

Electronic Supplementary Information

Effect of Azobenzene Derivatives on UV-Responsive Organic Thin-Film Transistors with 2,7-dipentylbenzo[b]benzo[4,5]thieno[2,3-d]thiophene Semiconductor[†]

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I. EXPERIMENTAL

A. Materials

4-(diethylamino)azobenzene (98%) (**Azo-2**) was purchased from Alfa Aesar and used as received. The following materials were purchased from Sigma Aldrich ferrocene ($\text{Fe}(\text{Cp})_2$), Bis(pentamethylcyclopentadienyl)iron(II) ($\text{Fe}(\text{Cp}^*)_2$), azobenzene (99%) (**Azo-1**), 4-nitroazobenzene (90%) (**Azo-3**), diethyl-(4-(4-nitro-phenylazo)-phenyl)-amine, disperse red 1 (95%) (**DR1**), 2-[Ethyl[4-[2-(4-nitrophenyl)ethenyl]phenyl]amino]ethanol (98%) (**Azo-4**), PMMA ($M_N=140,000$), HPLC grade CH_3CN , reagent grade isopropanol, toluene and 1,1,2,2-tetrachloroethane(TCE). ($\text{Fe}(\text{Cp})_2$) and ($\text{Fe}(\text{Cp}^*)_2$) were purified by sublimation. **Azo-3** was dissolved in ethyl acetate and filtered to remove impurities, the solvent was then removed using a rotary evaporator. It was then dried 60°C under vacuum overnight. All other samples were used as received. C5-BTBT was prepared using the methods outlined in reference ^{1,2}.

TABLE S I. Materials used to prepare solutions for spin coating^{a)}

Sample ^{b)}	Mass (mg)	mmoles	PMMA mass (mg)	C5-BTBT (mg) ^{c)}	TCE (g)
Azo-1	2.4	0.0133	37.6	40.0	3.92
Azo-2	3.4	0.0133	36.6	40.0	3.92
Azo-3	3.0	0.0133	37.0	40.0	3.92
Azo-4	4.0	0.0133	36.0	40.0	3.92
DR1	4.2	0.0133	36.0	40.0	3.92

^{a)}C5-BTBT and PMMA UV-vis spectra can be found in reference³

^{b)}All solutions were passed through a 0.45 μm filter before use

^{c)}The solutions used for UV-vis were the same composition except no C5-BTBT was added and its weight was replaced by an equivalent weight of TCE.

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B. UV-Vis Sample Preparation/Measurements

Glass microscope slides were cleaned with isopropanol and air dried. Solutions from table 1 were drop cast onto the glass slides where they sat for 2 minutes before being spin coated at 500 RPM for 90 sec using a 5 sec ramp time. These samples were used to acquire UV-Vis measurements on a Cary 5000 UV-Vis-NIR Spectrometer using a glass slide with a 40.0 mg PMMA, 3.96 g TCE solution spin coated on it as the background.

C. Cyclic Voltammetry Measurements

Pt was used as the working, reference and counter electrodes. Solutions were 2×10^{-3} M test compound and 0.1 M $N(\text{Bu}_4)\text{PF}_6$ as the supporting electrolyte in CH_3CN . Solutions containing the electrolyte, test compound and solvent were stirred with a bubbling stream of argon for 5 minutes before measurements were taken. During measurements, the chamber was sealed with a flow of argon over the solution. Scan rates of 100 mV/s and 200 mV/s were used. Data was collected on a PAR (Princeton Applied Research) model 283 potentiostat (using PAR PowerCV software). Ferrocene (1.9 mg, 0.002 M) was added as a reference to zero the spectra. For samples where the ferrocene halfwave could not be distinguished from the analyte, $\text{Fe}(\text{Cp}^*)_2$ (3.3. mg, 0.002 M) was used in its place. All samples were standardised vs SCE, where $E_{1/2}$ of the ferrocenium couple (Fc^+/Fc) in CH_3CN is given a value of 0.4 eV vs (SCE).⁴ These spectra were then converted to the vacuum scale by applying the following formula $E_{\text{HOMO}} = -(E_{[\text{onset, ox vs Fc}^+/\text{Fc}]} + 5.1)(\text{eV})$.⁵

TABLE S II. Materials used to prepare solutions for cyclic voltammetry

Sample	Mass (mg)	Molarity (mol/L)	$N(\text{Bu})_4\text{PF}_6$ mass (g)	$N(\text{Bu})_4\text{PF}_6$ molarity (mol/L)	CH_3CN (mL)
Azo-1	1.8	0.002	0.1937	0.1	5
Azo-2	2.5	0.002	0.1937	0.1	5
Azo-3	2.3	0.002	0.1937	0.1	5
Azo-4	3.0	0.002	0.1937	0.1	5
DR1	3.0	0.002	0.1937	0.1	5

C. Electrical Measurements

Sample preparation and characterization was performed in a similar manor to that outlined in our previous paper,³ with the following differences; Solution compositions are different and outlined above in Table S1. Spin coating conditions were changed from 2000 rpm to 3000 rpm. Measurements were no longer performed under humidity controlled conditions and instead measured under ambient conditions.

II. EXPERIMENTAL DATA

D. Optical Microscopy Measurements

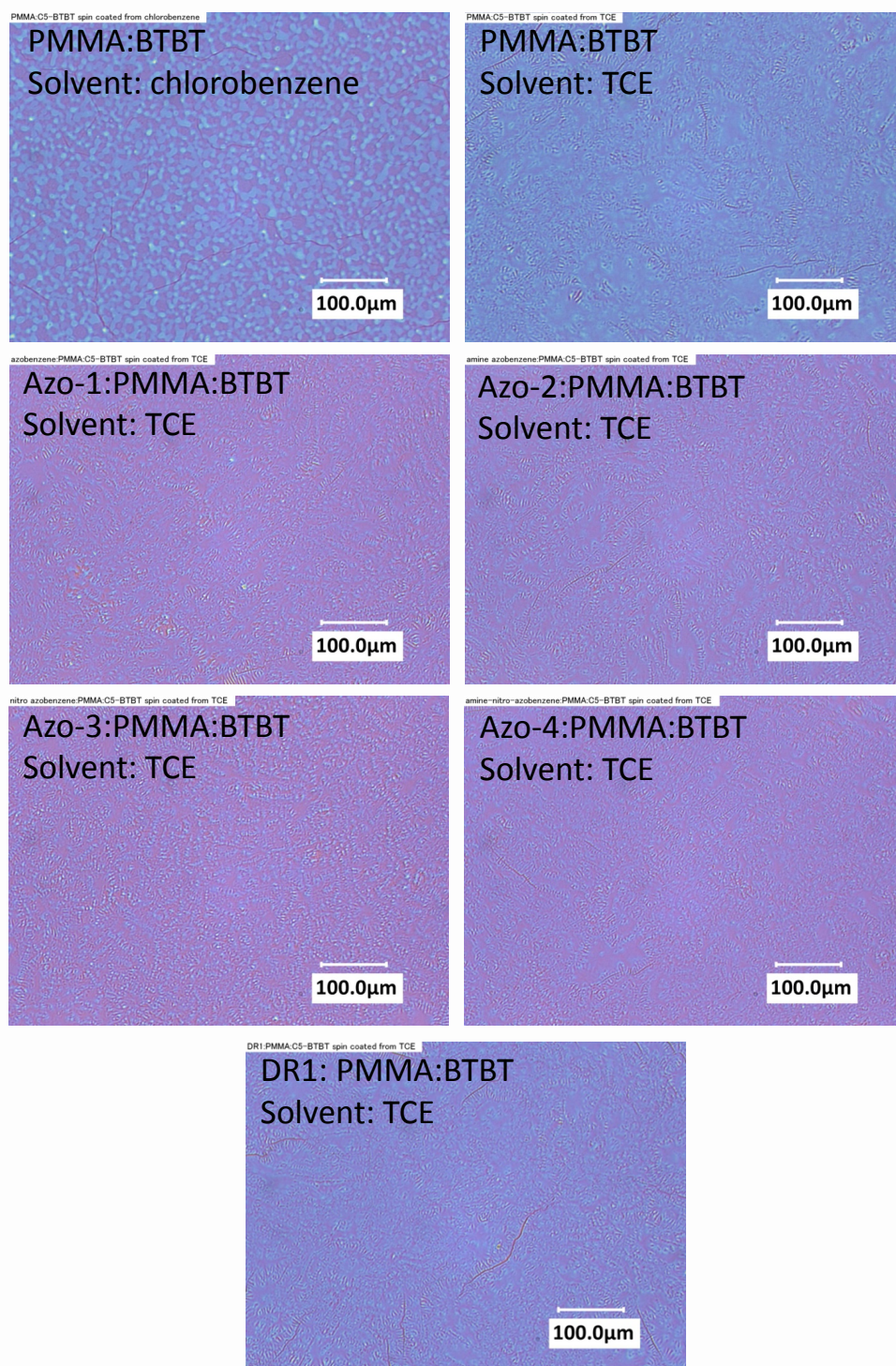


FIG. S1. Optical Microscope images of films spin coated from 1,1,2,2-tetrachlorethane (TCE) onto an HMDS modified Si/SiO₂ wafer, as well as a control film spin coated from chlorobenzene. All films show similar morphology when spin coated from the same solvent.

E. Transfer Curves

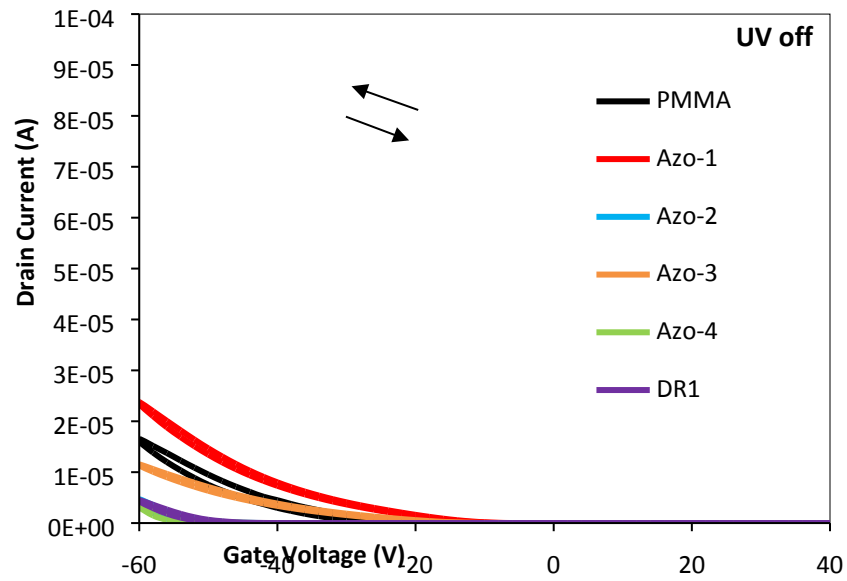


FIG. S2. Transfer curves for all systems studied under dark conditions showing a forward and backward sweep.

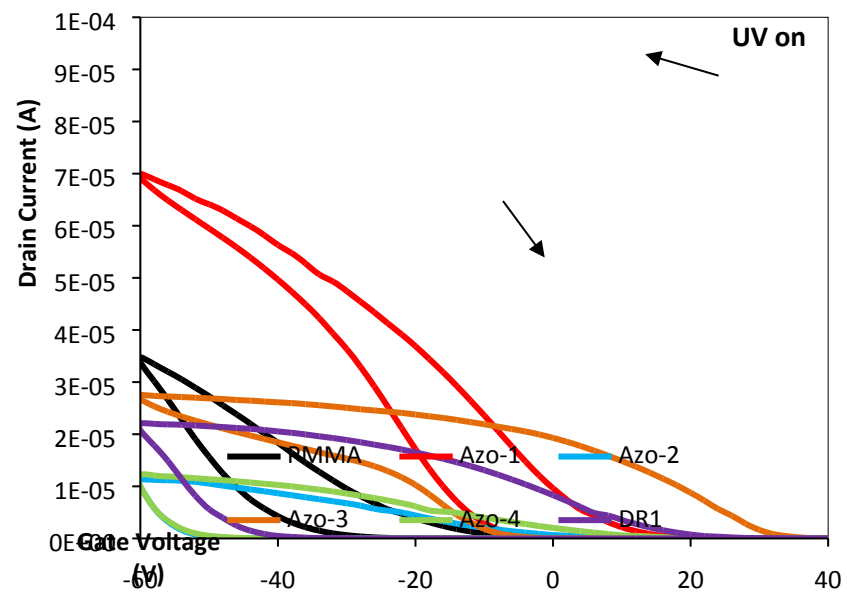


FIG. S3. Transfer curves for all systems studied under UV conditions showing a forward and backward sweep.

F. Cyclic Voltammetry Measurements

Table S III. Cyclic Voltammetry Data, all values in (eV)^a

Material	$E_{\text{Onset}}^{0/1+}$	$E_{1/2}^{0/1+}$	$E_{1/2}^{1+/2+}$	$E_{1/2}^{1-/0}$	$E_{1/2}^{2-/1-}$
C5-BTBT	1.21	1.31	----	----	----
Azo-1	----	----	----	-1.33	----
Azo-2	0.76	0.92 ^{b)}	1.61 ^{b)}	-1.76	----
Azo-3	1.84	2.13 ^{b)}	----	-0.83	-1.13
Azo-4	0.81	0.93 ^{b)}	----	-0.91	-1.32 ^{b)}
DR1	0.89	1.03 ^{b)}	----	-0.94	-1.29

^{a)}Values determined from cyclic voltammetry vs SCE, with the onset of oxidation or reduction reported

^{b)}Irreversible oxidation or reduction

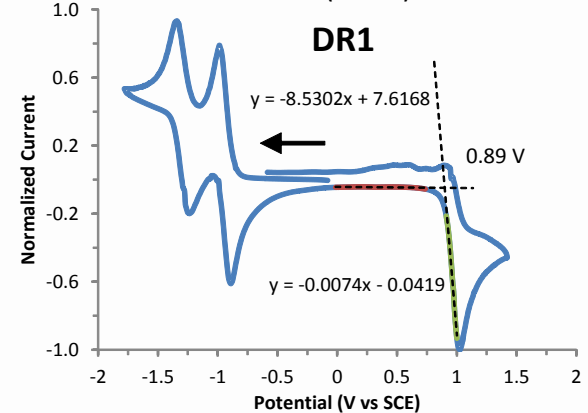
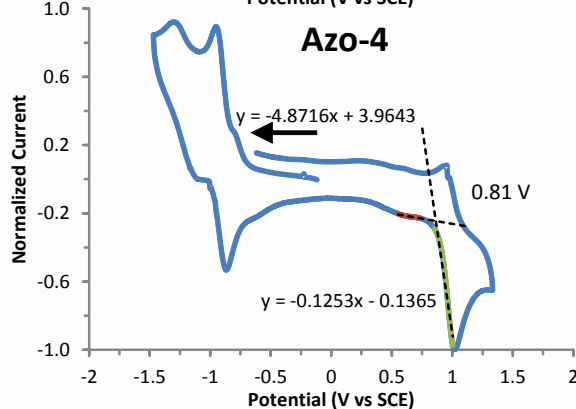
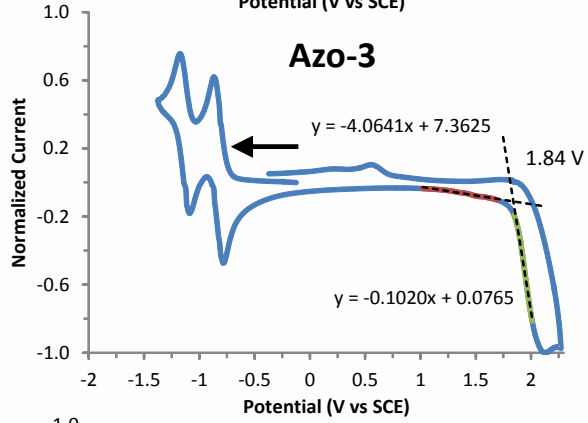
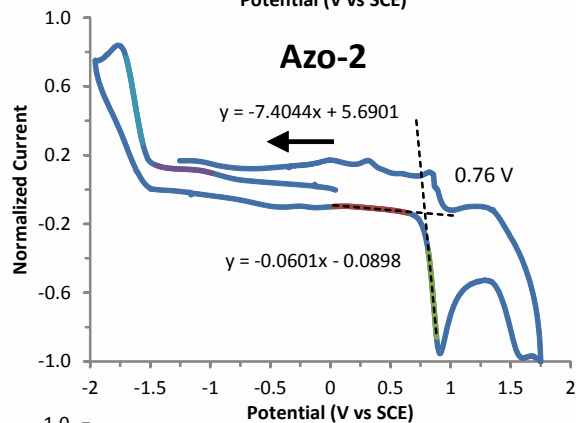
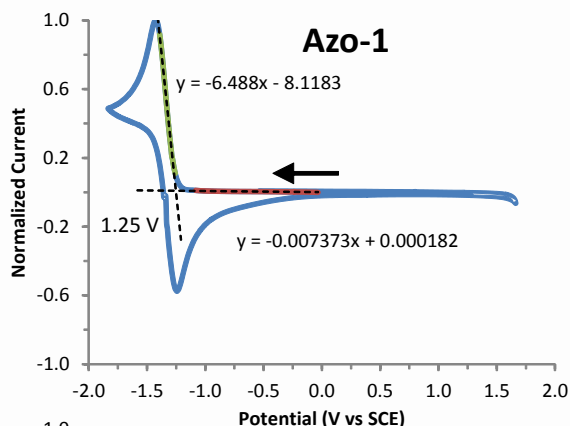
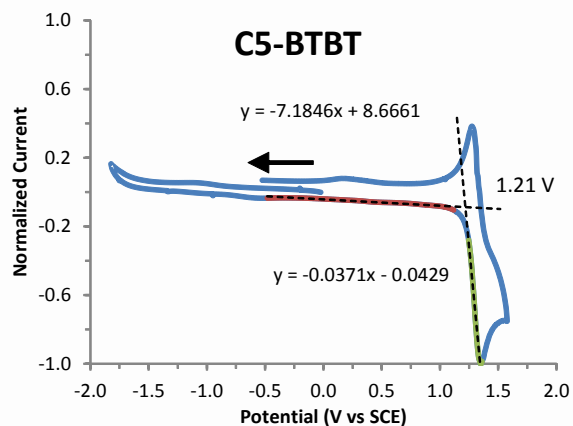


FIG. S4. Cyclic voltammograms of film materials (vs SCE) showing the onset of reduction or oxidation for.

G. UV-Vis Measurements

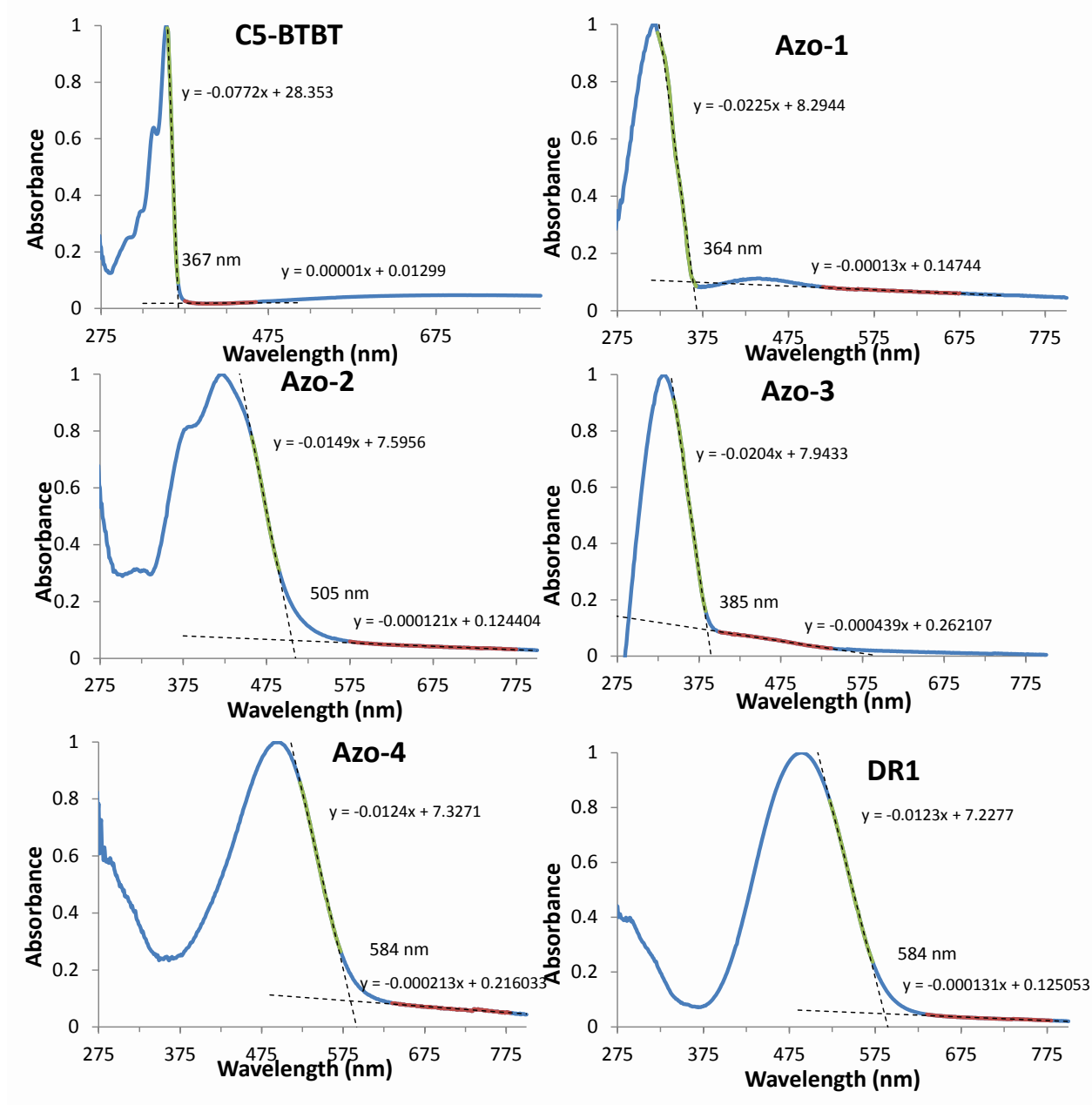


FIG. S5. UV-vis spectra of film materials with the absorption edge calculations shown.

H. Rise and Decay Measurements With Experimental Modeling

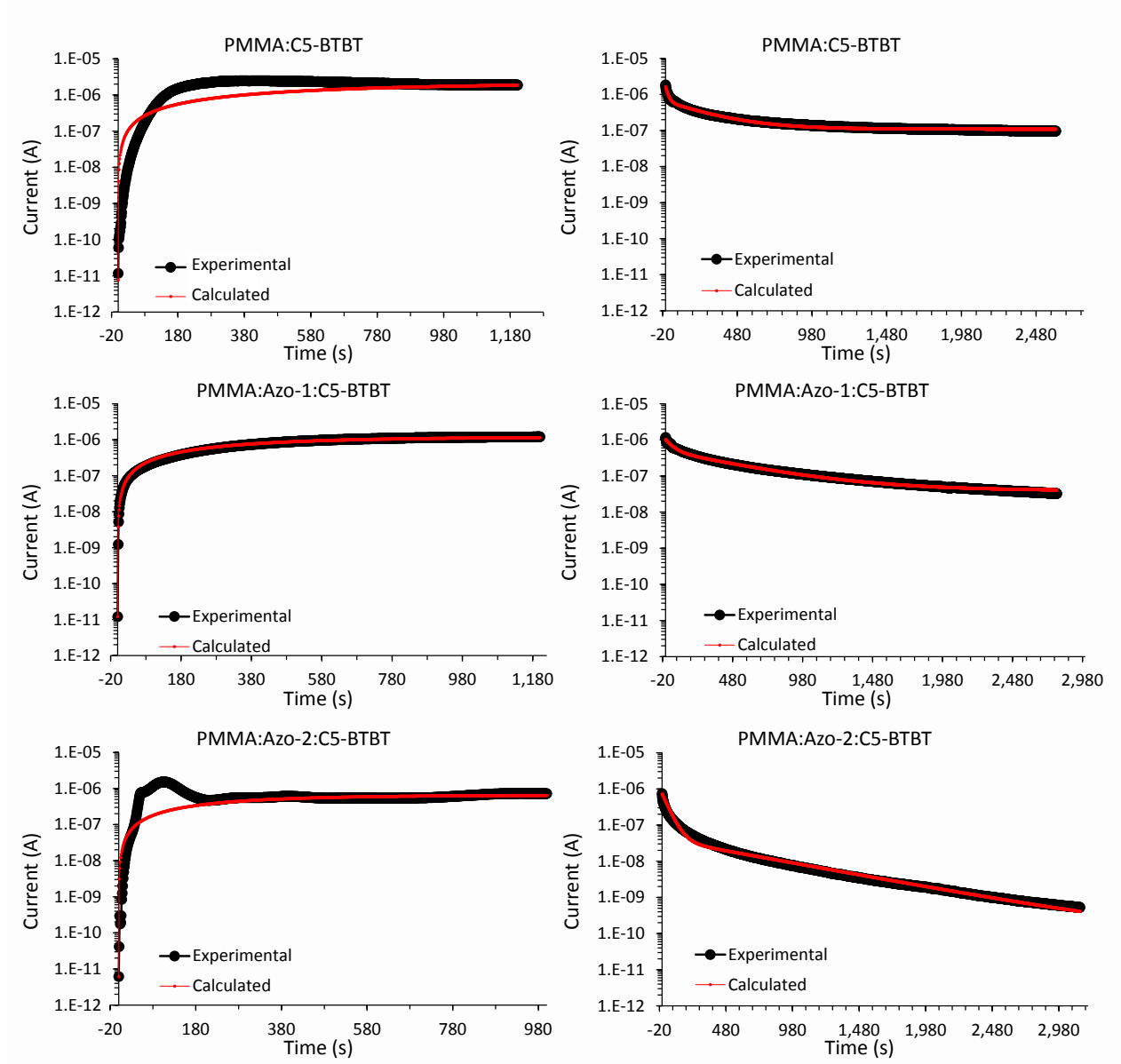


FIG. S6. (Left side), I_{DS} vs time showing the current rise over a 20 minute UV exposure with the experimental (black) and biexponential curve fitting (red). (Right) I_{DS} decay vs time starting after the 20 minute UV exposure with experimental (black) and biexponential curve fitting (red).

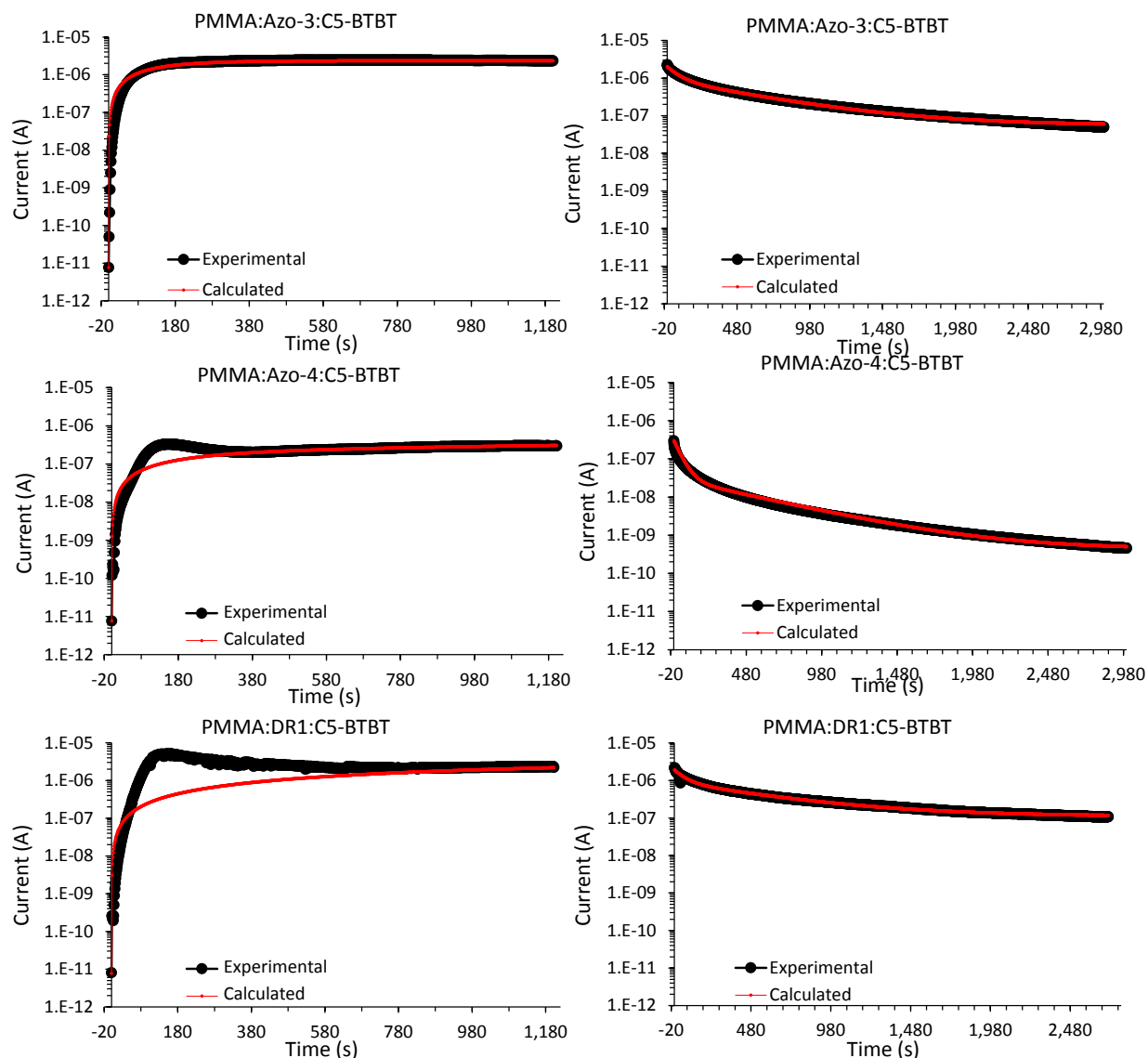


FIG. S7. (Left side), I_{DS} vs time showing the current rise over a 20 minute UV exposure with the experimental (black) and biexponential curve fitting (red). (Right) I_{DS} decay vs time starting after the 20 minute UV exposure with experimental (black) and biexponential curve fitting (red).

III. REFERENCES

- ¹ M. Saito, I. Osaka, E. Miyazaki, K. Takimiya, H. Kuwabara, and M. Ikeda, *Tetrahedron Lett.* **52**, 285 (2011).
- ² H. Ebata, T. Izawa, E. Miyazaki, K. Takimiya, M. Ikeda, H. Kuwabara, and T. Yui, *J. Am. Chem. Soc.* **129**, 15732 (2007).
- ³ C.S. Smithson, Y. Wu, T. Wigglesworth, and S. Zhu, *Adv. Mater.* **27**, 228 (2015).
- ⁴ N.G. Connelly and W.E. Geiger, *Chem. Rev.* **96**, 877 (1996).
- ⁵ C.M. Cardona, W. Li, A.E. Kaifer, D. Stockdale, and G.C. Bazan, *Adv. Mater.* **23**, 2367 (2011).