCM) as solvent using the Berny algorithm based on the eigenvalue-following method

augmented by Hessian techniques. The obtained equilibrium structures were checked by the normal mode analysis and no imaginary frequencies were found. The minimum of the potential energy surface was calculated at a restricted Hartree-Fock (RHF) level in C1 symmetry. The RMS force criterion was chosen as 10^{-4} Hartrees/Bohr. The SCF convergence criterion was equal to 10^{-8} Hartrees. The solvation effect was calculated by applying the polarizable continuum model (PCM) implemented in the Gaussian 16 package. The structural properties of the molecules **1** - **4** are presented in Table S2, namely the dihedral angles between the phenylene linker and the benzothiadiazole moiety for neutral molecules in vacuum and in DCM solvent as well as for cations and anions of these molecules with geometry optimized in DCM are discussed.

Table S2. Dihedral angles between the phenylene linker and the benzothiadiazole moiety for neutral molecules **1** - **4** with geometry optimized in vacuum and DCM as well as for cations and anions of these molecules with geometry optimized in DCM

	In vacuum	In DCM		
	neutral	neutral	cation	anion
1	37	39	40	26
	37	39	40	26
2	-59	-61	-61	-56
	59	60	60	56
3	39	38	37	25
	-39	-38	-37	-25
4	-35	-37	-36	-24
	6	14	13	0.2

The most stable geometry was calculated for molecule **4**. In vacuum its total energy per atom (E_{tot}/atom) is equal to -31.7131 Hartrees (see Table S3). The DCM generally stabilizes all investigated molecules lowering their E_{tot}/atom. However, the observed changes are insignificant.

Table S3. Total energy per atom calculated for the molecules **1** - **4**.

Molecule	In vacuum	In DCM	In vacuum	In DCM
	E_{tot} [Hartrees]	E_{tot} [Hartrees]	E_{tot}/atom [Hartrees]	E_{tot}/atom [Hartrees]
1	-2469.9857	-2469.9987	-27.1427	-27.1428
2	-2627.3238	-2627.3361	-25.5080	-25.5081
3	-3738.8431	-3738.8621	-25.0929	-25.0930
4	-2790.7495	-2790.7620	-31.7131	-31.7132

Electron and optical properties of the **1 - 4** molecules were computed quantum chemically for structures optimized in vacuum as well as in DCM. Calculations were carried out in Gaussian 16 by applying the DFT/B3LYP-GD3BJ/6-311++G(d,p) method at the ground state molecular geometries. The optical properties were determined using the time-dependent DFT (TDDFT) formalism. The SCF convergence criterion was chosen as 10^{-12} Hartrees in convergence on the RMS density matrix and 10^{-8} Hartrees in convergence in energy change. Vertical and adiabatic ionization potentials and electron affinities were evaluated from the differences in the total energies of the neutral molecules and respective radicals. In Table S4 the electron properties of the **1-4** molecules with geometries optimized in vacuum are presented.

Table S4. Electron parameters calculated in vacuum for **1 - 4** molecules with geometries optimized also in the vacuum by using the DFT/B3LYP-GD3BJ/6-311++G(d,p) method.

molecule	Geometry optimized in vacuum, electron parameters calculated in a vacuum			
	HOMO (eV)	LUMO (eV)	$\Delta E_{HOMO-LUMO}$ (eV)	μ (D)
1	-5.38	-2.99	2.39	1.11
2	-5.21	-2.88	2.33	1.05
3	-5.40	-3.09	2.31	1.20
4	-5.36	-3.04	2.32	2.00

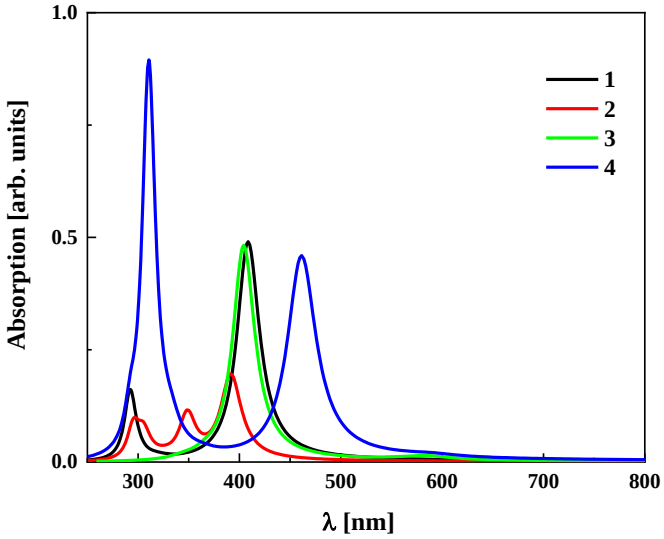
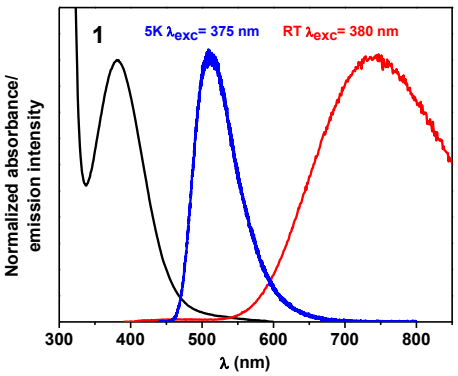


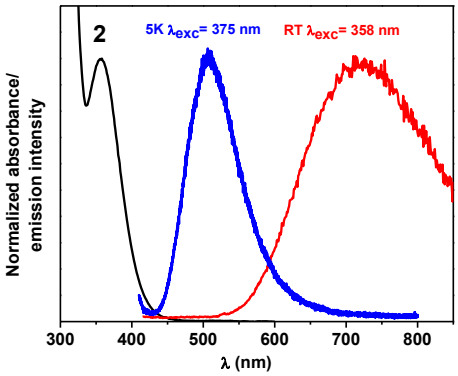
Fig. S12. UV-vis absorption spectra calculated in DCM for molecules with geometries optimized in DCM.

Optical Studies

Absorption spectra at room temperature were measured on a Perkin-Elmer Lambda 35 spectrophotometer. Emission spectra and fluorescence lifetimes at room temperature were collected on a Horiba Fluorolog 3 fluorimeter. Excitation for fluorescence lifetimes measurements was provided by Delta Diode 336 nm. The photoluminescence quantum yields were determined in diluted solutions by comparison with a known standard *i.e.* Coumarin 153 in EtOH (PLQY = 0.38). PLQYs of powders were determined using integrating sphere.

Solutions of the compounds diluted in toluene (T) and in dichloromethane (DCM) were first frozen in liquid nitrogen (77 K) and next inserted into a liquid helium cryostat, which temperature could be stabilized at any value between 5 and 300 K. Fluorescence and phosphorescence spectra at low temperatures (5 - 175 K) were detected using a Parker-type disc-chopper phosphorimeter. Emission spectra were collected at right angle and dispersed using a McPherson 207 monochromator and detected with an EMI9659 photomultiplier operating in photons counting mode. Transients were accumulated with the aid of a Stanford Research SR430 multi-channel scaler.





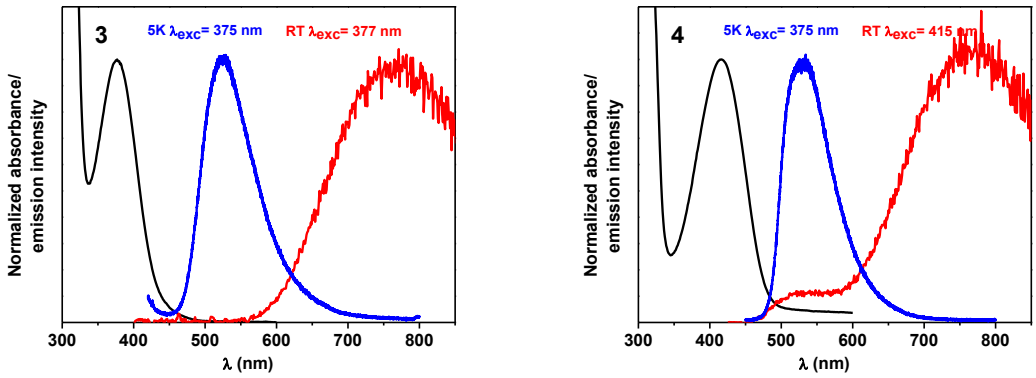


Fig. S13. Absorption (black) and fluorescence spectra of the compounds **1** - **4** in DCM at room temperature (red) and fluorescence at 5 K (blue).

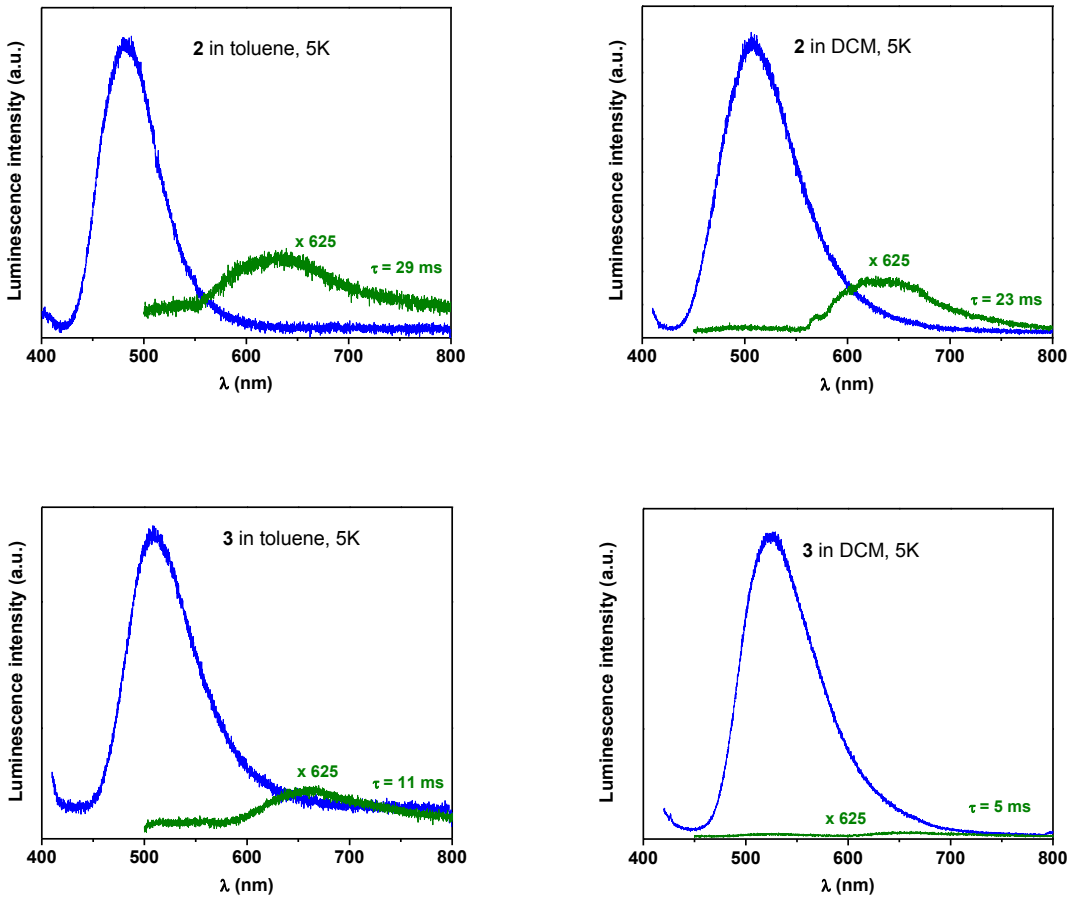


Fig. S14. Fluorescence (blue) and phosphorescence (green) spectra of the compounds **2** and **3** in toluene and DCM at 5 K.

1. Sheldrick, G. M. SHELXT, Integrated Space-Group and Crystal-Structure Determination. Acta Crystallogr. Sect. A 2015, 71 (1), 3–8. https://doi.org/10.1107/S2053273314026370.
2. Sheldrick, G. M. Crystal Structure Refinement with SHELXL. Acta Crystallogr. Sect. C 2015, 71 (1), 3–8. https://doi.org/10.1107/S2053229614024218].
3. crystallographic data deposition number: 2360338