

Electronic supplementary information

Efficient OFET-based optical memory and photodetectors using novel BODIPY dye

Filipp S. Talalaev,^a Lyubov A. Frolova,^a Andrei Y. Bochkov,^b Sergey D. Babenko,^c Lavrenty G. Gutsev,^a Sergey M. Aldoshin,^a Valery F. Traven,^b and Pavel A. Troshin^a

^a *Federal Research Center of Problems of Chemical Physics and Medicinal Chemistry of the Russian Academy of Sciences, Academician Semenov Avenue 1, Chernogolovka, Moscow Region, 142432, Russian Federation*

^b *D. I. Mendeleev University of Chemical Technology of Russia, Miusskaya sq. 9, Moscow, 125047, Russian Federation*

^c *Chernogolovka branch of the N.N. Semenov Federal Research Center for Chemical Physics of RAS, Academician Semenov St.1/10 Chernogolovka, 142432, Russian Federation*

† e-mail: troshin2003@inbox.ru

Contents

1. General information	2
2. Synthetic procedures	3
3. UV-vis and fluorescence spectra	6
4. NMR spectra	7
5. Cyclic voltammetry	12
6. Fabrication and characterization of devices	13
7. Electrical characteristics of the devices	14
8. References	22

1. General information

All reagents were obtained from Sigma-Aldrich and Acros Organics and used without further purification. Anhydrous solvents were obtained by distillation of standard grade solvents over phosphorous anhydride at atmosphere pressure (toluene and DCM) or in vacuum (DMF). Solvents for spectroscopy measurements were spectroscopy grade. Benzoylmethylenetriphenylphosphorane and diphenylmalonate were synthesized according to the reported procedures.¹

Analytical thin layer chromatography (TLC) was performed using Macherey-Nagel Alugram SILG/UV254 plates. Chromatograms were visualized by UV light (254 or 365 nm). Macherey-Nagel Kieselgel 60 H silica gel was used for column chromatography.

Stuart melting point apparatus SMP30 was used for measuring melting points. UV-vis absorption spectrometry measurements were performed using an SF-104 spectrophotometer (Interphotophysics LLC, Moscow, Russia). Fluorescence measurements were conducted using a Cary Eclipse (Varian) spectrofluorimeter.

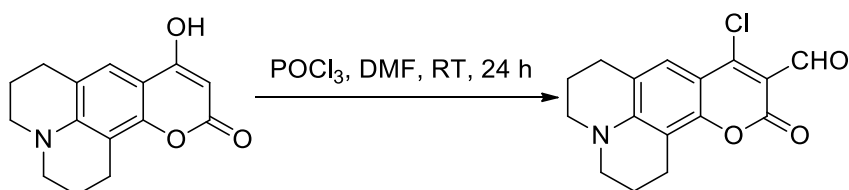
¹H and ¹³C NMR spectra were recorded on a Bruker AM 300, JEOL JNM ECX-400, Bruker 500 MHz NMR spectrometers in solvents as indicated. Chemical shifts (δ) are given in parts per million (ppm) downfield of tetramethylsilane, using the solvent signal as an internal reference (CDCl₃: δ H = 7.27 ppm, δ C = 77.16 ppm; DMSO-d₆: δ H = 2.50 ppm, δ C = 39.52 ppm). Abbreviations used in the description of resonances: s (singlet), d (doublet), t (triplet), q (quartet), br (broad). Coupling constants (J) are reported in Hertz (Hz) and quoted to the nearest 0.1 Hz.

Our spin-polarized DFT calculations were performed using the GAUSSIAN 16 suite of programs. Initial relaxations were performed with the B3PW91/6-311G* then optimizations were done with TPSSh/6-311G* and then finally with the Solvent Reaction Field taken into account with the parameters of acetonitrile. Where convergence was difficult, Gaussian's orbital shifting option was applied until convergence was achieved. The RMS force threshold was set to $3 \cdot 10^{-4}$ eV/Å and the total energy threshold to 10^{-8} a. u.

2. Synthetic procedures

Compounds (1) and (2) were synthesized as reported previously.²⁻⁴

9-chloro-11-oxo-2,3,5,6,7,11-hexahydro-1*H*-pyrano[2,3-*f*]pyrido[3,2,1-*ij*]quinoline-10-carbaldehyde (3)

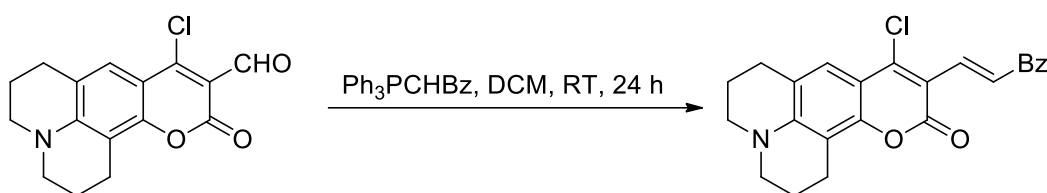


Starting material **2** (1.40 g, 4 mmol) was dissolved in DMF (25 ml) and POCl₃ (0.5 ml, 5.4 mmol) was added to the resulting solution. The reaction mixture was stirred for 24 hours until complete conversion of the starting materials (TLC control). Then the mixture was poured into 250 ml of water producing a red flaky precipitate, which was separated by filtration, dried, redissolved in methylene chloride (50 ml). Isopropyl alcohol (20 ml) was added to the resulting solution and then methylene chloride was removed in vacuum, thus producing a red precipitate, which was filtered out and dried (1.20 g). A certain amount of the target product was isolated from the solution in isopropyl alcohol by flash chromatography on silica gel column (h = 7 cm) using methylene chloride as eluent. Afterwards, 6 ml of EtOH was added to the eluate and the resulting solution was concentrated on a rotary evaporator producing a red precipitate formed from ethanol, which was filtered out and dried (0.19 g). Total yield: 1.39 g (88%), mp. 201 °C (decomp.), R_f = 0.38 (Petroleum ether : acetone 2:1).

201 °C (decomp.), R_f = 0.38 (Petroleum ether : acetone 2:1).

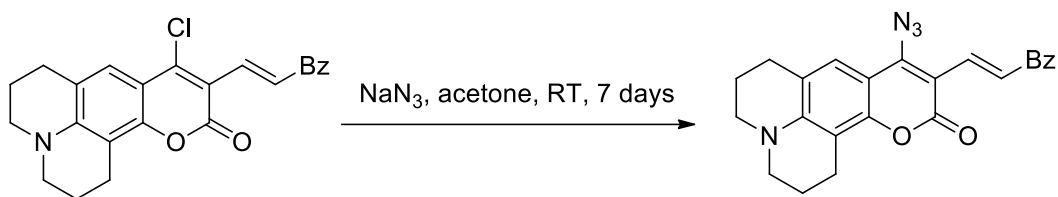
¹H NMR (500 MHz, CDCl₃): δ 1.98–2.02 (m, 4H), 2.80 (t, 2H, J = 6.1 Hz), 2.87 (t, 2H, J = 6.4 Hz), 3.37–3.41 (m, 4H), 7.42 (s, 1H), 10.25 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 19.43, 19.55, 20.40, 26.99, 49.45, 49.89, 105.05, 106.76, 109.07, 119.86, 124.35, 149.10, 150.86, 152.93, 159.64, 186.56. MS (ESI): m/z 303 (M⁺, 100%), 287 (29), 256 (34), 247 (29), 228 (30), 221 (26).

(*E*)-9-chloro-10-(3-oxo-3-phenylprop-1-en-1-yl)-2,3,6,7-tetrahydro-1*H*-pyrano[2,3-*f*]pyrido[3,2,1-*ij*]quinolin-11(5*H*)-one (4)



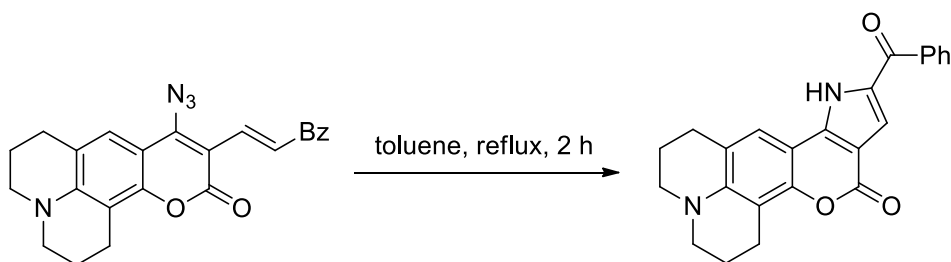
Compound **3** (476 mg, 1.2 mmol) was dissolved in distilled methylene chloride (10 ml) and benzoylmethylene triphenylphosphorane (985 mg, 2.2 mmol) was added to the resulting solution. The mixture was vigorously stirred at room temperature for 2 days. Upon completion of the reaction (TLC control), a red colored precipitate was filtered from the reaction mixture, washed with ethanol and dried. Yield: 551 mg (92%), mp. 180.8-181.5 °C, R_f = 0.49 (Petr.Ether:acetone 2:1). ¹H NMR (500 MHz, CDCl₃): δ 1.96–2.01 (m, 4H), 2.81 (t, 2H, J = 6.1 Hz), 2.91 (t, 2H, J = 6.4 Hz), 3.33 (t, 4H, J = 5.6 Hz), 7.34 (s, 1H), 7.51 (t, 2H, J = 7.3 Hz), 7.58 (t, 1H, J = 7.3 Hz), 8.11 (d, 2H, J = 7.30) 8.16 (d, 1H, J = 15.2 Hz), 8.45 (d, 1H, J = 15.2 Hz). ¹³C NMR (125 MHz, CDCl₃): δ 19.66, 19.69, 20.64, 27.08, 49.22, 49.63, 104.97, 107.08, 110.85, 119.17, 123.33, 124.32, 127.97, 128.09, 132.04, 135.52, 138.01, 147.36, 149.13, 150.71, 158.49, 190.27. MS (ESI): m/z 405 (M⁺, 100%), 322 (79), 291 (68), 243 (84), 226 (82).

(E)-9-azido-10-(3-oxo-3-phenylprop-1-en-1-yl)-2,3,6,7-tetrahydro-1H-pyrano[2,3-f]pyrido[3,2,1-ij]quinolin-11(5H)-one (5)



Compound 4 (370 mg, 0.74 mmol) was dissolved in acetone (75 ml) and NaN_3 (76 mg, 1.17 mmol) was added to the resulting mixture. The mixture was stirred vigorously for 7 days. After completion of the reaction (TLC control), a red precipitate was filtered from the reaction mixture and washed with water. 50 ml of H_2O was added to the mother liquor, acetone was distilled off from the resulting mixture, and the precipitate was filtered off. Yield: 347 mg (93%), mp. 200 ° C (decomp.), $R_f = 0.53$ (Petr. Ether : acetone 2:1).

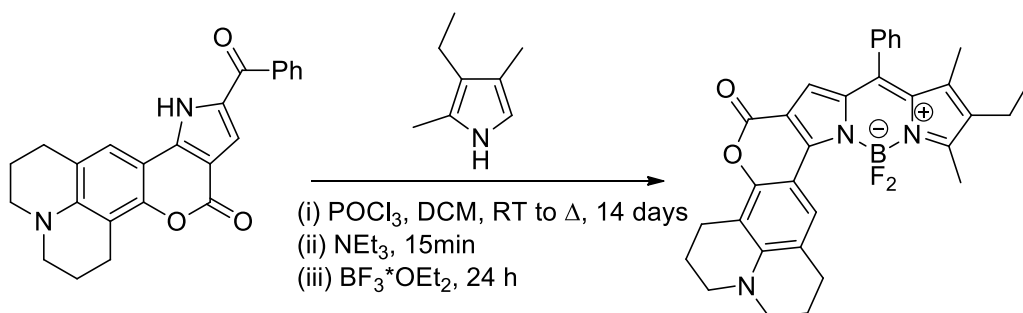
2-benzoyl-6,7,8,10,11,12-hexahydropyrido[3,2,1-ij]pyrrolo[2',3':4,5]pyrano[2,3-f]quinolin-4(1H)-one (6)



Compound 5 (347 mg, 0.7 mmol) was added to anhydrous toluene (10 ml). The resulting suspension was heated at reflux for two hours with vigorous stirring. The formed precipitate was filtered and washed with toluene. Yield: 276 mg (84%), mp. = 326-330.2 °C, $R_f = 0.43$ (Petr. Ether : acetone 2:1). ^1H NMR (500 MHz, CDCl_3): δ 1.95 (m, 2H), 2.52 (m, 1H, overlap with DMSO residual peak), 2.78 (m, 1H), 3.36 (m, 8H), 5.55 (s, 1H), 7.55 (m, 1H), 7.60 (m, 1H), 7.85 (m, 2H), 8.08 (m, 2H), 12.80 (br. s, <1H, NH). ^{13}C NMR (125 MHz, DMSO-d_6): δ 19.27, 20.30, 20.63, 26.18, 48.81, 49.34, 100.16, 106.56, 117.50, 120.45, 122.19, 127.50, 132.65, 132.69, 135.55, 136.81, 137.79, 140.75, 144.58, 149.63, 158.37, 187.63.

MS (ESI): m/z 383 ($\text{M}^+ - \text{H}$, 35%), 371 (31), 317 (36), 282 (48), 280 (65), 255 (95), 254 (100), 251 (36), 239 (35), 226 (31)

BODIPY compound (7)



To a solution of compound **6** (303 mg, 0.6 mmol) in anhydrous DCM (100 ml), 2,4-dimethyl-3-ethylpyrrole (537 mg, 4.4 mmol) and POCl₃ (385 μ l, 4.1 mmol) were added. The solution was left for 14 days with vigorous stirring at 40 °C. After complete conversion of the starting material (control by TLC), the reaction mixture was cooled to room temperature and triethylamine (11.2 mmol, 1.56 ml) was added; the resulting mixture was stirred for additional 15 minutes. Then BF₃·OEt₂ (12.7 mmol, 1.66 ml) was added and the mixture was stirred overnight. Next day, the mixture was analyzed by TLC to prove that dipyrromethene intermediate underwent complete conversion to the target product. The reaction mixture was mixed with water (3 ml) the organic layer was separated, concentrated on a rotary evaporator, while the resulting residue was subjected to gradient column chromatography using a mixture of petroleum ether - methylene chloride (in 1:1 v/v ratio). Compound **7** was isolated as dark green crystals with a metal lust. Yield: 271 mg (84%). Mp. 288-289 °C (decomp.). ¹H NMR (500 MHz, CDCl₃): δ 1.06 (t, 3H, *J* = 7.6 Hz), 1.49 (s, 3H), 2.02 (m, 4H), 2.41 (q, 2H, *J* = 7.6 Hz), 2.73 (s, 3H), 2.93 (m, 4H), 3.29 (m, 4H), 6.93 (s 1H), 7.36 (m, 2H), 7.50 (m, 3H), 8.22 (s, 1H). ¹³C NMR (125 MHz, DMSO-d₆): δ 11.73 (CH₃), 13.30 (CH₃), 16.72 (CH₂CH₃), 20.02 (CH₂), 20.07 (CH₂), 20.11 (CH₂), 27.63 (CH₂CH₃), 49.10 (CH₂), 49.70 (CH₂), 101.51, 107.05, 112.69, 117.96, 123.52, 125.99, 128.51, 128.74, 129.07, 133.39, 133.43, 136.88, 139.34, 140.94, 145.00, 148.58, 150.64, 153.89, 158.95, 162.94. ¹⁹F NMR (470 MHz, CDCl₃): δ -142.31.

MS (ESI): *m/z* 537 (M⁺, 91%), 370 (19), 317 (23), 282 (41), 280 (47), 254 (100), 251 (35), 239 (23), 226 (22).

3. UV-vis and fluorescence spectra

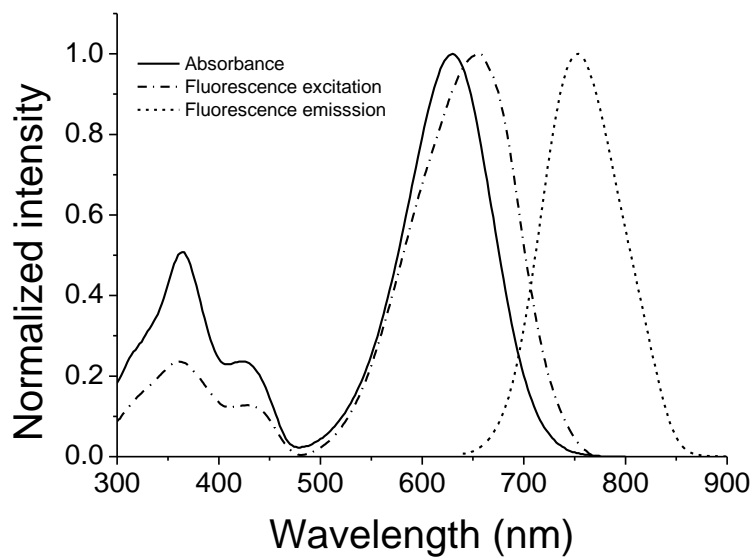


Figure S3-1 Normalized absorption, fluorescence excitation and emission spectra of **7** in DCM

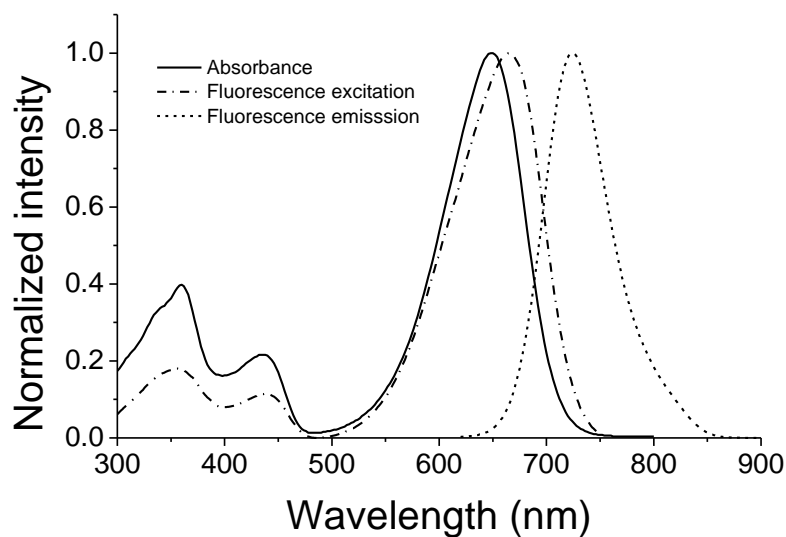


Figure S3-2 Normalized absorption, fluorescence excitation and emission spectra of **7** in toluene

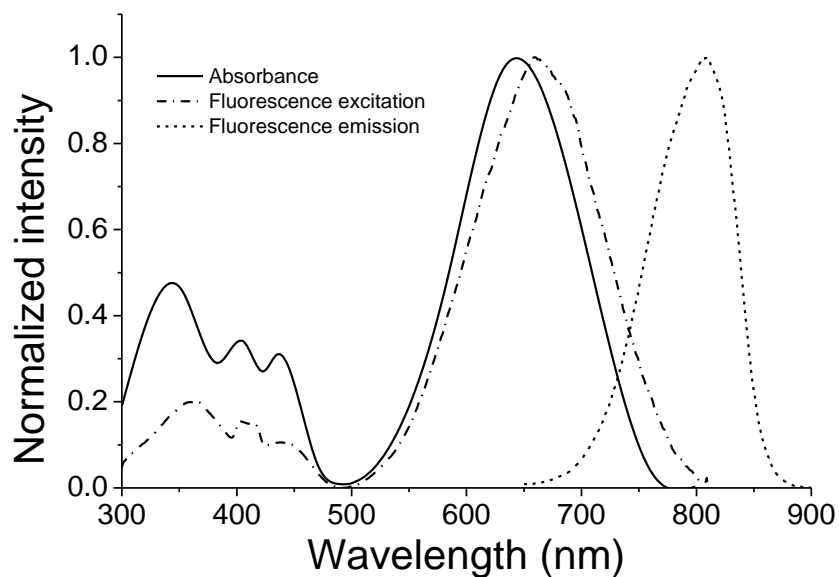


Figure S3-3 Normalized absorption, fluorescence excitation and emission spectra of **1** in DMF

4. NMR spectra

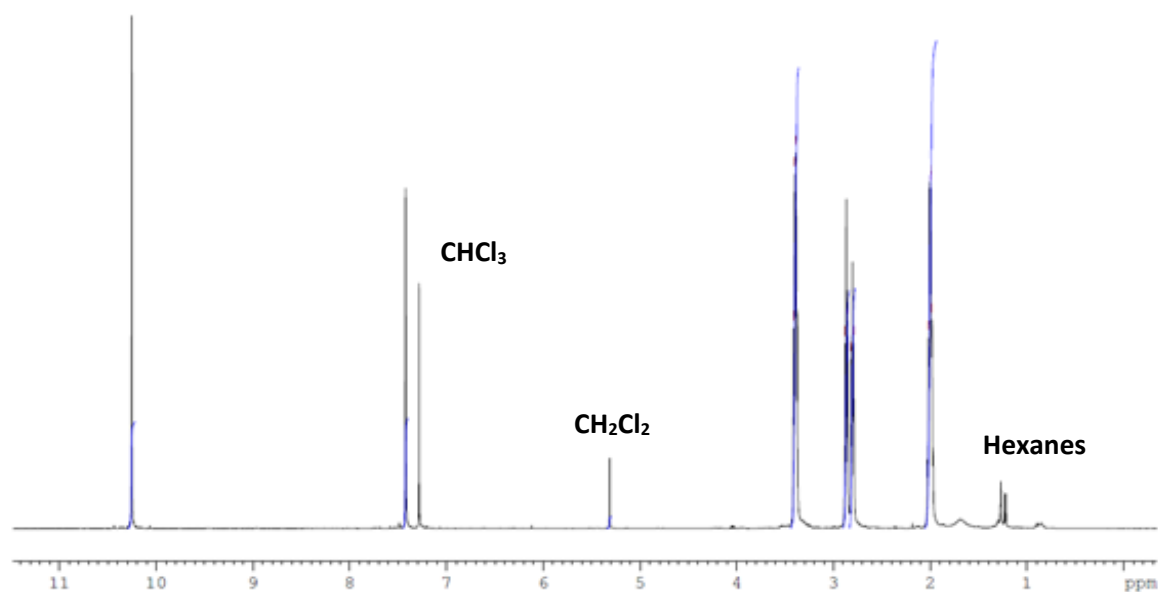


Figure S4-1 ^1H NMR spectrum of compound **3** (500 MHz, CDCl_3)

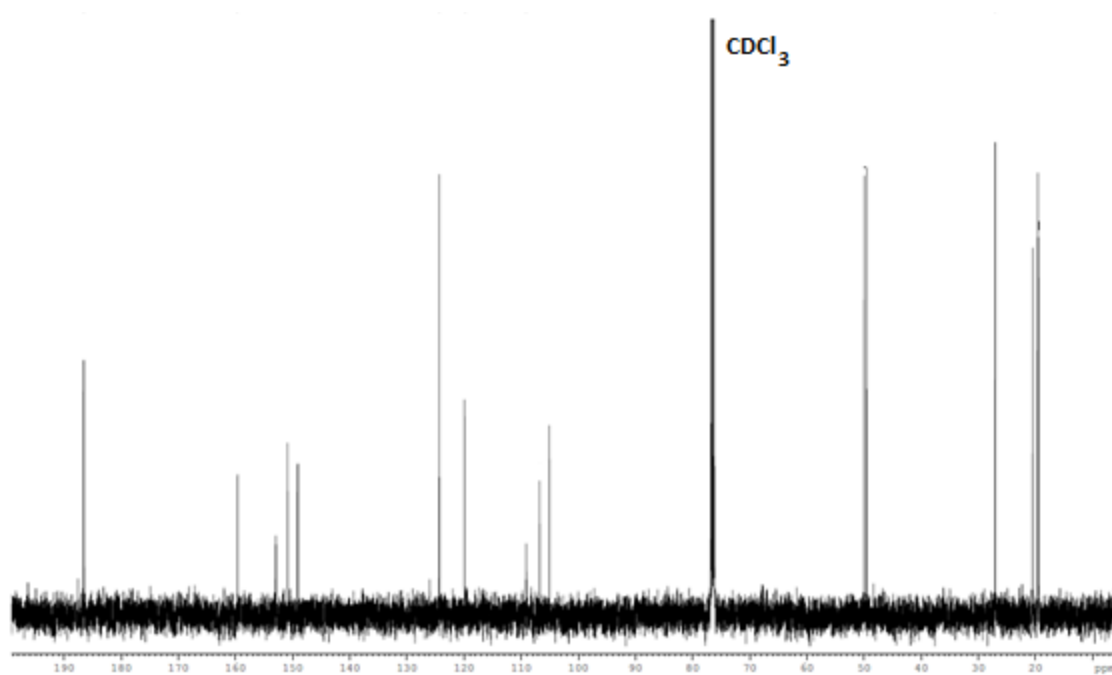


Figure S4-2 ^{13}C NMR spectrum of compound **3** (125 MHz, CDCl_3)

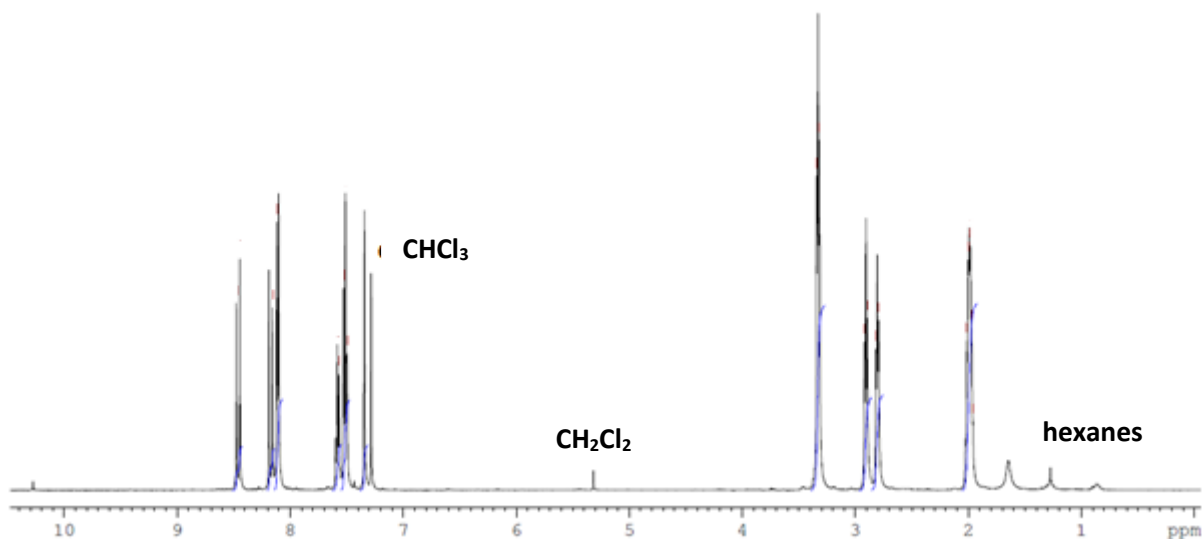


Figure S4-3 ^1H NMR spectrum of compound **4** (500 MHz, CDCl_3)

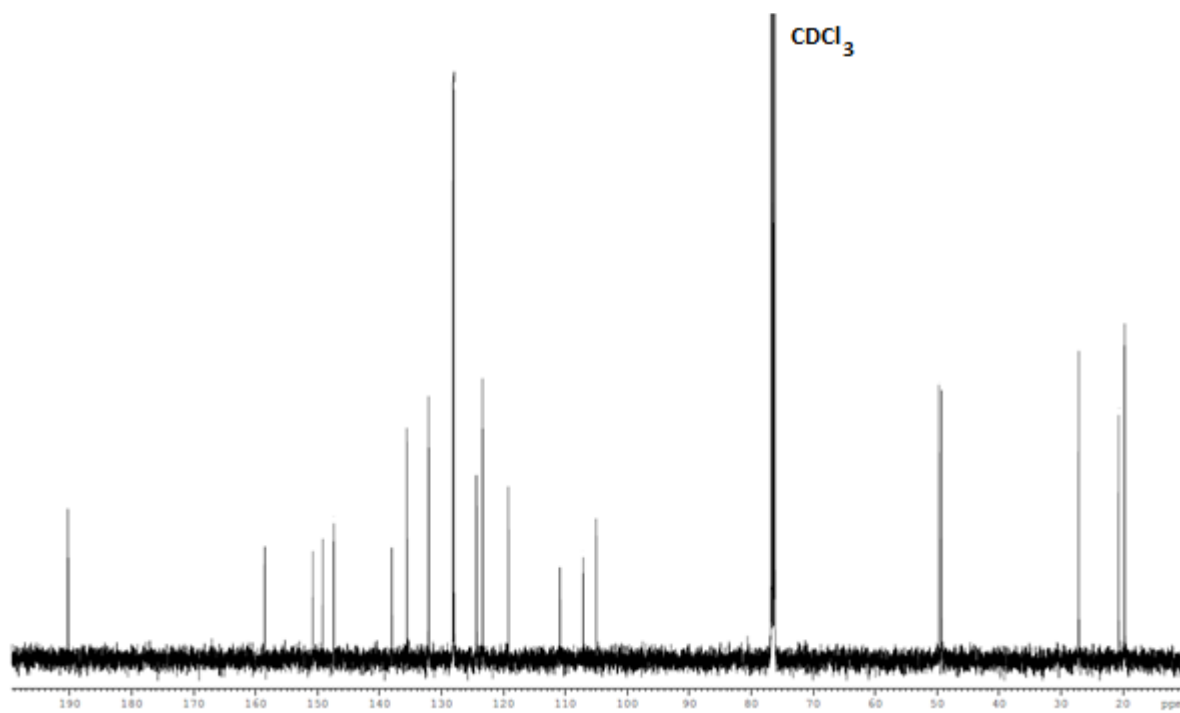


Figure S4-4 ^{13}C NMR spectrum of compound **4** (125 MHz, DMSO-d_6)

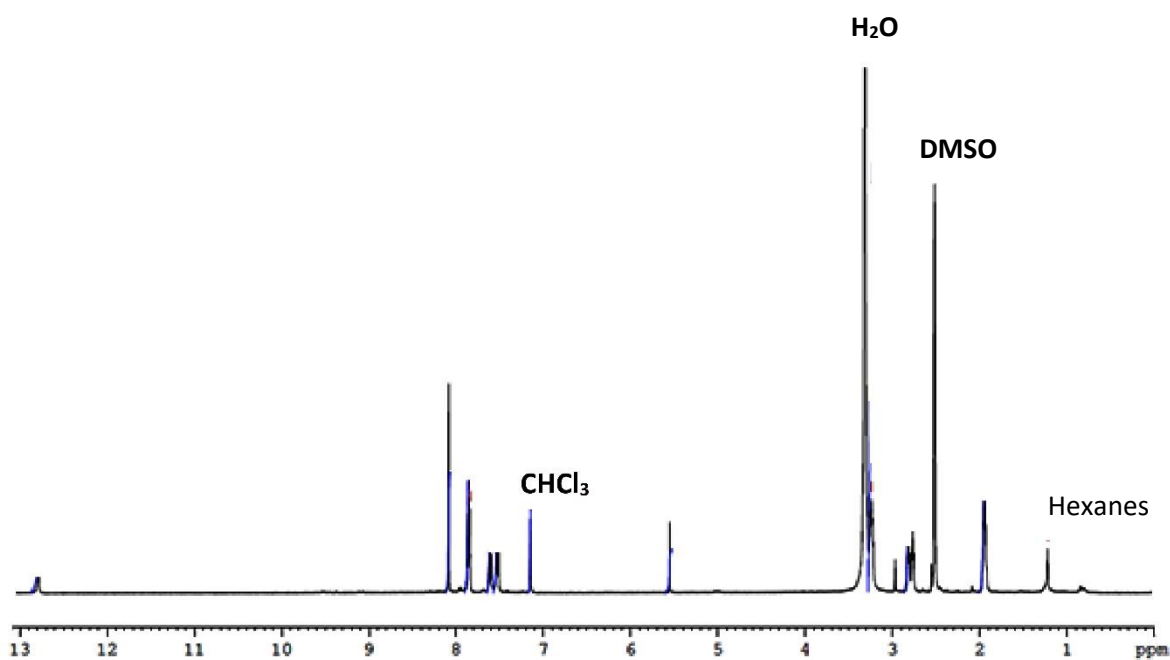


Figure S4-5 ¹H NMR spectrum of compound 6 (500 MHz, CDCl₃-DMSO-d₆ mixture)

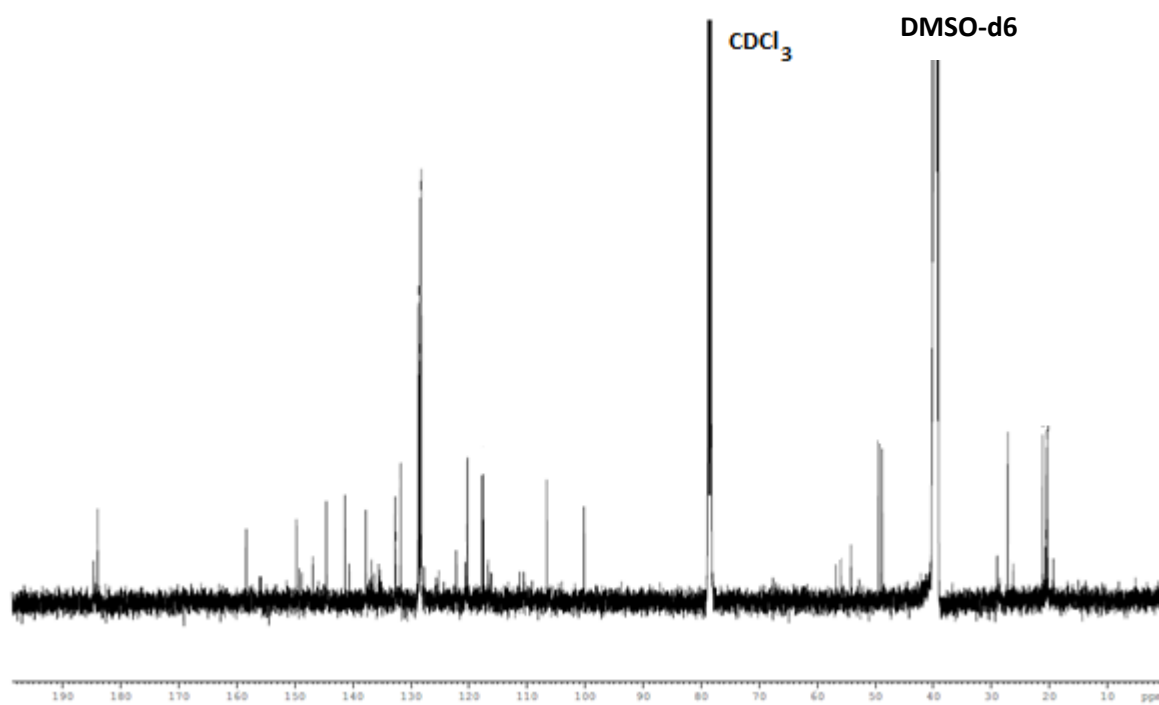


Figure S4-6 ¹³C NMR spectrum of compound 6 (125 MHz, CDCl₃-DMSO-d₆ mixture)

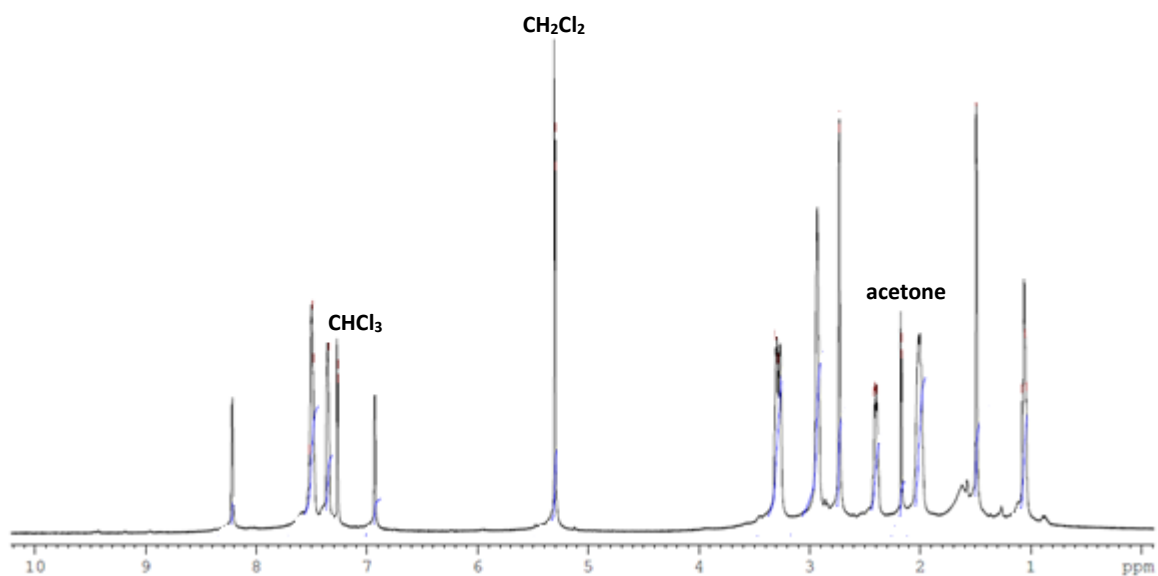


Figure S4-7 ^1H NMR spectrum of compound **7** (500 MHz, CDCl_3)

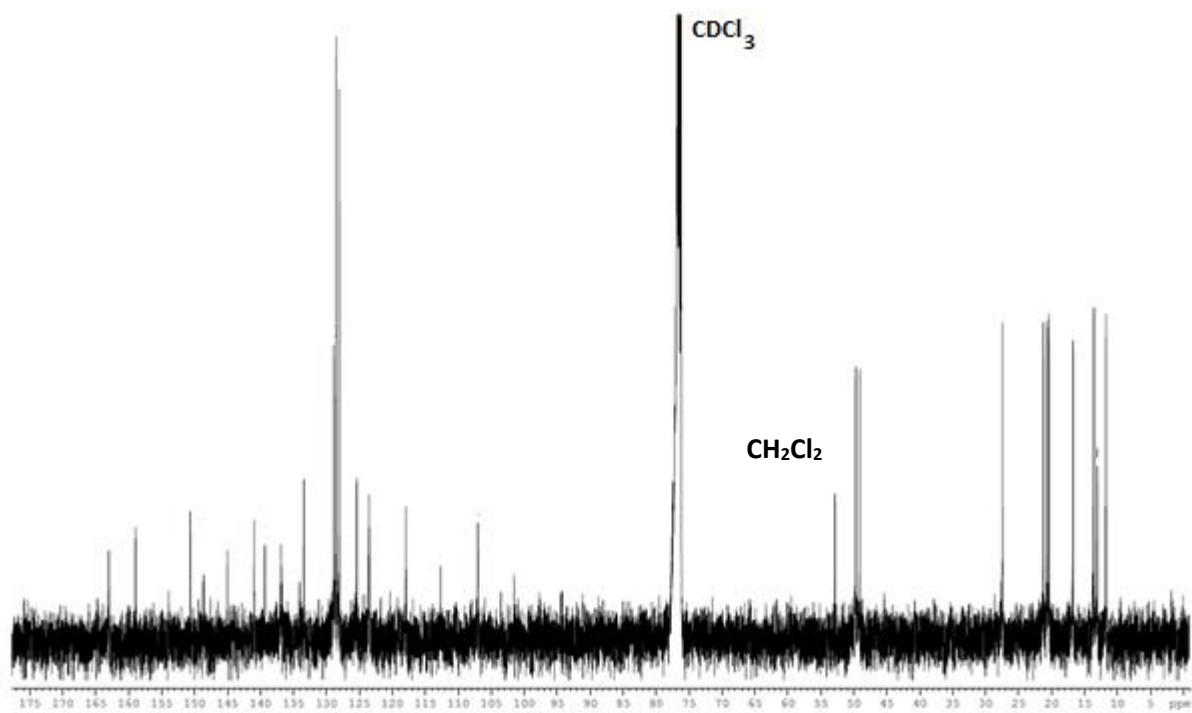


Figure S4-8 ^{13}C NMR spectrum of compound **7** (125 MHz, CDCl_3)

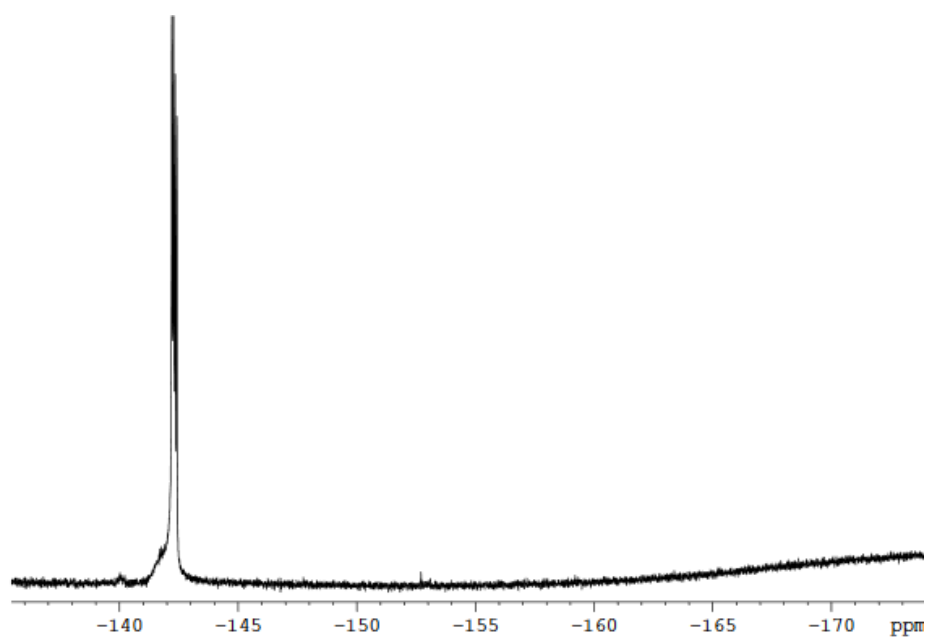


Figure S4-9 ^{19}F NMR spectrum of compound **7** (470 MHz, CDCl_3)

5. Cyclic voltammetry

The cyclic voltammetry measurements were performed for thin films (150–160 nm thick) of compounds **7** and **8** deposited on a glassy carbon disc electrode (working electrode, $d = 5$ mm, BAS Inc.) from solutions in chloroform. The measurements were performed in a three-electrode electrochemical cell using 0.1 M solution of Bu_4NPF_6 in acetonitrile as supporting electrolyte, platinum wire as a counter electrode and a silver wire immersed in 0.01 M solution of AgNO_3 in 0.1 M TBAP (CH_3CN) as a reference Ag/Ag^+ electrode (BAS Inc.). Ferrocene was used as an internal reference. The electrolyte solution was purged with argon before the measurements. The voltammograms were recorded using an ELINS P-30SM instrument at room temperature with a potential sweep rate of 50 mV s^{-1}

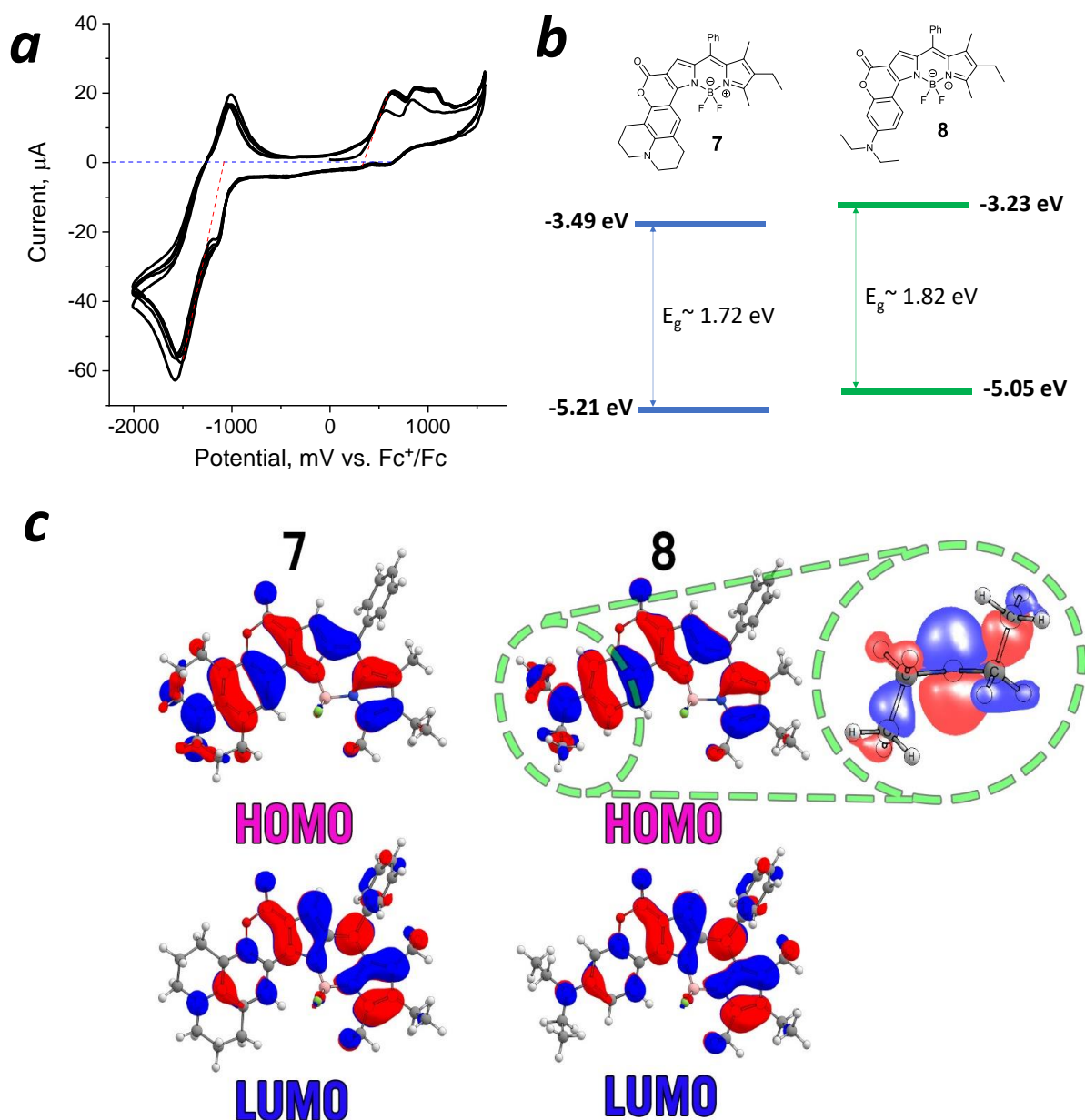


Figure S5-1 Cyclic voltammograms of BODIPY **7** (a), energies of HOMO and LUMO levels of **7** and **8** according to DFT (b) and the computed structures of frontier energy levels of **7** and **8** (c)

6. Fabrication and characterization of devices

The organic field-effect transistors (OFETs) with BODIPY **7** interlayer were fabricated as follows. The glass substrates (15x15 mm) were cleaned by RF plasma treatment for 10 min, transferred to glovebox and aluminum gate electrodes (100 nm) were deposited through a shadow mask by a thermal evaporation process in vacuum (10^{-6} mbar). Dielectric layer was formed by anodization of aluminum in citric acid solution (concentration 50 g/L) in a potentiostatic regime at 35 V until current drops below 1 μ A. Samples with the formed Al/AlO_x structure were thoroughly rinsed with water and isopropyl alcohol and then dried in an oven at 50 °C for 1 h. Afterwards, the samples were moved inside the MBraun nitrogen-filled glove box and BODIPY **7** films were deposited by spin-coating at 1500 rpm from CHCl₃ solution (concentration 10 mg/mL). Then a semiconductor layer (fullerene C₆₀ or pentacene, 100 nm) was deposited by thermal evaporation through a shadow mask followed by deposition of silver (when fullerene was used as a semiconductor) or gold (when pentacene was used as a semiconductor) source and drain electrodes.

The lateral 2-terminal photoresistor-type devices were fabricated inside a nitrogen-filled MBraun glove box as follows. The BODIPY **7** thin film was deposited by spin-coating at 1500 rpm from CHCl₃ solution directly onto the glass substrate. Then fullerene C₆₀ layer and two silver electrodes were deposited as described above for OFET fabrication.

The electrical characteristics of the devices were measured using Keithley 2612B 2-channel source-measurement unit inside the glovebox with inert (nitrogen) atmosphere with O₂ and H₂O levels below 1 ppm. The measurements of I-V curves were performed with integration time of 1 NPLC. Violet light (405 nm) irradiation of devices was provided by a laser diode, which was controlled by Advantest TR6240A instrument synchronized with the source-measurement unit collecting the I-V data. Coherent Field Max II-TO instrument with silicon diode OP-2 was used to measure the light intensity.

7. Electrical characteristics of the devices

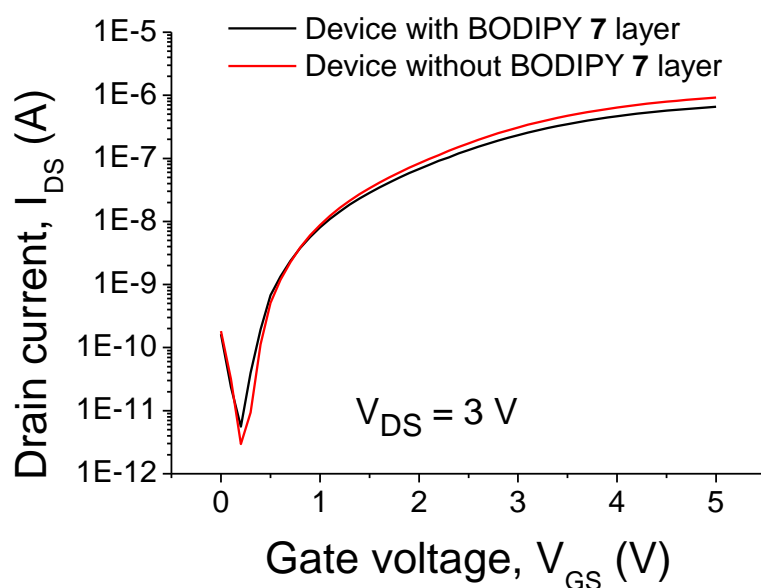


Figure S7-1 Comparison of the transfer characteristics of OFETs with and without BODIPY 7 layer

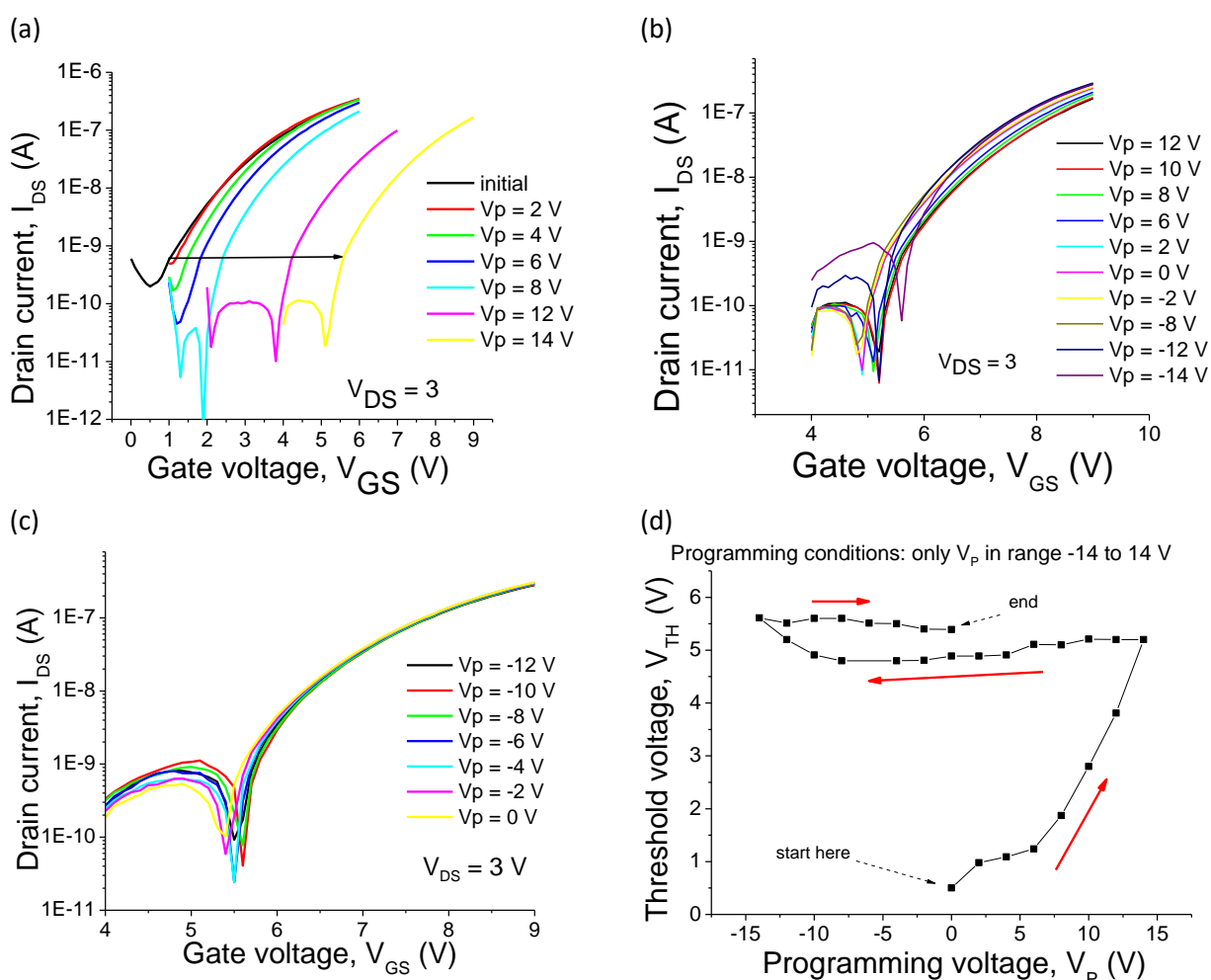


Figure S7-2 Evolution of transfer characteristics of OFETs comprising BODIPY 7/C₆₀ system while applying programming voltage V_p in range from 0 to +12 V (a), from +12 to -14 V (b), from -14 to 0 V (c) without

exposure to light. Dependence of the threshold voltage V_{TH} on the applied programming voltage V_p ($t_p=13$ s in each point) (d).

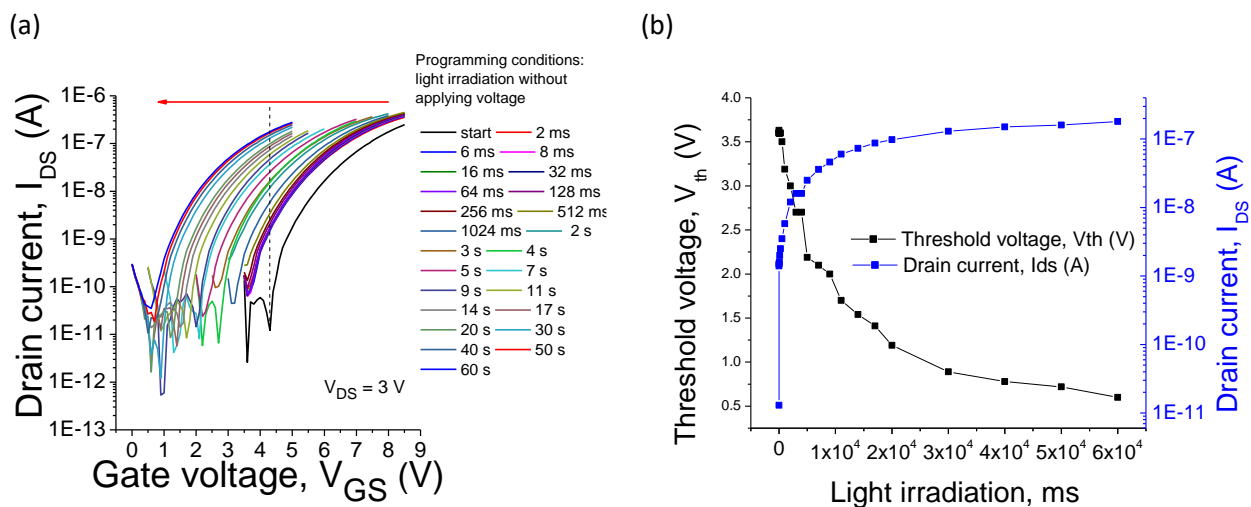


Figure S7-3 Evolution of transfer characteristics of the preprogrammed OFETs comprising BODIPY 7/C₆₀ system under light exposure without electric bias (a) and the corresponding time dynamics of I_{DS} at $V_{GS} = 4.5$ V and V_{TH} (b)

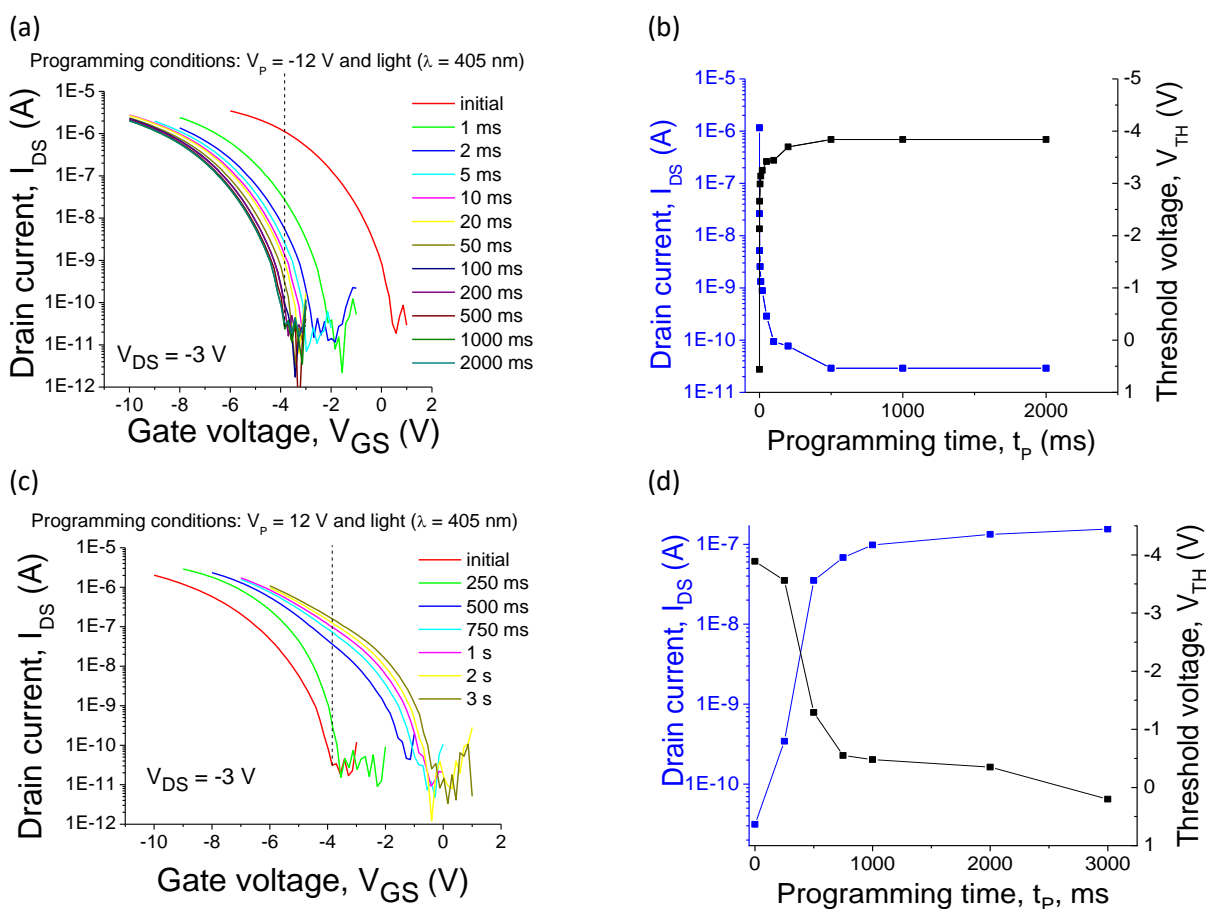


Figure S7-4 Evolution of the transfer characteristics of the OFETs comprising BODIPY 7/pentacene system (a, c), their drain currents (blue) and threshold voltages (black) (b, d) while programming with $V_P = -12$ V and light (a, b) or $V_P = 12$ V and light (c, d)

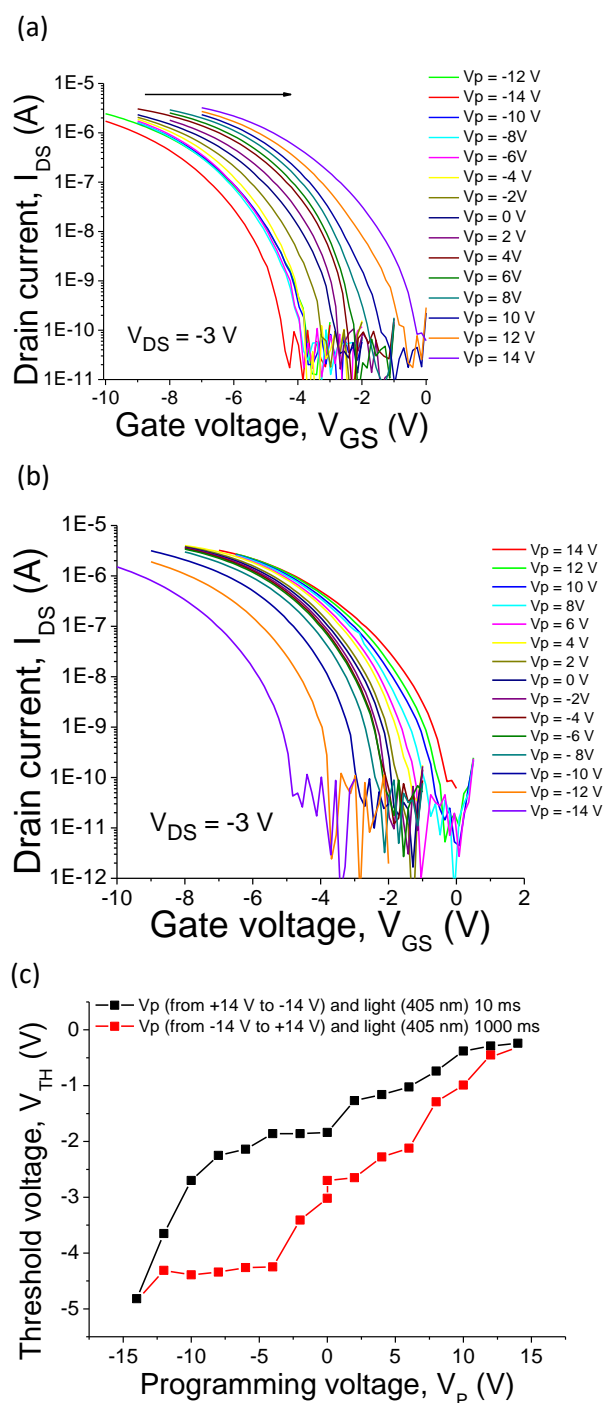


Figure S7-5 Evolution of transfer curves of OFETs comprising BODIPY 7/pentacene system under exposure to light and gradually increased (a) or decreased (b) programming voltages. The dependence of threshold voltage V_{TH} on the applied programming voltage V_p ($t_p = 13$ s in each point) (c).

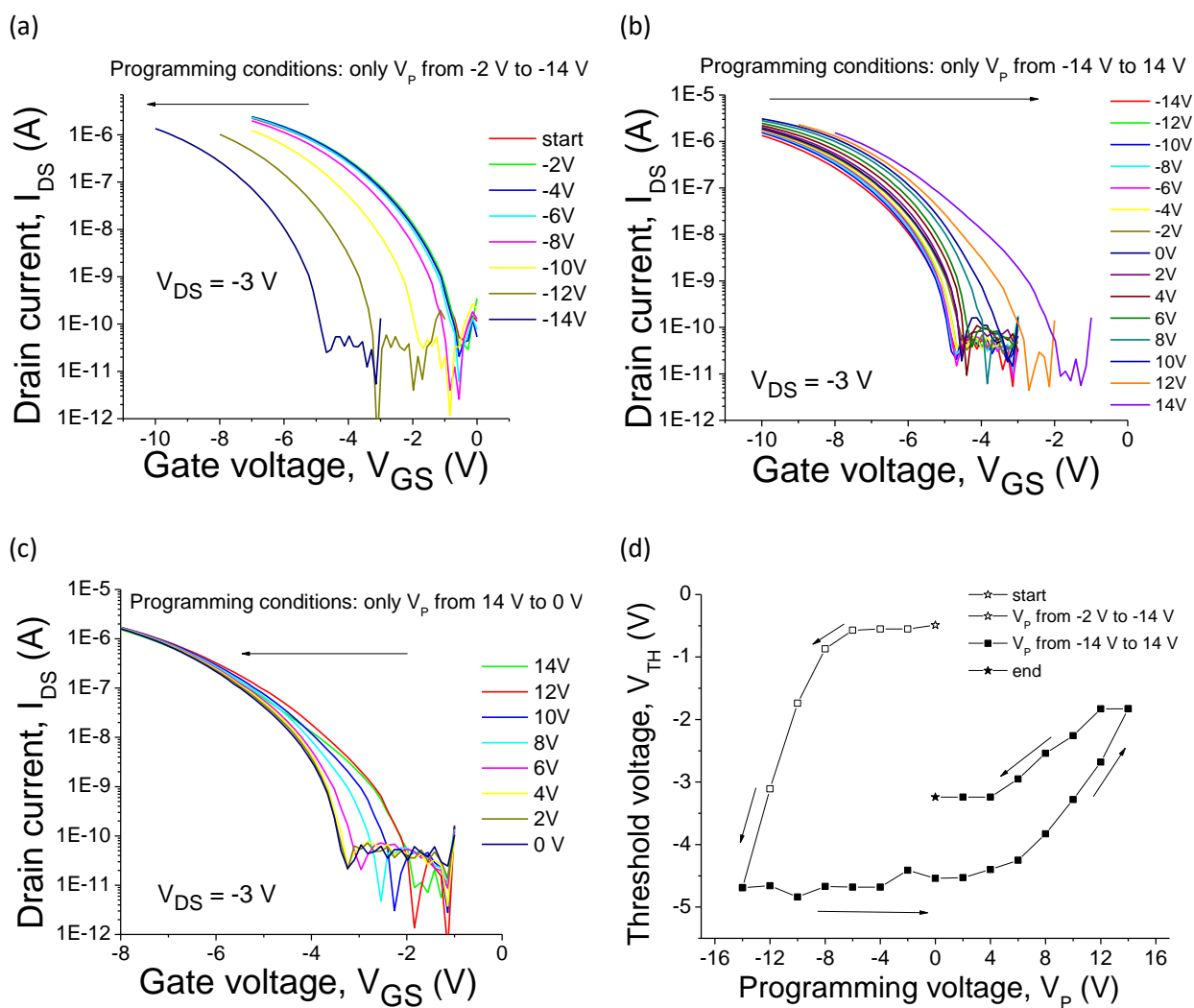


Figure S7-6 The evolution of transfer characteristics of OFETs with 7/pentacene system under exposure to electric bias V_p in the absence of light for 13 s in each point. V_p was varied in the range from -2 to -14 V (a), from -14 to +14 V (b), from +14 to 0 V (c). The dependence of threshold voltage V_{TH} on the applied programming voltage V_p (d).

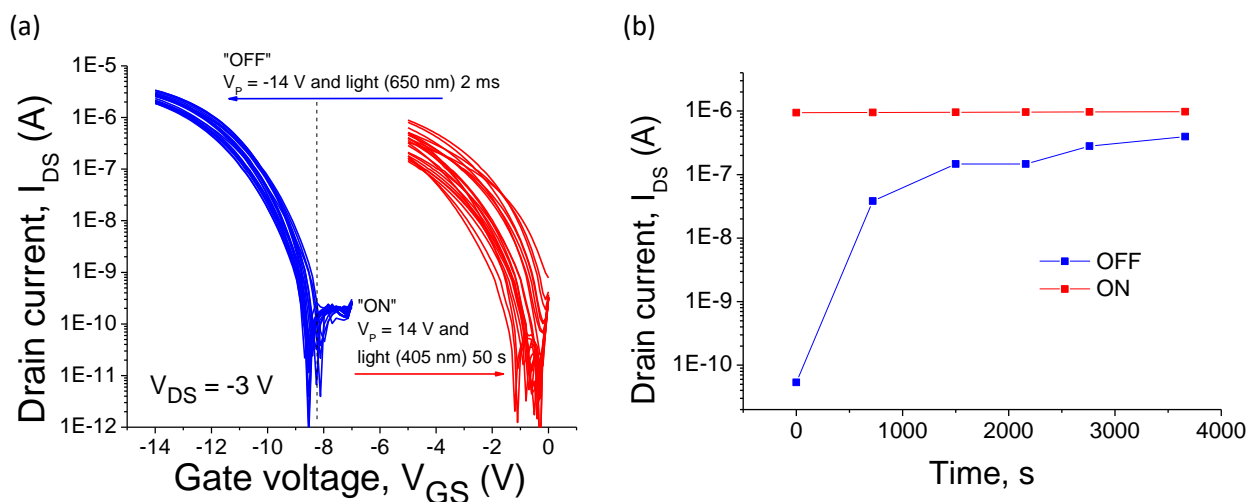


Figure S7-7 Multiple switching of the OFET assembled with BODIPY 7/pentacene system between two distinct electrical states (a). Retention characteristics of ON and OFF states (b)

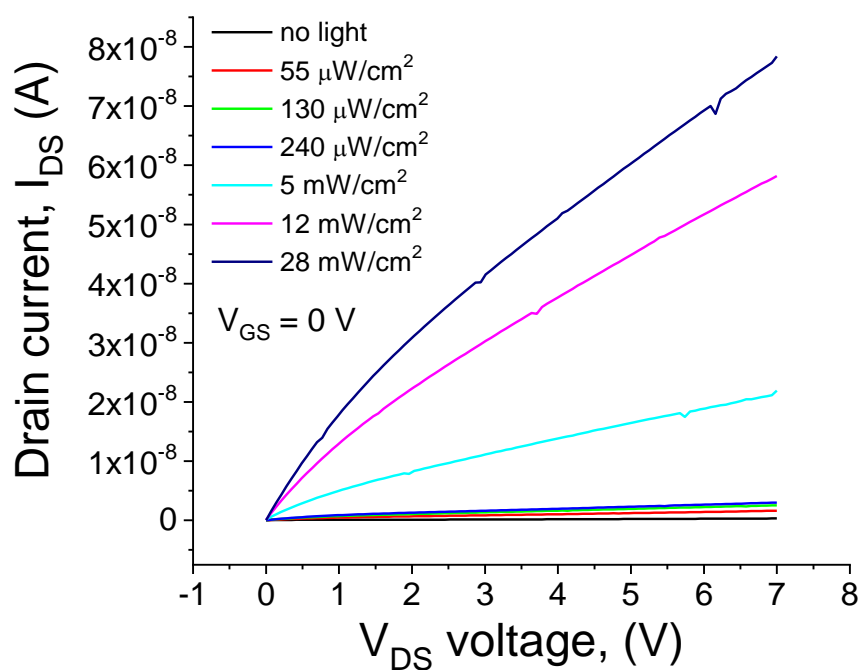


Figure S7-8 Evolution of the output characteristics of OFETs with BODIPY 7/ C_{60} system under light exposure

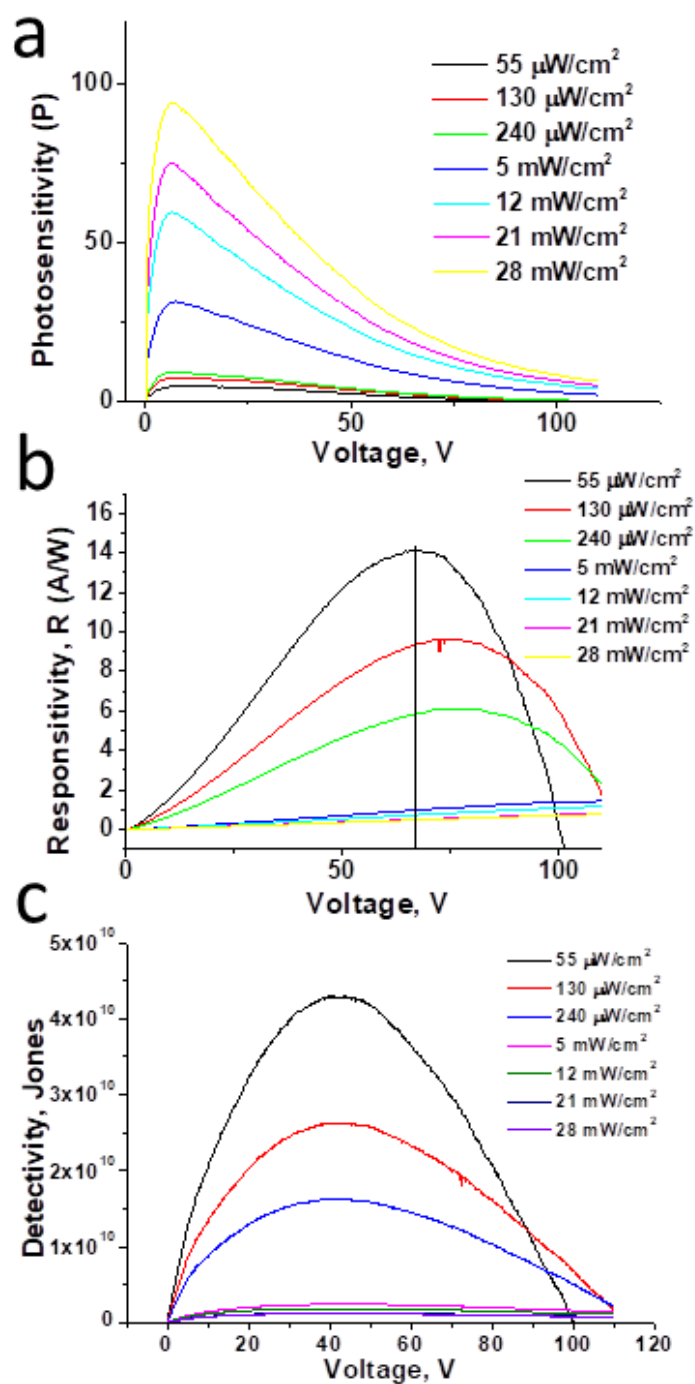


Figure S7-9. Photosensitivity (a), responsivity (b), and specific detectivity (c) of the photoresistor with the BODIPY 7/ C_{60} system measured at different light intensities and voltages

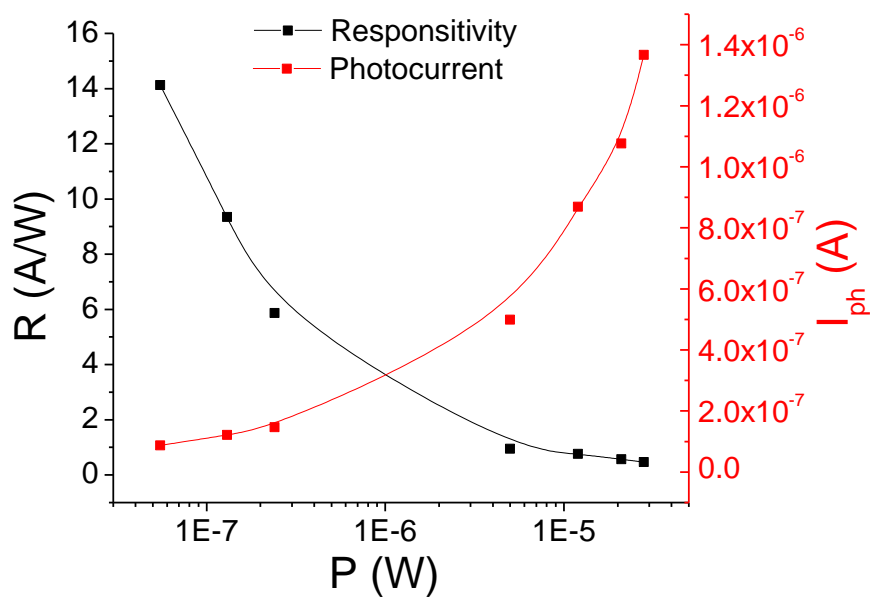


Figure S7-9 The dependence of responsivity R and photocurrent I_{ph} of the photoresistor with BODIPY **7**/ C_{60} system upon the light intensity P

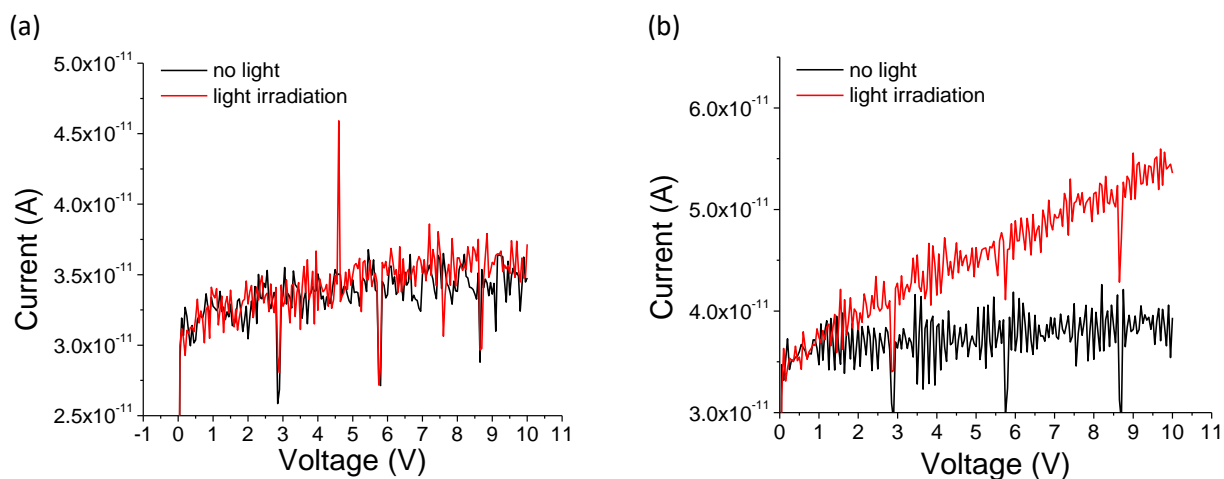


Figure S7-10 Current-voltage characteristics of the lateral 2-terminal resistors fabricated using single layers of BODIPY **7** (a) or fullerene C_{60} (b) showing no significant photoconductivity effect under light exposure (28 mW/cm^2)

8. References

1. A. Y. Bochkov, I. O. Akchurin, O. A. Dyachenko and V. F. Traven, *Chem Comm.*, 2013, **49**, 11653-11655.
2. S. Liu, W.-H. Wang, Y.-L. Dang, Y. Fu and R. Sang, *Tetrahedron Lett.*, 2012, **53**, 4235-4239.
3. J. Van Gompel and G. B. Schuster, *J. Org. Chem.*, 1987, **52**, 1465-1468.
4. J. Chen, W. Liu, B. Zhou, G. Niu, H. Zhang, J. Wu, Y. Wang, W. Ju and P. Wang, *J. Org. Chem.*, 2013, **78**, 6121-6130.