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Electronic Supplementary Information for:

Folding-induced exciton coupling in homo- and heterodimers of merocyanine dyes

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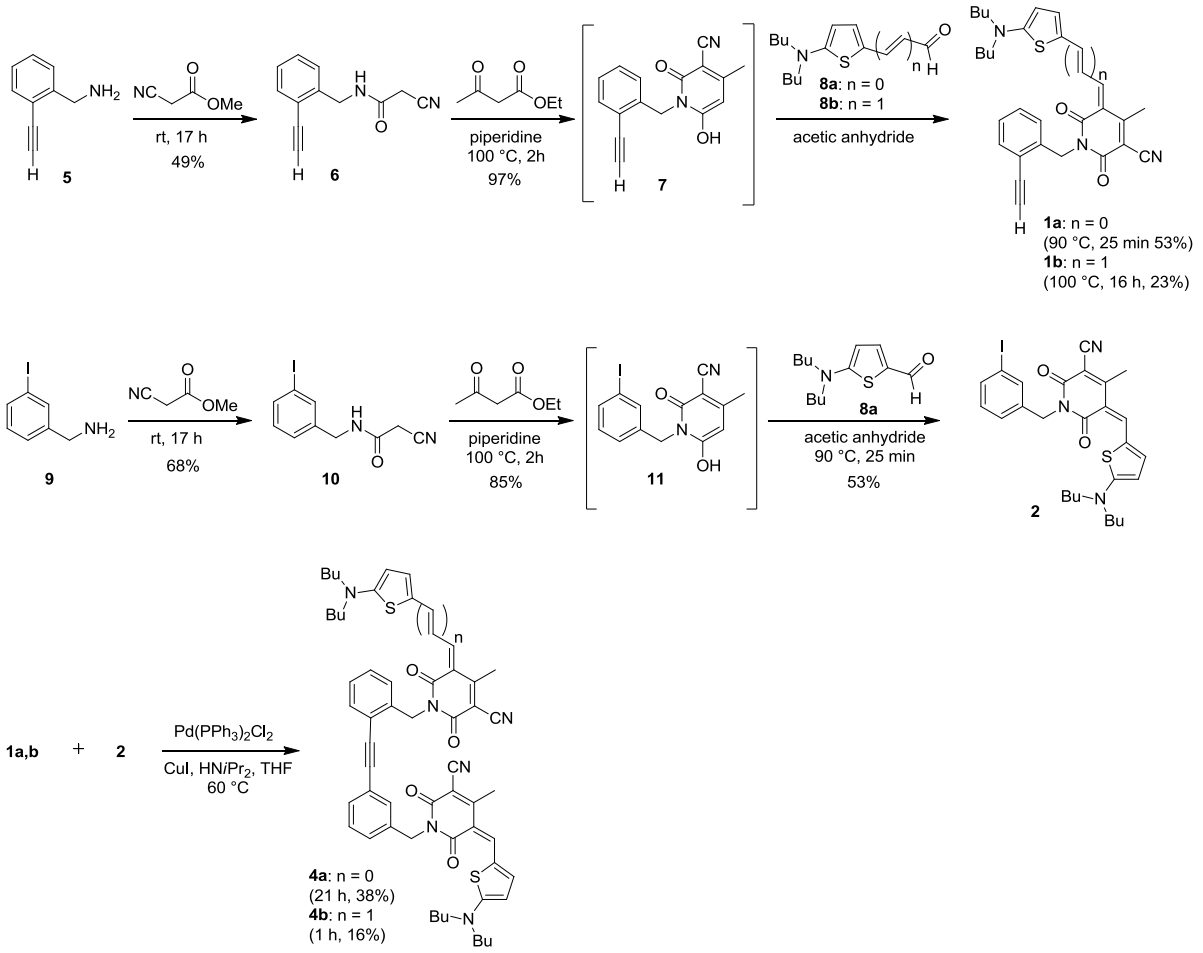
1. Materials and methods

All solvents and reagents were purchased from commercial sources and used as received without further purification. Column chromatography was performed using silica gel 60M (0.04-0.063 mm). NMR spectra were recorded on an Advance 400 or Advance DMX 600 spectrometer at 295 K, unless otherwise stated. The spectra were calibrated to the residual solvent peak and the chemical shifts δ are in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, dd = doublet of doublet, td = triplet of doublet, m = multiplet, br = broad. High-resolution mass spectra (ESI) were recorded on an ESI MicrOTOF Focus spectrometer. Melting points were determined on Olympus BX41 optical microscope with heating stage and are uncorrected. Solvents for spectroscopic studies were of spectroscopic grade and used as received. UV/Vis spectra were measured on a Lambda 950 or 40P spectrometer at 298 K in conventional quartz cell cuvettes with path lengths of 1–20 mm. For concentration-dependent studies freshly prepared stock solutions were subsequently diluted to adjust the desired concentration.

2. Synthetic procedures and product characterization data



Scheme S1 Synthetic route to bis(merocyanine) dyes **4a,b**.

Synthesis of mono(merocyanine) precursors **1a,b** and **2** were performed according to the route depicted in Scheme S1. The respective amines **5** and **9** were reacted with methyl cyanoacetate to afford cyanoacetamides **6** and **10**, respectively. While amine **9** is commercially available, compound **5** was prepared according to literature known procedures.[1] The hydroxypyridone intermediates **7** and **11** were synthesized by reacting the respective cyanoacetamide with ethyl acetoacetate in piperidine and subjected to a Knoevenagel condensation with aminothiophene aldehyde **8a,b**, which were prepared according to literature,[2] in acetic anhydride to give the desired mono(merocyanine) dyes **1a,b** and **2**. Finally, the target bis(merocyanine) dyes **4a** and **4b** were obtained *via* Sonogashira coupling of **2** with the respective acetylene compound **1a**,**b** under palladium catalysis in the presence of copper iodide and diisopropylamine in THF.

2-Cyano-*N*-(2-ethynylbenzyl)acetamide (6): (2-Ethynylphenyl)methanamine (636 mg, 4.85 mmol) was stirred with methyl cyanoacetate (470 µL, 5.33 mmol, 528 mg) at room temperature for 17 h. The solid was suspended in cold diethyl ether and collected by filtration to

give **6** (471 mg, 2.38 mmol, 49%) as a white solid. Mp 128 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, ^{3}J = 7.3 Hz, 1H), 7.36–7.27 (m, 3H), 6.68 (br. s, 1H), 4.63 (d, ^{3}J = 6.0 Hz, 2H), 3.40 (s, 1H), 3.38 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 160.7, 139.3, 133.4, 129.6, 129.1, 128.2, 121.6, 114.7, 82.7, 81.4, 43.2, 26.0 . HRMS (ESI, positive mode, acetonitrile/chloroform 1:1): *m/z* found 199.08639 $[M+H]^+$, calculated for $C_{12}H_{11}N_2O^+$ 199.08267.

1-(2-Ethynylbenzyl)-6-hydroxy-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (7): Cyanoacetamide **6** (450 mg, 2.27 mmol) was suspended in piperidine (4.5 mL) and ethyl acetoacetate (1.72 mL, 13.6 mmol, 1.77 g) was added to the suspension. The mixture was heated to 100 °C for 2 h and then concentrated HCl was added until pH 1 was reached. After the addition of water (20 mL), the solid was collected by filtration and washed with water and diethyl ether. Drying in vacuo afforded the hydroxyl pyridine intermediate **7** as a pale grey solid (583 mg, 2.20 mmol, 97%), which was used without further purification.

(*Z*)-5-{[5-(dibutylamino)thiophene-2-yl]methylene}-1-(2-ethynylbenzyl)-4-methyl-2,6-dioxo-1,2,5,6-tetrahydropyridine-3-carbonitrile (1a): A suspension of hydroxyl pyridine **7** (583 mg, 2.20 mmol) and 5-(dibutylamino)thiophene-2-carbaldehyde (528 mg, 2.20 mmol) in acetic anhydride (12 mL) was stirred for 25 min at 90 °C. The mixture was cooled down to room temperature, methanol (20 mL) was added and the resulting solution was concentrated in vacuo. The crude product was purified by column chromatography (silica gel, CH_2Cl_2/MeOH 99.1:0.9) to give merocyanine dye **1a** (567 mg, 1.17 mmol, 53%) as a purple solid. Mp 263 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (s, 1H), 7.54 (d, ^{3}J = 5.2 Hz, 1H), 7.47 (dd, ^{3}J = 7.5 Hz, ^{4}J = 1.3 Hz, 1H), 7.21 (td, ^{3}J = 7.5 Hz, ^{4}J = 1.4 Hz, 1H), 7.14 (td, ^{3}J = 7.5 Hz, ^{4}J = 1.4 Hz, 1H), 6.96 (dd, ^{3}J = 7.8 Hz, ^{4}J = 0.9 Hz, 1H), 6.35 (d, ^{3}J = 5.1 Hz, 1H), 5.42 (s, 2H), 3.49 (t, ^{3}J = 7.6 Hz, 4H), 3.36 (s, 1H), 2.55 (s, 3H), 1.74–1.66 (m, 4H), 1.44–1.35 (m, 4H), 0.97 (t, ^{3}J = 7.3 Hz, 6H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 176.8, 163.7, 162.6, 159.0, 153.0, 142.3, 140.3, 133.1, 129.3, 126.9, 125.2, 125.0, 120.8, 117.7, 111.7, 106.9, 94.5, 83.0, 81.6, 42.1, 29.6, 20.5, 19.2, 13.9. HRMS (ESI, positive mode, acetonitrile/chloroform 1:1): *m/z* found 485.21280 $[M]^+$, calculated for $C_{29}H_{31}N_3O_2S^+$ 485.21370. Elemental analysis (calcd., found for $C_{29}H_{31}N_3O_2S$): C (71.72, 71.69), H (6.43, 6.96), N (8.65, 8.65), S (6.60, 6.43). UV/Vis (CH_2Cl_2): λ / nm (ε / M^{-1} cm^{-1}) = 539 (152300).

(*Z*)-5-{(E)-3-[5-(dibutylamino)thiophene-2-yl]allylidene}-1-(2-ethynylbenzyl)-4-methyl-2,6-dioxo-1,2,5,6-tetrahydropyridine-3-carbonitrile (1b): A suspension of hydroxyl pyri-

dine **7** (445 mg, 1.68 mmol) and aminothiophene aldehyde **8b** (406 mg, 1.53 mmol) in acetic anhydride (5 mL) was stirred for 16 h at 100 °C. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel, CH_2Cl_2/ethyl acetate 10:1) to give merocyanine dye **1b** (180 mg, 352 μmol, 23%) as a green solid. Mp 195 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.00 (br, 1H), 7.57–7.34 (m, 4H), 7.29–7.16 (m, 2H), 6.89 (m, 1H), 6.25 (d, ^3J = 4.8 Hz, 4H), 5.33 (s, 2H, overlapped with solvent signal), 3.48 (s, 1H), 3.46 (t, ^3J = 7.8 Hz, 1H), 2.51 (s, 3H), 1.78–1.63 (m, 4H), 1.43–1.33 (m, 4H), 0.96 (t, ^3J = 7.3 Hz, 6H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 171.8, 163.6, 162.6, 158.4, 152.1, 149.6, 145.2, 140.6, 133.1, 129.4, 127.5, 126.8, 125.1, 120.6, 118.8, 117.7, 111.5, 110.6, 94.8, 83.0, 81.5, 55.1, 42.0, 29.5, 20.5, 19.0, 13.9. HRMS (ESI, positive mode, acetonitrile/chloroform 1:1): *m/z* found 511.22872 $[M]^+$, calculated for $C_{31}H_{33}N_3O_2S^+$ 511.22880. UV/Vis (CH_2Cl_2): λ / nm (ε / M^{-1} cm^{-1}) = 656 (223000).

2-Cyano-*N*-(3-iodobenzyl)acetamide (10): 3-Iodobenzylamine (450 μL, 3.38 mmol, 787 mg) and methyl cyanoacetate (330 μL, 3.71 mmol, 368 mg) were stirred for 17 h at room temperature. The solid was suspended in cold diethyl ether and collected by filtration to give **10** (685 mg, 2.28 mmol, 68%) as a white solid. Mp 122 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66–7.64 (m, 2H), 7.26 (d, ^3J = 7.6 Hz, 1H, overlapped with solvent signal), 7.09 (td, ^3J = 7.8 Hz, ^4J = 0.8 Hz, 1H), 6.36 (br. s, 1H), 4.42 (d, ^3J = 5.9 Hz, 2H), 3.42 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6): δ = 162.4, 141.3, 135.9, 135.8, 130.6, 126.9, 116.2, 94.9, 42.0, 25.4. HRMS (EI): *m/z* found 299.97485 $[M]^+$, calculated for $C_{12}H_{10}N_2O^+$ 299.97541.

6-Hydroxy-1-(3-iodobenzyl)-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (11): Cyanoacetamide **10** (1.06 g, 3.53 mmol) was suspended in piperidine (6 mL) and ethyl acetoacetate (890 μL, 7.06 mmol, 919 mg) was added to the suspension. The mixture was heated to 100 °C for 2 h and then concentrated HCl was added until pH 1 was reached. After addition of water (20 mL) the solid was collected by filtration and washed with water and diethyl ether. Drying in vacuo afforded the hydroxyl pyridine intermediate **11** as a pale grey solid (1.10 g, 3.00 mmol, 85%) which was used without further purification.

(*Z*)-5-{[5-(Dibutylamino)thiophene-2-yl]methylene}-1-(3-iodobenzyl)-4-methyl-2,6-dioxo-1,2,5,6-tetrahydropyridine-3-carbonitrile (2): A suspension of hydroxy pyridine **11** (1.10 g, 3.00 mmol) and 5-(dibutylamino)thiophene-2-carbaldehyde (791 mg, 3.30 mmol) in acetic anhydride (4 mL) was stirred for 25 min at 90 °C. The mixture was cooled down to

room temperature, methanol (20 mL) was added and the resulting solution was concentrated in vacuo. The crude product was purified by column chromatography (silica gel, CH_2Cl_2/MeOH 99.1:0.9) to give merocyanine dye **2** (937 mg, 1.60 mmol, 53%) as a purple solid. Mp 216 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.79 (m, 1H), 7.58–7.55 (m, 3H), 7.40 (d, ^3J = 8.0 Hz, 1H), 7.04 (m, 1H), 6.42 (d, ^3J = 8.0 Hz, 1H), 5.09 (s, 2H), 3.55 (t, ^3J = 8.0 Hz, 4H), 2.49 (s, 3H), 1.78–1.70 (m, 4H), 1.47–1.38 (m, 4H), 1.00 (t, ^3J = 8.0 Hz, 6H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 176.8, 163.5, 162.5, 158.8, 152.9, 142.2, 140.9, 137.9, 130.4, 130.3, 128.4, 125.0, 117.7, 111.7, 106.9, 94.3, 42.5, 29.7, 20.5, 19.1, 14.0. HRMS (ESI, positive mode, acetonitrile/chloroform 1:1): *m/z* found 587.10948 $[M]^+$, calculated for $C_{27}H_{30}IN_3O_2S^+$ 587.11034. Elemental analysis (calcd., found for $C_{27}H_{30}IN_3O_2S$): C (55.20, 55.12), H (5.15, 5.54), N (7.15, 7.21), S (5.46, 5.30). UV/Vis (CH_2Cl_2): λ / nm (ε / M^{-1} cm^{-1}) = 540 (146100).

Bis(merocyanine) 4a. Merocyanine **2** (181 mg, 309 μmol), bis(triphenylphosphine)-palladium(II) dichloride (4.33 mg, 6.18 μmol) and copper(I) iodide (1.18 mg, 6.18 μmol) were suspended in diisopropylamine (20 mL) and THF (60 mL) and the mixture was degassed by applying the freeze-pump-thaw method. A degassed solution of merocyanine **1a** (100 mg, 206 μmol) in THF (40 mL) was added dropwise under nitrogen atmosphere. After stirring for 21 h at 60 °C, the solvent was removed in vacuo and the crude product was purified by column chromatography (silica, $CHCl_3$/MeOH 99.8:0.2) to give **4a** as a purple solid (74.1 mg, 78.4 μmol, 38%). Mp 202 °C. ^{1}H NMR (600 MHz, DMF-d_7): δ = 8.11 (d, ^3J = 5.4 Hz, 1H), 8.08 (d, ^3J = 5.4 Hz, 1H), 8.01 (s, 1H), 7.95 (s, 1H), 7.77 (s, 1H), 7.53 (m, 2H), 7.44–7.37 (m, 2H), 7.34–7.25 (m, 2H), 7.10 (m, 1H), 6.89 (d, ^3J = 5.3 Hz, 1H), 6.88 (d, ^3J = 5.3 Hz, 1H), 5.40 (s, 2H), 5.16 (s, 2H), 3.69 (br, 4H), 3.50 (br, 4H, overlapped with solvent signal), 2.58 (s, 3H), 2.48 (s, 3H), 1.81–1.71 (m, 4H), 1.71–1.60 (br, 4H), 1.45–1.36 (m, 4H), 1.36–1.22 (br, 4H), 0.96 (t, ^3J = 7.4 Hz, 6H), 0.89 (br, 6H). ^{13}C NMR (101 MHz, DMF-d_7): δ = 177.6, 177.4, 163.5, 163.1, 159.3, 154.4, 154.3, 142.3, 142.2, 140.2, 139.3, 132.1, 131.5, 130.1, 129.1, 128.9, 128.7, 127.2, 126.3, 125.6, 125.4, 123.4, 122.0, 118.1, 118.0, 113.4, 113.1, 106.2, 106.1, 94.8, 92.6, 92.4, 87.7, 42.5, 41.4, 20.1, 20.0, 18.7, 18.6, 13.6. HRMS (ESI, positive mode, acetonitrile/chloroform 1:1): *m/z* found 945.41916 $[M+H]^+$, calculated for $C_{56}H_{61}N_6O_4S_2^+$ 945.41510. UV/Vis (CH_2Cl_2): λ / nm (ε / M^{-1} cm^{-1}) = 505 (125200), 538 (189800).

Bis(merocyanine) 4b. Merocyanine **2** (150 mg, 256 μmol), bis(triphenylphosphine)-palladium(II) dichloride (3.70 mg, 5.29 μmol) and copper(I) iodide (1.01 mg, 5.26 μmol) were suspended in diisopropylamine (20 mL) and THF (60 mL) and the mixture was degassed by applying the freeze-pump-thaw method. A degassed solution of compound **1b** (87.4 mg, 171 μmol) in THF (40 mL) was added dropwise under nitrogen atmosphere. After stirring for 1h at 60 °C, the solvent was removed in vacuo and the crude product was then purified by column chromatography (silica, CH_2Cl_2/ethyl acetate 10:1) to give **4b** as dark green solid (26.6 mg, 27.4 μmol, 16%). Mp 157 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.00 (br, 1H), 7.60 (m, 1H), 7.57 (s, 1H), 7.56–7.51 (m, 2H), 7.46 (m, 2H), 7.43 (m, 1H), 7.40–7.36 (m, 2H), 7.29 (m, 1H), 7.25–7.18 (m, 2H), 6.93 (m, 1H), 6.41 (d, ^3J = 5.2 Hz, 1H), 6.24 (d, ^3J = 4.7 Hz, 1H), 5.36 (s, 2H), 5.17 (s, 2H), 3.53 (t, ^3J = 7.8 Hz, 4H), 3.44 (t, ^3J = 7.8 Hz, 4H), 2.48 (s, 3H), 2.47 (s, 3H), 1.75–1.63 (m, 8H), 1.44–1.32 (m, 8H), 0.99–0.93 (m, 12H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 176.7, 172.0, 163.6, 163.4, 162.63, 162.61, 158.8, 158.2, 152.7, 151.7, 149.4, 145.2, 142.1, 139.9, 138.8, 132.5, 131.4, 130.7, 128.80, 128.77, 128.6, 127.7, 126.8, 125.4, 125.0, 123.6, 121.7, 118.9, 117.9, 117.8, 111.7, 111.5, 110.7, 107.0, 95.2, 94.6, 94.3, 87.4, 55.1, 42.8, 42.2, 29.5, 20.5, 19.1, 19.0, 13.9. HRMS (ESI, positive mode, acetonitrile/chloroform 1:1): *m/z* found 971.43384 $[M+H]^+$, calculated for $C_{58}H_{63}N_6O_4S_2^+$ 971.43467. UV/Vis (CH_2Cl_2): λ / nm (ε / M^{-1} cm^{-1}) = 540 (151000), 657 (192000).

3. UV/Vis spectroscopy

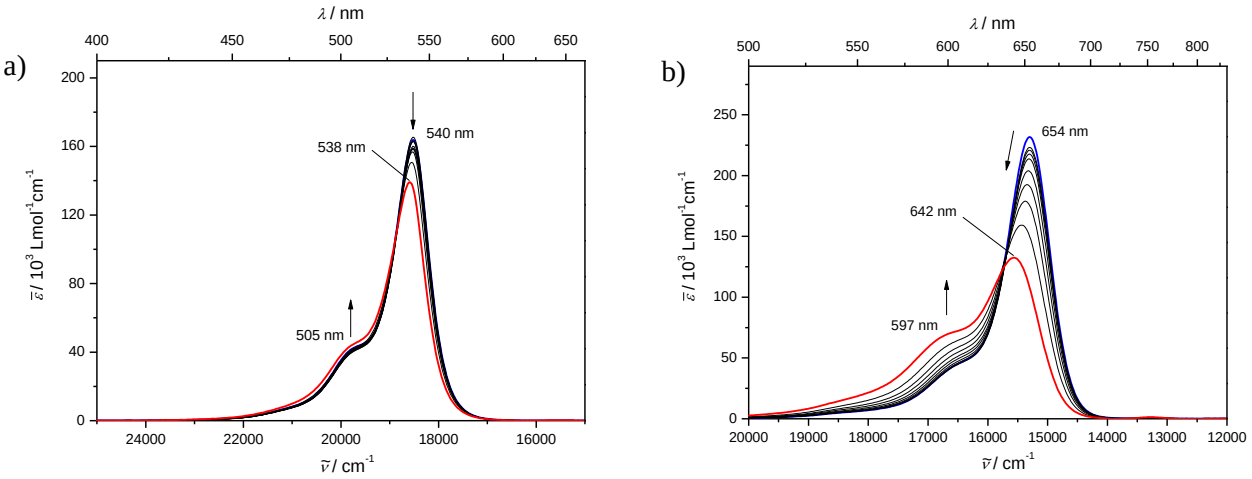


Fig. S1 Solvent-dependent UV/Vis spectra of merocyanine dyes (a) **3a** and (b) **3b** in dichloromethane/methylcyclohexane mixtures (c = 4 x 10^{-6} M) starting in pure dichloromethane (blue line) and successively increasing the volume fraction of methylcyclohexane in steps of 10 vol% up to 90 vol% (red line). The arrows indicate the spectral changes upon increasing the volume fraction of methylcyclohexane.

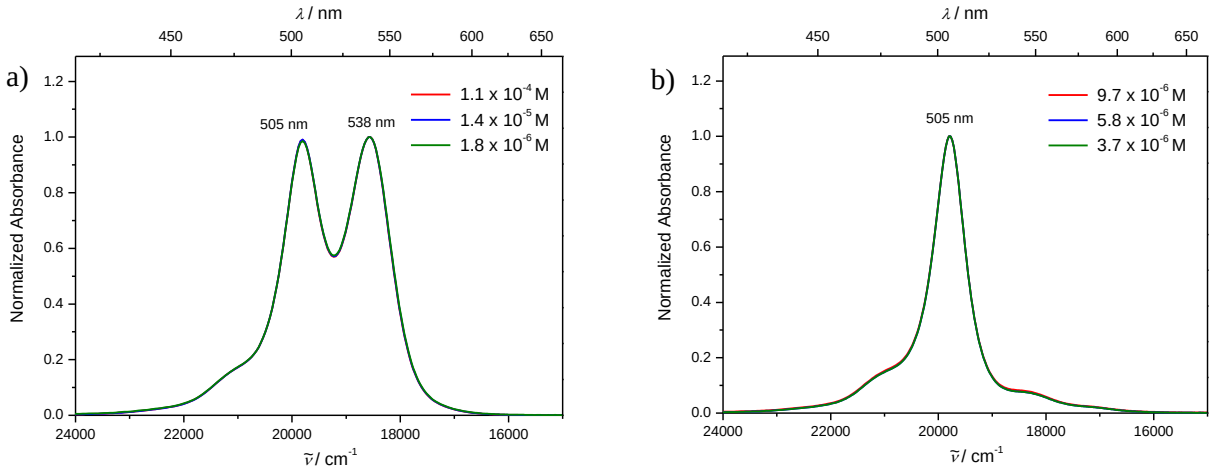


Fig. S2 Normalized UV/Vis absorption spectra of bis(merocyanine) **4a** in (a) dichloromethane and (b) DCM/MCH 10:90 at different concentrations.

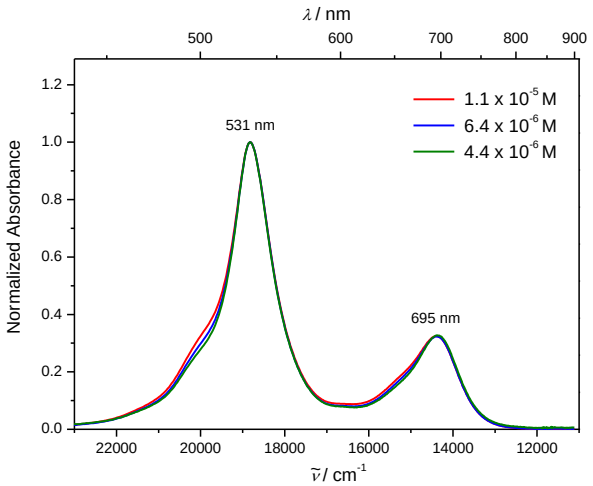


Fig. S3 Normalized UV/Vis absorption spectra of bis(merocyanine) **4b** in DCM/MCH 10:90 at different concentrations.

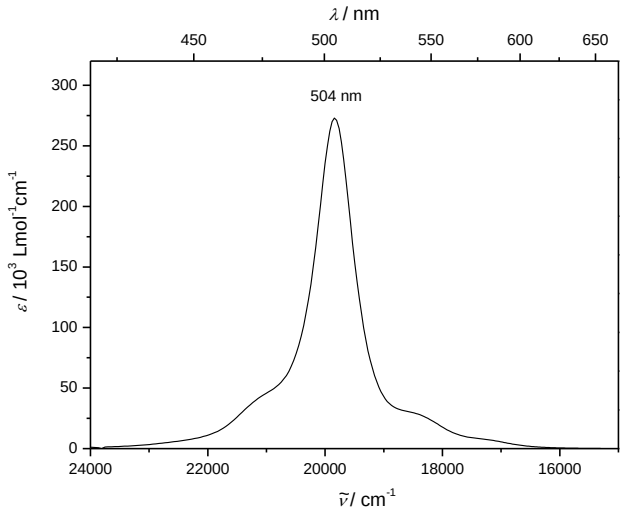


Fig. S4 UV/Vis absorption spectrum of bis(merocyanine) **4a** in dioxane (c = 5.0 x 10^{-6} M).

4. NMR spectroscopy

Table S1 Assignment of significant protons (for proton numbering, see following Fig. S5) and, chemical shifts δ (ppm), coupling constants J (Hz) and shift differences of ^{1}H NMR (600 MHz) signals of bis(merocyanine) **4a** in the folded (1,4-dioxane-d_8, c = 5 x 10^{-6} M, 333 K) and unfolded (DMF-d_7, c = 5 x 10^{-6} M, 298 K) conformation.

Proton	DMF-d_7 δ [ppm] (J [Hz])	1,4-Dioxan-d_8 δ [ppm] (J [Hz])	$\Delta\delta$ [ppm]
H2′	8.09 (d, 5.4, 1H)	7.42 (d, 5.0, 1H)	–0.67
H2	8.05 (d, 5.4, 1H)	7.31 (d, 4.8, 1H)	–0.74
H3′	7.98 (s, 1H)	7.35 (m, 1H)	–0.63
H3	7.91 (s, 1H)	7.20 (s, 1H)	–0.71
H4	7.76 (s, 1H)	8.04 (s, 1H)	+0.28
H1′	6.86 (d, 5.2, 1H)	6.50 (d, 5.2, 1H)	–0.36
H1	6.85 (d, 5.2, 1H)	6.44 (d, 5.2, 1H)	–0.41
CH_3′	2.57 (s, 3H)	2.39 (s, 3H)	–0.18
CH_3	2.46 (s, 3H)	2.14 (s, 3H)	–0.32

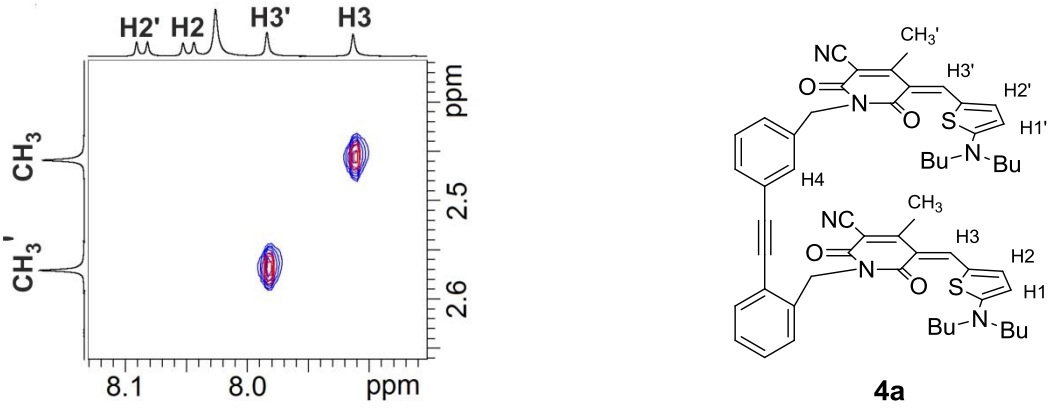


Fig. S5 Selected area of 2D (600 MHz) COSY (red signals) and ROESY (blue signals) NMR spectra of bis(merocyanine) dye **4a** in DMF-d_7 at 298 K (c = 5 x 10^{-6} M) and structure of bis(merocyanine) dye **4a** with assignment of relevant protons.

5. Computational details

All computational calculations were performed using the Gaussian 09 program package[3]. DFT calculations were carried out for bis(merocyanine)s **4a** and **4b** (butyl chains were replaced by methyl groups) and reference compounds **3a** and **3b** (benzyl and butyl groups were replaced by methyl groups) with B97D3[4] as functional and def2-SVP[5] as basis set. The structures were geometry optimized, followed by frequency calculations on the optimized structures. One very small imaginary frequency of 11i cm^{-1} was obtained for bis(merocyanine) dye **4b**. Small imaginary frequencies (<100i cm^{-1}) are considered most likely to be an artefact of the calculation[6], thus the resulting geometries can be seen as real minima. The geometry optimized structures and the electrostatic potential surfaces are shown in Fig. S6.

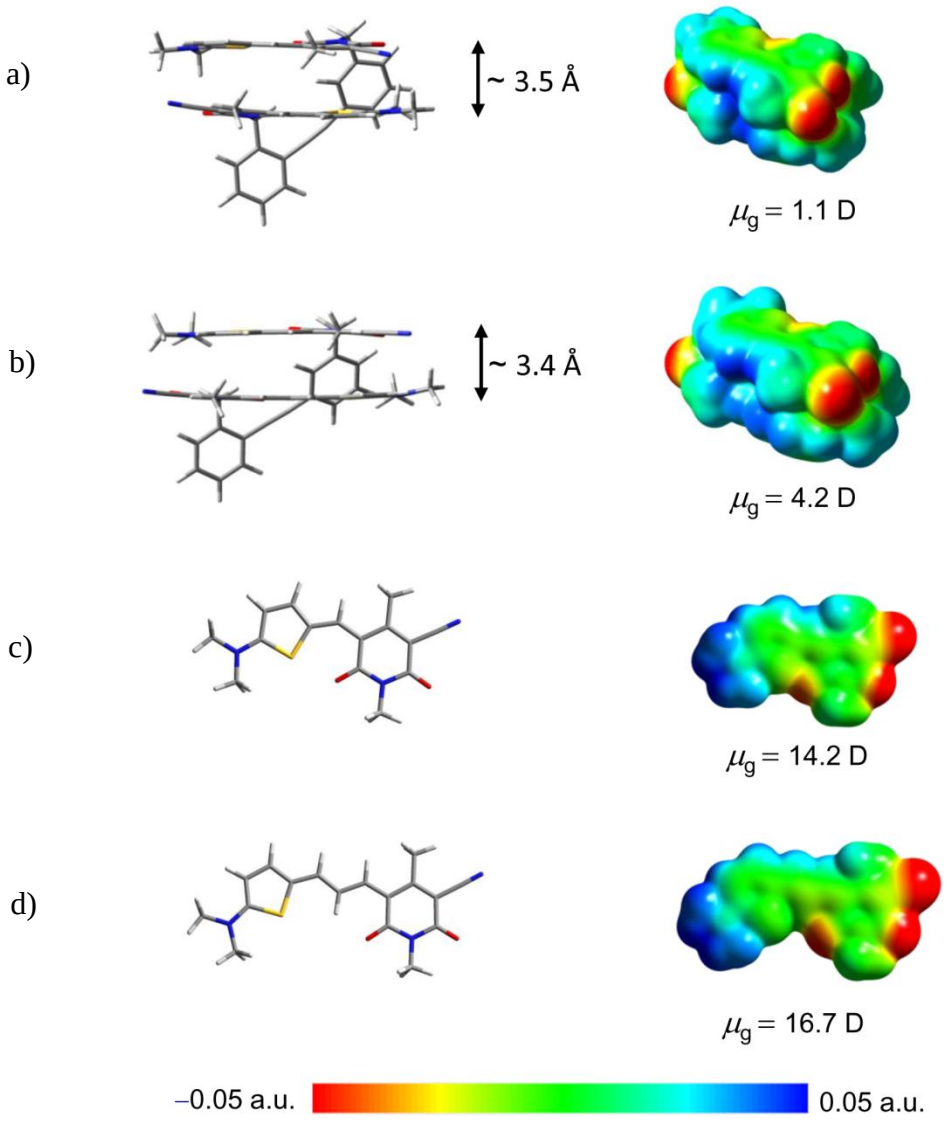


Fig. S6 Geometry optimized structures (B97D3, def2-SVP) and electrostatic potential surfaces of bis(merocyanine) dyes (a) **4a** and (b) **4b** as well as of reference compounds (c) **3a** and (d) **3b**.

ZINDO/S[7] calculations were performed on the geometry-optimized structures of bis(merocyanine) dyes **4a** and **4b** obtained by DFT calculations. The excited state energies as well as the corresponding oscillator strengths (*f*) are listed in Table S2. The UV/Vis spectra shown in Fig. S7a,b (top) were simulated with the help of the GaussView 5[8] visualization software package using the results obtained by ZINDO/S calculations with a half-width at half height of 0.15 eV.

Table S2 Excited state energies and corresponding oscillator strengths (*f*) of the two lowest Frenkel states in bis(merocyanine) dyes **4a** and **4b** obtained by ZINDO/S calculations.

	bis(merocyanine) **4a**	bis(merocyanine) **4b**
excited state energy	14874 cm^{-1} (f = 0)	14325 cm^{-1} (f = 0.211)
(oscillator strength)	19232 cm^{-1} (f = 1.617)	18892 cm^{-1} (f = 1.961)

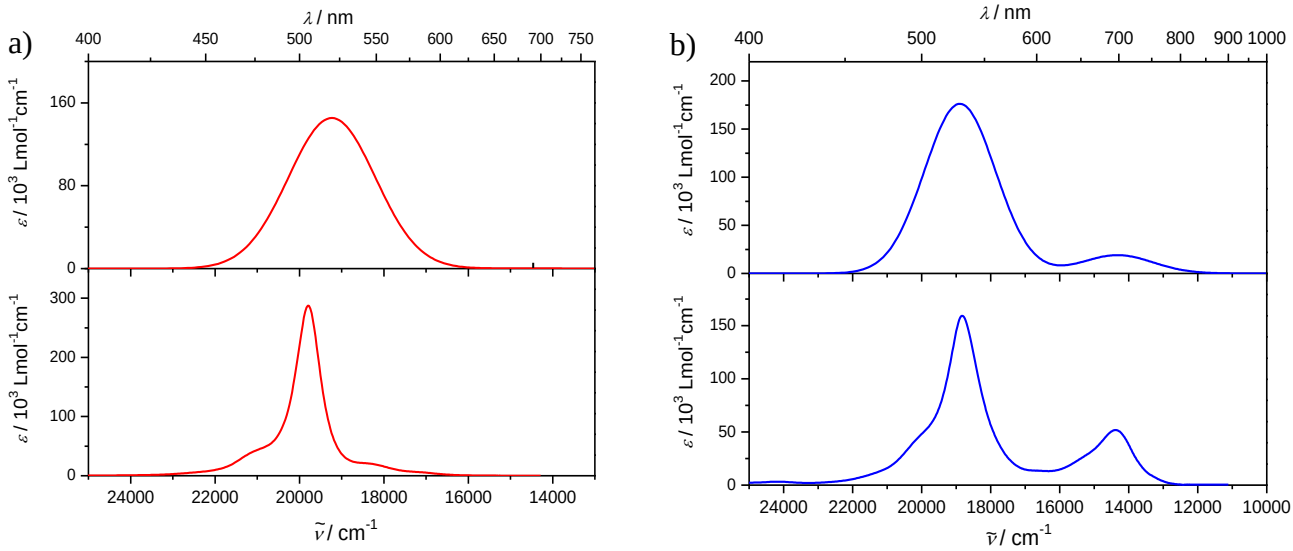


Fig. S7 Calculated absorption spectra obtained by ZINDO/S calculations (top) and experimental spectra in DCM/MCH 10:90 (c = 5 x 10^{-6} M, bottom) of bis(merocyanine) dyes (a) **4a** and (b) **4b**.

6. Theoretical Investigations

The excited state wave function Φ_E of a dimer of two chromophores 1, 2 can be described as follows[9]:

$$\Phi_E = c_1 \cdot \varphi^*_1 \, \varphi_2 + c_2 \cdot \varphi_1 \, \varphi^*_2 \qquad \text{(S1)}$$

where φ_1, φ_2 are the ground state wave functions of chromophores 1, 2 and φ^*_1, φ^*_2 the excited state wave functions of the corresponding chromophores. Furthermore, c_1 and c_2 represent coefficients that have to be determined.

The excited state energy E_E of the dimer is obtained by applying the Hamiltonian operator $\hat{H}$ on the excited state wave function Φ_E:

$$\hat{H}\,\Phi_E = E_E\,\Phi_E \qquad \text{(S2)}$$

Thus, one obtains the following Eigenwert equation:

$$\begin{pmatrix} E_1 & J \\ J & E_2 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E_E \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \quad \text{(S3)}$$

with E_1, E_2 as the excited state energies of monomeric chromophores 1, 2 and J as the exciton coupling energy. The eigenvalues of the Hamiltonian matrix represent the two excited state energies of the dimer:

$$E_{E1} = -0.5 \cdot \left(\sqrt{(E_1 - E_2)^2 + 4J^2} - E_1 - E_2\right) \quad \text{(S4)}$$

$$E_{E2} = 0.5 \cdot \left(\sqrt{(E_1 - E_2)^2 + 4J^2} + E_1 + E_2\right) \quad \text{(S5)}$$

Thus, the energy difference between both excited states is:

$$E_{E2} - E_{E1} = \sqrt{(E_1 - E_2)^2 + 4J^2} \quad \text{(S6)}$$

For a homodimer ($E_1 = E_2$) equation S6 simplifies to:

$$E_{E2} - E_{E1} = 2J \quad \text{(S7)}$$

Hence, one can determine the exciton coupling energies for the homo- and heteroaggregate of bis(merocyanine) dyes **4a** and **4b** based on the data obtained by UV/Vis spectroscopy.

Homoaggregate of bis(merocyanine) **4a**:

We obtain with Equation S7:

$$J = 0.5 \cdot (E_{E2} - E_{E1}) = 1400 \text{ cm}^{-1}$$

with E_{E2} = 19800 cm^{-1} (H-band of the spectrum of **4a** in DCM/MCH 10:90)
and E_{E1} = 17000 cm^{-1} (J-band of the spectrum of **4a** in DCM/MCH 10:90)

Heteroaggregate of bis(merocyanine) **4b**:

We obtain with Equation S6:

$$J = 0.5 \cdot \sqrt{(E_{E2} - E_{E1})^2 - (E_1 - E_2)^2} = 1609 \text{ cm}^{-1}$$

with E_{E2} = 18800 cm^{-1} (H-band of the spectrum of **4b** in DCM/MCH 10:90),
E_{E1} = 14400 cm^{-1} (J-band of the spectrum of **4b** in DCM/MCH 10:90)
E_1 = 18600 cm^{-1} (absorption maximum of **3a** in DCM/MCH 10:90)
E_2 = 15600 cm^{-1} (absorption maximum of **3b** in DCM/MCH 10:90)

7. ^{1}H and ^{13}C NMR spectra of new compounds

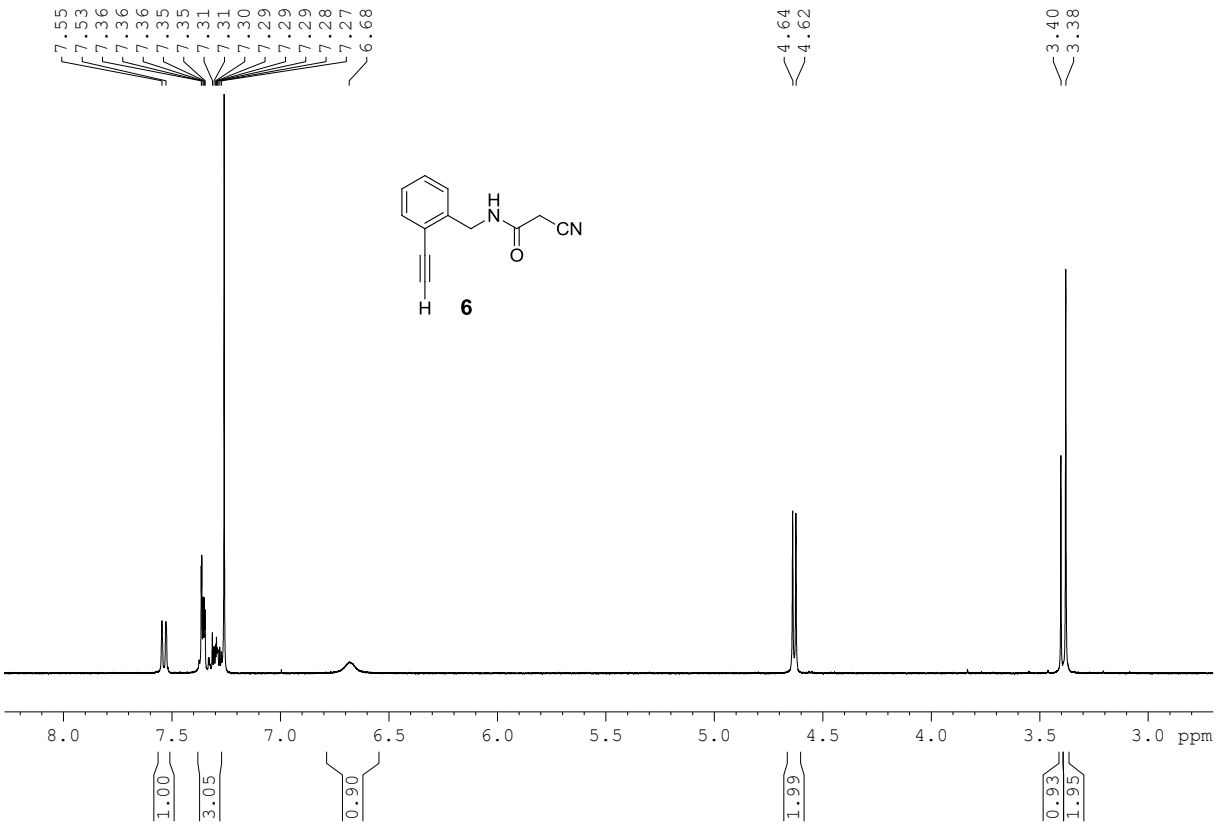


Fig. S8 ^{1}H NMR (400 MHz) spectrum of **6** in $CDCl_3$ at 295 K.

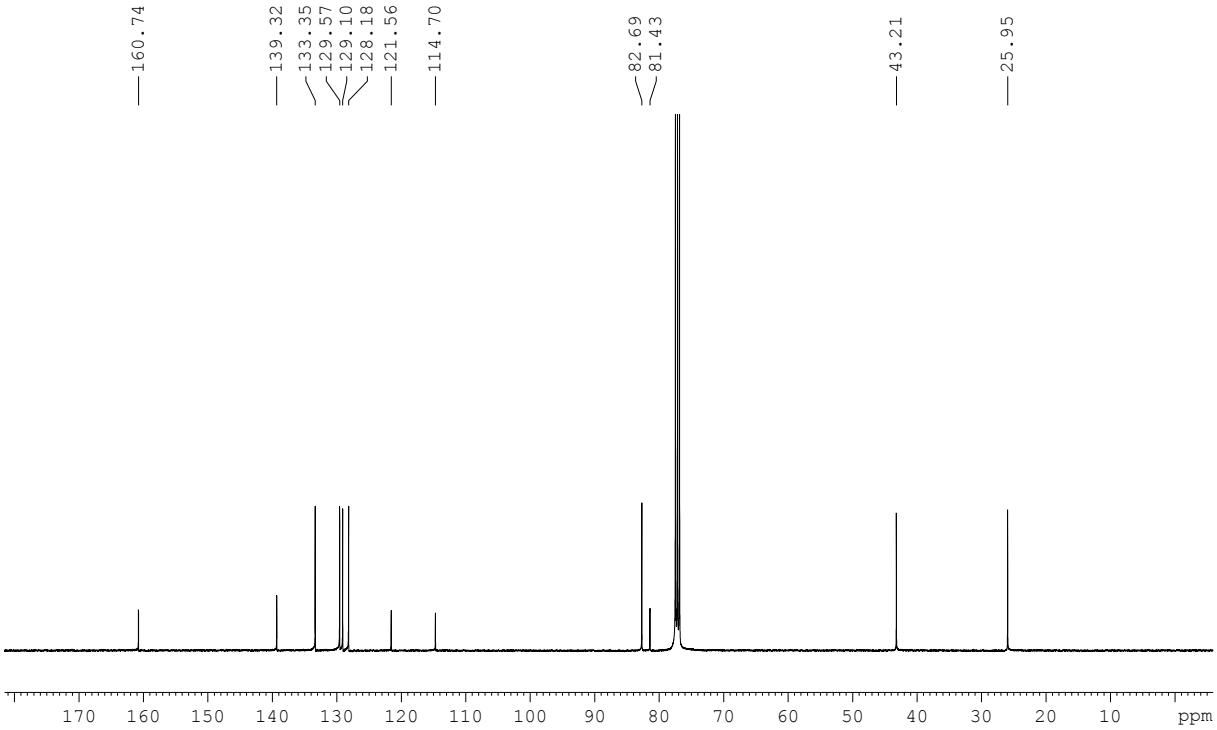


Fig. S9 ^{13}C NMR (101 MHz) spectrum of **6** in $CDCl_3$ at 295 K.

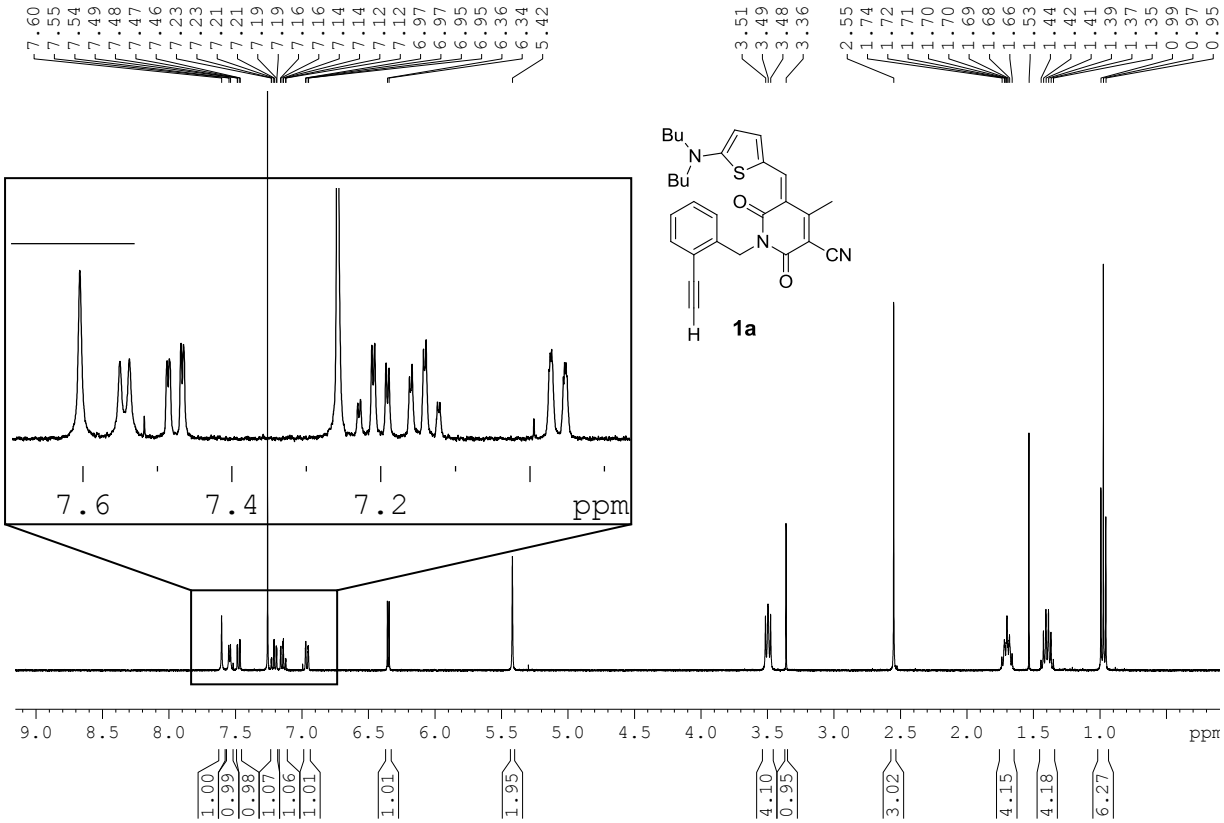


Fig. S10 ^{1}H NMR (400 MHz) spectrum of **1a** in $CDCl_3$ at 295 K.

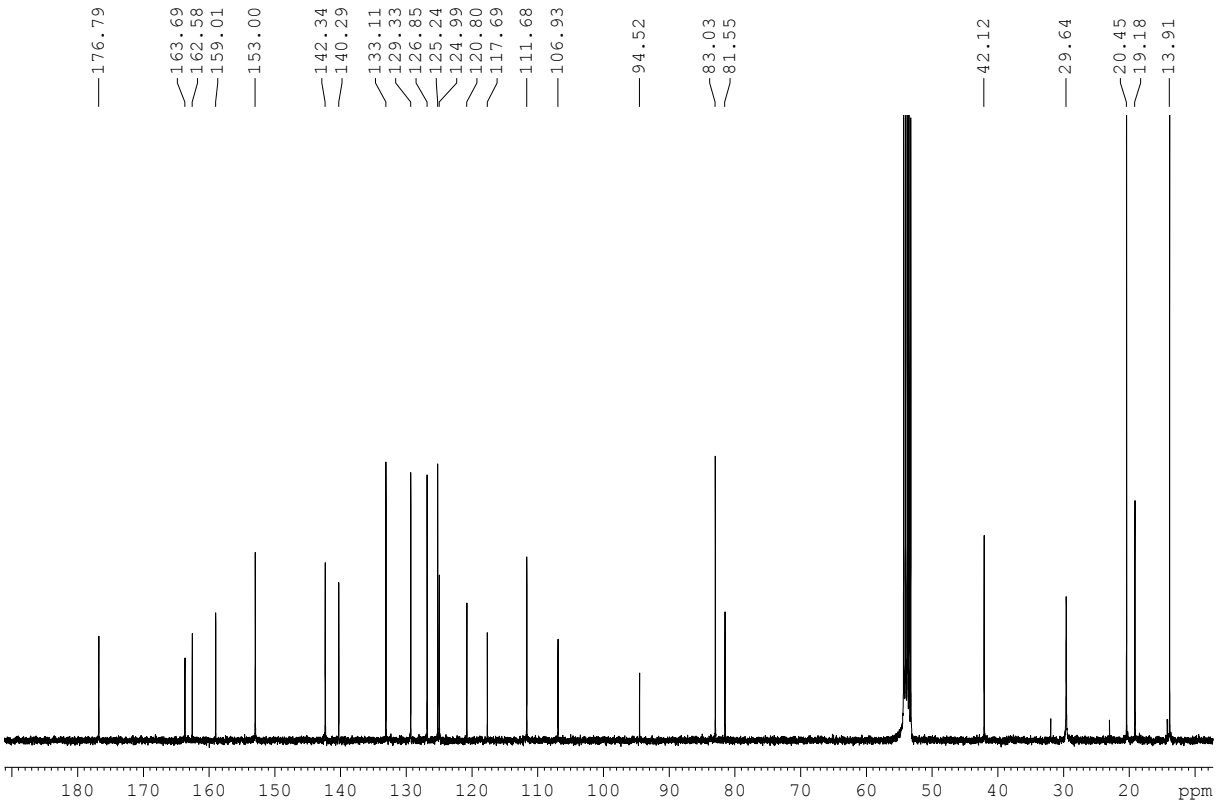


Fig. S11 ^{13}C NMR (101 MHz) spectrum of **1a** in CD_2Cl_2 at 295 K.

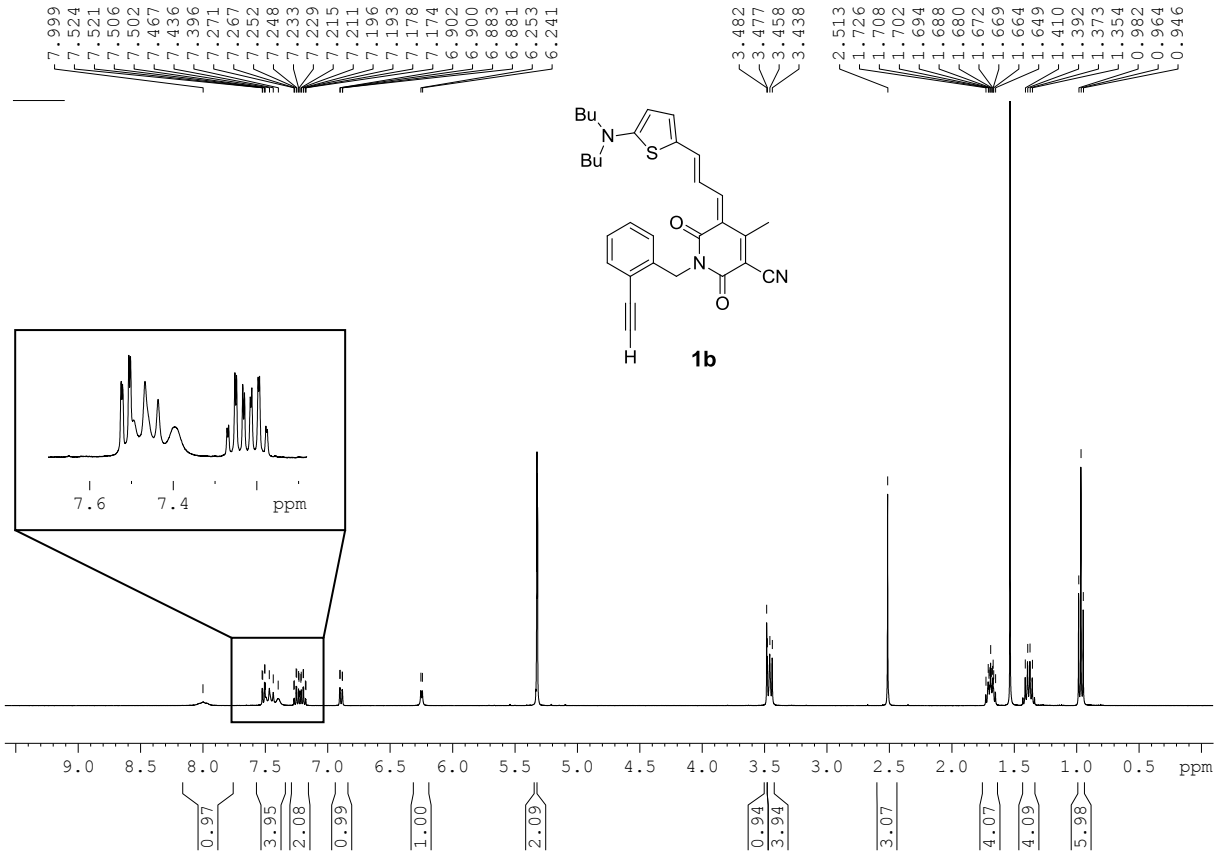


Fig. S12 ^{1}H NMR (400 MHz) spectrum of **1b** in CD_2Cl_2 at 295 K.

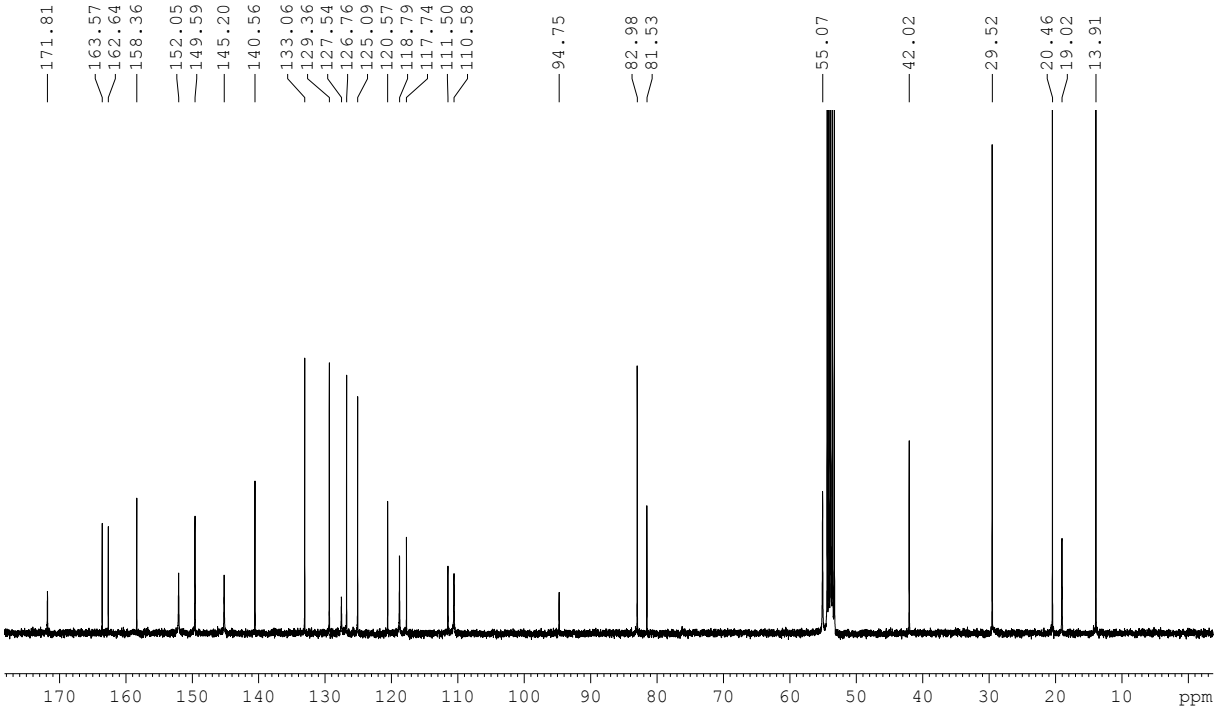


Fig. S13 ^{13}C NMR (101 MHz) spectrum of 1**b** in CD_2Cl_2 at 295 K.

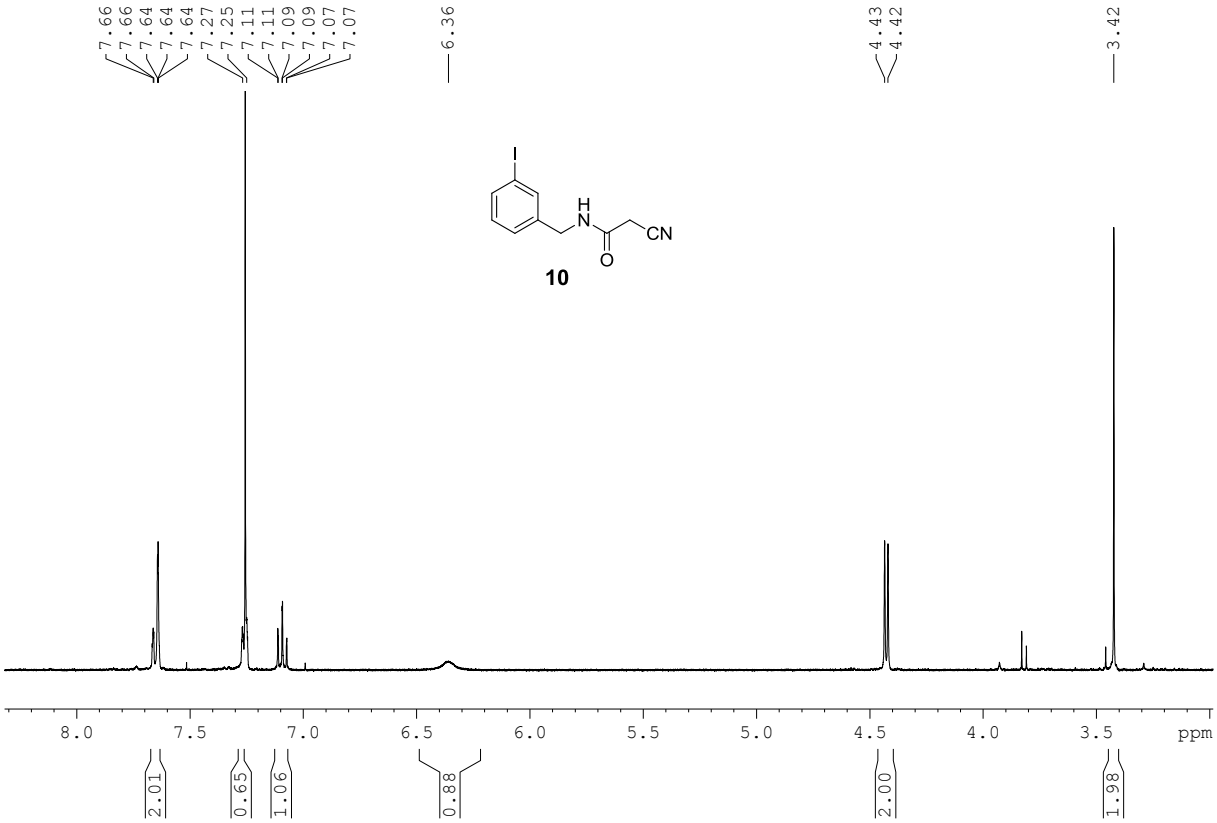


Fig. S14 ^{1}H NMR (400 MHz) spectrum of **10** in $CDCl_3$ at 295 K.

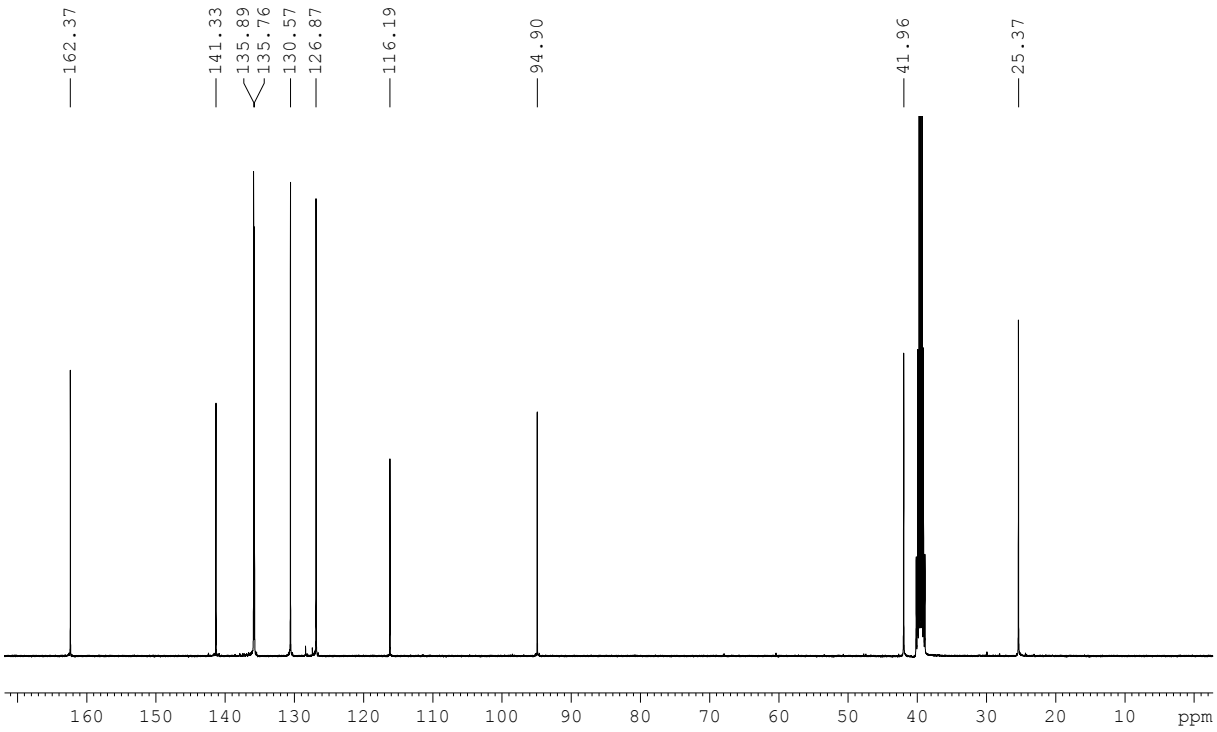


Fig. S15 ^{13}C NMR (101 MHz) spectrum of **10** in DMSO-d_6 at 295 K.

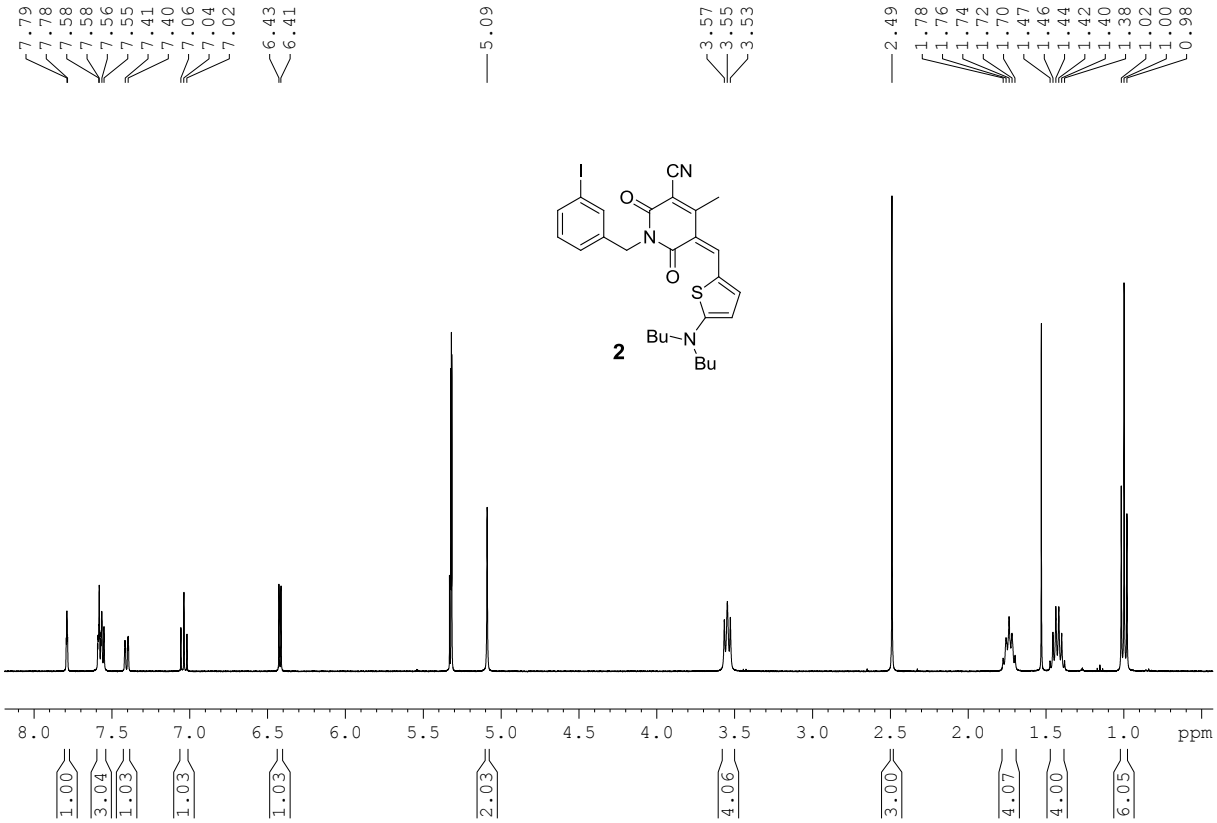


Fig. S16 ^{1}H NMR (400 MHz) spectrum of **2** in CD_2Cl_2 at 295 K.

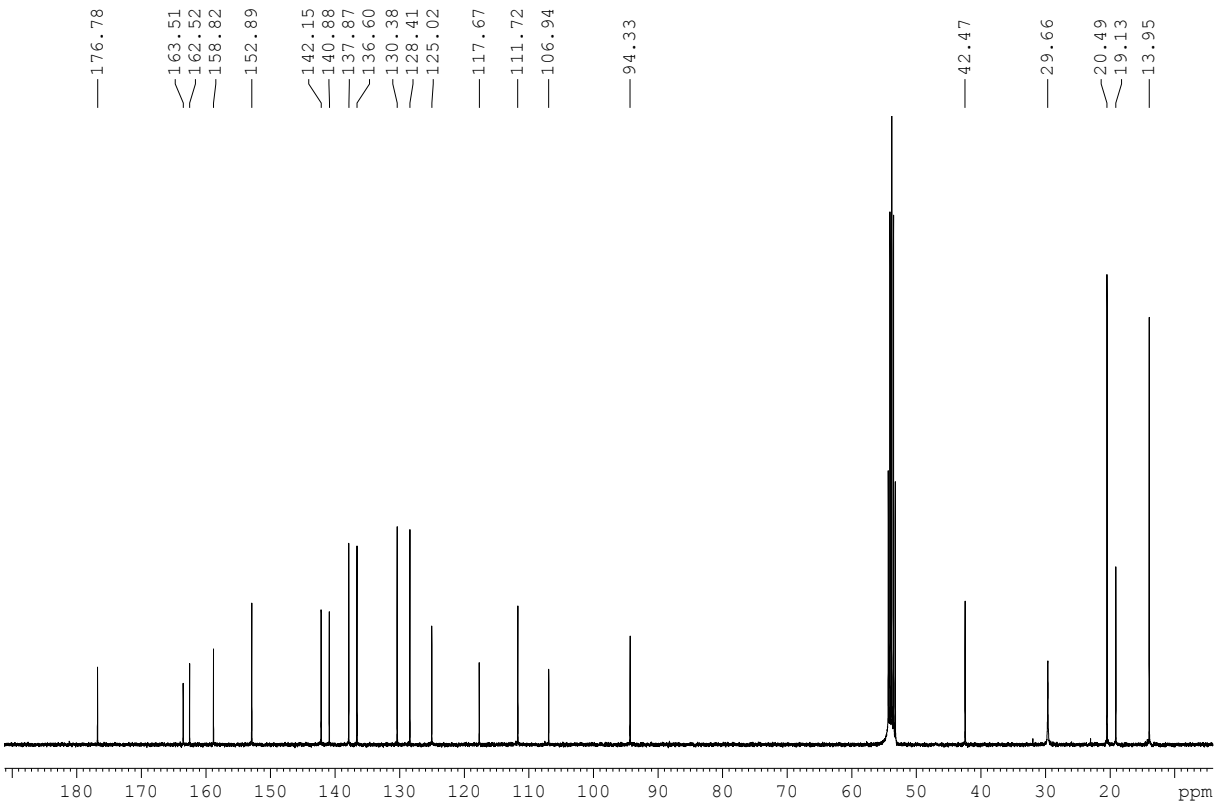


Fig. S17 ^{13}C NMR (101 MHz) spectrum of **2** in CD_2Cl_2 at 295 K.

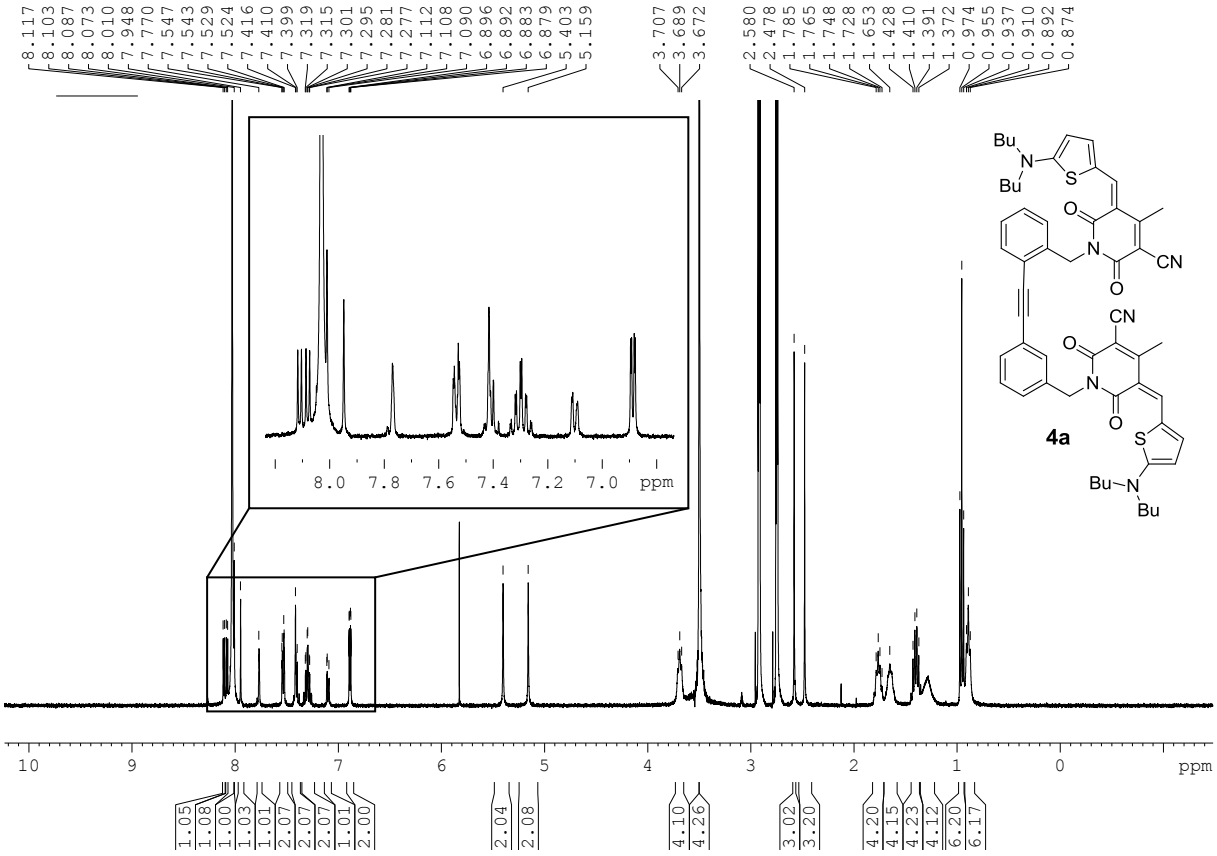


Fig. S18 ^{1}H NMR (600 MHz) spectrum of **4a** in DMF-d_7 at 295 K.

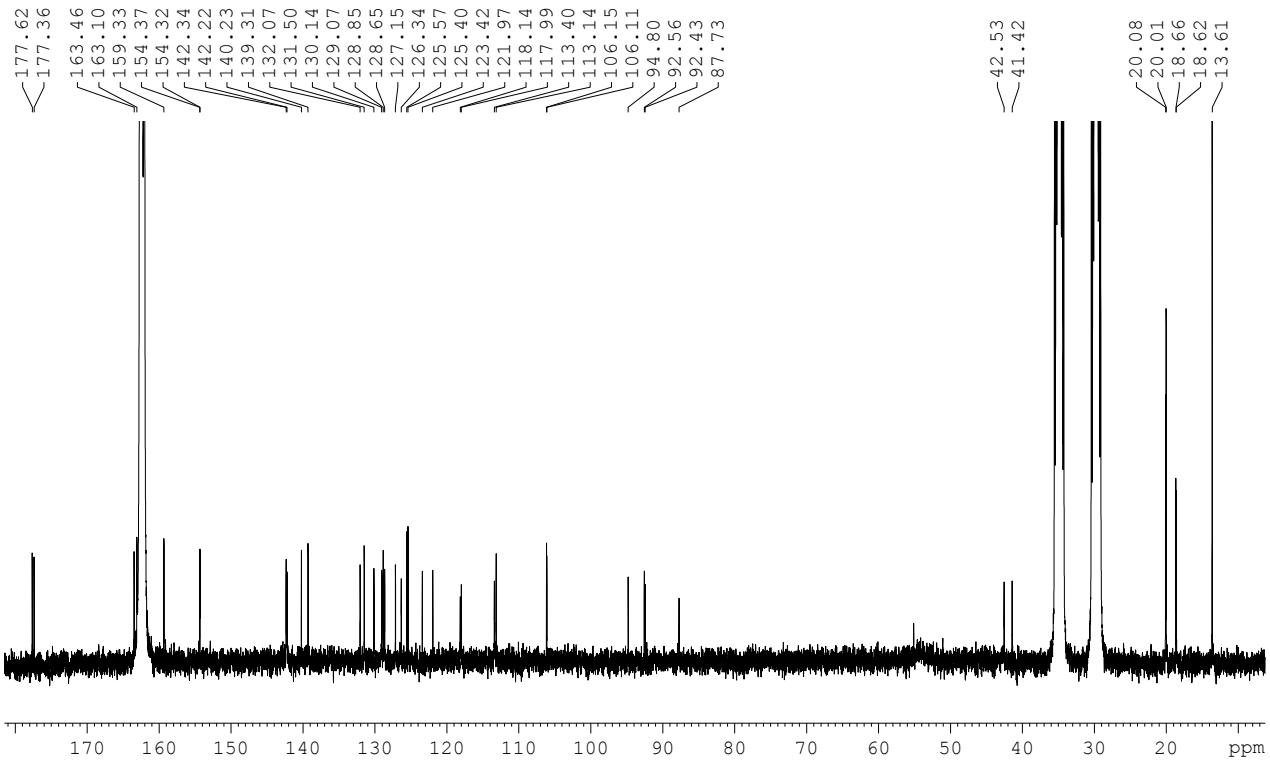


Fig. S19 ^{13}C NMR (101 MHz) spectrum of **4a** in DMF-d_7 at 295 K.

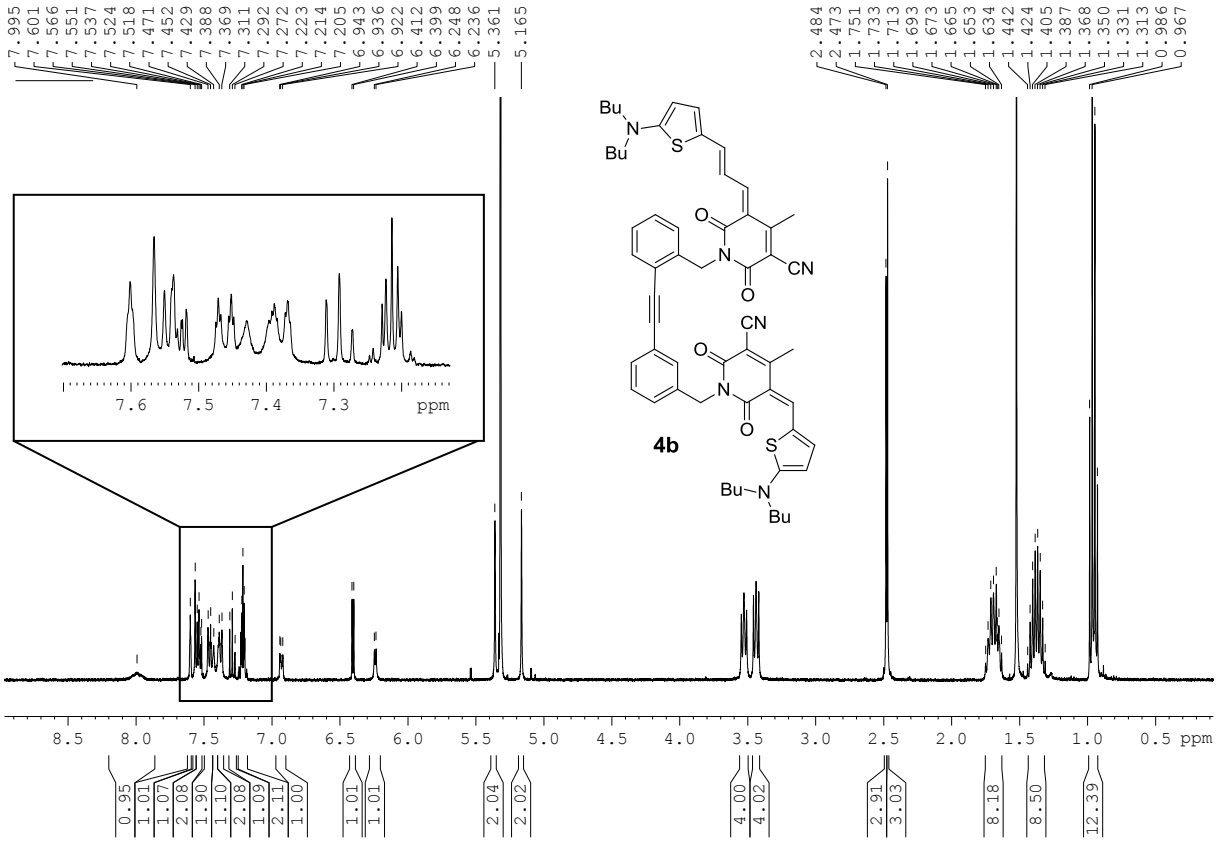


Fig. S20 ^{1}H NMR (400 MHz) spectrum of **4b** in CD_2Cl_2 at 295 K.

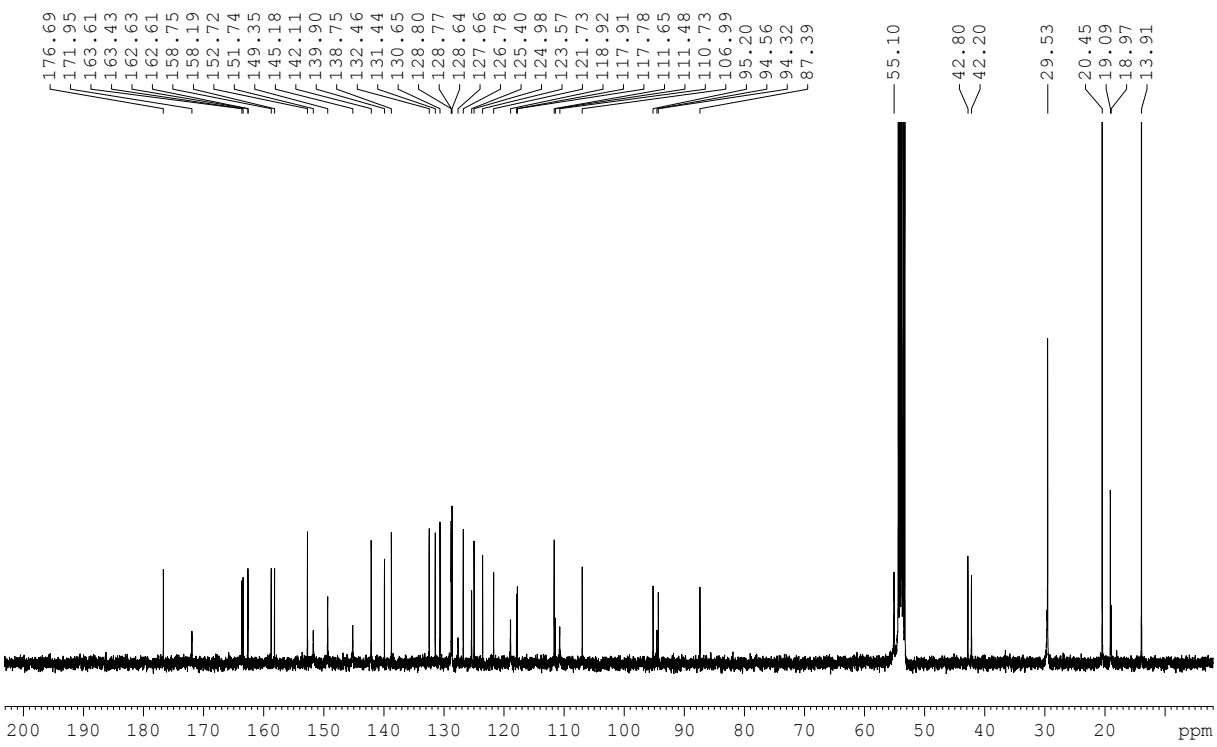


Fig. S21 ^{13}C NMR (101 MHz) spectrum of **4b** in CD_2Cl_2 at 295 K.

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