

SUPPORTING INFORMATION FOR

Proton-assisted seven-electron acceptor properties of di-iso-propylphenyl-bis-iminoacenaphthene

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General information. All manipulations were carried out in vacuo or under nitrogen using the standard Schlenk technique or in a glovebox. The solvents (THF, diethyl ether, and pentane) were distilled from sodium/benzophenone and stored over 3 Å molecular sieves under nitrogen. MeCN with a purity 99.99 % were stored under 3 Å molecular sieves or septum in a glove box atmosphere and used without additional purification. Acenaphthenequinone (95 %), 2,6-diisopropylphenyl aniline (98 %), metallic sodium (99, 9%), and Bu₄NPF₆ (>99.0 %) were purchased and used without any preliminary purification. Dpp-bian, dpp-bianH₂ was synthesized according to the published procedure.¹

NMR measurements were performed using Bruker spectrometers AVANCE-400 (399.93 MHz (¹H), 100.6 MHz (¹³C)) and AVANCE-600 (600.1 MHz (¹H), 150.9 MHz (¹³C)) equipped with a pulsed gradient unit capable of producing magnetic field pulse gradients in the z-direction of 53.5 G cm⁻¹. Chemical shifts are reported on the δ (ppm) scale relative to the residual solvent signals for ¹H and ¹³C.

Electrochemical measurements. Cyclic voltammetry measurements were performed with an E2P potentiostat of BASi Epsilon (USA). A stationary glassy-carbon electrode (with diameter of 3.0 mm) was used as a working electrode. Ferrocene was used as an internal standard. Ag/AgBF₄ was used as a comparison electrode. Before and after each CV and DPV experiments, a 1.5 mM solution of ferrocene was recorded under similar conditions. The potential was reproduced and remained constant in all the cases. E_{1/2} (Fc/Fc⁺) relative to the Ag/AgCl reference electrode in THF is +0.594 V. A platinum wire of 0.5 mm diameter was used as an auxiliary electrode. Measurements were performed under an inert nitrogen atmosphere of a glovebox.

Controlled potential electrolysis. *In situ* electrochemical reduction and oxidation of 2 mM dpp-bianH₂ THF solution was carried out using BASi Epsilon potentiostat in controlled-potential mode. Dpp-bianH₂ was dissolved in 0.1M solution of Bu₄NPF₆ in THF. The electrolysis potential was found from cyclic voltammetry studies performed earlier. Electrolysis was performed in three electrode divided cell. The surface area of the platinum cylindrical electrode used as the working electrode was 10.0 cm². A

ceramic plate with a pore size of 10 μm was used as a membrane. A platinum grid served as a counter electrode. During electrolysis, the electrolyte was stirred using a magnetic stirrer. The potential of reaction was measured vs. Ag/AgBF₄ system. Bu₄NPF₆ was used as supporting electrolyte in both cathode and anode sides. The number of electrons transferred at each stage (CV peaks) was determined by the amount of electricity passed through the solution at a certain CV potential (was used CV potential +200 mV).

EPR spectroscopy. EPR spectra were registered on a Bruker ELEXSYS E500 Xrange spectrometer. The solution or powder of samples were prepared and placed to quartz calcined ampule in glove box inert atmosphere and then soldered. For EPR-spectroelectrochemical experiments the EPR-cuvette describe earlier was used.² The 1 mM of sample was dissolved in 0.1 M Bu₄NPF₆ solution of THF in glovebox nitrogen atmosphere. Then, the prepared solution was poured into a EPR-spectroelectrochemical cell a pipette and removed from a glove box for studying.

UV/Vis spectroscopy. UV/Vis spectra were recorded at room temperature on a PerkinElmer Lambda 365 spectrometer. Spectra were registered with a scan speed of 480 nm/min, using a spectral width of 1 nm with use 10 mm quartz cuvettes. A thin layer quartz glass spectroelectrochemical cell with a Pt counter electrode and a Pt gauze working electrode were used for UV/Vis spectroelectrochemical experiments. A solution of sample was placed in a spectroelectrochemical UV/Vis quartz cuvette in a glove box and after that the reduced samples were obtained in situ in the spectroelectrochemical cell using BASi Epsilon potentiostat.

Synthesis of dpp-bianH₂ (I). Compound **I** was synthesized according to a previously published procedure.¹ The spectroscopic data are fully consistent with the literature data.

Synthesis of sodium complex (II). To solution of compound **I** in THF was added a small excess (2-3 equiv.) of sodium metal, that afford to change color from violet to dark blue. The solution was filtered by PTFE syringe filter and concentrated. The blue crystals of **II** suitable for XRD was obtained by THF/Et₂O layered system at -30°C during few days. The complex **II** was previously described.¹

Synthesis of sodium complex (III). The addition of a big piece of sodium (significant excess) to solution of sodium complex (**II**) or dpp-bian-H₂ (**I**) in THF leads to change color to red after mixing during few hours. Then, THF solution of complex **III** was decanted from sodium piece and concentrated. The red crystals of **III** were obtained from THF/Et₂O layered system at room temperature. Yield of crystalline sample is 50%. Elemental analysis calcd (%) for C₈₈H₁₁₄N₄Na₆O₄: C 73.92, H 8.04, N 3.92, O 4.48; found (%):C 73.92, H 8.05, N 3.90, O 4.49.

IR (KBr, cm^{-1}): 1589, 1617, 1645, 1669.

Synthesis of sodium complex (IV).

Compound **I** (dpp-bian-H₂) was synthesised according to a previously published procedure¹ as a result of the addition of water (3-4 equiv.) to the disodium complex of dpp-bian in Et₂O. After keeping the reaction mixture at cold, NaOH was precipitated as the solid. Then the NaOH was filtered and the reaction mixture was used for the synthesis of complex **IV** without further purification. To this dpp-bian-H₂ solution in Et₂O a large piece of sodium metal was added and mixed until the color of the solution became yellow. The solution was then decanted and concentrated under vacuum. The solution of complex **IV** was kept at -30°C overnight, resulting in the formation of yellow crystals suitable for X-ray diffraction analysis. Yield of crystalline product is 60%. Elemental analysis calcd (%) for C₄₄H₆₃N₂NaO₂: C 78.30, H 9.41, N 4.15, O 4.74; found (%): C 78.33, H 9.42, N 4.16, O 4.75. IR (KBr, cm^{-1}): 1591, 1640, 1650, 1671.

Synthesis of compound V. The small excess (10 equiv.) of water were added to solution of complexes **III** and **IV**. The reaction mixture color immediately turned pink. The solution of **V** was dried under MgSO₄ and dried under vacuum. The crystals of **V** suitable for XRD were obtained by THF/hexane layered system at room temperature. Yield of crystalline sample is 60%. ¹H NMR (500 MHz, THF-d₈, 298 K): δ = 7.37 (t, 1H, J = 7.5 Hz), 7.30 (m, 2H), 7.22 (d, 2H, J = 7.0 Hz), 7.16 (t, 1H, J = 7.5 Hz), 6.80 (d, 1H, J = 7.5 Hz), 6.72 (s, 1H), 6.66 (t, 1H, J = 7.5 Hz), 6.20 (d, 1H, J = 7.0 Hz), 5.30 (m, 2H), 5.06 (d, 1H, J = 6.5 Hz), 3.76 (d, 1H, J = 11.5 Hz), 3.70 (m, 2H), 1.33 (m, 20H); 1.24 (d, 4H, J = 7.0 Hz). ¹³C NMR (500 MHz, THF-d₈, 298 K): δ = 147.37, 146.41, 142.70, 142.19, 141.57, 136.70, 127.30, 126.09, 125.21, 123.68, 123.30, 123.22, 122.42, 122.28, 120.86, 120.59, 104.75, 30.64, 29.64, 29.27, 26.69, 25.62, 25.04, 24.39, 23.58. Elemental analysis calcd (%) for C₃₆H₄₄N₂: C 85.66, H 8.79, N 5.55; found (%): C 85.63, H 8.80, N 5.56. IR (KBr, cm^{-1}): 1574, 1590, 1612, 1644.

The X-ray structure determination details

Data sets for the single crystals were collected on a Bruker D8 QUEST diffractometer with a PHOTON III area detector and an I μ S DIAMOND microfocus X-ray tube using Mo K α (0.71073 Å) radiation at low temperature. The data reduction package APEX4 v2021.10-0 was used for data processing. The data were corrected for systematic errors and absorption: Numerical absorption correction based on integration over a multifaceted crystal model and empirical absorption correction based on spherical harmonics according to the point group symmetry using equivalent reflections.

The structures were solved by the intrinsic phasing approach using *SHELXT*-2018/2³ and refined by the full-matrix least-squares on F^2 using *SHELXL*-2018/3.⁴ Non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms [N-H] were found from Fourier difference maps, and these atoms were refined

isotropically. The positions of hydrogen atoms of methyl groups were found using rotating group refinement with idealized tetrahedral angles. The other hydrogen atoms were inserted at the calculated positions and refined as riding atoms.

Detailed information about crystal structure determination can be accessed via supplementary cif files. Deposition numbers CCDC 2345338-2345341 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures

References:

1. I. L. Fedushkin, V. A. Chudakova, G. K. Fukin, S. Dechert, M. Hummert, H. Schumann, *Russ. Chem. Bull.*, 2004, **53**, 2744–2750.
2. K. Kholin, M. Valitov, V. Burilov, E. Tselischeva, S. Strekalova, A. Mustafina, Y. Budnikova, M. Kadirov, *Electrochimica Acta*, 2015, **182**, 212-216.
3. G. M. Sheldrick, *SHELXT* – Integrated space-group and crystal-structure determination, *Acta Crystallogr., Sect. A: Found. Adv.* **2015**, *71*, 3–8.
4. G. M. Sheldrick, Crystal structure refinement with *SHELXL*, *Acta Crystallogr., Sect. C: Struct. Chem.* **2015**, *71*, 3–8.

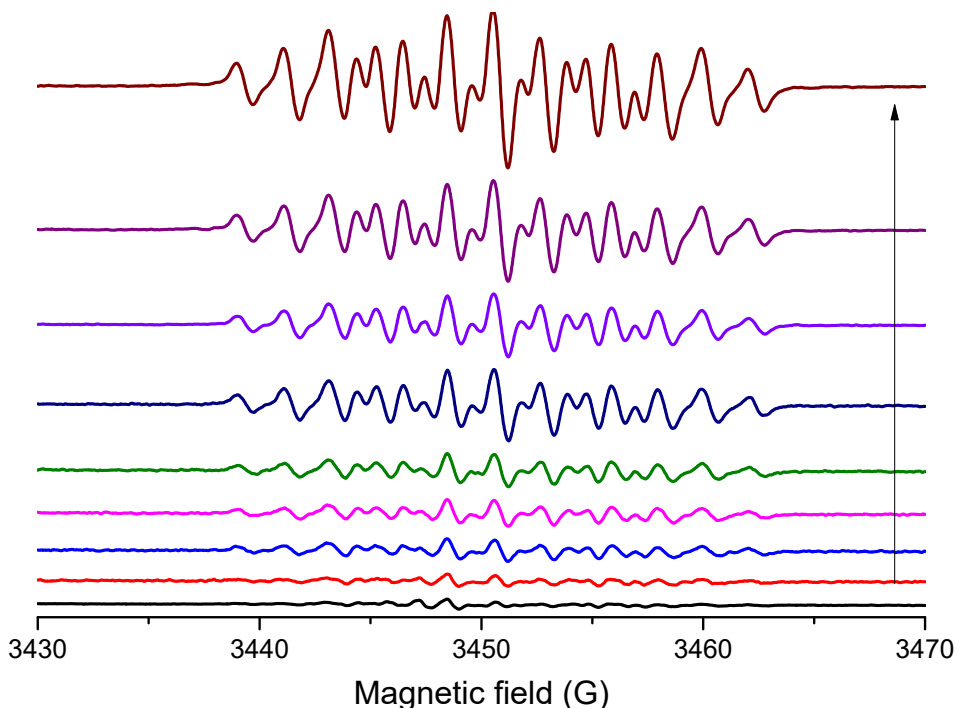


Figure S1. EPR – spectroelectrochemical reduction of dpp-bian-H₂ (I) at second CV reduction potential. Arrow shown the appearance and growth of signal of tri-anion radical [I]³⁻, forming during electrolysis.

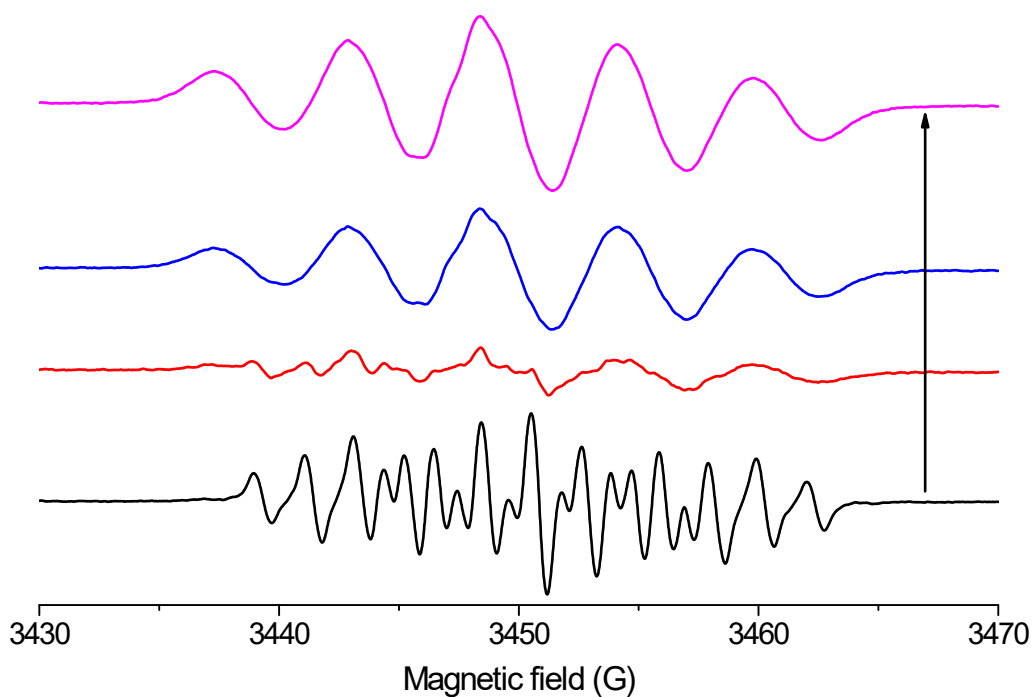


Figure S2. EPR spectra of tri-anion radical $[I]^{3-}$ after potential disconnection. Arrow shown the transformation of signal $[I]^{3-}$ (19 lines) to the signal of anion-radical $[I]^{-}$ (5 lines) during the time.

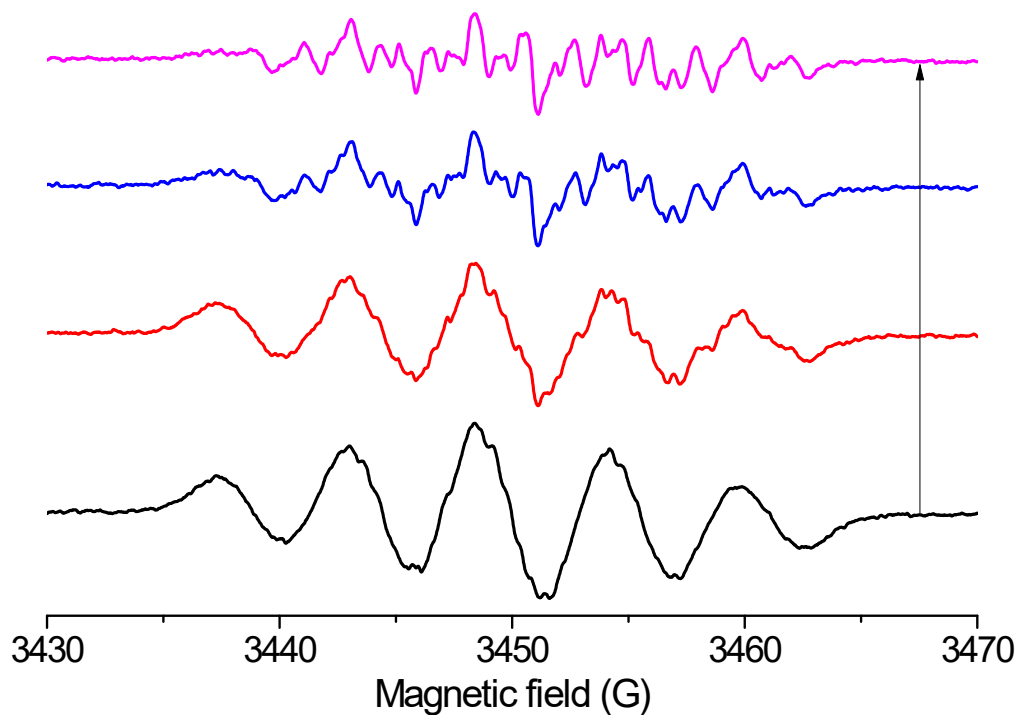


Figure S3. EPR spectra of anion radical $[I]^{-}$ after potential connection. Arrow shown the transformation of signal $[I]^{-}$ (5 lines) to the signal of tri-anion-radical $[I]^{3-}$ (19 lines) during electrolysis.

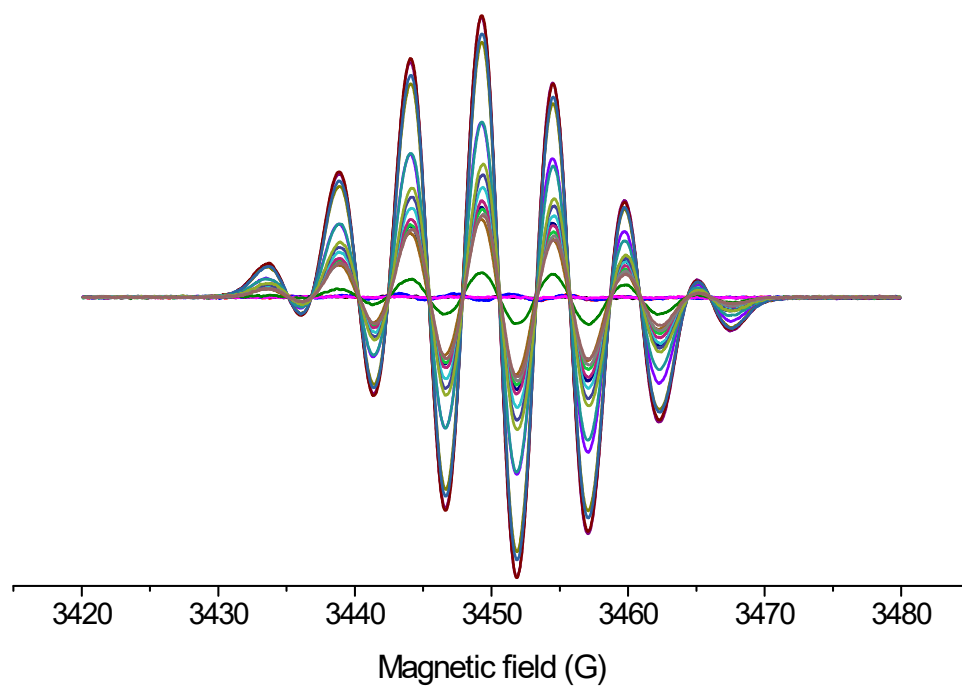


Figure S4. EPR – spectroelectrochemical oxidation of dpp-bian-H2 (I) at first CV oxidation potential.

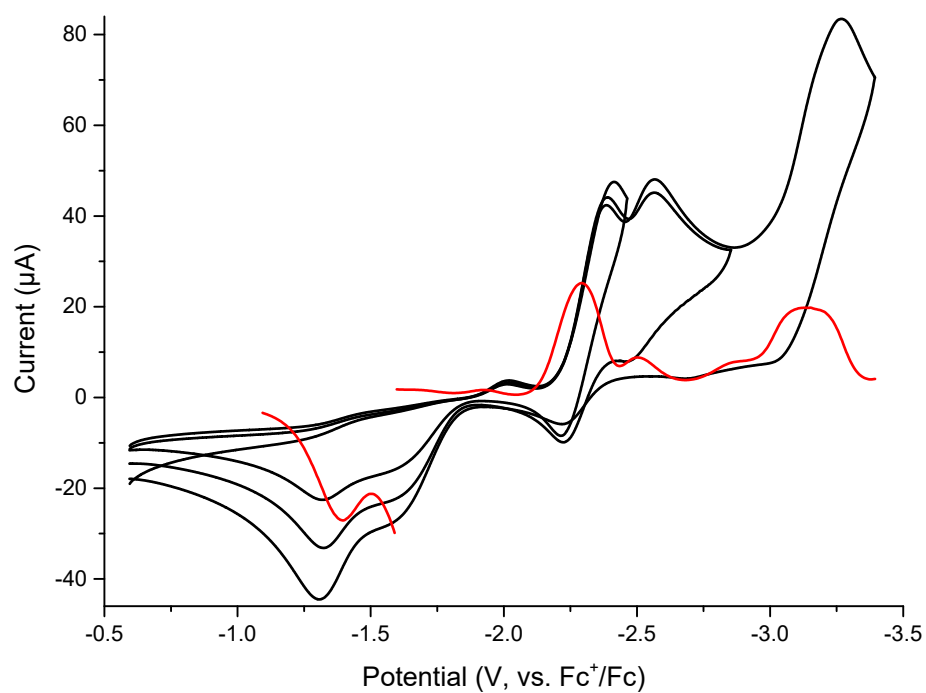


Figure S5. CV (shown in black) and DPV (shown in red) for 1mM THF solution of the sodium complex IV measured on GC electrode at scan rate 100 mV s⁻¹

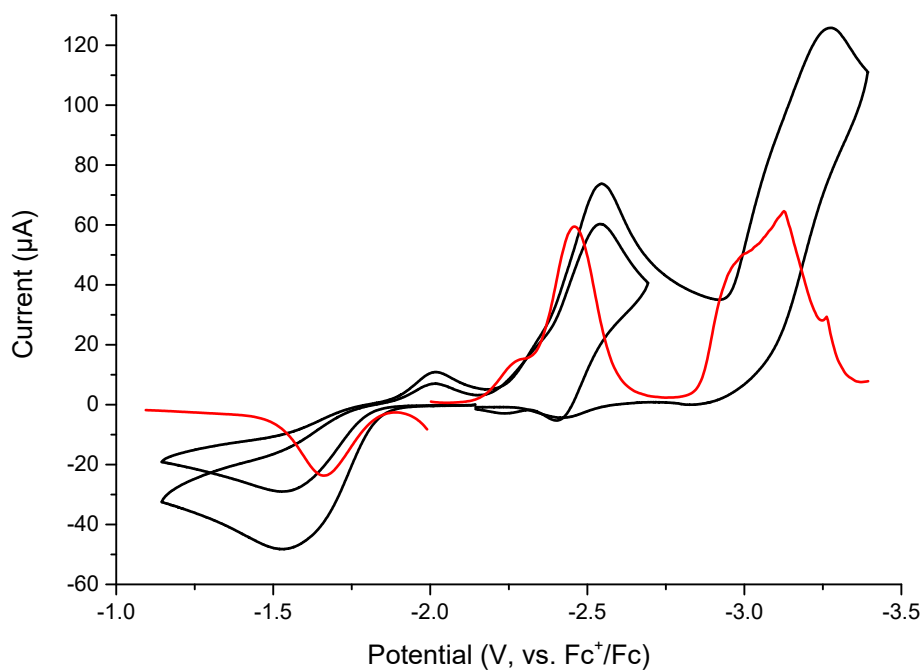


Figure S6. CV (shown in black) and DPV (shown in red) for 1mM THF solution of the sodium complex **II** measured on GC electrode at scan rate 100 mV s^{-1}

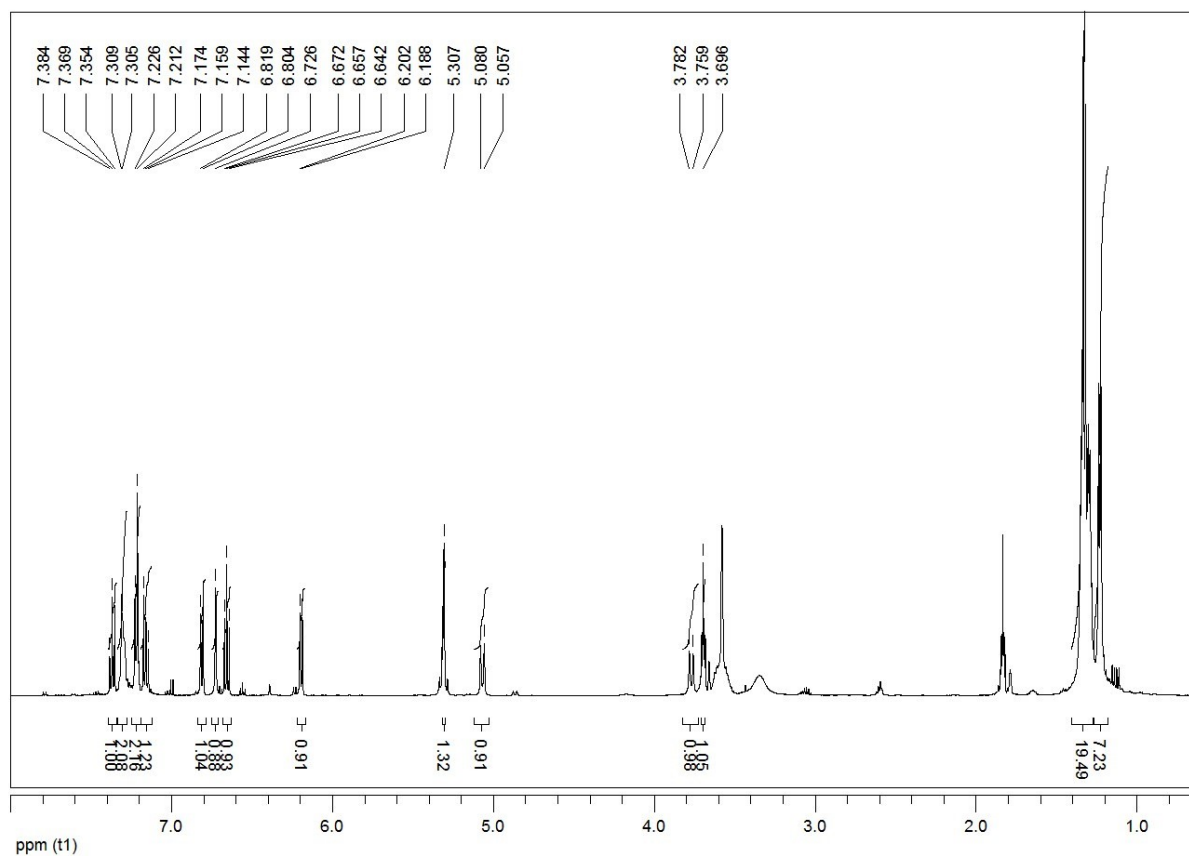


Figure S7. ^1H NMR (400 MHz) spectra for compound **V** in THF-d_8 .

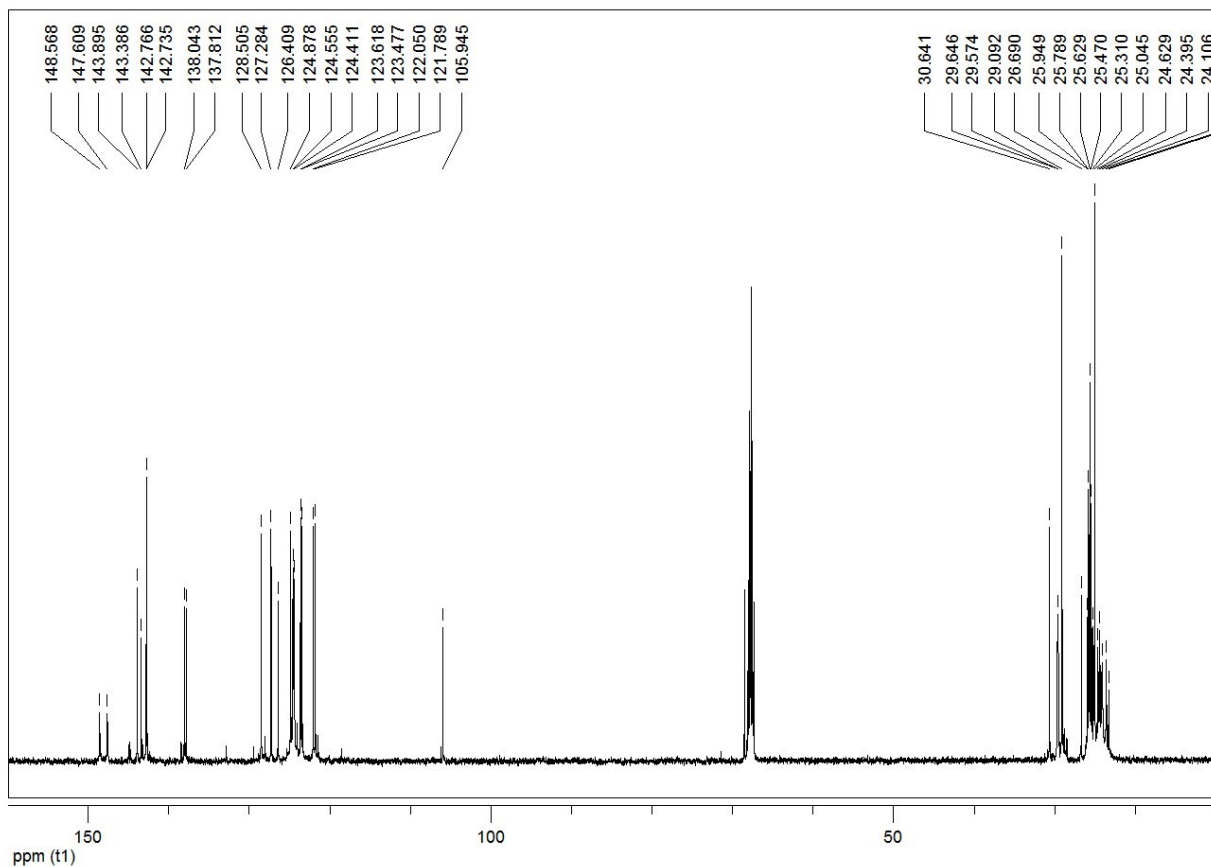


Figure S8. ^{13}C NMR (400 MHz) spectra for compound **V** in THF-d_8 .

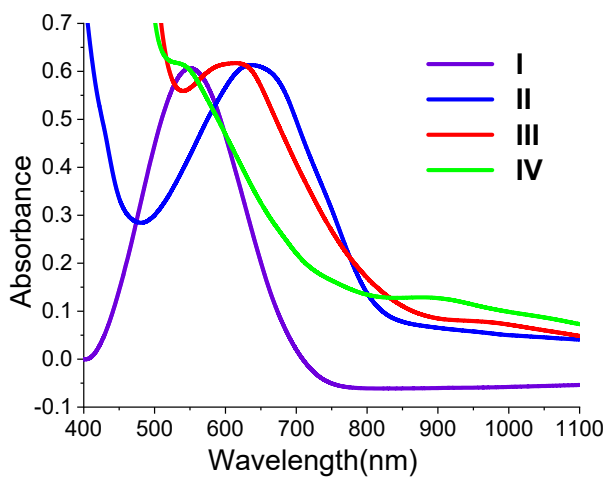


Figure S9. UV-vis spectra of compounds **I-IV** in THF.

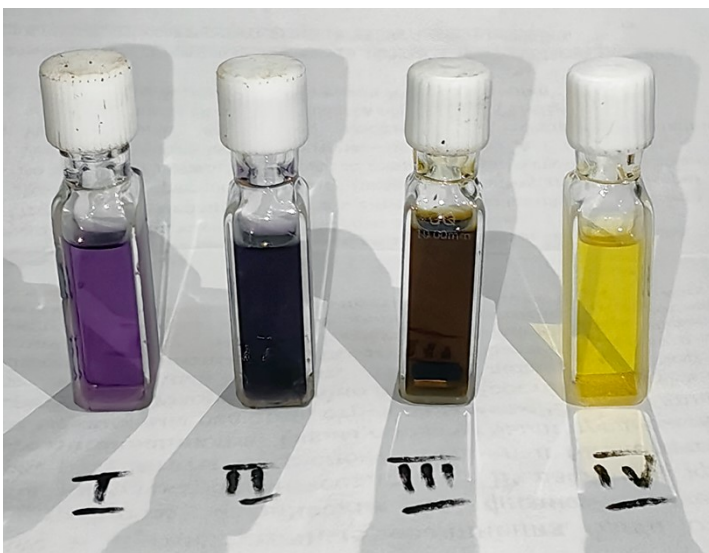


Figure S10. Demonstration of the colour of solutions of compounds I-IV in THF.



Figure S11. Photo of the three-electrode electrochemical cell used in the current work.