

Supporting Information

Croconaines as molecular materials for organic electronics: synthesis, solid state structure and transistor devices

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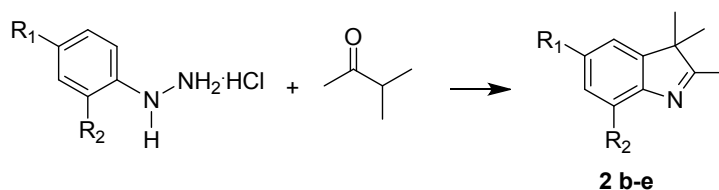
1 General information

Reagents were purchased at the highest commercial quality from Sigma-Aldrich, Apollo Scientific, TCI Europe N.V. and Fluorochem and used without further purification. Preparative column chromatography was carried out using Macherey-Nagel silica gel (60, particle size 0.063-0.2 mm). Macherey-Nagel aluminum sheets with silica gel 60 F₂₅₄ were used for TLC analyses. All new compounds were characterized by ¹H NMR, ¹³C NMR, FT-IR spectroscopy and LC-MS analysis. ¹H NMR and ¹³C NMR spectra were recorded on a Varian Inova at 400 and at 100.6 MHz, on a Varian Inova at 500 and at 126 MHz and on a Bruker Avance 2 at 600 and at 151 MHz respectively, by using the residual proton peak of CDCl₃ at δ = 7.26 ppm as internal standard for ¹H spectra and the signal of CDCl₃ at δ = 77 ppm as internal standard for ¹³C spectra. IR spectra were recorded on a Perkin-Elmer IR Spectrum Bx. Mass spectra were recorded on a Thermo Electron Corporation Polaris Q mass spectrometer instrument. High-resolution mass spectra were acquired on a Shimadzu high performance liquid chromatography-ion trap-time of flight mass spectrometer (LCMS-IT-TOF) via direct infusion of the samples using methanol as the elution solvent. Melting points were determined on a Stuart Scientific Melting point apparatus SMP3. UV-Vis absorption measurements have been performed on a Shimadzu UV-2401PC spectrophotometer. Cyclic voltammetry measurements were carried out with an Autolab potentiostat (model PGSTAT128N) by Metrohm using a conventional three electrode configuration consisting of a platinum working electrode, a platinum counter electrode and an Ag/AgCl reference electrode. All CV measurements were recorded at room temperature under nitrogen atmosphere in anhydrous dichloromethane solution (scan rate 0.1 Vs⁻¹). The solutions were prepared as follows: a 0.1 M solution of *n*-Bu₄NPF₆ solution in anhydrous dichloromethane as supporting electrolyte was prepared in a glove-box, the proper amount of croconaine was dissolved afterward in the desired volume of *n*-Bu₄NPF₆ solution at a final concentration of 10⁻³ M and put inside the three electrode cell. All measurements were calibrated using the Fc/Fc⁺ redox couple as external standard. LUMO-HOMO energy levels were calculated according to the following equations: $E_{\text{HOMO}} = -e(E_{\text{ox}} + 5.1\text{V})$ and $E_{\text{LUMO}} = -e(E_{\text{red}} + 5.1\text{V})$ where E is the average value between the first peak potential and the related reverse one measured for the compounds in solution versus Fc⁺/Fc reference and -5.1eV is the position of the formal potential of the Fc⁺/Fc redox couple in the Fermi scale.^[1]

Organic Thin Film Transistor Fabrication and characterization: bottom-contact bottom-gate configuration transistors were purchased from Fraunhofer Institute. They consist of *n*⁺-Si substrates with 230-nm thick thermally grown SiO₂ as the gate dielectric (15 nF capacitance) and pre-patterned pairs of interdigitated gold electrodes as the source and drain ($W = 10$ mm, $L = 2.5, 5, 10$ and 20 μm). All samples were prepared and measured in a N₂ filled glovebox to avoid oxidative doping of the materials and ensure reproducibility of the experiments. The silicon oxide surface was treated with hexamethyldisilazane (HMDS) in order to screen electron trapping arising from the hydroxyl groups present at the surface of the silicon oxide. The solution preparation and deposition (spincoating) as well as the HMDS treatment were performed under inert nitrogen atmosphere. The electrical measurements were performed via a Keithley 2636A connected to a Cascade probe station with micromanipulators. Ambient photoelectron spectroscopy measurements for the determination of the ionization energy were performed by sampling an area of about 4 mm² (beam size) by using a PhotoElectron Yield counter operating in Ambient conditions (PEYA), Model AC-2 from Riken Keike Co.

X-ray diffraction data were collected by a Bruker AXS X8 APEXII automated diffractometer equipped with a CCD detector and graphite-monochromatized MoK α radiation ($\lambda = 0.71073$ Å). The instrument operated at 50 kV, 30 mA and 40 mm crystal-to-detector distance. The collection strategy was optimized by the Apex program suite^[2] by combining several ω and ϕ rotation scans and recording the whole Ewald sphere ($\pm h, \pm k, \pm l$). The SAINT package^[3] was used for the integration of the intensities of reflections and for the correction of Lorentz-polarization (Lp). The SADABS software^[4] was employed for the absorption correction. Iterative method The SUPERFLIP program^[5], based on an iterative dual space algorithm, revealed the positions of all non H-atoms, difference Fourier syntheses located all remaining H-atoms. The structure refinements were carried out using the CRYSTALS software.^[6] The minimization function is $w(|F_o|^2 - |F_c|^2)^2$, where w is the weight of $|F_o|^2$ provided by an optimized weighting scheme. The refined parameters were: scale factors, atomic positions and anisotropic displacement parameters (H isotropic). Croconaine thin films for XRD analysis were deposited on glass substrates using spin coating method (CHCl₃ solution, 10mg/mL, 1000rpm/60s). A PANanalytical Empyrean XRD Diffractometer equipped with a PIXcel-3D detector with Cu K α radiation ($\lambda=1.540562$ Å) was employed to determine the XRD spectra of the thin films. The explored 2θ range was: 8-62°. Data from XRD was examined by using the PANalytical HighScore software.

2.1 General procedure for the preparation of indolenines 2 b-e.



To a solution of hydrazine hydrochloride (1 equiv.) in acetic acid, 3-methylbutan-2-one (1.1 or 1.9 equiv.) was added. The reaction mixture was heated at 80 °C for 6 h, then cooled to room temperature and stirred for further 18 h. After removing the acetic acid under vacuum, 50 mL of an aqueous solution of KOH (10%w/w) were added. The resulting mixture was extracted with diethyl ether (3×50 mL), then the combined organic layers were dried over Na₂SO₄ and concentrated under vacuum. Compounds **2b** and **2c** were used without further purification. Compounds **2d-e** were purified by column chromatography.

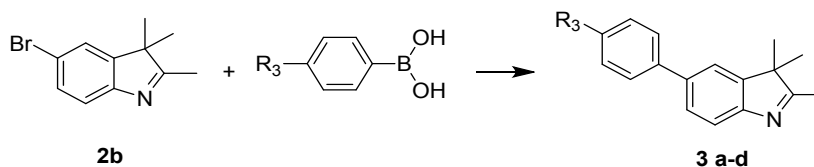
5-bromo-2,3,3-trimethyl-3H-indole (2b).^[7] Compound **2b** was synthesized from 4-bromophenylhydrazine hydrochloride (2.39 g, 11 mmol) and 3-methylbutan-2-one (2 mL, 21 mmol) in acetic acid (15 mL) in accordance with the general procedure. Red oil, yield 90%; GC-MS (70 eV) *m/z* 239 (M+2, 88%), 237 (M+, 92), 224 (96), 222 (100), 143 (90), 115 (92); ¹H NMR (CDCl₃, 400 MHz) δ: 7.42 - 7.36 (m, 3H), 2.25 (s, 3H), 1.28 (s, 6H); ¹³C NMR (CDCl₃, 100.6 MHz) δ: 188.2, 152.4, 147.6, 130.4, 124.6, 121.0, 118.6, 53.9, 22.7, 15.2; IR (KBr, cm⁻¹) ν: 2965, 1574, 1446, 1245, 1199, 824.

5-Iodo-2,3,3-trimethyl-3H-indole (2c).^[8] Compound **2c** was synthesized from 4-iodophenylhydrazine hydrochloride (1.5 g, 6.41 mmol) and 3-methylbutan-2-one (0.753 mL, 7.05 mmol) in acetic acid (15 mL) in accordance with the general procedure. The solvent was evaporated yielding the desired product. Orange oil, yield 87%; GC-MS (70 eV) *m/z* 285 (M+, 100), 270 (42), 143 (50), 115 (84); ¹H NMR (CDCl₃ 400 MHz) δ: 7.56 - 7.53 (m, 2H), 7.22 (d, *J* = 7.9 Hz; 1H), 2.17 (s, 3H), 1.22 (s, 6H); ¹³C NMR (CDCl₃ 100.6 MHz) δ: 188.3, 153.4, 148.2, 136.7, 130.7, 121.8, 89.9, 54.0, 22.9, 15.4; IR (KBr, cm⁻¹) ν: 2961, 1686, 1484, 1332, 1289, 1171, 938.

5-Fluoro-2,3,3-trimethyl-3H-indole (2d).^[9] Compound **2d** was synthesized from 4-fluorophenylhydrazine hydrochloride (1.7 g, 11 mmol) and 3-methylbutan-2-one (2 mL, 21 mmol) in acetic acid (15 mL) in accordance with the general procedure. The crude mixture was purified by column chromatography (silica gel, diethyl ether/chloroform, 1:1) yielding the desired product. Orange oil, yield 98%; LCMS-IT-TOF calculated for C₁₁H₁₂NF (M+H)⁺: 178.1027, found: *m/z* 178.1021; ¹H NMR (CDCl₃ 400 MHz) δ: 7.47 - 7.41 (m, 1H), 7.00 - 6.93 (m, 2H), 2.25 (s, 3H), 1.29 (s, 6H); ¹³C NMR (CDCl₃ 100.6 MHz) δ: 187.8 (d, *J* = 3.6 Hz), 161.3 (d, *J* = 243.5 Hz), 149.7 (d, *J* = 2.1 Hz), 147.7 (d, *J* = 8.4 Hz), 120.5 (d, *J* = 8.8 Hz), 114.2 (d, *J* = 23.6 Hz), 109.1 (d, *J* = 24.3 Hz), 54.2 (d, *J* = 2.3 Hz), 23.1, 15.5; IR (KBr, cm⁻¹) ν: 2965, 1581, 1460, 1267, 1178, 895, 824.

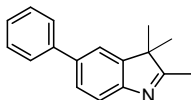
7-Fluoro-2,3,3-trimethyl-3H-indole (2e). Compound **2e** was synthesized from 2-fluorophenylhydrazine hydrochloride (1.7 g, 11 mmol) and 3-methylbutan-2-one (2 mL, 21 mmol) in acetic acid (15 mL) in accordance with the general procedure. The crude mixture was purified by column chromatography (silica gel, diethyl ether/chloroform, 1:1) yielding the desired product. Red oil, yield 77%; LCMS-IT-TOF calculated for C₁₁H₁₂NF [M+H]⁺: 178.1027, found: *m/z* 178.1024; ¹H NMR (CDCl₃ 500 MHz) δ: 7.19 - 7.11 (m, 1H), 7.08 - 6.96 (m, 2H), 2.30 (s, 3H), 1.30 (s, 6H); ¹³C NMR (CDCl₃ 126 MHz) δ: 188.5, 153.8 (d, *J* = 253.0 Hz), 149.2 (d, *J* = 3.4 Hz), 140.3 (d, *J* = 11.1 Hz), 126.4 (d, *J* = 6.4 Hz), 117.0 (d, *J* = 3.5 Hz), 114.7 (d, *J* = 18.6 Hz), 54.4 (d, *J* = 1.5 Hz), 23.0, 15.5; IR (KBr, cm⁻¹) ν: 2965, 1615, 1577, 1482, 1458, 1242, 752.

2.2 Procedures for the preparation of indolenines 3 a-d.

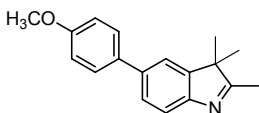


General procedure for the preparation of indolenines 3 a-c: To a solution of 5-bromo-2,3,3-trimethyl-3H-indole **2b** (1 equiv.) in tetrahydrofuran and water, potassium carbonate (17.5 equiv.) and Pd(PPh₃)₄ (0.04 equiv.) were added under nitrogen atmosphere. The reaction mixture was heated at 70 °C for 30 minutes, then arylboronic acid (1.5 equiv.) was added. The reaction mixture was refluxed and stirred for 24 h, then cooled to room temperature, quenched with water and extracted with ethyl acetate (3×50 mL). The combined organic layers were dried over Na₂SO₄ and concentrated under vacuum. Compounds **3a-c** were purified by column chromatography (silica gel, diethyl ether/ethyl acetate, 1:1).

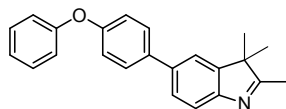
2,3,3-Trimethyl-5-phenyl-3H-indole (3a). Compound **3a** was synthesized from 5-bromo-2,3,3-trimethyl-3H-indole **2b** (600 mg, 2.53 mmol), potassium carbonate (6.11 g, 44.26 mmol), Pd(PPh₃)₄ (58.44 mg, 0.05 mmol) and 4-phenylboronic acid (463 mg, 3.78 mmol) in dry tetrahydrofuran (31 mL) and water (10 mL) in accordance with the general procedure. Orange oil, yield 88%; LCMS-IT-TOF calculated for C₁₇H₁₇N [M+H]⁺: 236.1434, found: *m/z* 236.1410; ¹H NMR (CDCl₃ 400 MHz) δ: 7.59 - 7.56 (m, 3H), 7.52 - 7.46 (m, 2H), 7.44 - 7.36 (m, 2H), 7.33 - 7.29 (m, 1H), 2.28 (s, 3H), 1.32 (s, 6H); ¹³C NMR (CDCl₃ 100.6 MHz) δ: 188.1, 152.9, 146.1, 140.2, 138.3, 128.5, 127.0, 126.8, 126.6, 120.9, 119.8, 53.6, 25.0, 15.3; IR (KBr, cm⁻¹) ν: 2961, 1573, 1461, 1207, 756, 698.



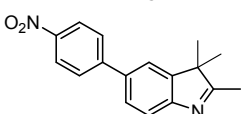
5-(4-Methoxyphenyl)-2,3,3-trimethyl-3H-indole (3b). Compound **3b** was synthesized from 5-bromo-2,3,3-trimethyl-3H-indole **2b** (600 mg, 2.53 mmol), potassium carbonate (6.1 g, 44.28 mmol), Pd(PPh₃)₄ (58.44 mg, 0.05 mmol) and 4-methoxyphenylboronic acid (577 mg, 3.8 mmol) in dry tetrahydrofuran (31 mL) and water (10 mL) in accordance with the general procedure. Red-orange oil, yield 82%; LCMS-IT-TOF calculated for C₁₈H₁₉NO [M+H]⁺: 266.1539, found: *m/z* 266.1514; ¹H NMR (CDCl₃ 400 MHz) δ: 7.53 (d, *J* = 8.0 Hz; 1H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.46 - 7.41 (m, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 3.82 (s, 3H), 2.26 (s, 3H), 1.31 (s, 6H); ¹³C NMR (CDCl₃ 100.6 MHz) δ: 187.7, 158.8, 152.5, 146.1, 137.9, 133.8, 128.0, 126.1, 119.7, 119.7, 114.0, 55.2, 53.5, 23.0, 15.3; IR (KBr, cm⁻¹) ν: 2961, 1571, 1515, 1465, 1246, 1036, 841.



2,3,3-Trimethyl-5-(4-phenoxyphenyl)-3H-indole (3c). Compound **3c** was synthesized from 5-bromo-2,3,3-trimethyl-3H-indole **2b** (638 mg, 2.69 mmol), potassium carbonate (6.5 g, 47.07 mmol), Pd(PPh₃)₄ (62.14 mg, 0.054 mmol) and 4-phenoxyphenylboronic acid (638 mg, 2.69 mmol) in dry tetrahydrofuran (31 mL) and water (10 mL) in accordance with the general procedure. Yellow-orange oil, yield 68%; LCMS-IT-TOF calculated for C₂₃H₂₁NO [M+H]⁺: 328.1696, found: *m/z* 328.1672; ¹H NMR (CDCl₃ 400 MHz) δ: 7.56 - 7.52 (m, 3H), 7.48 - 7.46 (m, 1H), 7.43 (d, *J* = 1.7 Hz; 1H), 7.35 - 7.31 (m, 2H), 7.23 (s, 1H), 7.11 - 7.02 (m, 4H), 2.27 (s, 3H), 1.32 (s, 6H); ¹³C NMR (CDCl₃ 100.6 MHz) δ: 188.3, 157.3, 156.8, 153.1, 146.5, 137.9, 136.7, 129.9, 128.6, 126.6, 123.5, 120.2, 120.1, 119.3, 119.1, 53.9, 23.3, 15.6; IR (film, cm⁻¹) ν: 2961, 1586, 1487, 1459, 1231, 1117, 826.



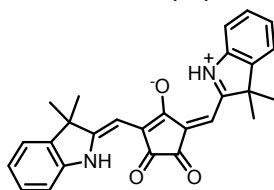
2,3,3-Trimethyl-5-(4-nitrophenyl)-3H-indole (3d). To a solution of 5-bromo-2,3,3-trimethyl-3H-indole **2b** (500 mg, 2.1 mmol) in dry toluene (30 mL), ethanol (10 mL) and water (20 mL), potassium carbonate (1.16 g, 8.4 mmol) and Pd(PPh₃)₄ (242 mg, 0.21 mmol) were added under nitrogen atmosphere. The reaction mixture was heated at 70 °C for 30 minutes, then 4-nitrophenylboronic acid (522 mg, 3.1 mmol) was added. The reaction mixture was refluxed and stirred for 24 h, then cooled to room temperature, quenched with water and extracted with ethyl acetate (3×50 mL). The combined organic layers were dried over Na₂SO₄ and concentrated under vacuum. The crude mixture was purified by column chromatography (silica gel, hexane/ethyl acetate, 7:3), yielding the desired product. Brown solid, yield 78%; m.p. 142 - 143 °C; LCMS-IT-TOF calculated for C₁₇H₁₆N₂O₂ [M+H]⁺: 281.1285, found: *m/z* 281.1259; ¹H NMR (CDCl₃ 400 MHz) δ: 8.25 (d, *J* = 7.96 Hz, 2H), 7.71 (d, *J* = 7.96 Hz, 2H), 7.60 - 7.49 (m, 3H), 2.29 (s, 3H), 1.34 (s, 6H); ¹³C NMR (CDCl₃ 100.6 MHz) δ: 189.7, 154.7, 148.0, 147.0, 146.9, 136.0, 127.9, 127.4, 124.2, 120.5, 120.5, 54.1, 23.2, 15.7; IR (KBr, cm⁻¹) ν: 2971, 1593, 1514, 1107, 828.



2.3 General procedure for the preparation of croconaine dyes **4 a-e** and **5 a-d**^[10]

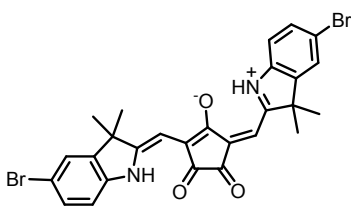
To a solution of indolenine (2 equiv.) in dry toluene and butanol, croconic acid (1 equiv.) was added. The reaction mixture was refluxed at 110 °C for 3 h, using Dean-Stark apparatus to remove water, and then cooled to -20 °C for 24 h. The reaction mixture was warmed to room temperature and the precipitate was filtered off and washed with diethyl ether and hexane. Pure compounds **4b-d** and **5a-d** were obtained. Compound **4a** was purified by column chromatography (silica gel, chloroform/methanol 97:3); compound **4e** was purified by column chromatography (silica gel, diethyl ether/chloroform 9:1).

3-(3,3-Dimethyl-1,3-dihydro-indol-2-ylidene-methyl)-5-(3,3-dimethyl-3H-indol-2-ylmethylene)-4-hydroxy-cyclopent-3-ene-1,2-dione (4a).^[11] Compound **4a** was synthesized from 2,3,3-trimethyl-3H-indole **2a** (318 mg, 2 mmol) and croconic acid (142 mg, 1 mmol) in 1-butanol (5 mL) and dry toluene (5 mL) in accordance with the general procedure. Bronze solid, yield 60%; m.p. 325 - 327 °C; LCMS-IT-TOF calculated for C₂₇H₂₄N₂O₃ [M-H]⁻: 423.1741, found: *m/z* 423.1727; ¹H NMR (CDCl₃ 500 MHz) δ: 15.75 - 14.45 (m, 2H), 7.37 - 7.27 (m, 6H), 7.24 - 7.13 (m, 2H), 6.14 - 5.95 (m, 2H), 1.54 - 1.51 (m, 12H); ¹³C NMR (126 MHz, CDCl₃) δ: 186.2, 185.7, 185.4, 185.3, 185.2, 177.1, 176.6, 174.9, 146.6, 145.5, 145.0, 141.3, 141.2, 141.1, 141.1, 140.8, 140.3, 128.7, 128.6, 128.6, 125.4, 125.0, 124.5, 122.7, 122.5, 122.5, 113.5, 113.3, 112.8, 94.6, 93.8, 91.2, 50.5, 50.2, 49.9, 26.2, 25.7, 25.5; IR (KBr, cm⁻¹) ν: 2962, 1670, 1486, 1460, 1340, 1293, 1172, 938.



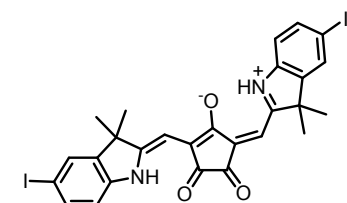
26.2, 25.7, 25.5; IR (KBr, cm⁻¹) ν: 2962, 1670, 1486, 1460, 1340, 1293, 1172, 938.

3-(5-bromo-3,3-dimethyl-1,3-dihydro-indol-2-ylidene-methyl)-5-(5-bromo-3,3-dimethyl-3H-indol-2-ylmethylene)-4-hydroxy-cyclopent-3-ene-1,2-dione (4b).



Compound **4b** was synthesized from **2b** (410 mg, 1.74 mmol) and croconic acid (124 mg, 0.87 mmol) in 1-butanol (5 mL) and dry toluene (5 mL) in accordance with the general procedure. Purple solid, yield 80%; m.p. 298 - 300 °C; LCMS-IT-TOF calculated for C₂₇H₂₂Br₂N₂O₃ [M-H]⁻: 578.9924, found: *m/z* 578.9900; ¹H NMR (CDCl₃ 600 MHz) δ: 15.96 - 14.44 (m, 2H), 7.51 - 7.42 (m, 4H), 7.19 - 7.06 (m, 2H), 6.13 - 5.93 (m, 2H), 1.55 - 1.52 (m, 12H); ¹³C NMR (100.6 MHz, CDCl₃) δ: 186.0, 185.7, 185.5, 184.9, 177.1, 176.3, 174.3, 146.7, 145.9, 145.3, 143.2, 142.9, 142.4, 140.4, 140.2, 131.8, 131.7, 126.3, 126.2, 118.9, 118.5, 117.7, 114.9, 114.7, 114.0, 95.2, 94.4, 91.6, 50.8, 50.5, 50.1, 26.3, 25.8, 25.5; IR (KBr, cm⁻¹) ν: 2963, 1685, 1485, 1452, 1334, 1291, 1173, 938.

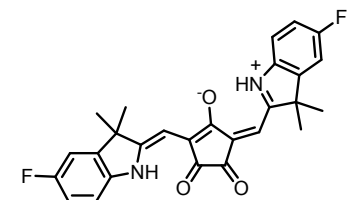
3-(5-Iodo-3,3-dimethyl-1,3-dihydro-indol-2-ylidenemethyl)-5-(5-iodo-3,3-dimethyl-3H-indol-2-ylmethylene)-4-hydroxy-cyclopent-3-ene-1,2-dione (4c).



Compound **4c** was synthesized from **2c** (855 mg, 3 mmol) and croconic acid (213 mg, 1.5 mmol) in 1-butanol (7.5 mL) and dry toluene (7.5 mL) in accordance with the general procedure. Red solid, yield 47%; m.p. 333 - 335 °C; LCMS-IT-TOF calculated for C₂₇H₂₂I₂N₂O₃ [M-H]⁻: 674.9647, found: *m/z* 674.9647; ¹H NMR (500 MHz, CDCl₃) δ: 15.95 - 14.40 (m, 2H), 7.70 - 7.58 (m, 4H), 7.10 - 7.00 (m, 2H), 6.12 - 5.90 (m, 2H), 1.51 (s, 12H); ¹³C NMR (126 MHz, CDCl₃) δ: 185.9, 185.6, 185.4, 185.4, 184.8, 176.7, 175.9, 173.9, 146.7, 145.9, 145.3, 143.4, 143.1, 142.6, 140.9, 140.8, 137.7, 137.6, 137.5, 131.9, 131.8, 131.7, 115.2, 115.0, 114.4, 95.1, 94.3, 91.5, 89.3, 88.8, 87.9, 77.3, 77.0, 76.8, 50.5, 50.2, 49.8, 26.2, 25.7, 25.4; IR (KBr, cm⁻¹) ν: 1686, 1484,

1332, 1289, 1171, 938.

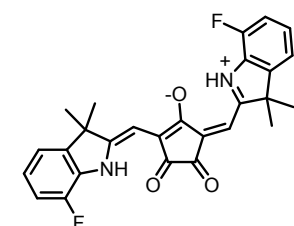
3-(5-Fluoro-3,3-dimethyl-1,3-dihydro-indol-2-ylidenemethyl)-5-(5-fluoro-3,3-dimethyl-3H-indol-2-ylmethylene)-4-hydroxy-cyclopent-3-ene-1,2-dione (4d).



Compound **4d** was synthesized from **2d** (500 mg, 2.82 mmol) and croconic acid (200 mg, 1.41 mmol) in 1-butanol (10 mL) and dry toluene (10 mL) in accordance with the general procedure. Golden solid, yield 55%; m.p. 277 - 279 °C; LCMS-IT-TOF calculated for C₂₇H₂₂F₂N₂O₃ [M-H]⁻: 459.1526, found: *m/z* 459.1537; ¹H NMR (500 MHz, CDCl₃) δ: 15.90 - 14.45 (m, 2H), 7.25 - 6.95 (m, 6H), 6.11 - 5.90 (m, 2H), 1.53 - 1.51 (m, 12H); ¹³C NMR (126 MHz, CDCl₃) δ: 186.1, 185.6, 185.3, 185.2, 185.0, 177.3, 176.7 (d, *J* = 1.2 Hz), 174.8, 161.0 (d, *J* = 246.7 Hz), 160.7 (d, *J* = 246.0 Hz), 159.7 (d, *J* = 245.0 Hz), 146.3, 145.3, 144.8, 143.2 (d, *J* = 8.1 Hz), 142.8 (d, *J* = 8.2 Hz), 142.2 (d, *J* = 7.8 Hz), 137.3, 137.2, 137.1, 115.5 (d, *J* = 27.8 Hz), 115.4 (d, *J* = 24.5 Hz), 115.3 (d, *J* = 27.6 Hz), 114.2 (d, *J* = 8.7 Hz), 114.1 (d, *J* = 8.7 Hz), 113.4 (d, *J* = 8.6 Hz), 110.8 (d, *J* = 25.3 Hz), 110.6 (d, *J* = 25.0 Hz), 110.6 (d, *J* = 25.8 Hz), 94.7, 93.9, 91.1, 50.9 (d, *J* = 2.0 Hz), 50.6 (d, *J* = 2.3 Hz), 50.2 (d, *J* = 1.8 Hz) 26.1, 25.7, 25.4; IR (KBr, cm⁻¹) ν: 2966, 1670, 1458, 1332, 1268, 1162, 950.

Hz), 137.3, 137.2, 137.1, 115.5 (d, *J* = 27.8 Hz), 115.4 (d, *J* = 24.5 Hz), 115.3 (d, *J* = 27.6 Hz), 114.2 (d, *J* = 8.7 Hz), 114.1 (d, *J* = 8.7 Hz), 113.4 (d, *J* = 8.6 Hz), 110.8 (d, *J* = 25.3 Hz), 110.6 (d, *J* = 25.0 Hz), 110.6 (d, *J* = 25.8 Hz), 94.7, 93.9, 91.1, 50.9 (d, *J* = 2.0 Hz), 50.6 (d, *J* = 2.3 Hz), 50.2 (d, *J* = 1.8 Hz) 26.1, 25.7, 25.4; IR (KBr, cm⁻¹) ν: 2966, 1670, 1458, 1332, 1268, 1162, 950.

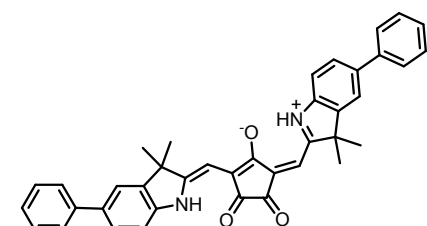
3-(7-Fluoro-3,3-dimethyl-1,3-dihydro-indol-2-ylidenemethyl)-5-(7-fluoro-3,3-dimethyl-3H-indol-2-ylmethylene)-4-hydroxy-cyclopent-3-ene-1,2-dione (4e).



Compound **4e** was synthesized from **2e** (500 mg, 2.82 mmol) and croconic acid (200 mg, 1.41 mmol) in 1-butanol (10 mL) and dry toluene (10 mL) in accordance with the general procedure. Green solid, yield 49%; m.p. 279 - 281 °C; LCMS-IT-TOF calculated for C₂₇H₂₂F₂N₂O₃ [M-H]⁻: 459.1526, found: *m/z* 459.1553; ¹H NMR (500 MHz, CDCl₃) δ: 16.35 - 14.65 (m, 2H), 7.20 - 7.05 (m, 6H), 6.19 - 6.03 (m, 2H), 1.56 - 1.53 (m, 12H); ¹³C NMR (CDCl₃ 126 MHz) δ: 185.8, 185.7, 185.4, 185.3, 184.8, 177.3, 176.3, 174.5, 149.5 (d, *J* = 250.4 Hz), 149.2 (d, *J* = 252.0 Hz), 148.9 (d, *J* = 252.1 Hz), 146.7, 145.9, 145.2, 144.1, 143.6 (d, *J* = 1.7 Hz), 129.2 (d, *J* = 22.5 Hz), 129.0 (d, *J* = 26.7 Hz), 128.9 (d, *J* = 16.4 Hz), 126.5 (d, *J* = 6.1 Hz), 126.2 (d, *J* = 5.6 Hz), 125.5 (d, *J* = 5.0 Hz), 118.3 (d, *J* = 3.1 Hz), 118.2 (d, *J* = 3.5 Hz), 118.1, 115.6, 115.5, 115.4, 95.5, 94.5, 92.1, 51.3, 51.0, 50.6, 26.3, 25.8, 25.5; IR (KBr, cm⁻¹) ν: 2922, 1681, 1495, 1340, 1303, 1176, 900.

(d, *J* = 1.7 Hz), 129.2 (d, *J* = 22.5 Hz), 129.0 (d, *J* = 26.7 Hz), 128.9 (d, *J* = 16.4 Hz), 126.5 (d, *J* = 6.1 Hz), 126.2 (d, *J* = 5.6 Hz), 125.5 (d, *J* = 5.0 Hz), 118.3 (d, *J* = 3.1 Hz), 118.2 (d, *J* = 3.5 Hz), 118.1, 115.6, 115.5, 115.4, 95.5, 94.5, 92.1, 51.3, 51.0, 50.6, 26.3, 25.8, 25.5; IR (KBr, cm⁻¹) ν: 2922, 1681, 1495, 1340, 1303, 1176, 900.

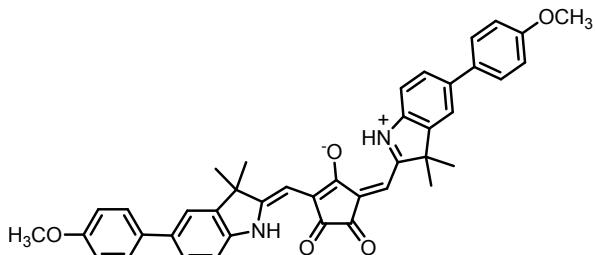
3-(3,3-Dimethyl-5-phenyl-1,3-dihydro-indol-2-ylidenemethyl)-5-(3,3-dimethyl-5-phenyl-3H-indol-2-ylmethylene)-4-hydroxy-cyclopent-3-ene-1,2-dione (5a).



Compound **5a** was synthesized from **3a** (623.7 mg, 2.65 mmol) and croconic acid (188 mg, 1.33 mmol) in 1-butanol (10 mL) and dry toluene (10 mL) in accordance with the general procedure. Green solid, yield 67%; m.p. 299 - 301 °C; LCMS-IT-TOF calculated for C₃₉H₃₂N₂O₃ [M+Na]⁺: 599.2305, found: *m/z* 599.2286; ¹H NMR (500 MHz, CDCl₃) δ: 15.85 - 14.50 (m, 2H), 7.60 - 7.31 (m, 16H), 6.18 - 5.99 (m, 2H), 1.60 - 1.56 (m, 12H); ¹³C NMR (126 MHz, CDCl₃) δ: 186.3, 185.7, 185.4, 185.4, 185.2, 176.8, 176.3, 174.6, 146.3, 145.2, 144.8, 141.9, 141.6, 141.1, 140.7, 140.6, 140.6, 140.5, 140.4, 138.9, 138.6, 138.0, 129.0, 128.9, 128.9, 127.8, 127.7, 127.7, 127.6, 127.5, 127.4, 127.0, 127.0, 127.0, 121.5, 121.4, 121.3, 113.7, 113.5, 112.9, 94.9, 94.2, 91.6, 50.5, 50.2,

49.9, 26.3, 25.8, 25.6; IR (KBr, cm⁻¹) ν: 2972, 1671, 1494, 1346, 1170, 1128, 841.

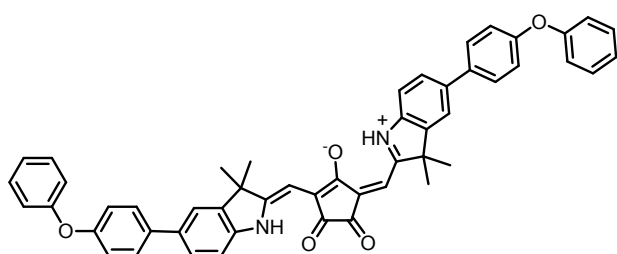
4-Hydroxy-3-[5-(4-methoxyphenyl)-3,3-dimethyl-1,3-dihydro-indol-2-ylidenemethyl]-5-[5-(4-methoxy-phenyl)-3,3-dimethyl-3H-indol-2-ylmethylene]-cyclopent-3-ene-1,2-dione (5b). Compound **5b** was synthesized from **3b** (403 mg,



1.52 mmol) and croconic acid (108 mg, 0.76 mmol) in 1-butanol (10 mL) and dry toluene (10 mL) in accordance with the general procedure. Red solid, yield 75%; m.p. 295 - 297 °C; LCMS-IT-TOF calculated for $C_{41}H_{36}N_2O_5$ [M-H]⁻: 635.2551, found: m/z 635.2534; ¹H NMR (500 MHz, CDCl₃) δ: 15.80 - 14.50 (m, 2H), 7.55 - 7.45 (m, 8H), 7.35 - 7.20 (m, 2H), 6.98 (d, J = 8.4 Hz; 4H), 6.14 - 5.95 (m, 2H), 3.85 (s, 6H), 1.58 - 1.55 (m, 12H); ¹³C NMR (126 MHz, CDCl₃) δ: 186.4, 185.7, 185.4, 185.3, 176.5, 176.1, 174.4, 159.4, 159.3, 159.3, 146.1, 145.0, 144.5, 141.9, 141.6, 141.1, 140.2, 140.1, 140.0, 138.6,

138.2, 137.7, 133.1, 133.0, 132.9, 128.1, 128.1, 128.0, 127.2, 127.2, 127.2, 121.0, 120.9, 120.9, 114.4, 114.4, 114.4, 113.6, 113.5, 112.9, 94.8, 94.1, 91.5, 55.4, 50.5, 50.2, 49.9, 26.3, 25.8, 25.6; IR (KBr, cm⁻¹) ν: 2960, 1487, 1332, 1290, 1184, 1119, 947,

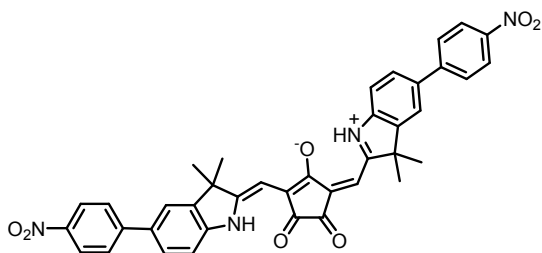
3-[3,3-Dimethyl-5-(4-phenoxyphenyl)-1,3-dihydro-indol-2-ylidenemethyl]-5-[3,3-dimethyl-5-(4-phenoxy-phenyl)-3H-indol-2-ylmethylene]-4-hydroxy-cyclopent-3-ene-1,2-dione (5c). Compound **5c** was synthesized from **3c** (654 mg,



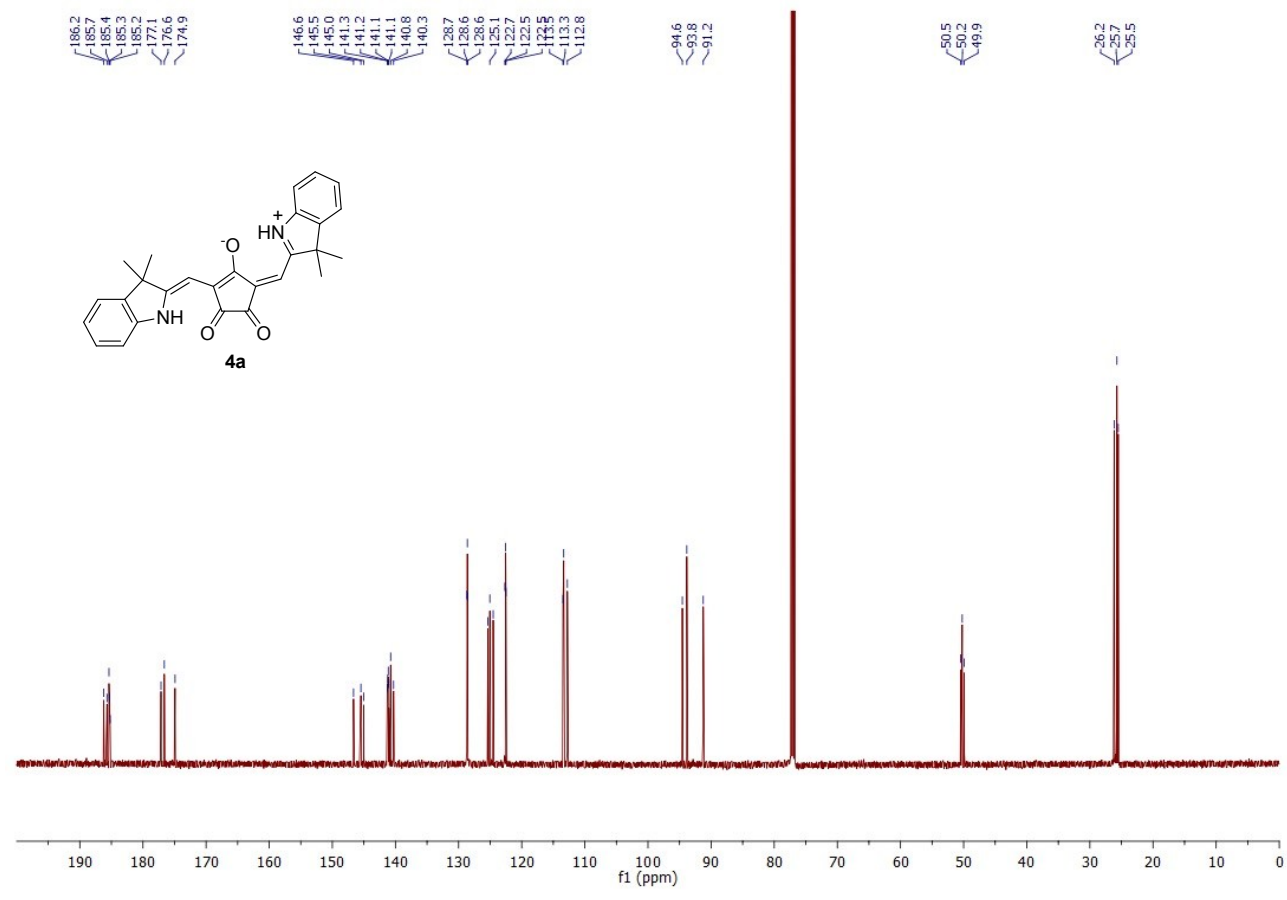
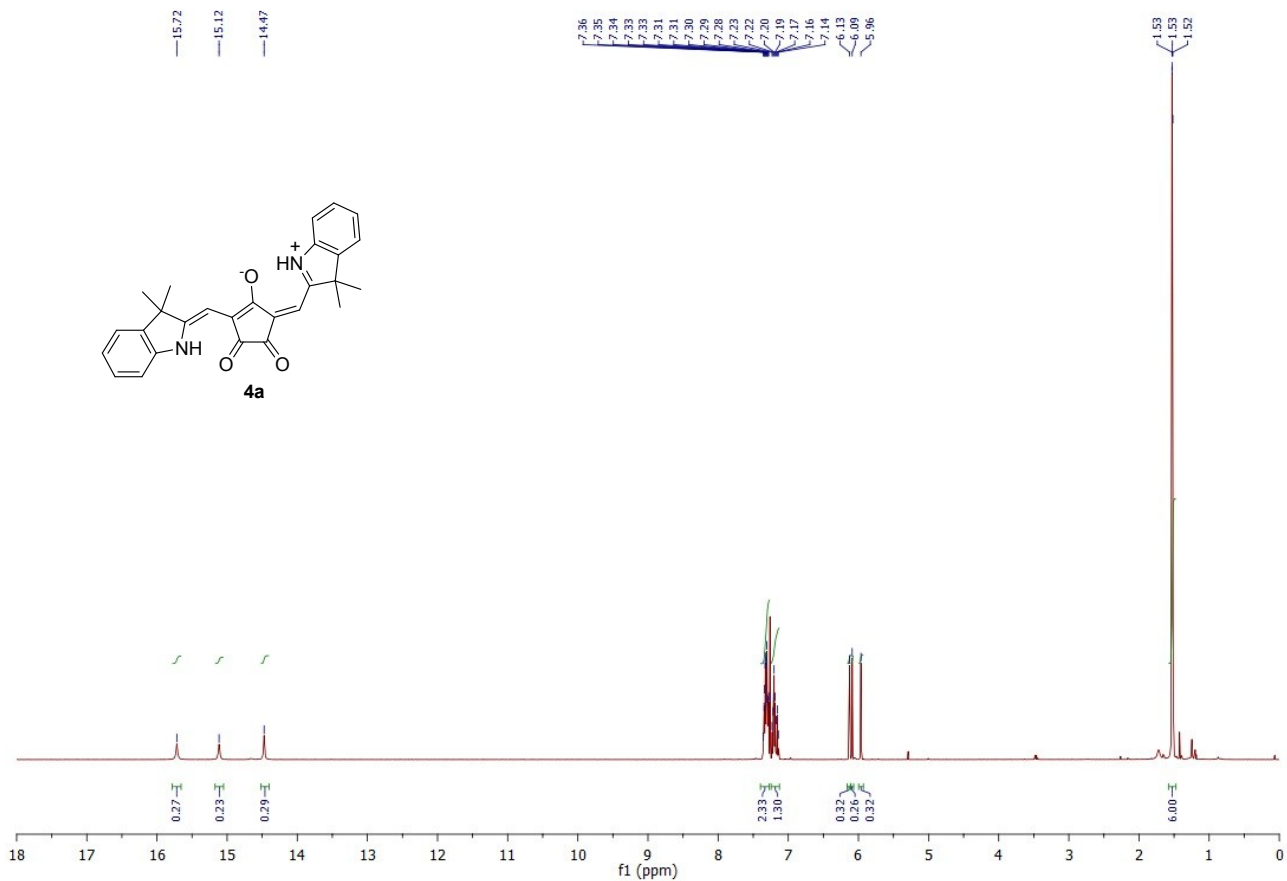
2 mmol) and croconic acid (142 mg, 1 mmol) in 1-butanol (10 mL) and dry toluene (10 mL) in accordance with the general procedure. Blue solid, yield 64%; m.p. 299 - 302 °C; LCMS-IT-TOF calculated for $C_{51}H_{40}N_2O_5$ [M-H]⁻: 759.2864, found: m/z 759.2861; ¹H NMR (500 MHz, CDCl₃) δ: 15.85 - 14.53 (m, 2H), 7.58 - 7.48 (m, 8H), 7.39 - 7.31 (m, 6H), 7.16 - 7.05 (m, 10H), 6.20 - 5.98 (m, 2H), 1.58 (s, 12H); ¹³C NMR (126 MHz, CDCl₃) δ: 186.3, 185.8, 185.4, 185.4, 185.3, 176.7, 176.2, 174.5, 157.2, 157.1, 157.0, 157.0, 156.9, 146.2, 145.1, 144.7, 141.9, 141.6, 141.1, 140.5, 140.4,

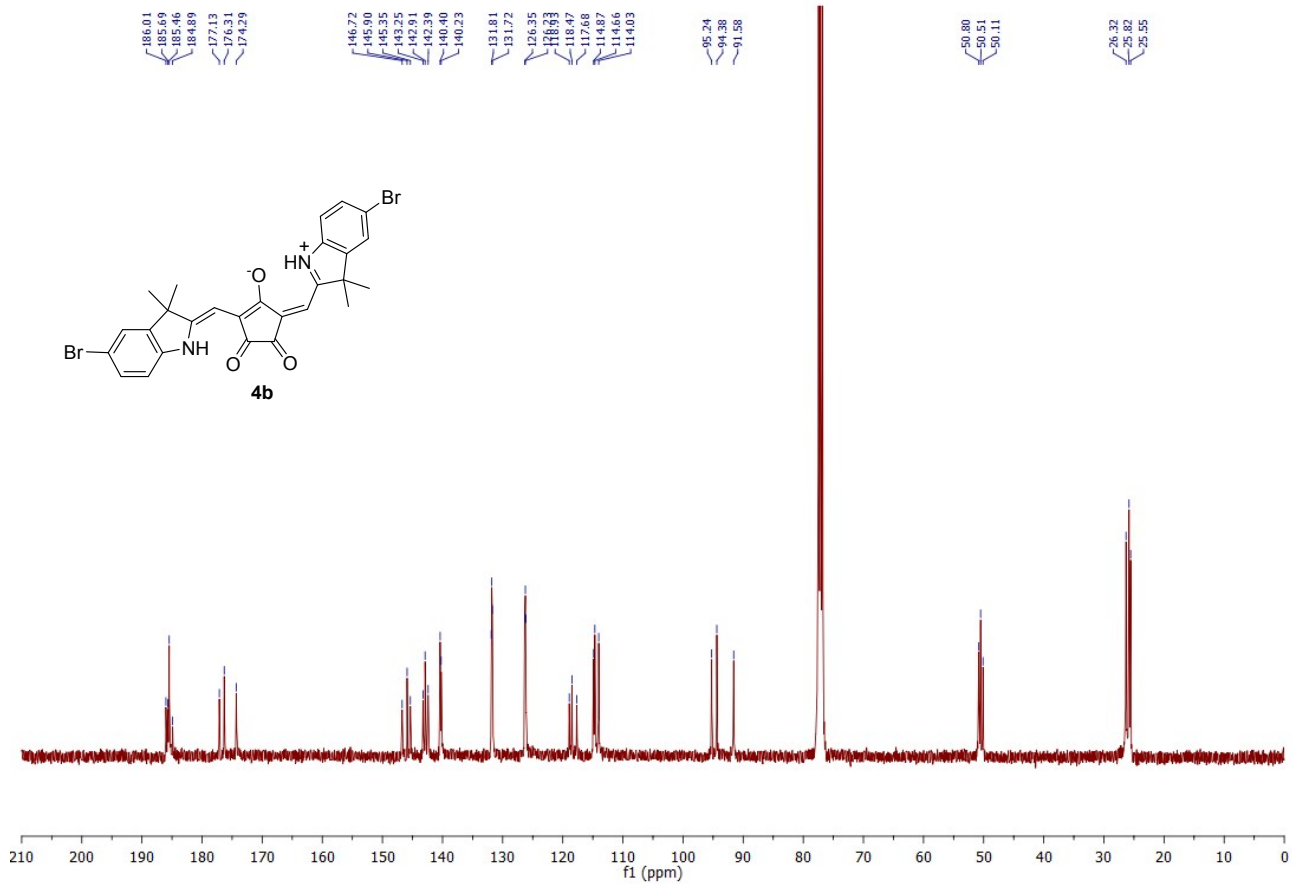
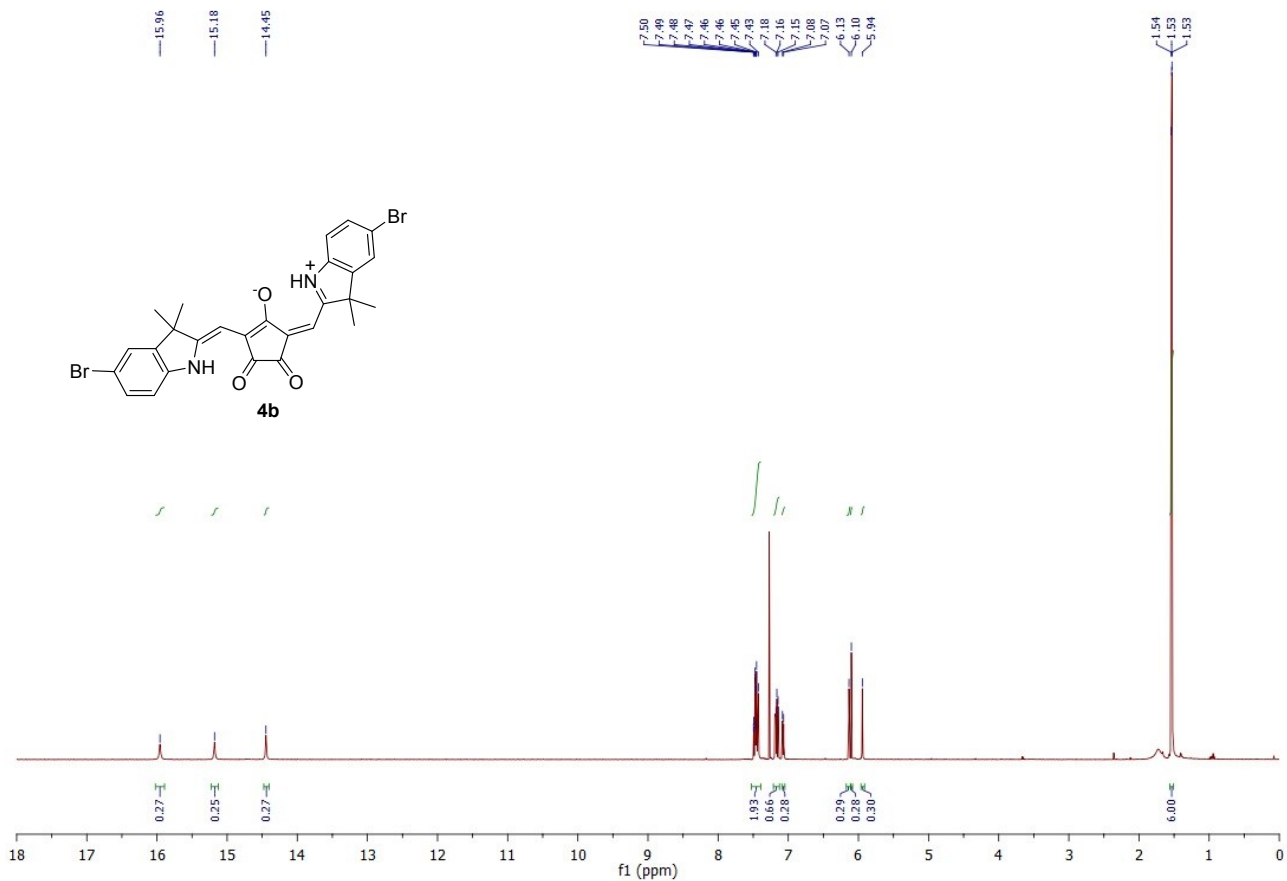
140.3, 138.3, 137.9, 137.4, 135.6, 135.5, 135.4, 129.8, 128.4, 128.3, 128.3, 127.5, 127.4, 127.4, 123.6, 123.5, 123.5, 121.2, 121.1, 121.1, 119.2, 119.1, 119.1, 119.0, 119.0, 113.7, 113.6, 113.0, 95.0, 94.2, 91.6, 50.5, 50.3, 49.9, 26.3, 25.9, 25.6; IR (KBr, cm⁻¹) ν: 2964, 1526, 1470, 1339, 1162, 939, 823.

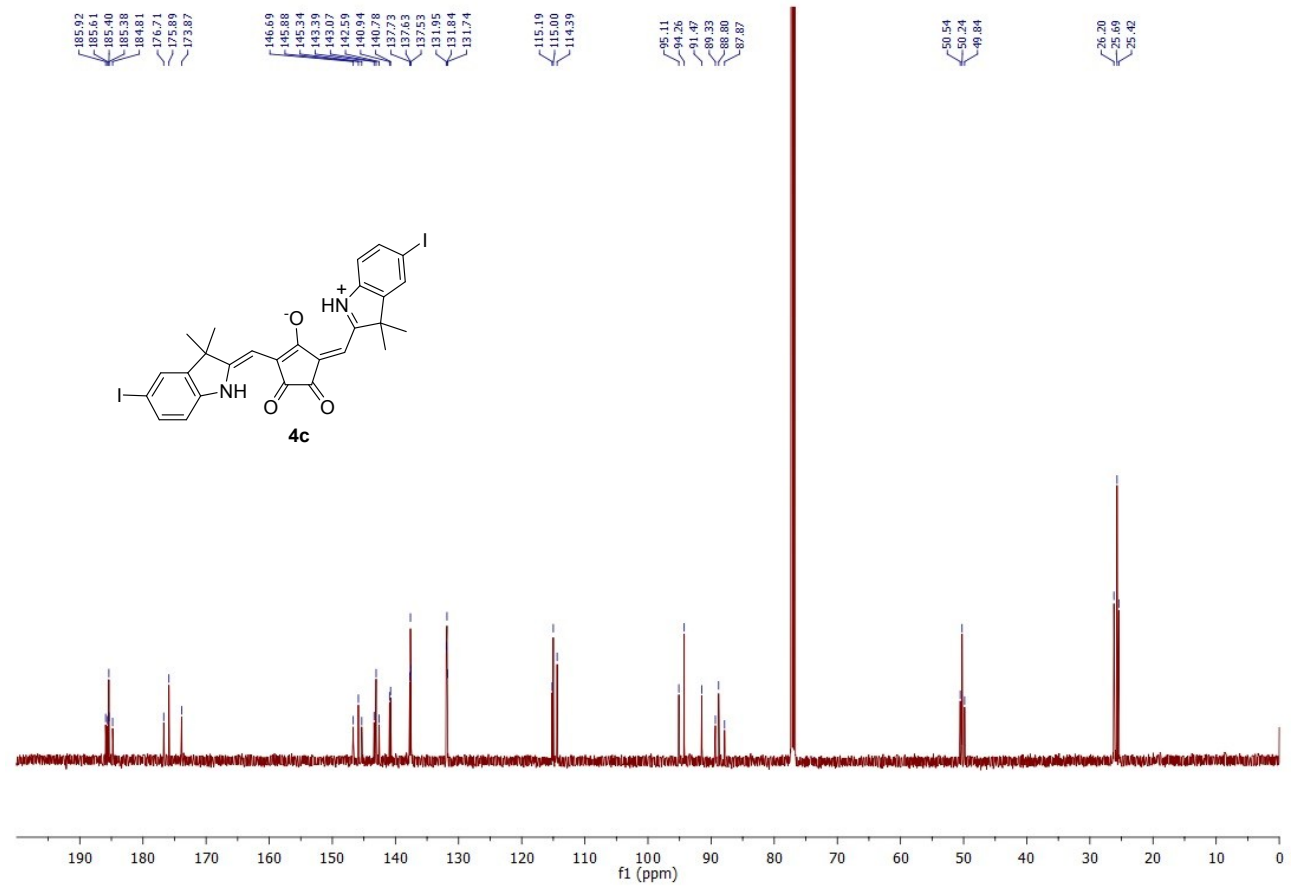
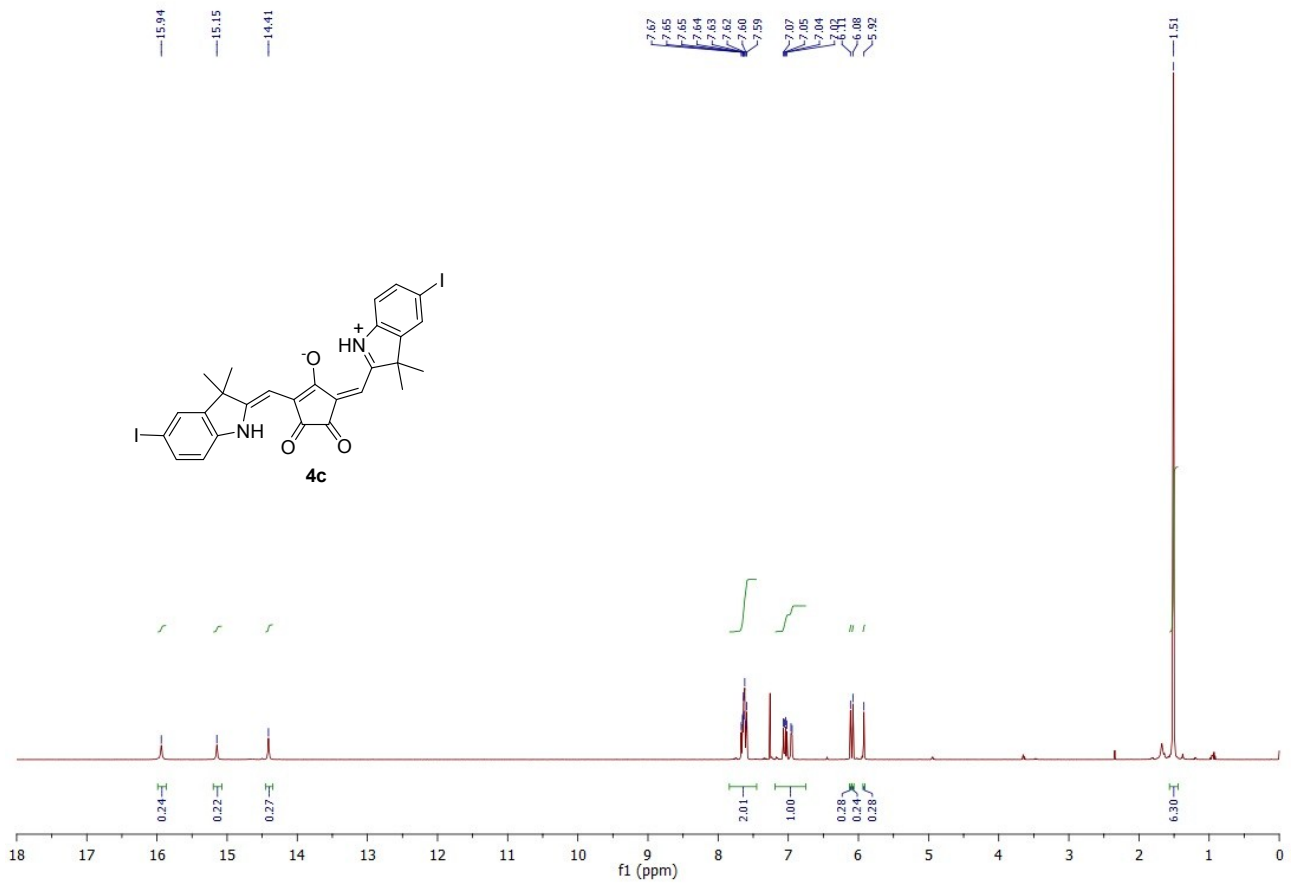
3-[3,3-Dimethyl-5-(4-nitrophenyl)-1,3-dihydro-indol-2-ylidenemethyl]-5-[3,3-dimethyl-5-(4-nitro-phenyl)-3H-indol-2-ylmethylene]-4-hydroxy-cyclopent-3-ene-1,2-dione (5d). Compound **5d** was synthesized from **3d** (500 mg, 1.78

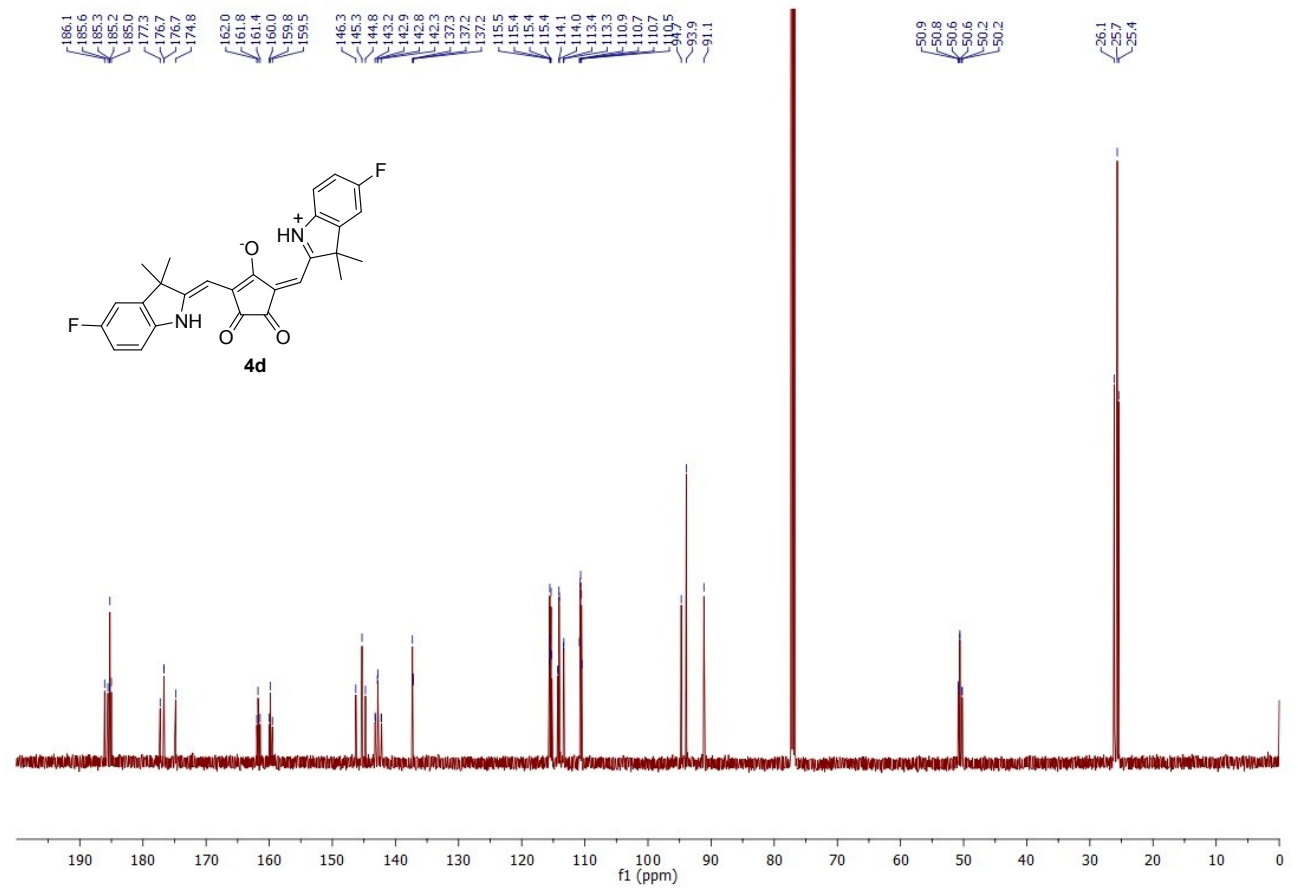
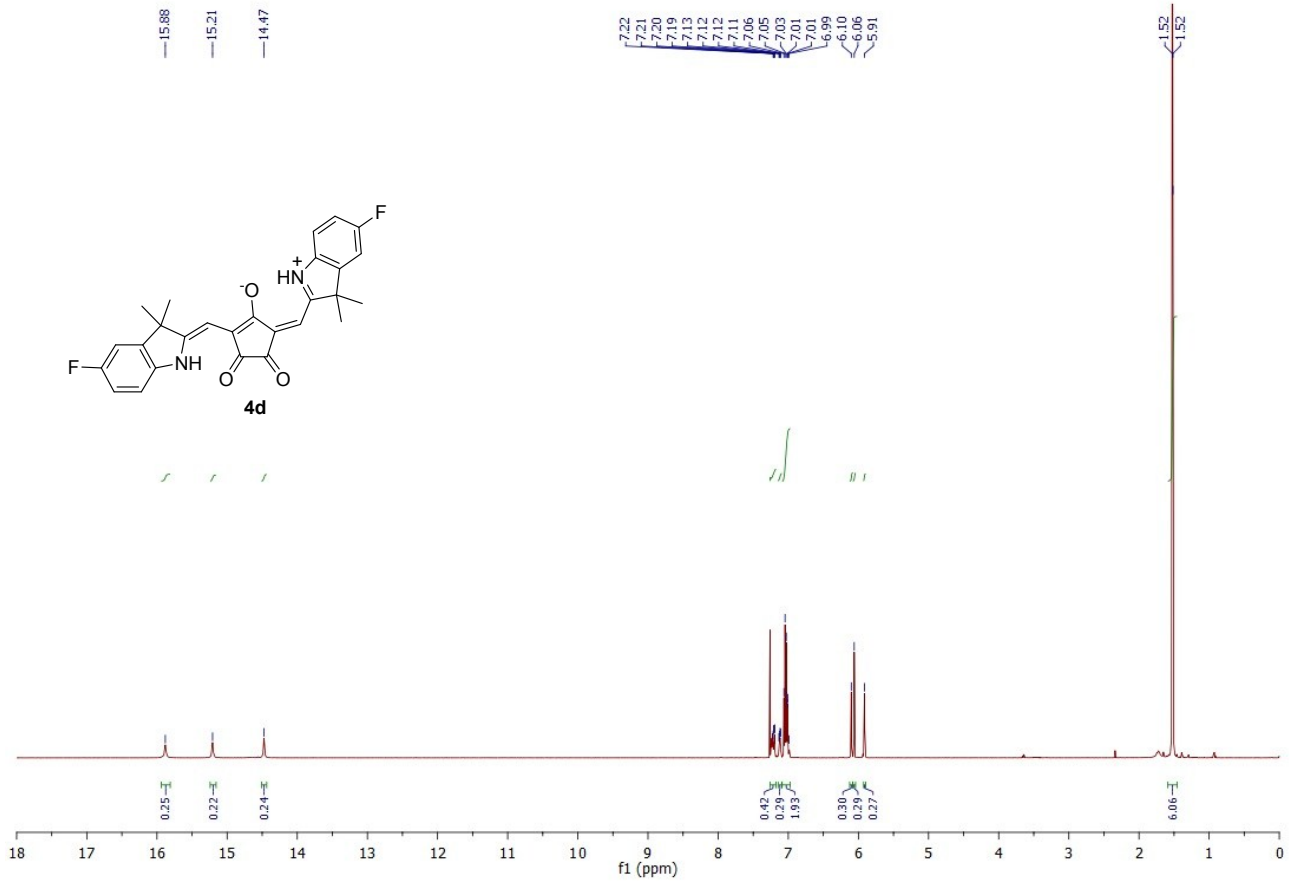


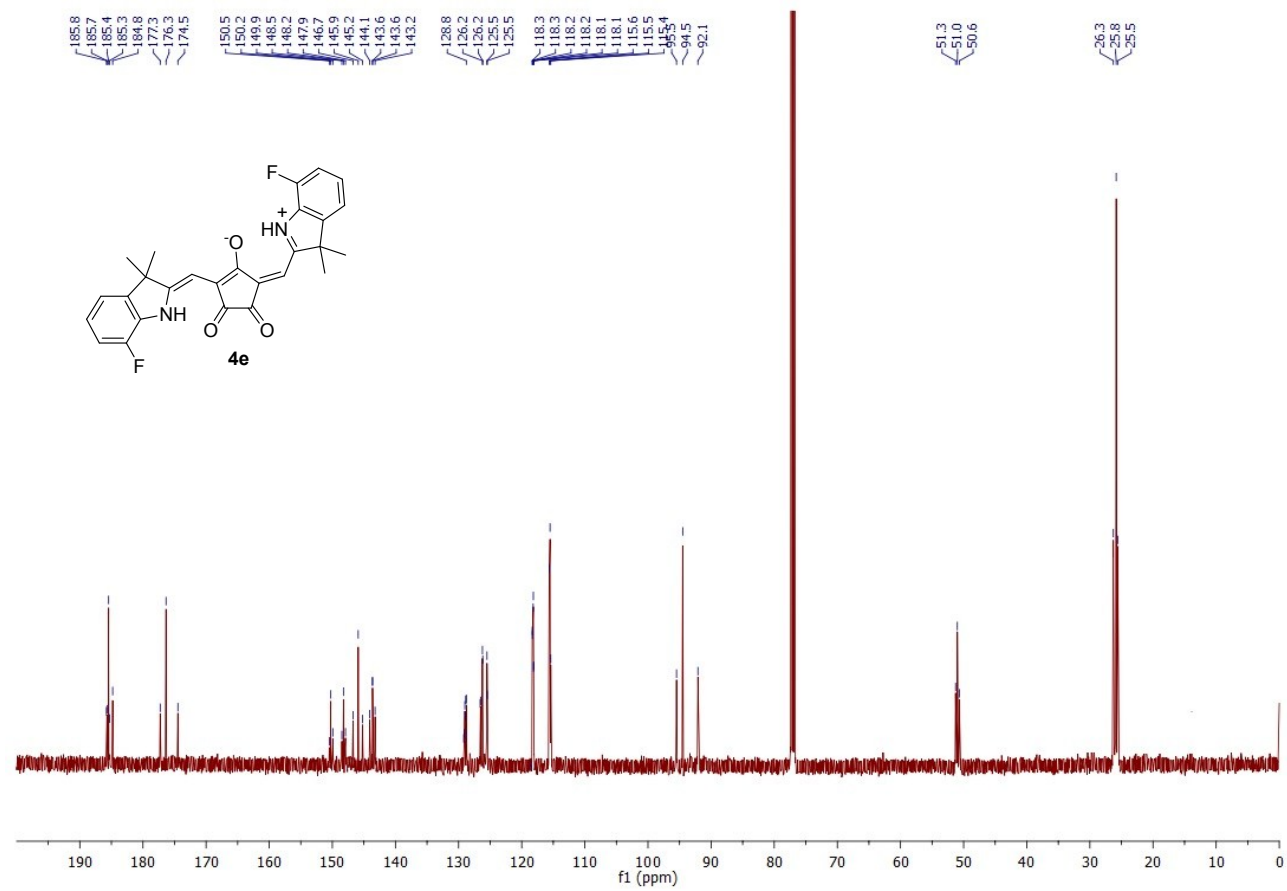
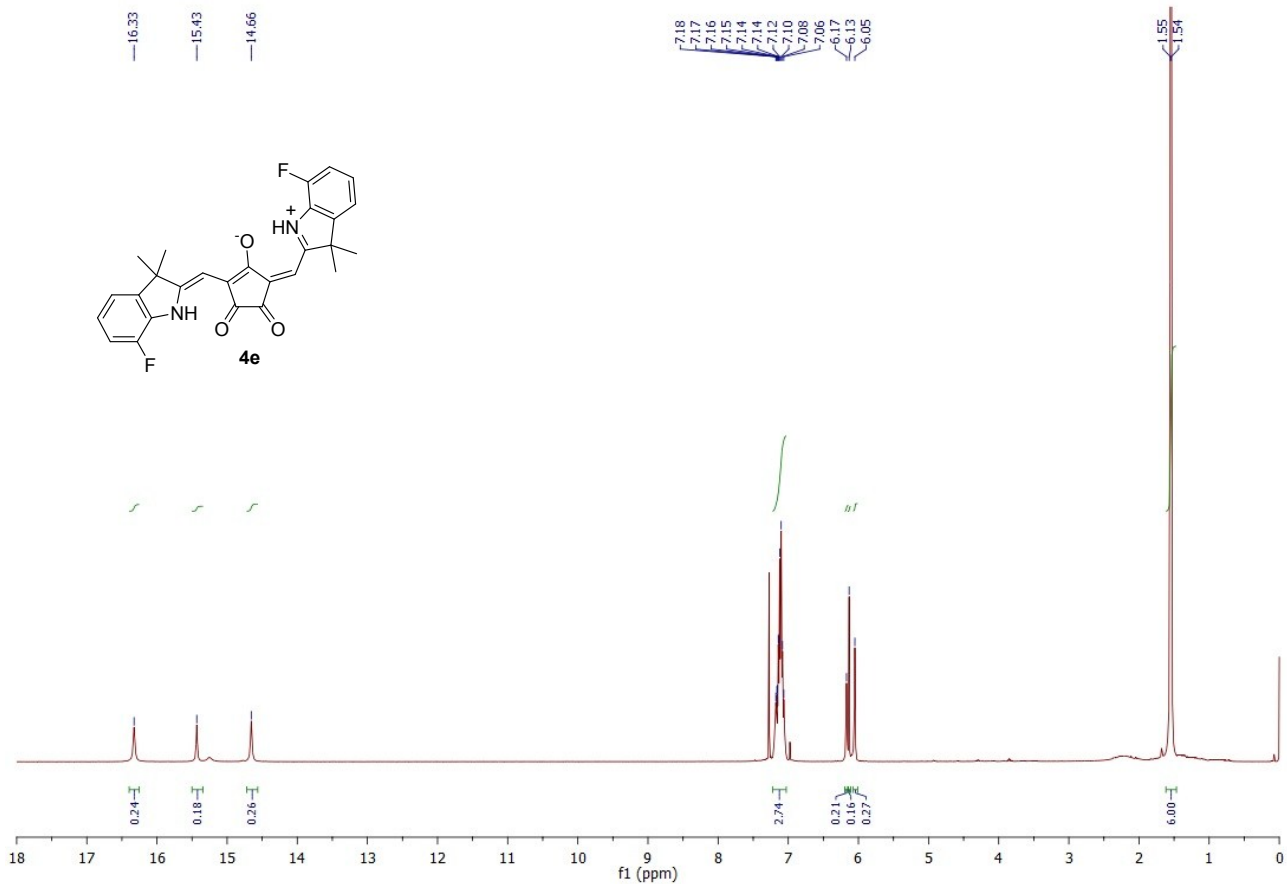
mmol) and croconic acid (126 mg, 0.89 mmol) in 1-butanol (10 mL) and dry toluene (10 mL) in accordance with the general procedure. Purple solid, yield 87%; 299 - 301 °C; LCMS-IT-TOF calculated for $C_{39}H_{30}N_4O_7$ [M-H]⁻: 665.2042, found: m/z 665.2060; ¹H NMR (500 MHz, CDCl₃) δ: 16.05 - 14.53 (m, 2H), 8.34 - 8.30 (m, 4H), 7.75 (d, J = 8.5 Hz, 4H), 7.65 - 7.53 (m, 6H), 6.22 - 6.01 (m, 2H), 1.62 - 1.58 (m, 12H); IR (KBr, cm⁻¹) ν: 1665, 1592, 1486, 1331, 1172, 941, 840; ¹³C-NMR spectrum was not collected because of the poor solubility of the product.

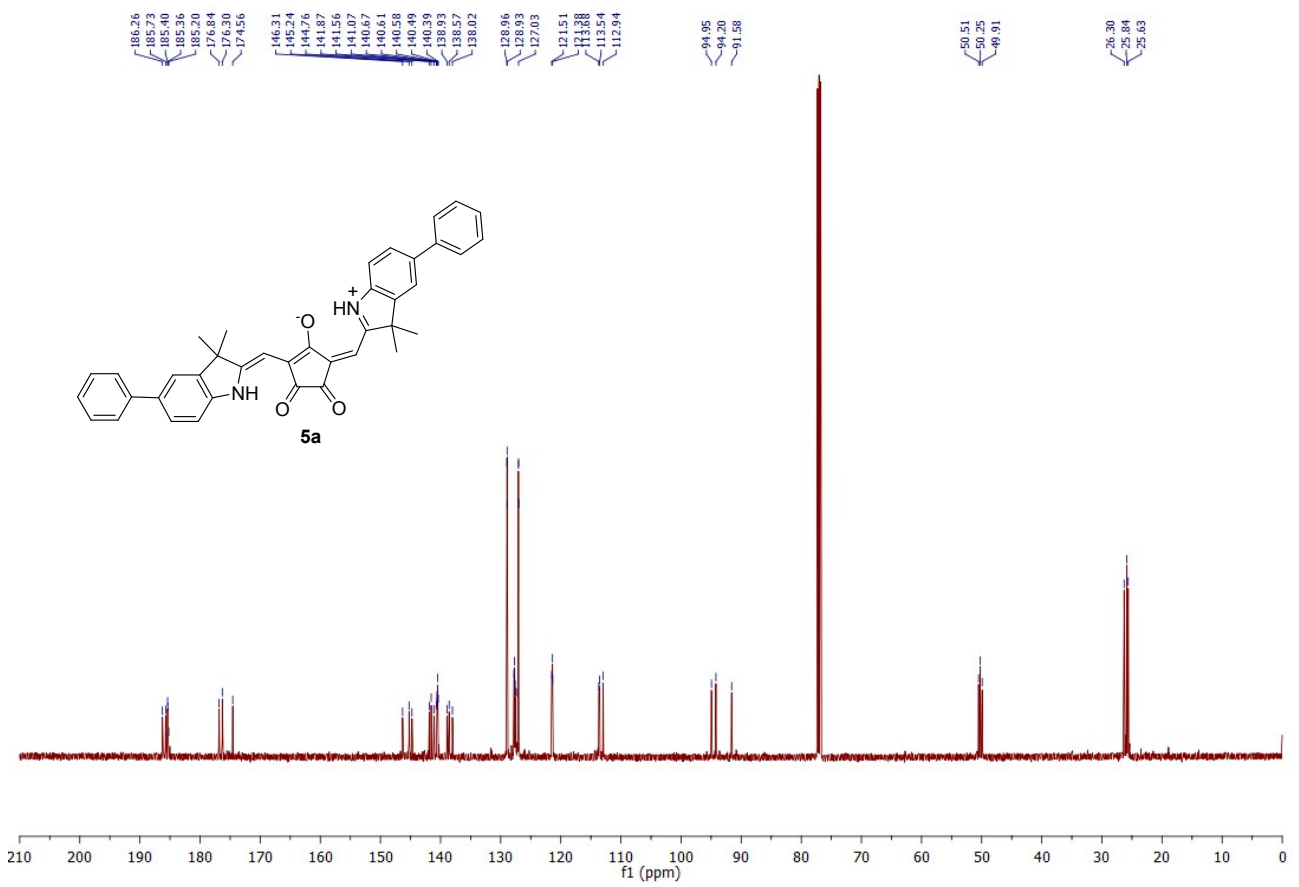
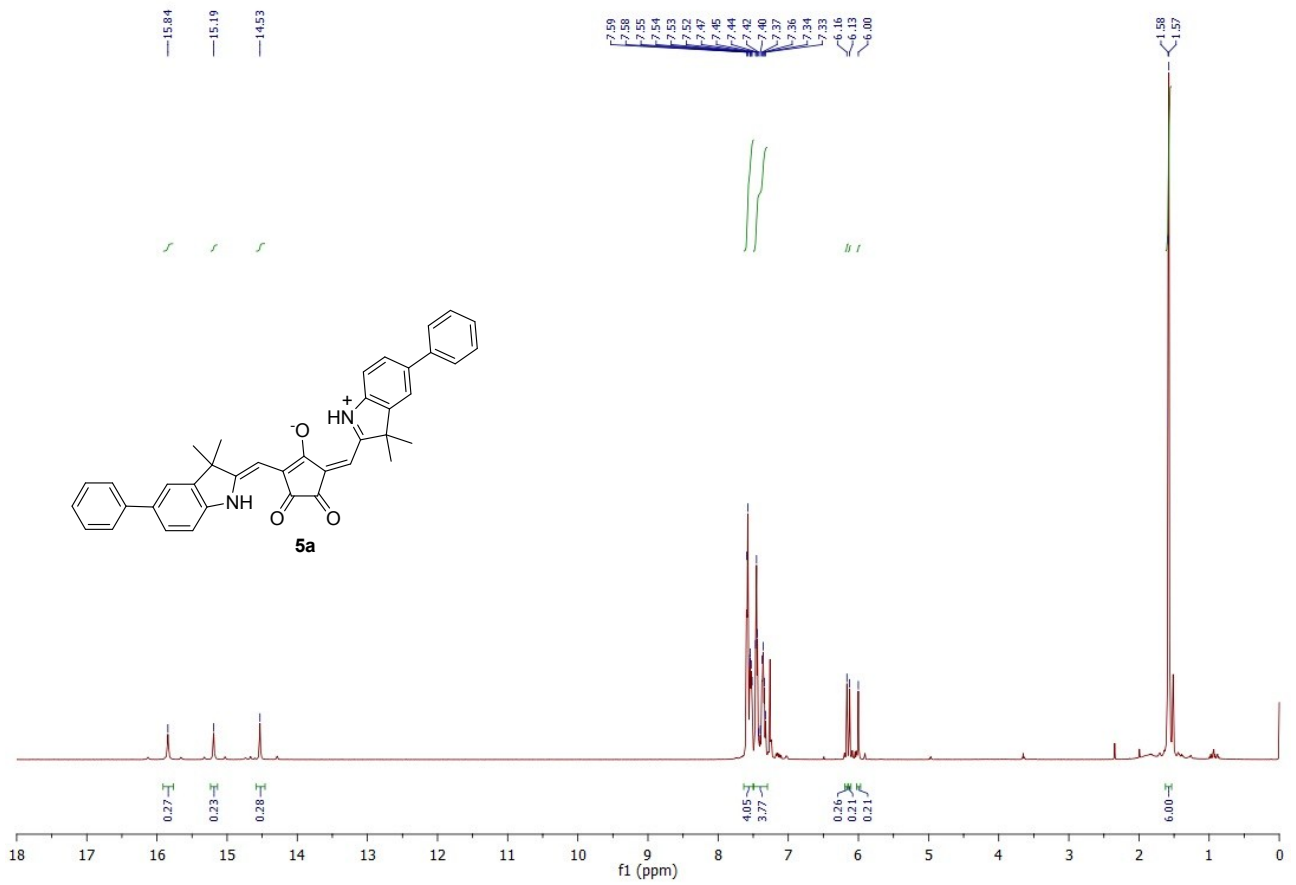


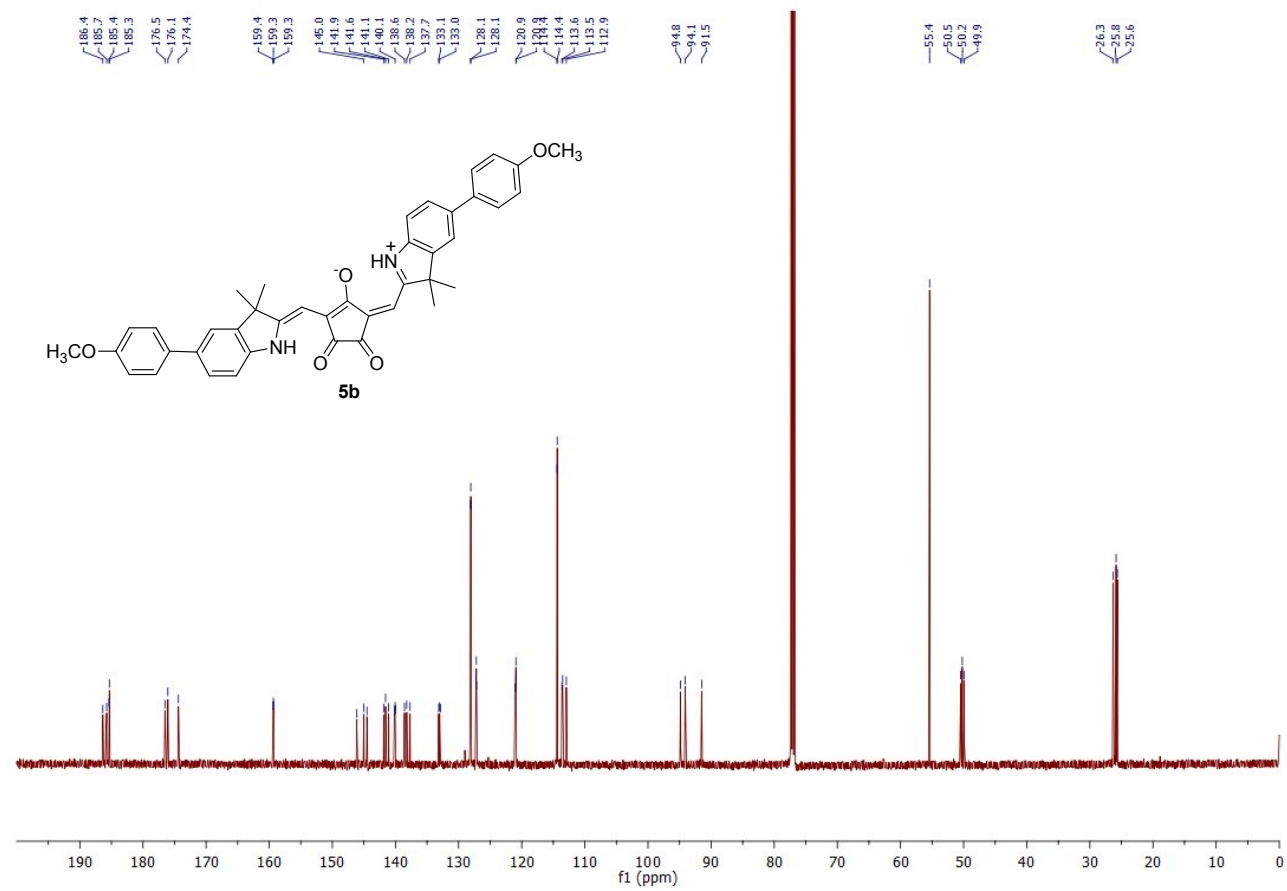
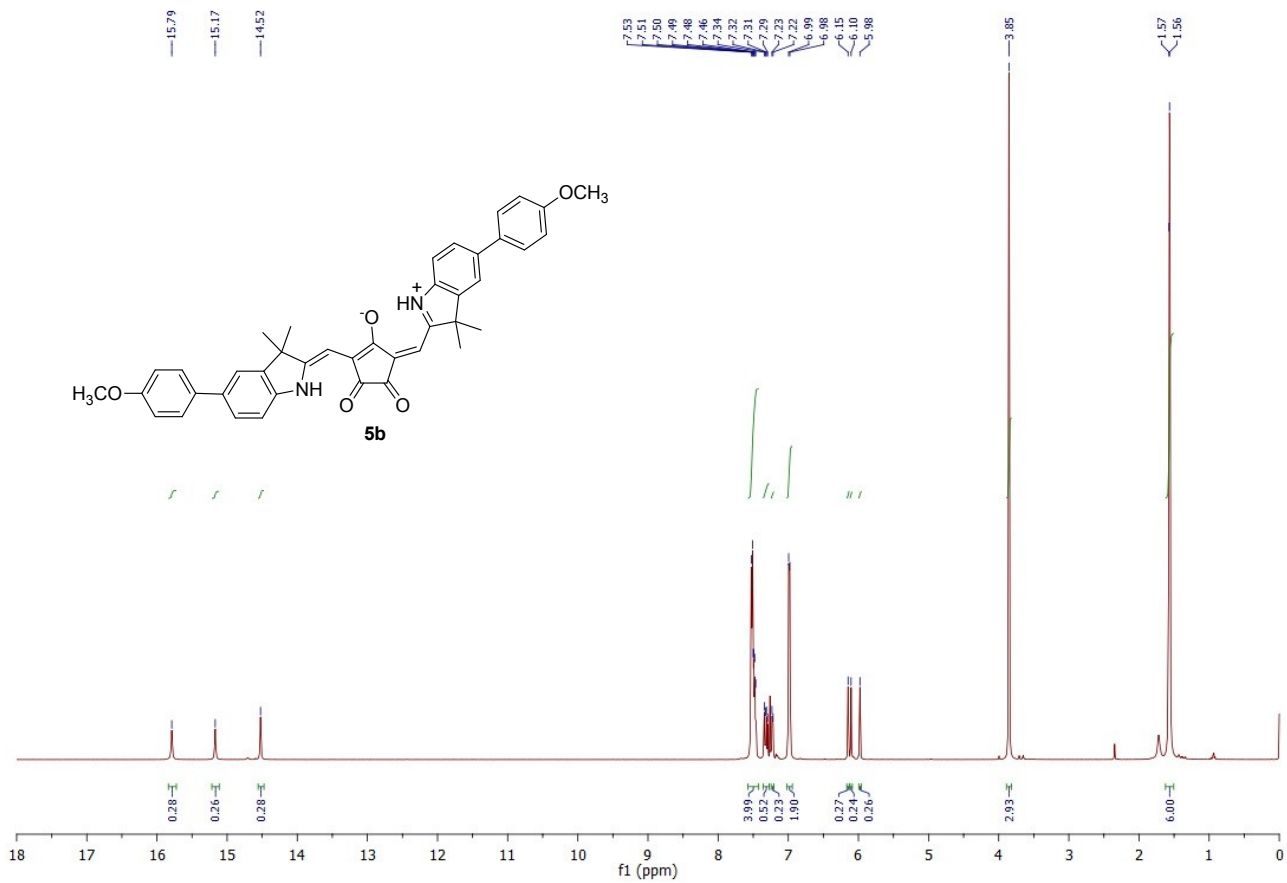


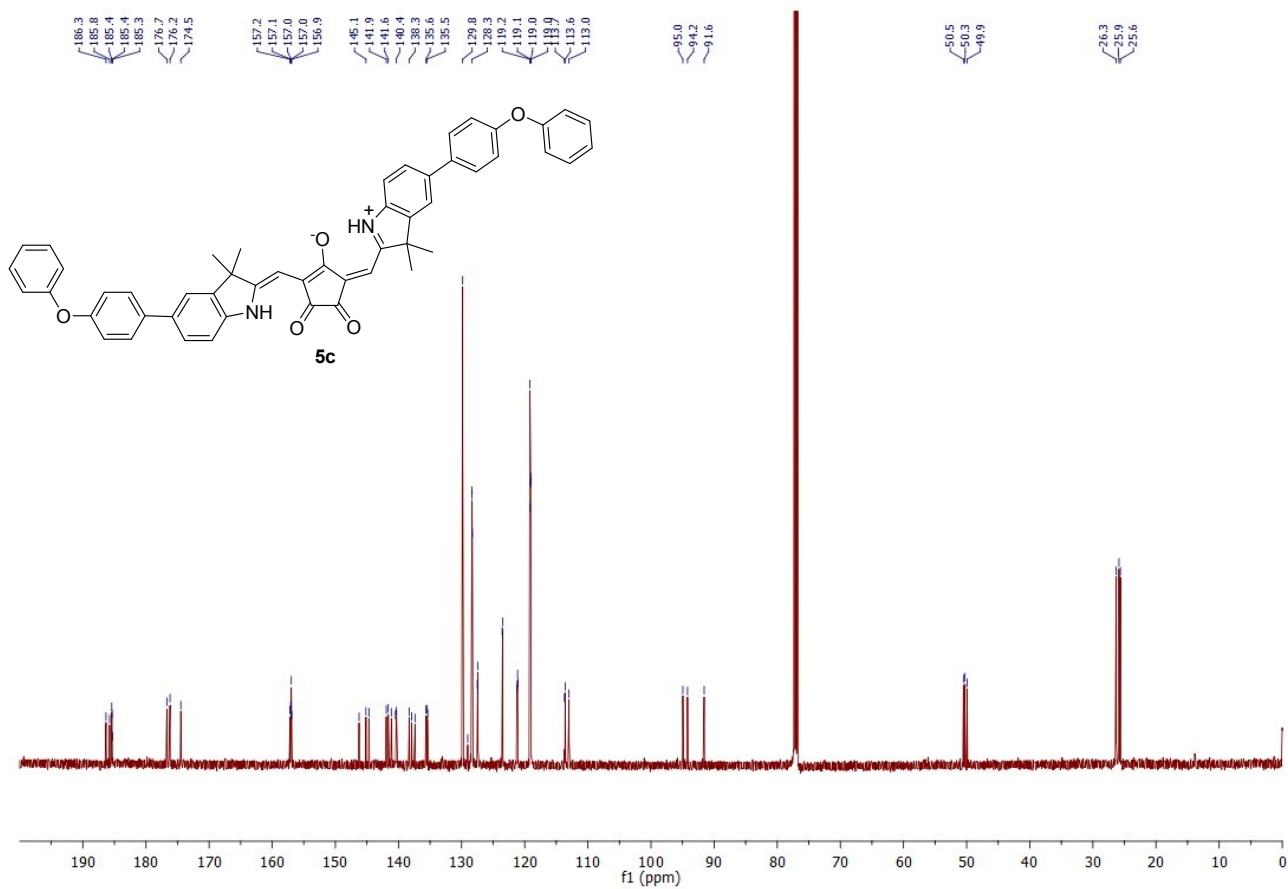
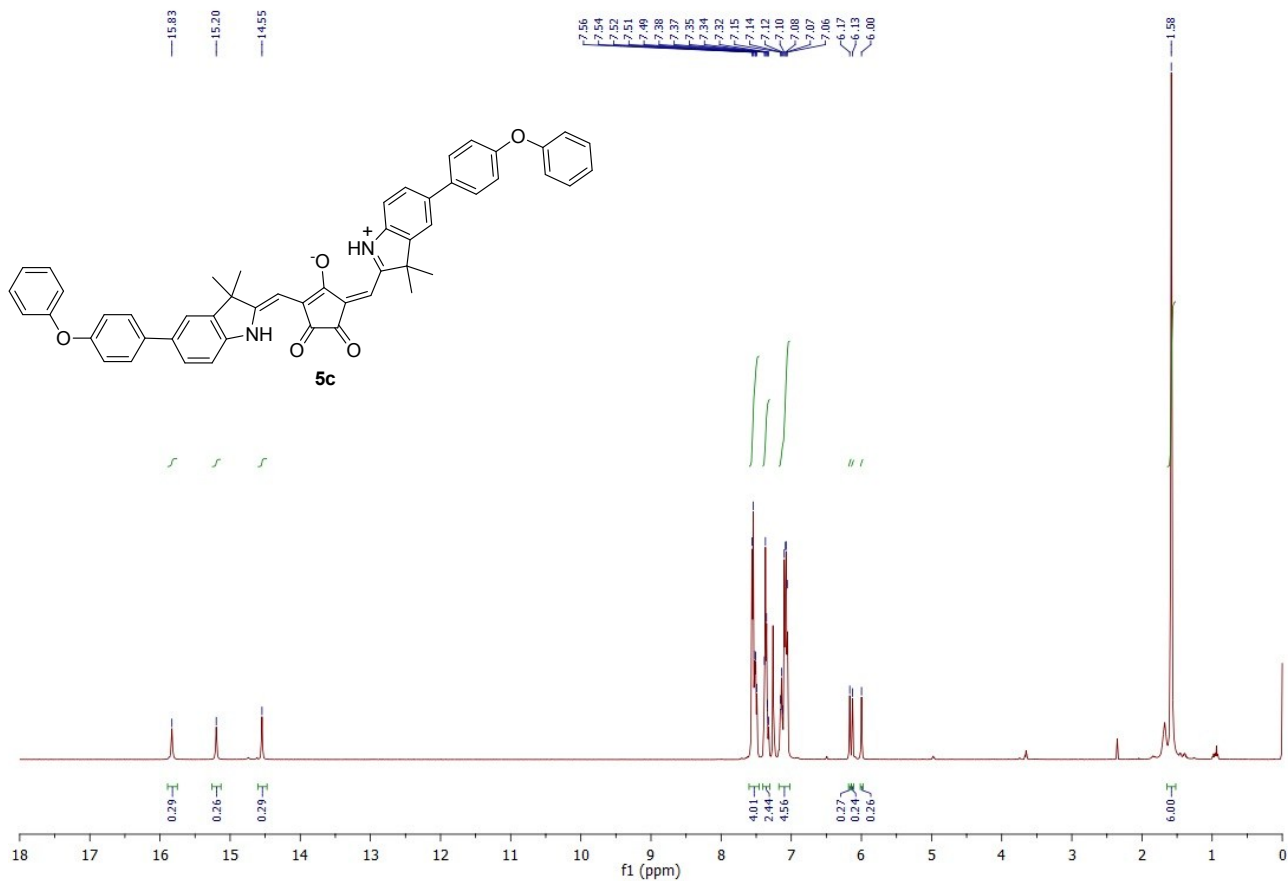


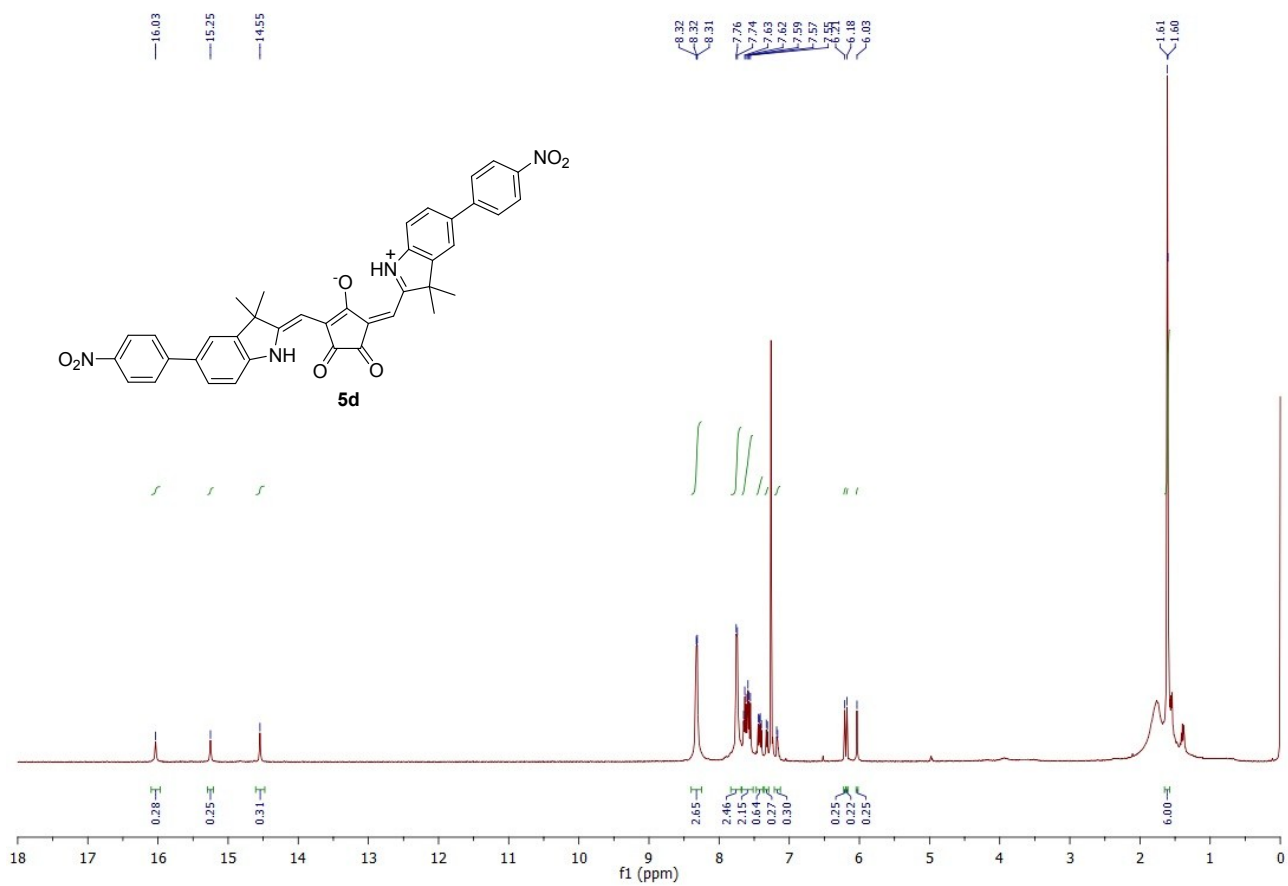
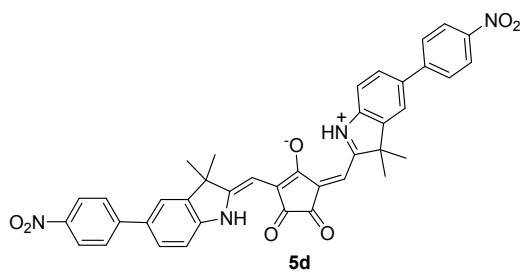












3 Cyclic voltammetry

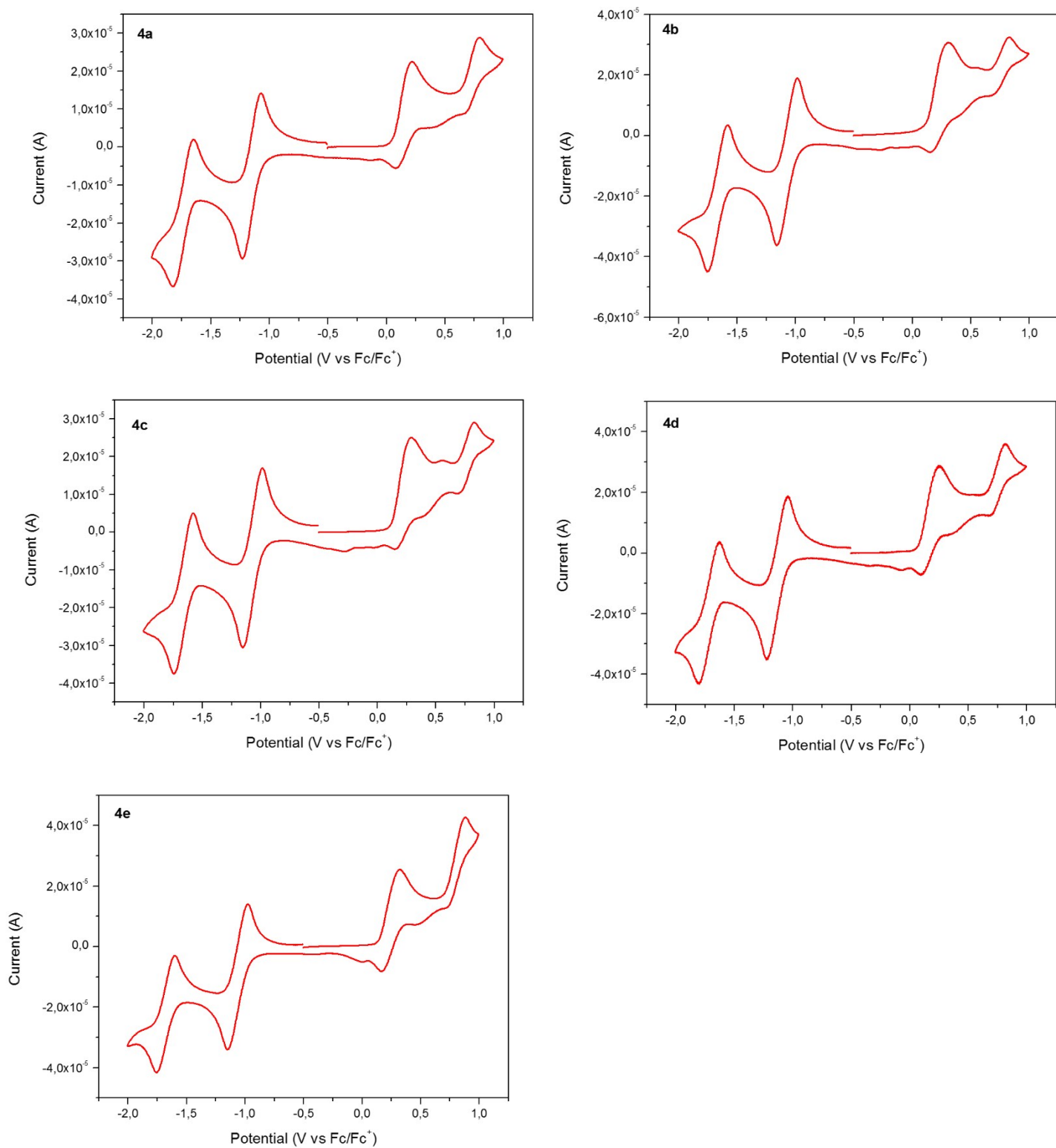


Figure S1. Cyclic voltammograms of croconaine dyes **4 a-e**

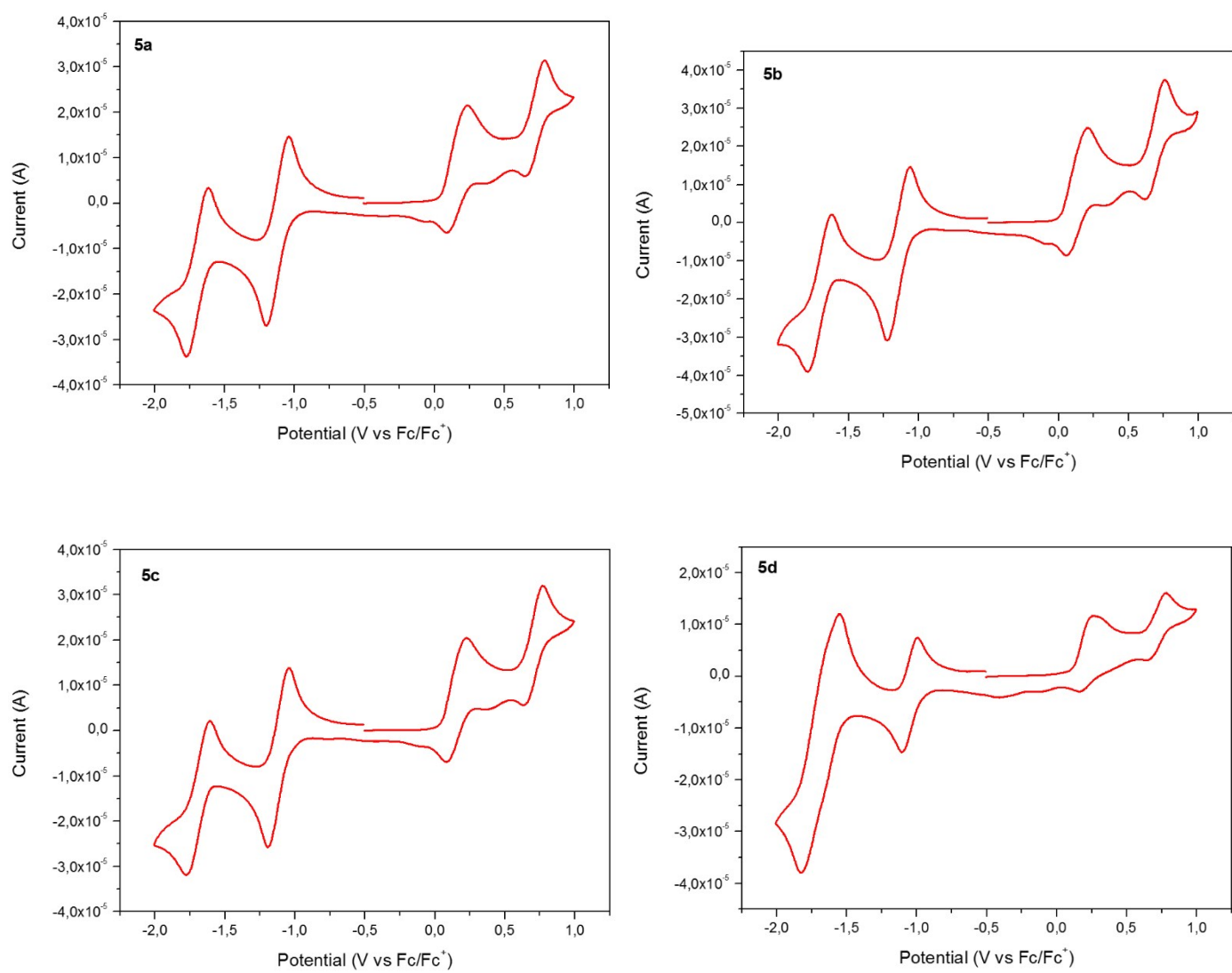


Figure S2. Cyclic voltammograms of croconaine dyes **5 a-d**

4 Emission spectra of 4a and 4b

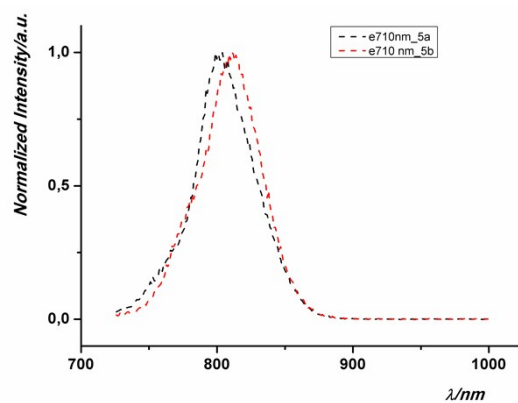


Figure S3. Emission spectra of **4a** and **4b** in CHCl₃ solution (5 mg/mL) at RT (λ_{exc} = 710 nm).

5 X-ray diffraction

Experimental details and figures of merit of the structure refinements are reported in Table S1. The hydrogen atoms were all located in a difference map, and those bound to carbon atoms were repositioned geometrically. The hydrogen atoms were initially refined with soft constraints on the bond lengths and angles to regularize their geometry (C-H in the range 0.93–0.98 Å) and $U_{\text{iso}}(\text{H})$ (in the range 1.2–1.5 times U_{eq} of the parent atom); then their positions were refined with riding constraints.^[12] The crystal **4a** was weakly diffracting and repeated attempts to grow a better quality crystal failed. Although the diffraction behavior remained poor, the data-to-parameter ratio is almost ten (9.3).

In addition, the **4a** crystal required a different refinement strategy, because the residual peaks of the difference Fourier map suggested the occurrence of highly disordered solvent molecules. All attempts to model them were unsuccessful, so in the final cycles of refinement, the contribution to electron density corresponding to disordered molecules was removed from the observed data using the SQUEEZE option in PLATON.^[13] Owing to the influence of the solvent, the rigid-bond model^[14] might be violated for some bonds. To achieve a better correspondence for these atom pairs, default rigid-bond restraints and similar Anisotropic Displacement Parameters (ADP) restraints on neighbouring atoms^[15] were applied.

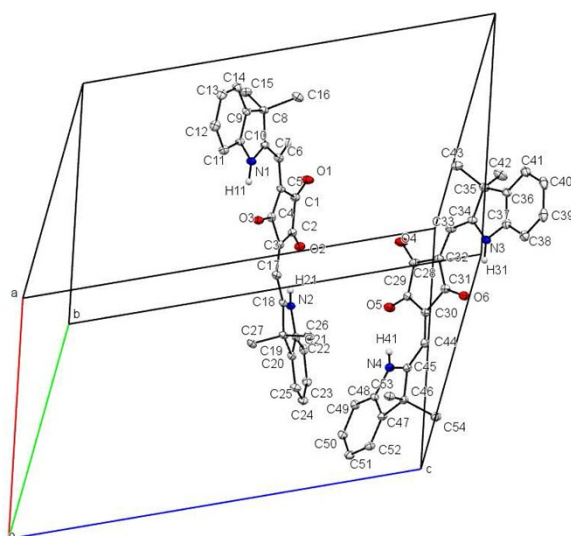


Figure S4. The asymmetric unit of **4a** with displacement ellipsoids drawn at the 30% probability level showing the atom labels used in the structure refinement. H atoms are omitted, for clarity, with the exception of those involved in intramolecular H-bonds.

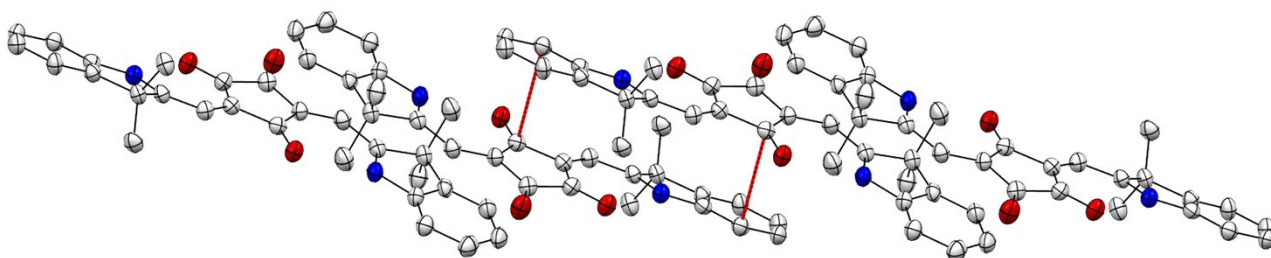


Figure S5. The crystal packing of **4a**.

Experimental details and structural refinements figures of merit are reported in Table S1.

Table S1 Experimental data collection, data reduction details and structure refinements details

	4b	4a
Crystal data		
Chemical formula	C ₂₇ H ₂₂ Br ₂ N ₂ O ₃	C ₂₇ H ₂₄ N ₂ O ₃
<i>M</i> _r	582.29	424.50
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Triclinic, <i>P</i> 1
Temperature (K)	293	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.8186 (2), 10.0198 (2), 23.1493 (5)	11.0823 (3), 14.6505 (5), 18.1033 (6)
α, β, γ (°)	90, 103.090 (1), 90	66.188 (2), 81.891 (2), 72.294 (2)
<i>V</i> (Å ³)	2444.18 (9)	2561.12 (15)
<i>Z</i>	4	4
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	3.35	0.07
Crystal size (mm)	0.38 × 0.20 × 0.07	0.48 × 0.28 × 0.13
Data collection		
Diffractometer	Bruker Kappa Apex2 diffractometer	Bruker Kappa Apex2 diffractometer
Absorption correction	Multi-scan SADABS ^[4]	Multi-scan SADABS ^[4]
<i>T</i> _{min} , <i>T</i> _{max}	0.79, 1.00	0.97, 1.00
No. of measured, independent and observed [<i>I</i> > 2.0σ(<i>I</i>)] reflections	27449, 3509, 2536	5370, 5370, 3300
<i>R</i> _{int}	0.068	0.054
θ _{max} (°)	23.3	20.9
(sin θ/λ) _{max} (Å ⁻¹)	0.556	0.502
Refinement		
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.042, 0.091, 0.97	0.059, 0.160, 0.90
No. of reflections	3491	5331
No. of parameters	307	577
No. of restraints	0	14
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.60, -0.63	0.31, -0.28

Computer programs ^[1-6]**Table S2** Selected geometric parameters (Å, °) for compound **4b**

Br1—C13	1.905 (4)	C8—C15	1.540 (6)
Br2—C24	1.899 (4)	C8—C16	1.523 (6)
N1—C7	1.322 (5)	C9—C10	1.388 (6)
N1—C10	1.414 (5)	C9—C14	1.372 (6)
N2—C18	1.340 (6)	C10—C11	1.372 (6)
N2—C21	1.390 (5)	C11—C12	1.403 (6)
O1—C1	1.220 (5)	C12—C13	1.370 (6)
O2—C2	1.245 (5)	C13—C14	1.385 (6)

O3—C4	1.256 (5)	C17—C18	1.381 (6)
C1—C2	1.482 (6)	C18—C19	1.526 (6)
C1—C5	1.465 (6)	C19—C20	1.525 (6)
C2—C3	1.446 (6)	C19—C26	1.527 (6)
C3—C4	1.453 (6)	C19—C27	1.526 (6)
C3—C17	1.395 (6)	C20—C21	1.381 (6)
C4—C5	1.440 (6)	C20—C25	1.372 (6)
C5—C6	1.380 (6)	C21—C22	1.383 (7)
C6—C7	1.386 (6)	C22—C23	1.387 (7)
C7—C8	1.525 (6)	C23—C24	1.380 (7)
C8—C9	1.516 (6)	C24—C25	1.379 (6)
C7—N1—C10	112.4 (3)	N1—C10—C11	128.3 (4)
C18—N2—C21	112.6 (4)	C9—C10—C11	123.6 (4)
O1—C1—C2	124.8 (4)	C10—C11—C12	116.5 (4)
O1—C1—C5	127.2 (4)	C11—C12—C13	119.9 (4)
C2—C1—C5	108.1 (4)	Br1—C13—C12	117.9 (4)
C1—C2—O2	123.2 (4)	Br1—C13—C14	119.3 (4)
C1—C2—C3	107.2 (4)	C12—C13—C14	122.8 (4)
O2—C2—C3	129.6 (4)	C13—C14—C9	117.8 (4)
C2—C3—C4	107.8 (4)	C3—C17—C18	128.9 (4)
C2—C3—C17	130.7 (4)	C17—C18—N2	126.3 (4)
C4—C3—C17	121.5 (4)	C17—C18—C19	125.2 (4)
C3—C4—O3	123.0 (4)	N2—C18—C19	108.5 (4)
C3—C4—C5	109.8 (4)	C18—C19—C20	101.1 (3)
O3—C4—C5	127.1 (4)	C18—C19—C26	111.0 (4)
C1—C5—C4	106.8 (4)	C20—C19—C26	111.5 (4)
C1—C5—C6	120.5 (4)	C18—C19—C27	111.5 (4)
C4—C5—C6	132.7 (4)	C20—C19—C27	110.9 (4)
C5—C6—C7	128.1 (4)	C26—C19—C27	110.5 (4)
C6—C7—N1	125.9 (4)	C19—C20—C21	108.8 (4)
C6—C7—C8	125.0 (4)	C19—C20—C25	131.5 (4)
N1—C7—C8	109.1 (4)	C21—C20—C25	119.7 (4)
C7—C8—C9	101.1 (3)	N2—C21—C20	109.0 (4)
C7—C8—C15	109.4 (4)	N2—C21—C22	128.4 (4)
C9—C8—C15	109.4 (4)	C20—C21—C22	122.6 (4)
C7—C8—C16	111.8 (4)	C21—C22—C23	117.2 (5)
C9—C8—C16	113.9 (4)	C22—C23—C24	120.1 (4)
C15—C8—C16	110.7 (4)	Br2—C24—C23	119.2 (4)
C8—C9—C10	108.9 (4)	Br2—C24—C25	118.8 (4)
C8—C9—C14	131.7 (4)	C23—C24—C25	122.0 (4)
C10—C9—C14	119.3 (4)	C24—C25—C20	118.4 (5)
N1—C10—C9	108.1 (4)		

Table S3 Selected geometric parameters (Å, °) for **4a**

C1—C2	1.501 (6)	C28—C29	1.458 (6)
C1—C5	1.463 (6)	C28—C32	1.470 (6)
C1—O1	1.229 (5)	C28—O4	1.240 (5)
C2—C3	1.417 (6)	C29—C30	1.430 (6)
C2—O2	1.238 (5)	C29—O5	1.244 (5)
C3—C4	1.481 (6)	C30—C31	1.480 (6)
C3—C17	1.397 (5)	C30—C44	1.374 (6)
C4—C5	1.436 (6)	C31—C32	1.426 (6)

C4—O3	1.260 (5)	C31—O6	1.254 (5)
C5—C6	1.371 (6)	C32—C33	1.399 (6)
C6—C7	1.397 (6)	C33—C34	1.376 (6)
C7—C8	1.528 (6)	C34—C35	1.500 (6)
C7—N1	1.317 (5)	C34—N3	1.340 (5)
C8—C9	1.488 (6)	C35—C36	1.509 (7)
C8—C15	1.525 (6)	C35—C42	1.525 (7)
C8—C16	1.559 (6)	C35—C43	1.532 (7)
C9—C10	1.372 (6)	C36—C37	1.390 (6)
C9—C14	1.379 (6)	C36—C41	1.373 (7)
C10—C11	1.358 (6)	C37—C38	1.376 (7)
C10—N1	1.414 (5)	C37—N3	1.392 (6)
C11—C12	1.399 (6)	C38—C39	1.392 (7)
C12—C13	1.400 (7)	C39—C40	1.410 (8)
C13—C14	1.369 (7)	C40—C41	1.389 (8)
C17—C18	1.378 (6)	C44—C45	1.386 (6)
C18—C19	1.531 (5)	C45—C46	1.530 (6)
C18—N2	1.333 (5)	C45—N4	1.339 (5)
C19—C20	1.517 (6)	C46—C47	1.505 (6)
C19—C26	1.536 (6)	C46—C53	1.531 (6)
C19—C27	1.521 (6)	C46—C54	1.541 (6)
C20—C21	1.386 (6)	C47—C48	1.370 (6)
C20—C25	1.373 (6)	C47—C52	1.374 (6)
C21—C22	1.386 (6)	C48—C49	1.374 (6)
C21—N2	1.406 (5)	C48—N4	1.414 (5)
C22—C23	1.377 (6)	C49—C50	1.371 (6)
C23—C24	1.378 (6)	C50—C51	1.379 (6)
C24—C25	1.394 (6)	C51—C52	1.426 (6)
C2—C1—C5	107.8 (4)	C32—C28—O4	126.4 (4)
C2—C1—O1	125.9 (4)	C28—C29—C30	108.7 (4)
C5—C1—O1	126.3 (4)	C28—C29—O5	122.8 (4)
C1—C2—C3	107.8 (4)	C30—C29—O5	128.5 (4)
C1—C2—O2	122.3 (4)	C29—C30—C31	106.9 (4)
C3—C2—O2	130.0 (4)	C29—C30—C44	132.3 (4)
C2—C3—C4	107.6 (4)	C31—C30—C44	120.6 (4)
C2—C3—C17	131.7 (4)	C30—C31—C32	109.3 (4)
C4—C3—C17	120.5 (4)	C30—C31—O6	122.4 (4)
C3—C4—C5	109.6 (4)	C32—C31—O6	128.3 (4)
C3—C4—O3	122.7 (4)	C28—C32—C31	107.1 (4)
C5—C4—O3	127.7 (4)	C28—C32—C33	121.0 (4)
C1—C5—C4	106.9 (4)	C31—C32—C33	131.9 (5)
C1—C5—C6	121.8 (4)	C32—C33—C34	129.1 (4)
C4—C5—C6	131.3 (4)	C33—C34—C35	125.2 (5)

C5—C6—C7	129.7 (4)	C33—C34—N3	125.2 (4)
C6—C7—C8	125.4 (4)	C35—C34—N3	109.6 (4)
C6—C7—N1	125.2 (4)	C34—C35—C36	101.3 (4)
C8—C7—N1	109.4 (4)	C34—C35—C42	110.4 (4)
C7—C8—C9	100.5 (4)	C36—C35—C42	112.2 (5)
C7—C8—C15	110.4 (4)	C34—C35—C43	110.5 (4)
C9—C8—C15	112.0 (4)	C36—C35—C43	110.8 (4)
C7—C8—C16	110.3 (4)	C42—C35—C43	111.1 (5)
C9—C8—C16	111.7 (4)	C35—C36—C37	108.9 (4)
C15—C8—C16	111.5 (4)	C35—C36—C41	131.3 (5)
C8—C9—C10	110.7 (4)	C37—C36—C41	119.8 (6)
C8—C9—C14	130.9 (4)	C36—C37—C38	123.1 (5)
C10—C9—C14	118.4 (5)	C36—C37—N3	108.4 (5)
C9—C10—C11	124.3 (4)	C38—C37—N3	128.5 (5)
C9—C10—N1	107.6 (4)	C37—C38—C39	117.8 (5)
C11—C10—N1	128.1 (4)	C38—C39—C40	119.3 (6)
C10—C11—C12	117.1 (5)	C39—C40—C41	121.9 (6)
C11—C12—C13	119.7 (5)	C40—C41—C36	118.3 (6)
C12—C13—C14	120.8 (5)	C30—C44—C45	128.5 (4)
C9—C14—C13	119.7 (5)	C44—C45—C46	125.6 (4)
C3—C17—C18	128.2 (4)	C44—C45—N4	125.6 (4)
C17—C18—C19	124.9 (4)	C46—C45—N4	108.7 (4)
C17—C18—N2	125.9 (4)	C45—C46—C47	101.2 (3)
C19—C18—N2	109.1 (3)	C45—C46—C53	110.5 (3)
C18—C19—C20	100.7 (3)	C47—C46—C53	112.6 (4)
C18—C19—C26	109.3 (3)	C45—C46—C54	111.3 (4)
C20—C19—C26	111.3 (4)	C47—C46—C54	111.7 (4)
C18—C19—C27	112.2 (4)	C53—C46—C54	109.4 (4)
C20—C19—C27	112.9 (3)	C46—C47—C48	109.8 (4)
C26—C19—C27	110.1 (4)	C46—C47—C52	130.5 (4)
C19—C20—C21	109.7 (4)	C48—C47—C52	119.7 (4)
C19—C20—C25	130.5 (4)	C47—C48—C49	124.1 (4)
C21—C20—C25	119.8 (4)	C47—C48—N4	108.7 (4)
C20—C21—C22	122.9 (4)	C49—C48—N4	127.2 (4)
C20—C21—N2	108.1 (4)	C48—C49—C50	116.7 (4)
C22—C21—N2	129.0 (4)	C49—C50—C51	121.5 (5)
C21—C22—C23	116.4 (4)	C50—C51—C52	120.6 (5)
C22—C23—C24	121.7 (5)	C51—C52—C47	117.4 (4)
C23—C24—C25	121.1 (5)	C10—N1—C7	111.8 (4)
C24—C25—C20	118.1 (4)	C21—N2—C18	112.4 (3)
C29—C28—C32	107.9 (4)	C37—N3—C34	111.7 (4)
C29—C28—O4	125.7 (5)	C48—N4—C45	111.6 (4)

Table S4 Hydrogen-bond geometry (Å, °) for compound **4b**

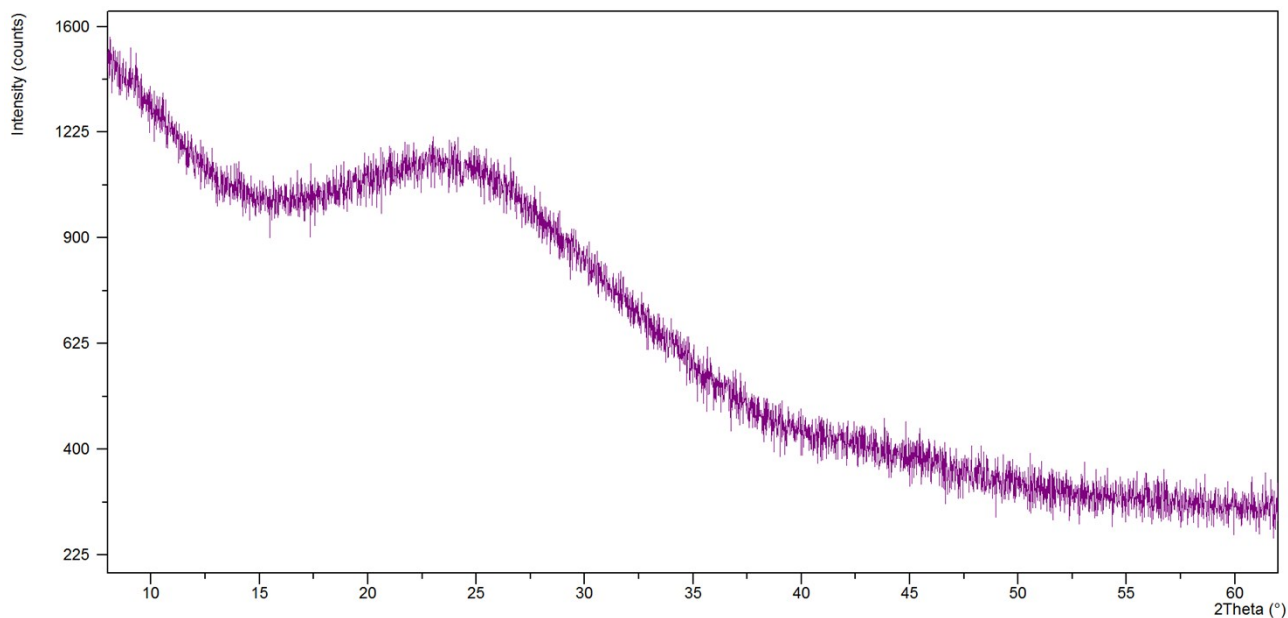
<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N1—H11···O3	0.85	1.85	2.630 (7)	152 (1)
N2—H21···O2	0.87	1.85	2.654 (7)	153 (1)
C11—H111···O1 ⁱ	0.92	2.33	3.008 (7)	130 (1)
C15—H153···O2 ⁱⁱ	0.95	2.55	3.462 (7)	160 (1)
C26—H262···O2 ⁱⁱⁱ	0.96	2.56	3.454 (7)	155 (1)

Symmetry codes: (i) *x*, *y*-1, *z*, (ii) -*x*, -*y*+1, -*z*+1, (iii) -*x*+1, -*y*+1, -*z*+1.

Table S5 Hydrogen-bond geometry (Å, °) for compound **4a**

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C25—H251···O1 ⁱ	0.93	2.45	3.355 (8)	163
C52—H521···O4 ⁱⁱ	0.95	2.42	3.349 (8)	165
N3—H31···C31	0.87	2.57	3.138 (8)	124
N3—H31···O6	0.87	1.86	2.648 (8)	151
N1—H11···C4	0.88	2.57	3.140 (8)	123
N1—H11···O3	0.88	1.84	2.634 (8)	150
N2—H21···O2	0.86	1.93	2.677 (8)	144
N4—H41···O5	0.87	1.91	2.656 (8)	144

Symmetry codes: (i) *x*-1, *y*, *z*; (ii) *x*+1, *y*, *z*.

**Figure S6.** XRD of the spin-coated thin films of compound **4b**.

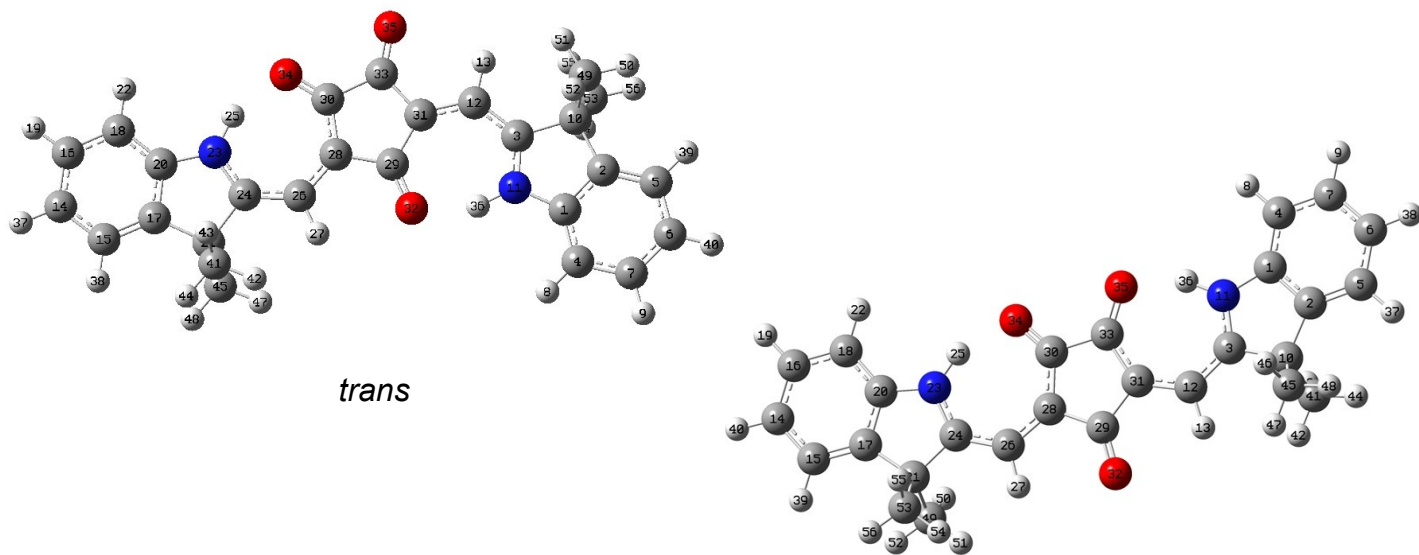
6 Computational Details

All calculations were performed on the ground electronic state in vacuo and in CHCl_3 solution at DFT^[16] level of approximation. The GAUSSIAN03^[17] program was used. The DFT method investigated was the Becke's method with the Perdew and Wang's 1991 gradient corrected exchange and functional, known as B3PW91^[18], with the 6-311G(d,p) basis set for all atoms. Various basis sets were tested, but no significant variations were observed. Firstly, molecular geometries were fully optimized in vacuo starting from standard bond lengths and angles as input data. Then, molecular geometries were optimized in CHCl_3 starting from the best geometries calculated in vacuo. Solvent effects were modelled using the Integral Equation Formalism for the Polarisable Continuum Model (IEF-PCM).^[19] NBO Natural Bond Orbital (NBO) analysis^[20] was used to examine hyperconjugative interactions due to electron transfers from carbonyl oxygen lone-pairs (donor) to empty antibonding N-H orbitals (acceptor) and calculate the energies of the hydrogen bonds in the three conformers of **4a**.

7 Calculated geometries and energies of N-H...O=C hydrogen bonds

Tables S6-S7

Geometries (distances in Å and angles in °) and energies (in kcal mol⁻¹) of the hydrogen bonds calculated in CHCl₃ solution for *trans*, *cis1* and *cis2* conformational isomers of **4a**. *cis1* and *cis2* conformational isomers are symmetric and only one hydrogen bond has been reported.

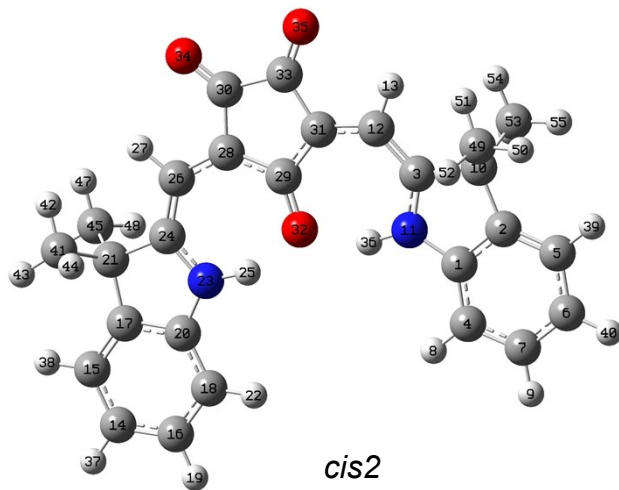


trans

cis1

Table S6

<i>trans</i>	
N23-H35	1.038
C30=O34	1.237
N23-H25...O34	1.710
<N23-H25...O34	153.6
<H25...O34-C30	110.4
<i>Energy</i>	<i>24.5 kcal mol⁻¹</i>
N11-H36	1.044
C29=O32	1.248
N11-H36...O32	1.675
<N11-H36...O32	154.8
<H36...O32-C29	111.5
<i>Energy</i>	<i>28.2 kcal mol⁻¹</i>



cis2

Table S7

<i>cis1</i>		<i>cis2</i>	
N-H	1.040	N-H	1.042
C30(33)=O34(35)	1.240	C29=O32	1.271
N-H...O34(35)	1.699	N-H...O32	1.678
<N-H...O34(35)	154.0	<N-H...O32	154.1
<H...O34(35)-C30(33)	110.5	<H...O32-C29	113.4
<i>Energy</i>	<i>25.6 kcal mol⁻¹</i>	<i>Energy</i>	<i>24.4 kcal mol⁻¹</i>

8 Electrical characterization of compound 5a and hysteresis measurements on compound 4a and 4b.

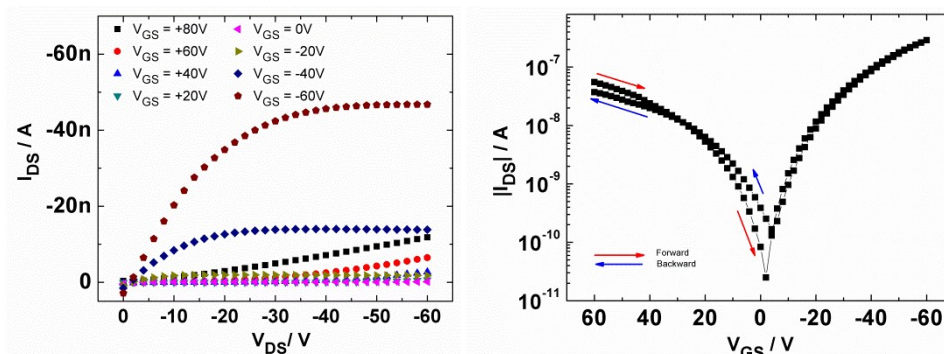


Figure S7: (left) Output characteristics (I_{DS} - V_{DS}) and (right) forward and backward transfer characteristics (I_{DS} - V_{GS}) of molecule **5a**. [$V_{DS} = -30$ V; $L = 10$ μm]

MOLECULE 5a	Saturation Regime	Linear Regime
Avg Mobility (cm^2/Vs)		
Electrons	$\mu_{e,\text{sat}} = 3,13 \times 10^{-7}$	$\mu_{e,\text{lin}} = 1,47 \times 10^{-7}$
Holes	$\mu_{h,\text{sat}} = 1,02 \times 10^{-5}$	$\mu_{h,\text{lin}} = 7,17 \times 10^{-6}$

Table S8: Average hole and electron mobility for molecule **5a** extracted from the I_{DS} - V_{GS} in different regimes. [$L = 10$ μm]

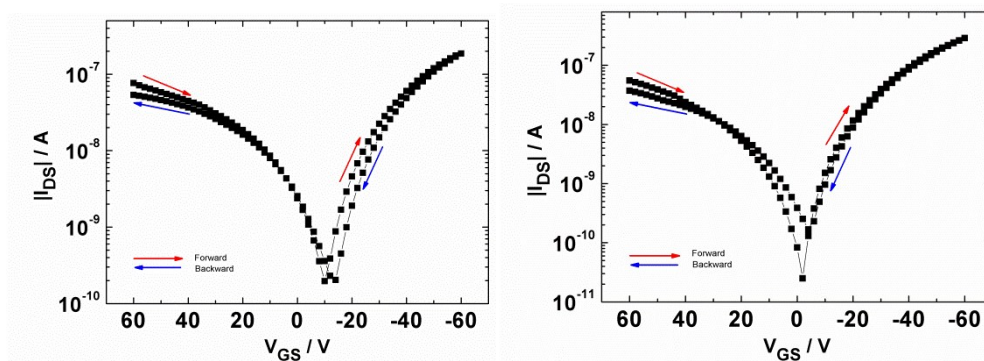


Figure S8: Forward and backward transfer characteristics (I_{DS} - V_{GS}) of molecule **4a** and **4b**. [$V_{DS} = -30$ V; $L = 10$ μm]

9 References and notes

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