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Synthesis and photophysical properties of heptamethine cyanine–fullerene C_{60} dyads with non-quenched fluorescence

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Materials and equipment

Materials. The following commercially available materials were used in the work: chloroform (chemically pure), tetrahydrofuran (chemically pure), toluene (chemically pure), methanol (analytically pure), dichloromethane (chemically pure), silica gel (Acros organics, 40–60 μm, 60 Å), pyridine (chemically pure), *N*-methylglycine, trifluoroacetic acid (chemically pure), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), acetonitrile, ethanolamine, 2-mercaptoethanol, 4-formylbenzoic acid, N,N′-dicyclohexylcarbodiimide, 4-dimethylaminopyridine. Purification of solvents: chloroform and dichloromethane were distilled over K_2CO_3; THF was boiled over KOH for 4 hours, stored over metallic Na for 24 hours, and then distilled over metallic Na; pyridine was stored over KOH for 24 hours and then distilled; toluene was stored over metallic sodium. The remaining substances were used without prior purification.

For Electrochemistry: Acetonitrile (AN, Sharlau, HPLC gradient grade, it was specially dried with 4 Å molecular sieves) and THF (Lab Scan, HPLC gradient grade) were used as solvents. Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, Fluka, >99%) used as the supporting electrolyte was dried at 80°C for at least 24 h prior to use.

Equipment. The rotary evaporator IKA RV-10 was used to evaporate the solvents. The ^{1}H NMR spectra were recorded on a Bruker AVANCE 50 (500 MHz) and Bruker AM-200 (200 MHz) spectrometers. Absorption spectra were recorded on a Cary-60 and Hitachi U-2900 spectrophotometer (UV-vis), and stationary fluorescence spectra were recorded on a Cary-Eclipse spectrofluorometer. ***For Electrochemistry*** – the working electrode potential was controlled by Autolab PGSTAT302N (Metrohm, Switzerland) potentiostate. ***Electrospray mass spectra*** (ESI) were obtained using an Exactive Orbitrap high resolution mass spectrometer (ThermoFisher Scientific, Germany).

Synthesis of the dyads and precursors

Fullerene derivative **1** was obtained by the Prato reaction according to the literature [S1]. Mass and NMR spectra coincide with those given in [S1]. Dye **2a** was obtained as follows. Dye IR-780 (100 mg, 0.15 mmol) was dissolved in dry dichloromethane. Then, under argon, 2-mercaptoethanol (12 μL, 0.16 mmol) and *N*-ethyldiisopropylamine (29 μL, 0.16 mmol) were added. The reaction mixture was left overnight at room temperature. After completion of the reaction, the product was purified by column chromatography on silica gel eluting with gradient CH_2Cl_2-MeOH up to 9:10; yield: 98 mg (92%).

Dye **2b** was obtained as described [S2], the mass and NMR spectra coincide with those given in this work.

Dyads **3a** and **2b** were obtained as follows. Compound **1** (317 mg, 0.35 mmol), DCC (73 mg, 0.35 mmol) and DMAP (4.3 mg, 35 mmol) were dissolved in dry THF and stirred at room temperature for 2 h under argon. Then THF solution of dye **2a** or **2b** (0.42 mmol) was added, and the mixture was refluxed for 16 h and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel with toluene/pyridine (1:1 vol.) as eluent.

Characterization of new compounds

Compound **2a.** VIS/NIR abs., λ_{max} (lg ε) in DCM: 794 nm (5.41).

^{1}H NMR (DMSO-d_6): 8.76 (2H, d, ^3J =14.21 Hz), 7.60 (2H, d, ^3J =7.45 Hz), 7.42 (4H, m), 7.25 (2H, t, J^3=7.25 Hz), 4.97 (1H, t, ^3J =5.36 Hz), 4.17 (4H, t, ^3J =7.35 Hz), 3.51 (2H, q, ^3J =6.56 Hz), 2.86 (2H, t, ^3J =6.56 Hz), 2.64 (4H, t, ^3J =5.86 Hz), 1.82-1.75 (6H, m), 1.70 (12H, s), 0.96 (6H, t, ^3J =7.35 Hz).

MS (ESI+), m/z: calculation for $C_{38}H_{49}N_2OS$: 581.3565 [M$^+$]; found: 581.3554.

Dyad **3a** yield 340 mg (60 %). VIS/NIR abs., λ_{max} (lg ε) in Py: 783 nm (5.20).

^{1}H NMR (DMSO-d_6): 8.58 (2H, d, ^3J =7.33 Hz), 8.02 (2H, d, ^3J =14.27 Hz), 7.80 (1H, t, ^3J =7.63 Hz), 7.47 (2H, d, ^3J =7.33 Hz), 7.41 (7H, m), 7.22 (3H, m), 6.18 (2H, d, ^3J =14.27Hz), 4.26 (2H, t, ^3J =5.85 Hz), 4.12 (4H, t, 7.35 Hz), 3.51 (3H, s), 3.43 (2H, t, ^3J =5.85 Hz), 2.58 (4H, t, ^3J =5.35 Hz), 1.79 (2H, qui, ^3J =5.35 Hz), 1.72 (4H, q, ^3J =7.35 Hz), 1.64 (12H, s), 0.92 (6H, t, ^3J =7.35 Hz).

MS (ESI+), m/z: calculation for $C_{108}H_{58}N_3O_2S$: 1460.425 [M$^+$]; found: 1460.426.

Dyad **3b** yield 323 mg (58 %). VIS/NIR abs. λ_{max} (lg ε) in Py: 652 (4.81).

^{1}H NMR (DMSO-d_6): 8.58 (2H, d, ^3J =3.89 Hz), 7.78 (2H, t, ^3J =6.78 Hz), 7.69 (2H, d, ^3J =12.46 Hz), 7.44 (2H, d, ^3J =7.18 Hz), 7.39 (3H, m), 7.29 (2H, t, ^3J =7.68 Hz), 7.15 (2H, d, ^3J =7.93 Hz), 7.06 (2H, t, ^3J =7.43 Hz), 5.79 (2H, d, ^3J =13.76 Hz), 5.05 (1H, s), 3.93 (2H, t, ^3J =6.98 Hz), 3.72 (6H, m), 3.51 (3H, s), 2.48, 1.72 (6H, m), 1.6 (12H, s), 0.94 (6H, t, ^3J =7.38 Hz).

MS (ESI+), m/z: calculation for $C_{108}H_{59}N_4O_2$: 1443.463 [M$^+$]; found: 1443.472.

Experimental methods

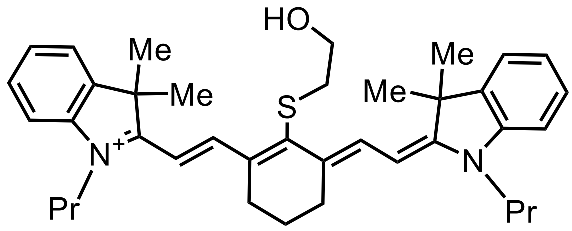
Electrospray ionization mass spectra (ESI MS) were acquired using an Exactive Orbitrap mass spectrometer (ThermoFisher Scientific, Germany). The working resolution of the mass spectrometer in the reported studies was 10000 (FWHM). The ratio error of the m/z values measurement was better than 10^{-5}. Analysis of the isotopic structure of the registered ion peaks and the accurate measurement of the ion masses allowed identifying all the main ions that were detected.

Electrochemical experiments were carried out in a non-separated three-electrode electrochemical cell. Cross-sections of Pt wire or glassy carbon (GC) rod (geometric area of 0.785 mm^2) was used as working electrode. An auxiliary electrode was Pt foil; its surface area was several tens as large as the working electrode one. Insertion of solution's components and of electrodes into the cell as well as the implementation of electrochemical measurements was performed with the use of Schlenk line under a slight excessive argon pressure (~ 20 mbar) over the solution. Silver wire immersed into 10 mM Ag^+ + 0.1 M Bu_4NPF_6 solution in acetonitrile served as reference electrode; its potential was -100 mV with respect to the formal potential of the Fc/Fc^+ couple in acetonitrile + 0.1 M Bu_4NPF_6 or about 200 mV with respect to aq. SCE. All values of the potential below are given *vs.* this reference electrode, Ag/Ag^+ (in acetonitrile). Working electrode potential was controlled by Autolab PGSTAT302N (Metrohm, Switzerland) potentiostate.

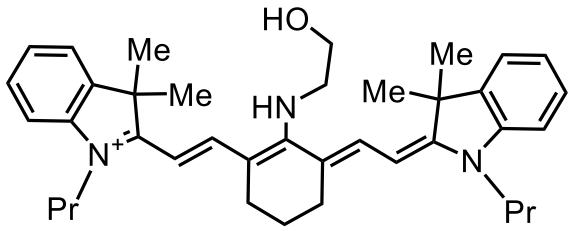
Procedure: Pretreatment of working electrodes: Pt and GC disk electrodes were polished with synthetic grinding short-pile felt (polishing cloth) coated with Aka-Poly (Akasel) diamond powder suspension (grain size: 1 μm). The supporting electrolyte solution was prepared by placing a weighed portion of Bu_4NPF_6 into the cell and introducing a certain volume of acetonitrile or THF there. A portion of the compound under study was added to the electrochemical cell containing 10 mL of 0.1 M Bu_4NPF_6 background electrolyte solution. The solution was de-aerated by alternately applying a vacuum and filling the cell with argon; then, electrodes were installed. The redox properties of the compound under study were investigated in THF (for compound **1**) or acetonitrile (for all other compounds under study) by cyclic voltammetry (CV) with a Pt or GC electrode.

Acid-base properties evaluation. Spectrophotometric titration of compounds **2b** and **3b** was carried out with solutions of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and trifluoroacetic acid (TFA) in acetonitrile at 23 °C. The concentration ratio of the acid forms in equilibrium, $I=C_i/C_{i-1}$, was determined spectrophotometrically at wavelengths corresponding to the absorption maxima. The values $I=C_i/C_{i-1}$ of the concentration constants of stability of acid forms pK_{si} were determined by analyzing the dependence $lg(I) = pK_{si} + m{\cdot}lg[TFA/DBU]$, where m is the number of acid or base particles participating in the formation of this acid form i.

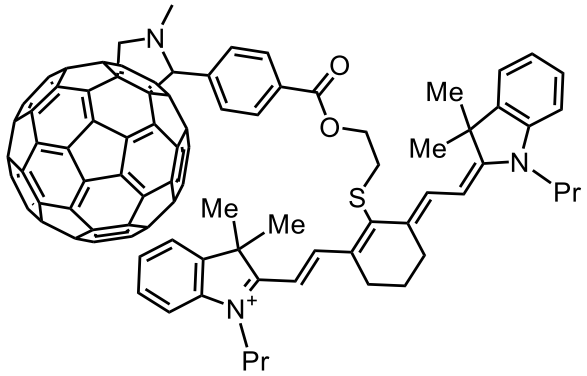
Chemical structures of compounds under study



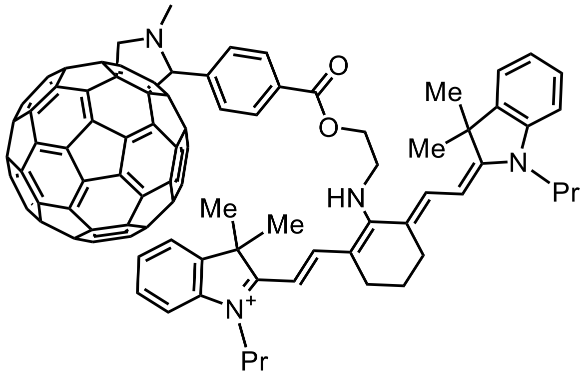
2a



2b



3a



3b

Figure S1. Chemical structures of compounds under study.

Mass spectra of compounds under study

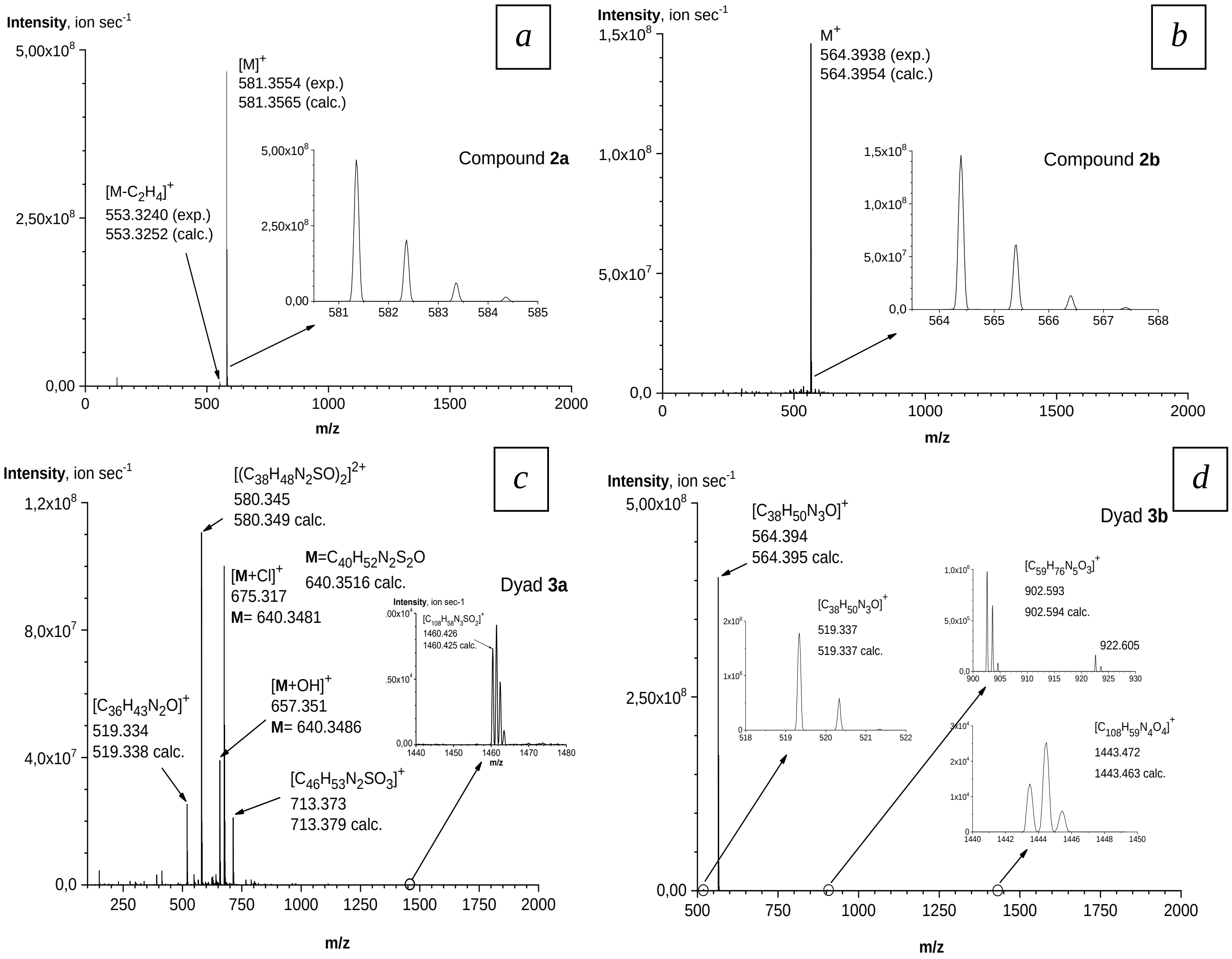


Figure S2. ESI HRMS spectra of compounds **2a** (*a*), **2b** (*b*), dyad **3a** (*c*) and dyad **3b** (*d*).

^{1}H NMR spectrum of compound 2a

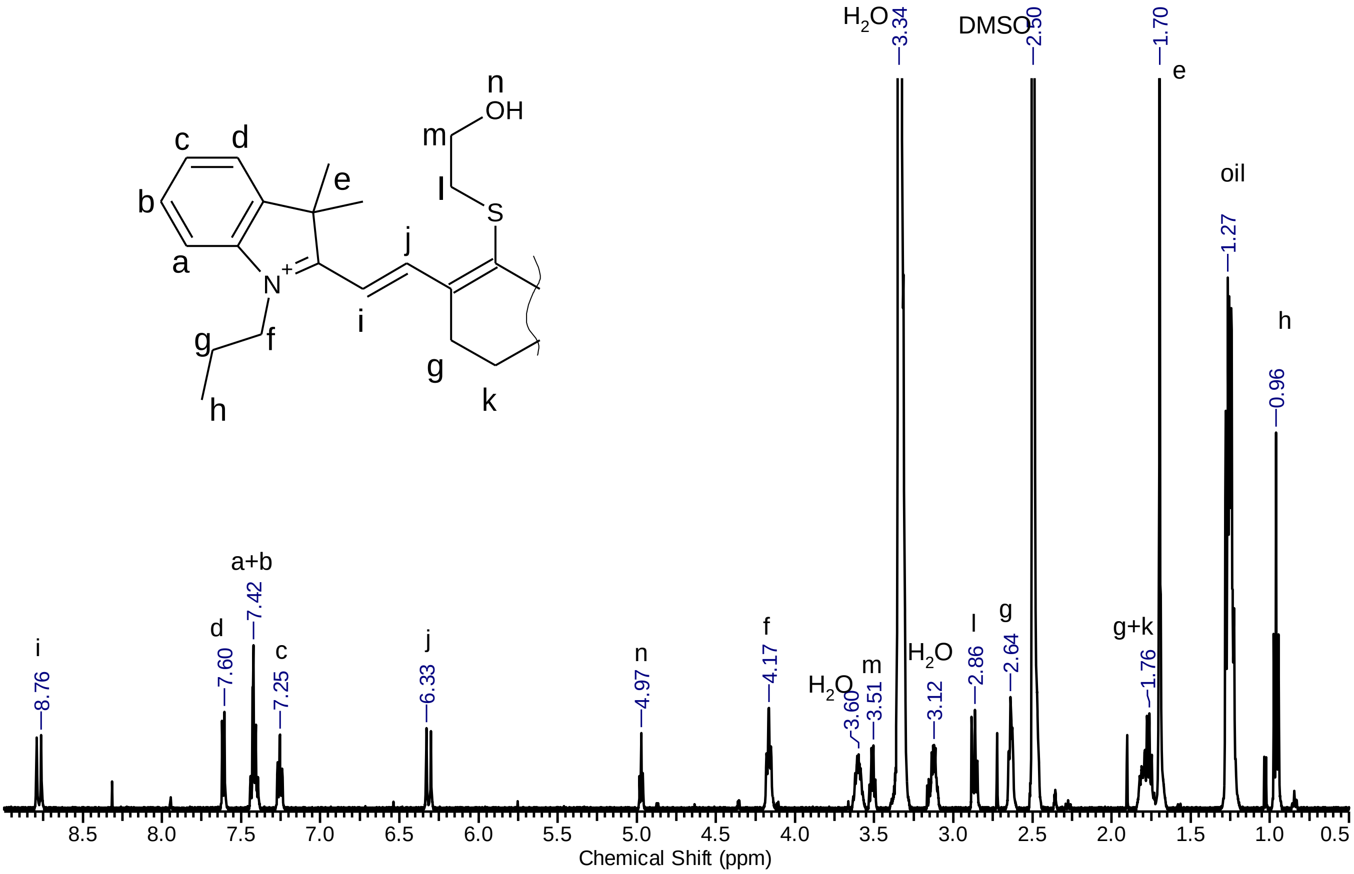


Figure S3. Compound **2a** ^{1}H NMR spectrum in DMSO-*d*$_6$.

Dyad 3a ^{1}H NMR spectrum

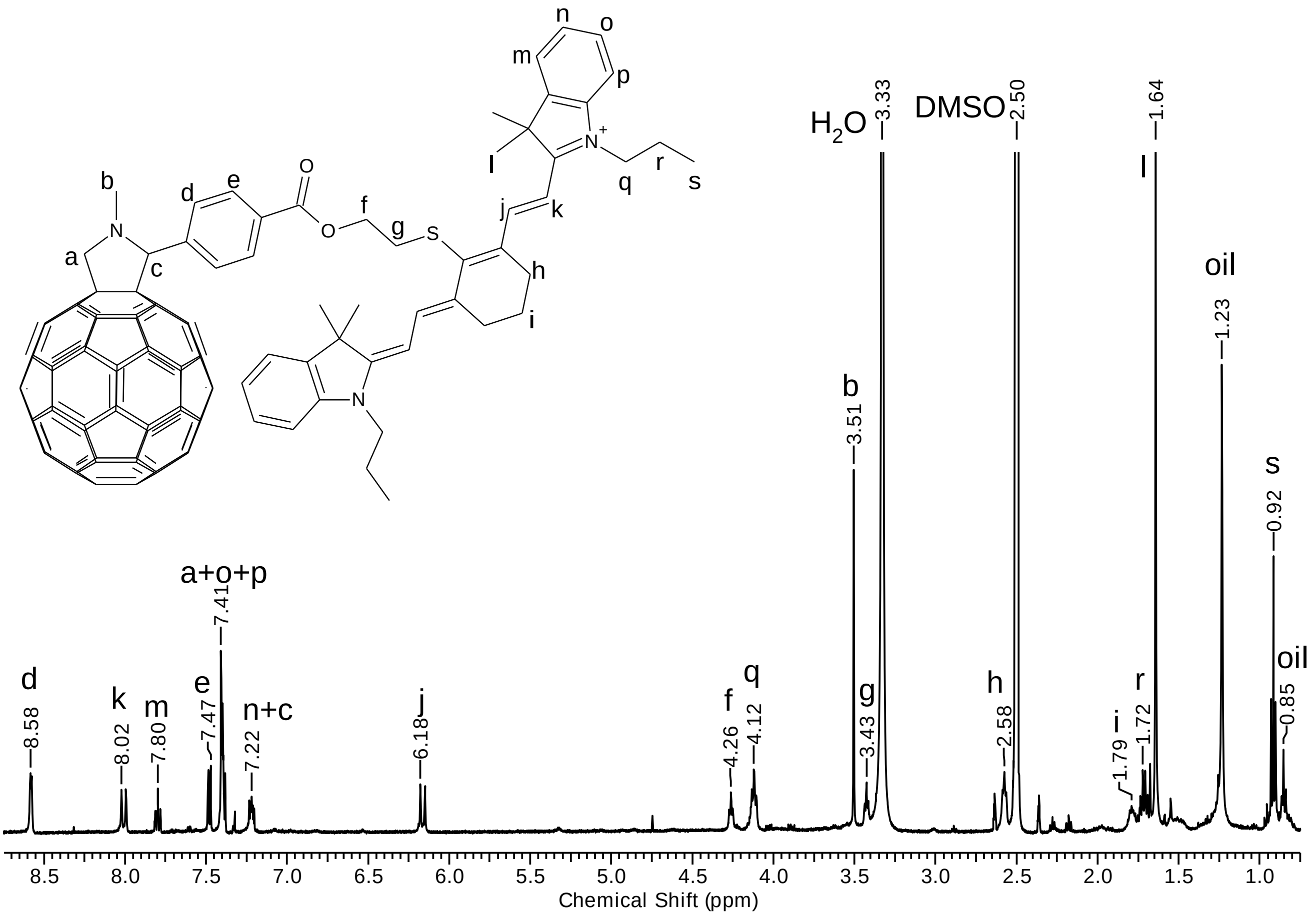
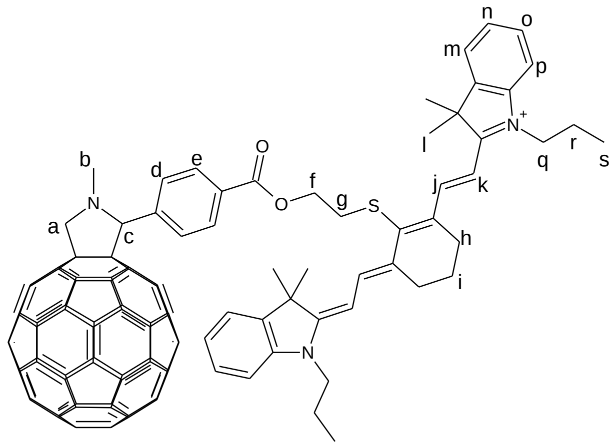


Figure S4. ^{1}H NMR spectrum of dyad **3a** in DMSO-d_6.

Dyad 3a ^{1}H-^{1}H COSY NMR spectrum



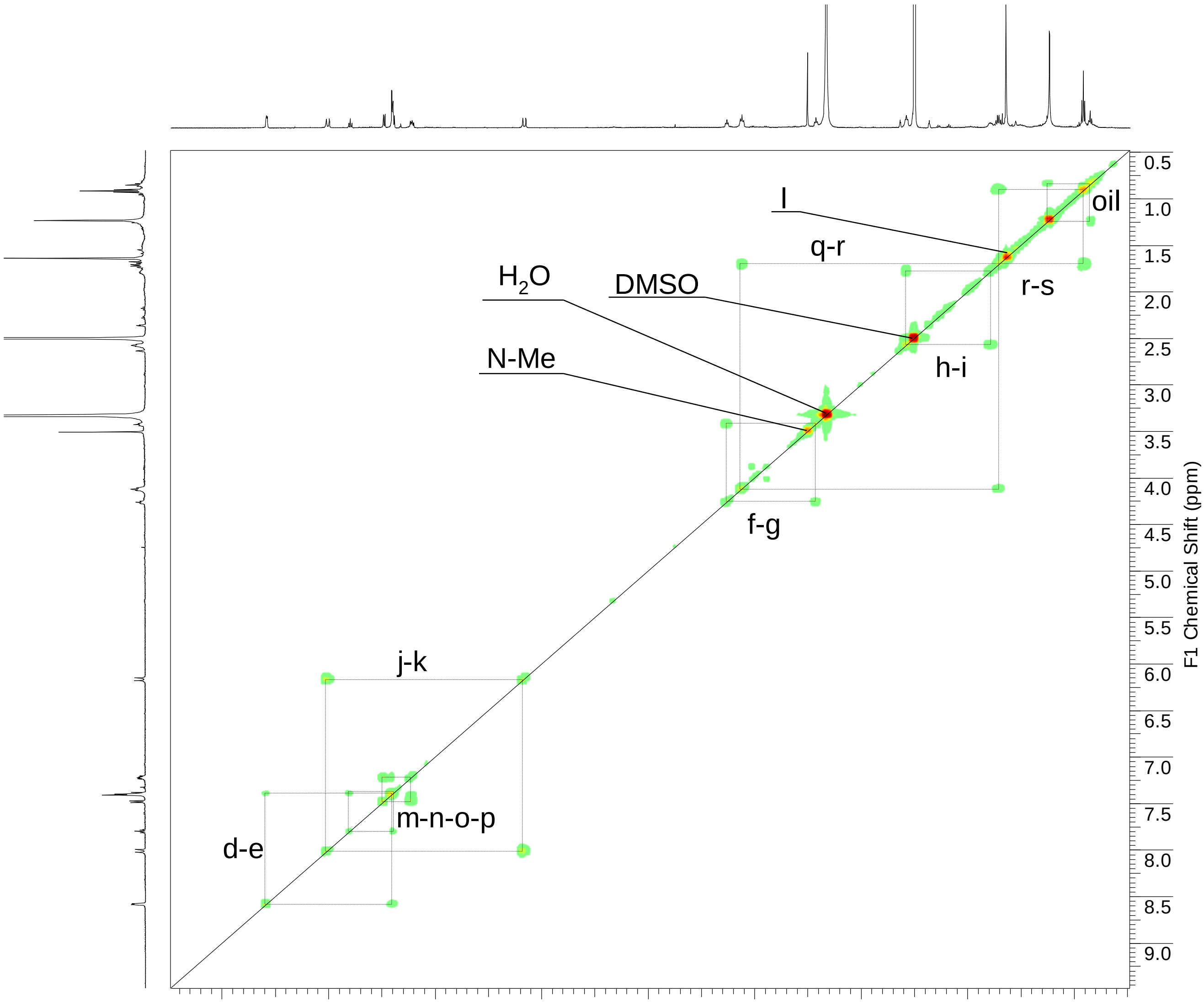


Figure S5. ^{1}H-^{1}H COSY NMR spectrum of dyad **3a** in DMSO-d_6.

Dyad 3b ^{1}H NMR spectrum

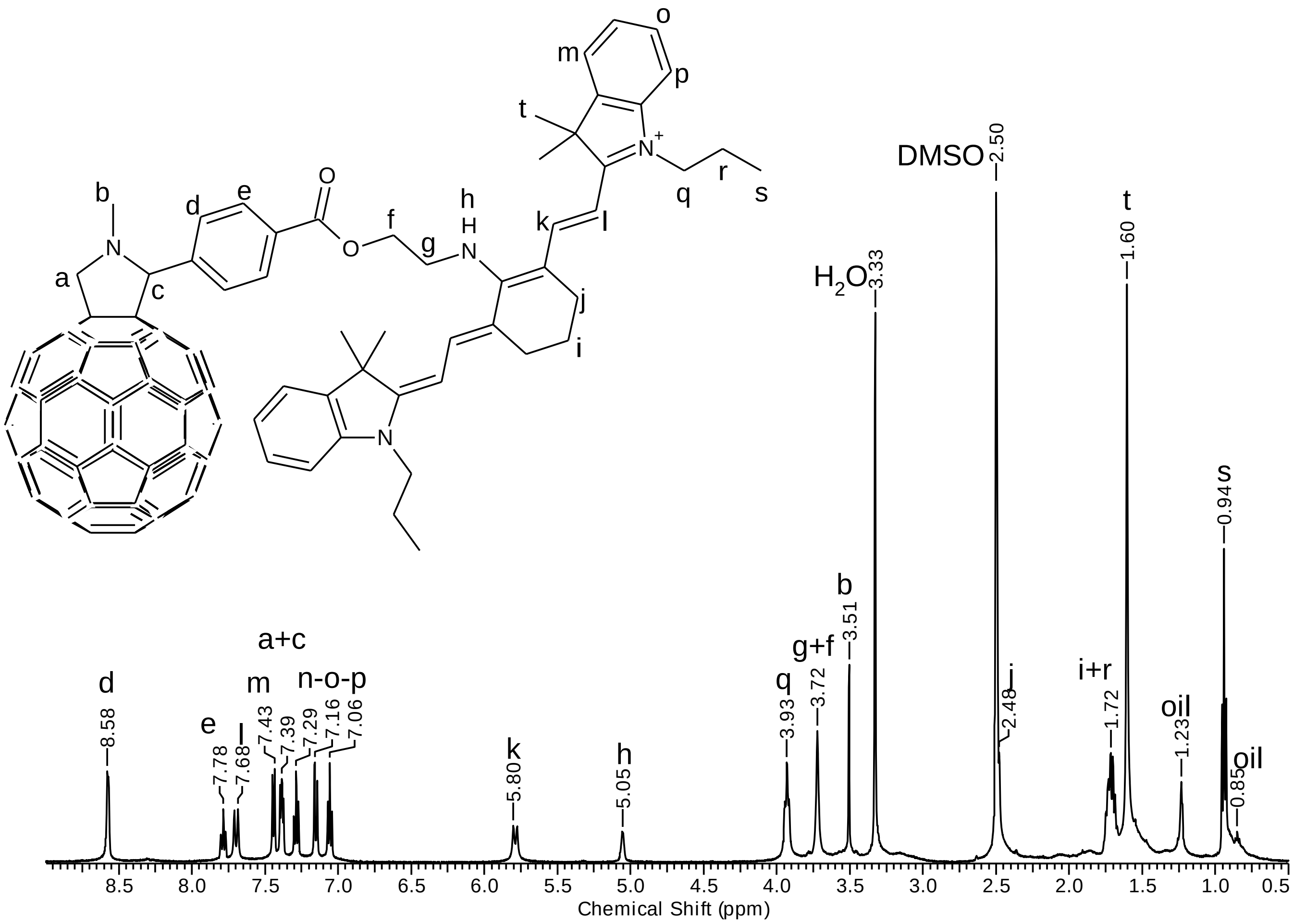
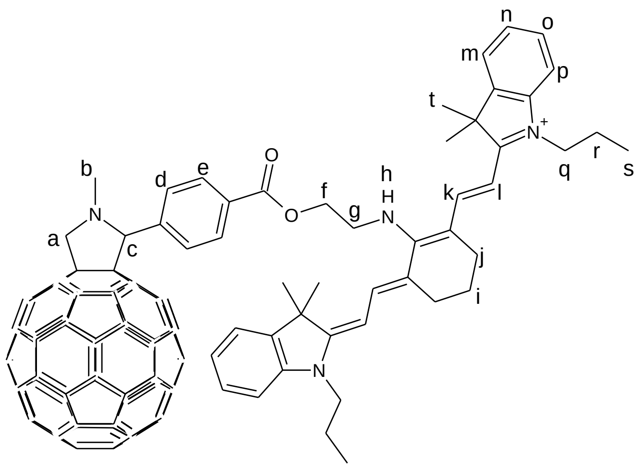


Figure S6. ^{1}H NMR spectrum of dyad **3b** in DMSO-d_6.

Dyad 3b ^{1}H-^{1}H COSY NMR spectrum



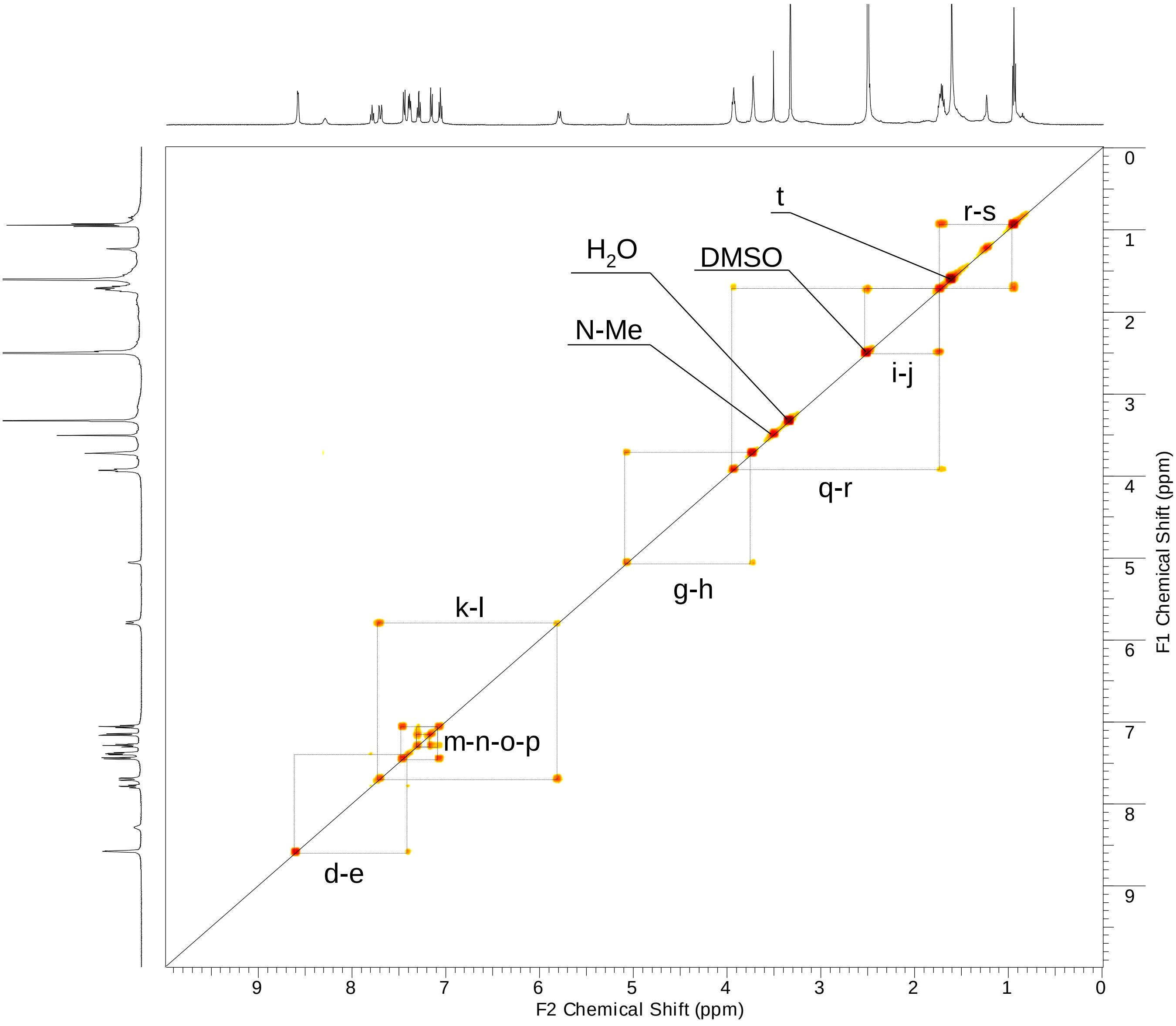


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Figure S7. ^{1}H-^{1}H COSY NMR spectrum of dyad **3b** in DMSO-d_6.

Compound 1 cyclic voltammetry curves

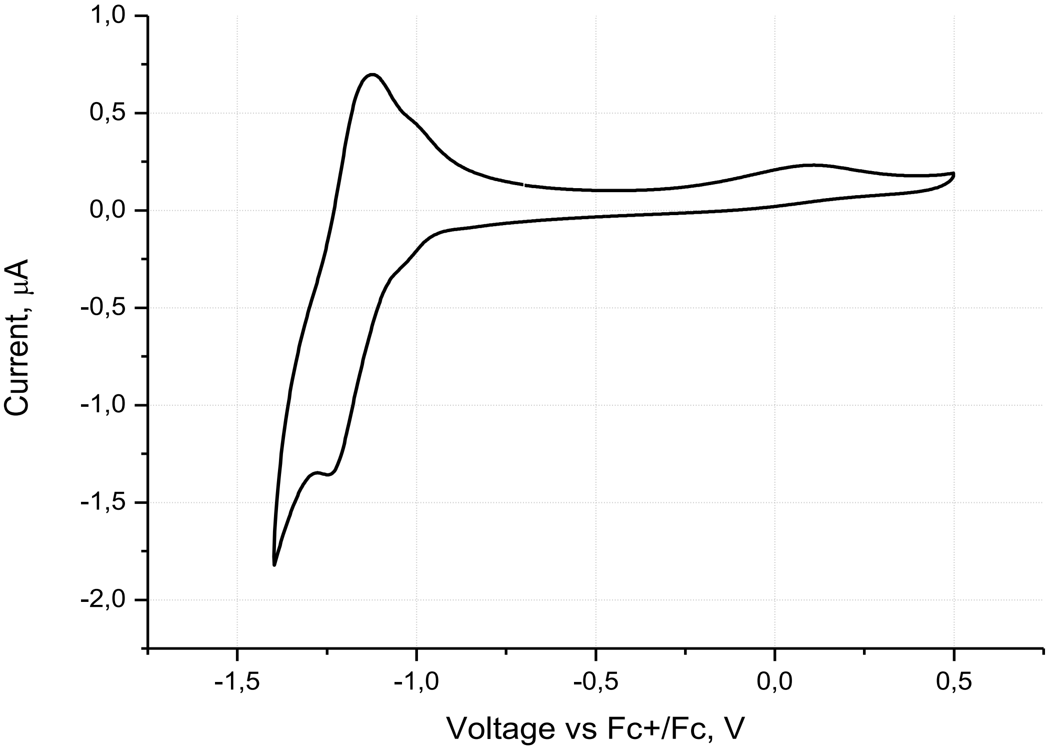


Figure S8. CV curves of compound **1** (precursor fullerene derivative). Solvent – THF with 0.1 M Bu_4NPF_6 as a supporting electrolyte.

Compound 2a cyclic voltammetry curves

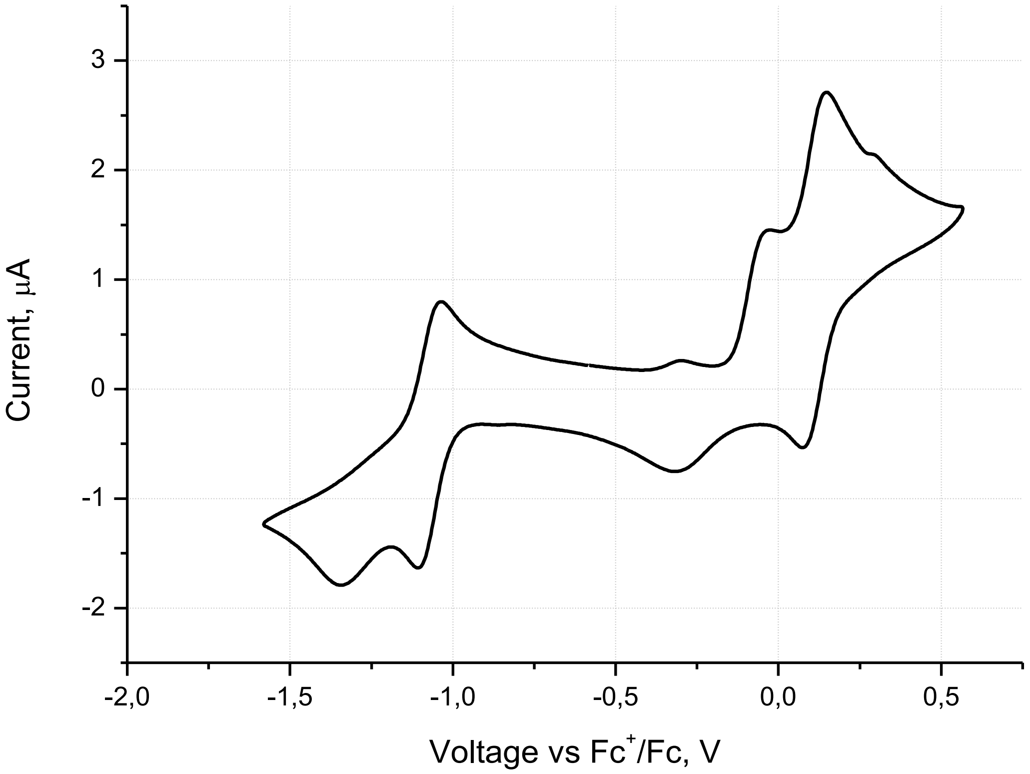


Figure S9. CV curves of compound **2a**.
Solvent – THF with 0.1 M Bu_4NPF_6 as a supporting electrolyte.

Compound 2b cyclic voltammetry curves

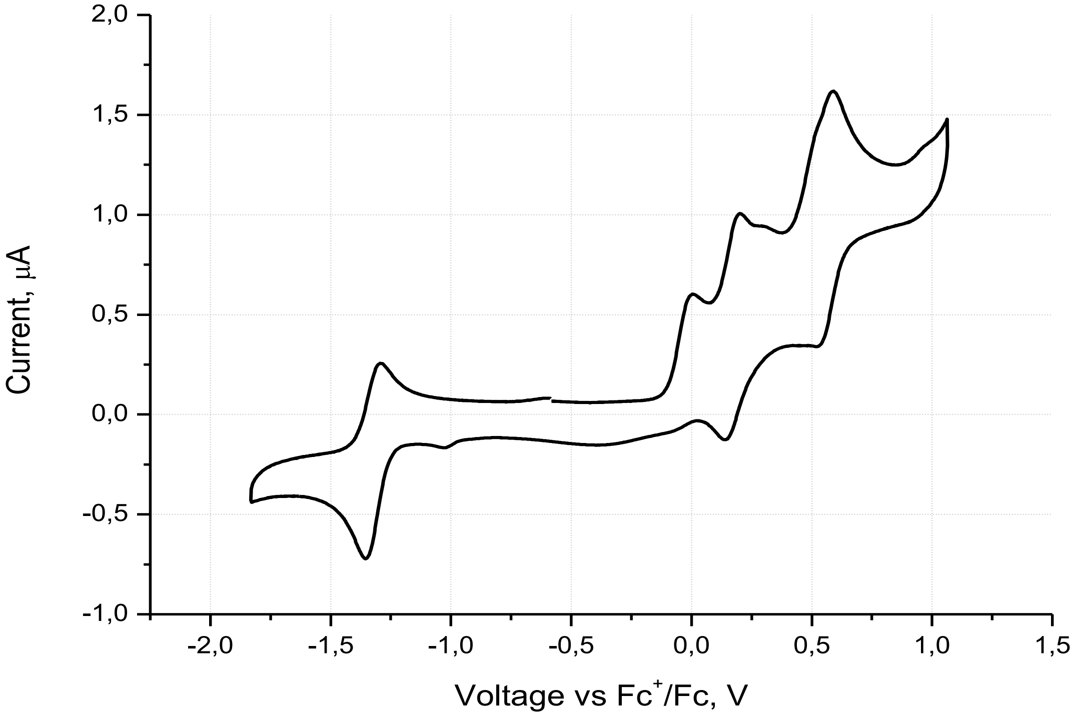


Figure S10. CV curves of compound **2b**.
Solvent – THF with 0.1 M Bu_4NPF_6 as a supporting electrolyte.

Dyad 3a cyclic voltammetry curves

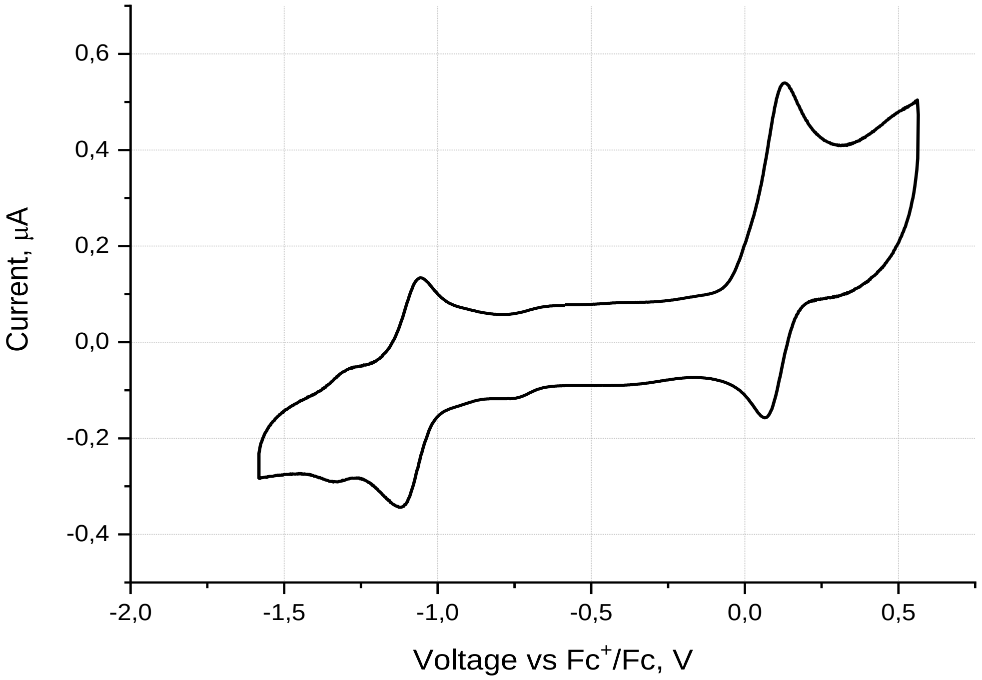


Figure S11. CV curves of compound **3a**.
Solvent – THF with 0.1 M Bu_4NPF_6 as a supporting electrolyte.

Dyad 3b cyclic voltammetry curves

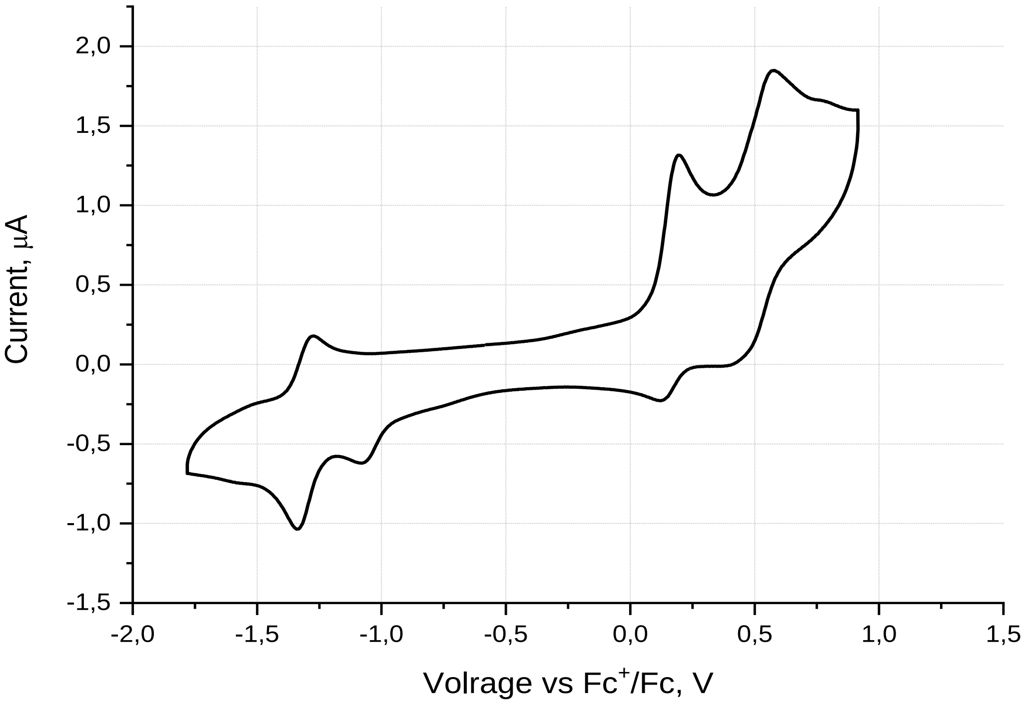


Figure S12. CV curves of compound **3b**.
Solvent – THF with 0.1 M Bu_4NPF_6 as a supporting electrolyte.

Compound 2b acid-base properties

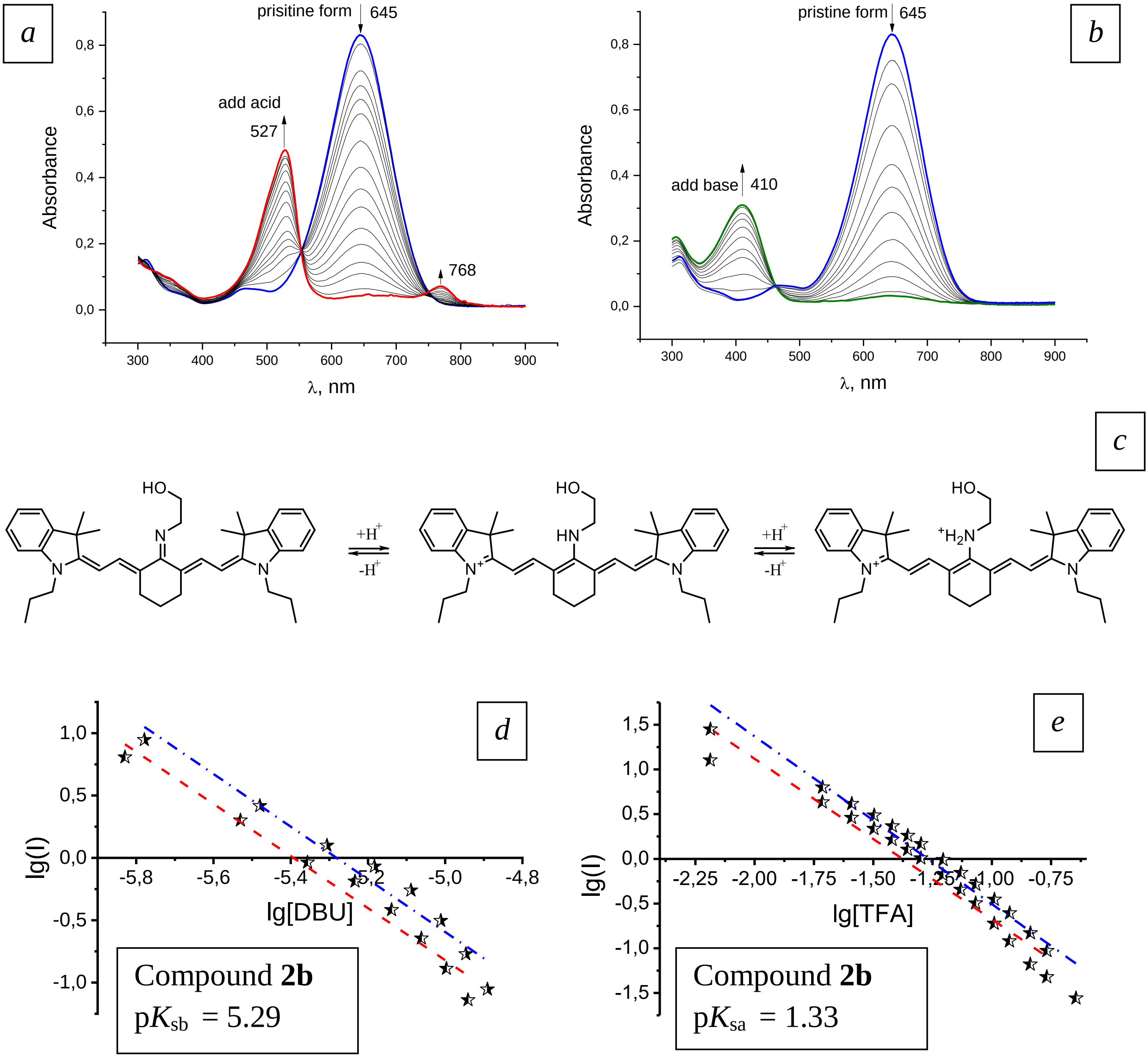


Figure S13. Compound **2b** acid-base properties:

a – absorption spectra of **2b** in acetonitrile upon addition of trifluoroacetic acid (TFA).

b – absorption spectra of **2b** in acetonitrile upon addition of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).

c – scheme for possible protonation and deprotonation processes for compound **2b**.

d – titration curves of substance **2b** in the presence of DBU.

e – titration curves of substance **2b** in the presence of TFA.

Dyad 3b acid-base properties

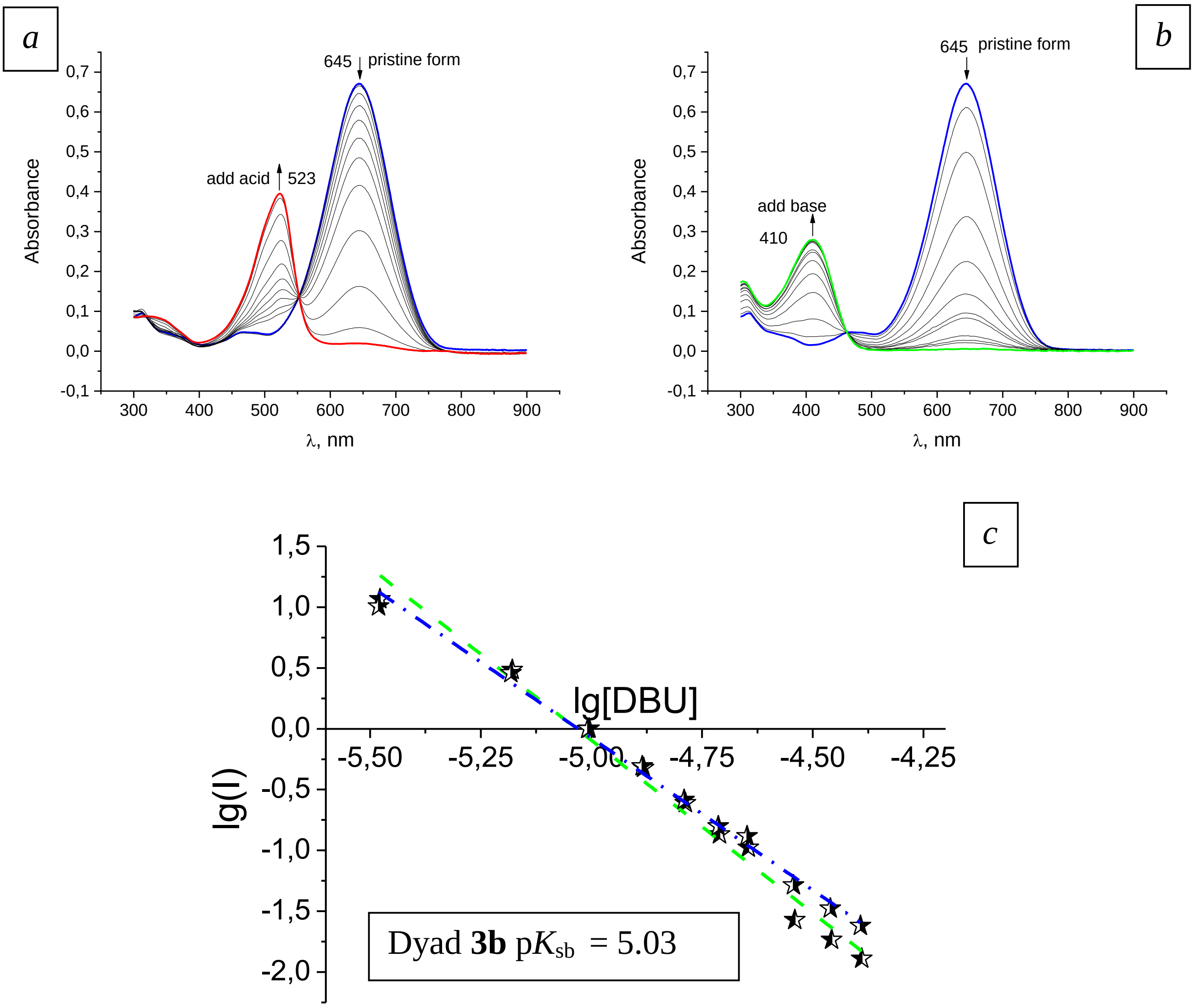
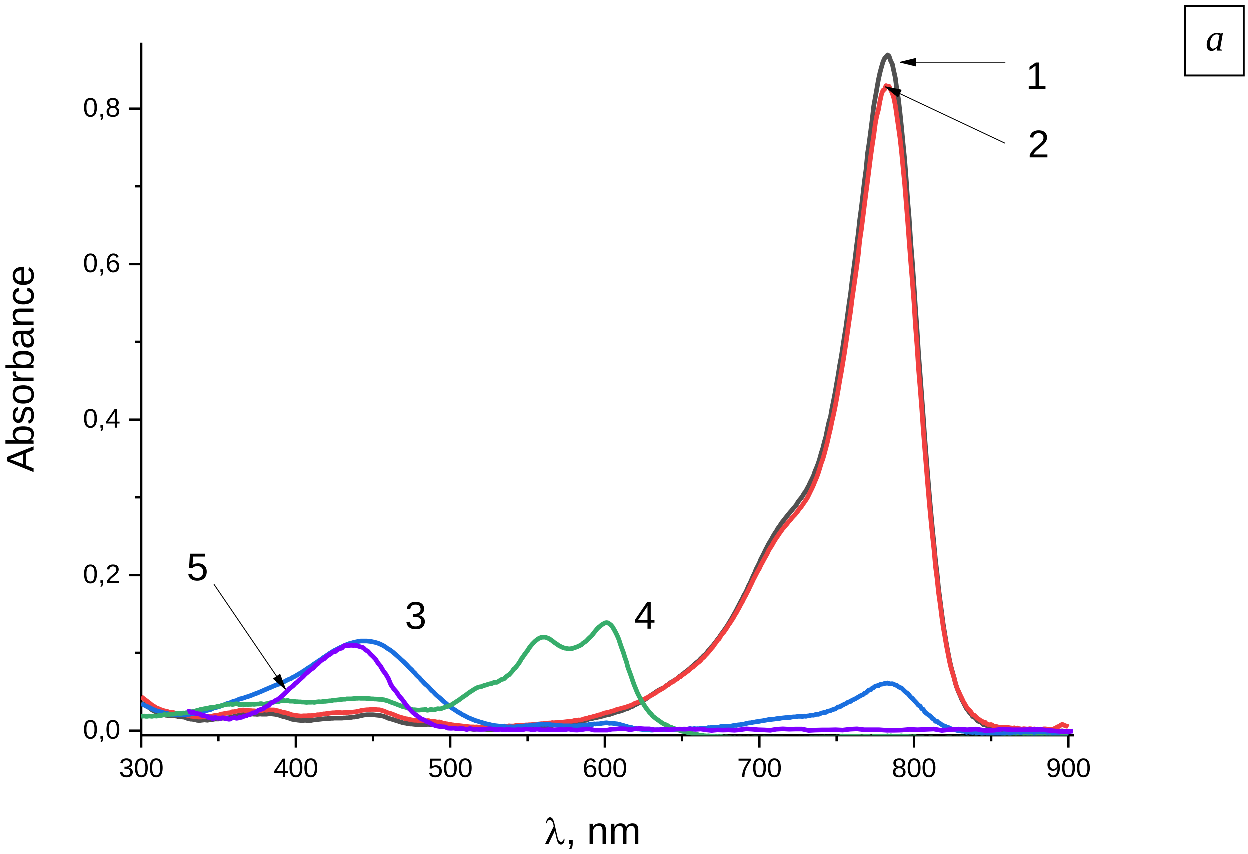


Figure S14. Compound **3b** acid-base properties:
a – absorption spectra of **3b** in acetonitrile upon addition of trifluoroacetic acid (TFA).
b – absorption spectra of **3b** in acetonitrile upon addition of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).
c – titration curves of substance **3b** in the presence of DBU.

Compound 2a acid-base properties



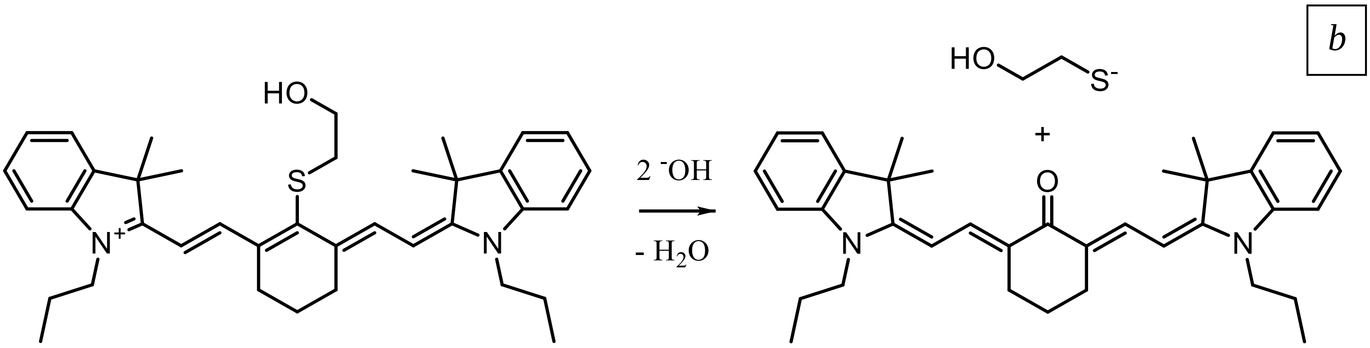


Figure S15. Compound **2a** acid-base properties:
a: absorption spectra of **2a** in acetonitrile (*1*);
absorption of **2a** in acetonitrile upon addition of 20 μl 100% TFA (*2*);
absorption of **2a** in acetonitrile upon addition of 100 μl 100% TFA (*3*);
absorption of **2a** in acetonitrile upon addition of 100 μl 100% TFA and an excess of K_2CO_3 (*4*);
absorption of **2a** in acetonitrile upon addition an excess of DBU (*5*).
b: scheme for the possible basic hydrolysis for compound **2a**.

References

[S1] S. K. Hau, Y.-J. Cheng, H.-L. Yip, Y. Zhang, H. Ma and A. K.-Y. Jen, *ACS Appl. Mater. Interfaces*, 2010, **2**, 1892.

[S2] X. Ma, M. Laramie and M. Henary, *Bioorg. Med. Chem. Lett.*, 2018, **28**, 509.