

Supporting Information

Optical and photovoltaic properties of thieno[3,2-*b*]thiophene based push-pull organic dyes with different anchoring groups for dye-sensitized solar cells

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Table S1. Spectroscopic properties (absorption and fluorescence emission maxima) and fluorescence quantum yields (ϕ_F) obtained in ethanol solution together with IR and ^1H NMR data for the compounds studied.

Cpds	Yield [%]	UV-vis	Fluorescence				IR ^{b)} ν [cm ⁻¹]					¹ H NMR ^{c)} δ [ppm]		
			λ_{max} [nm]	ε [M ⁻¹ cm ⁻¹]	λ_{em} [nm]	Stokes' Shift [cm ⁻¹]	Φ_F	C=O	O-H	C $\equiv$ N	C=S	H _{vinyl}	π -bridge	
													H-3	H-6
3a	55	422	22,079	575	6305	0.36	1584	3360	2204	-	8.45	7.89	8.25	
3b	82	476	13,627	654	5718	0.02	1581	3362	-	1279	8.06	7.85	8.08	

a) Fluorescence quantum yields obtained using rhodamine-6G in ethanol solution as reference b) IR spectra were performed in Nujol. (c) ^1H NMR spectra were performed at 400 MHz, using DMSO- d_6 as solvent.

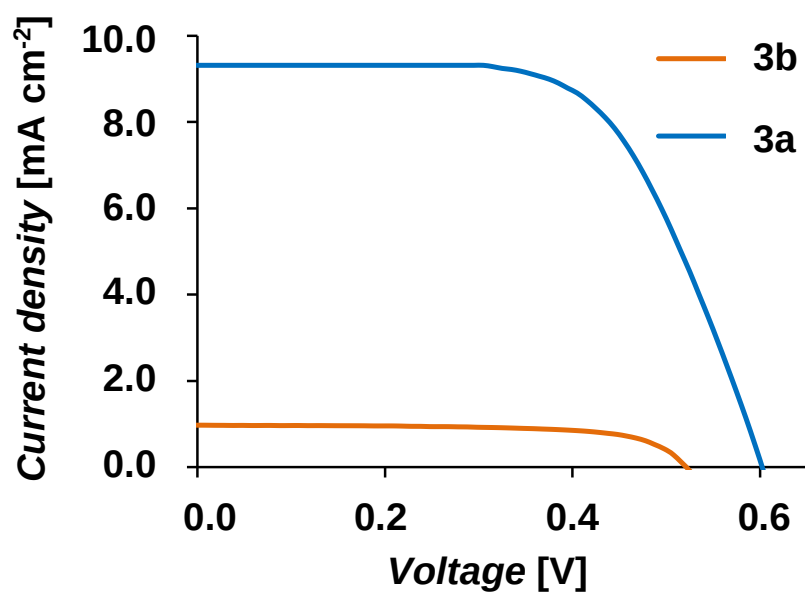


Figure S1. Photocurrent density-voltage plots of the devices prepared with dyes **3a-b**.

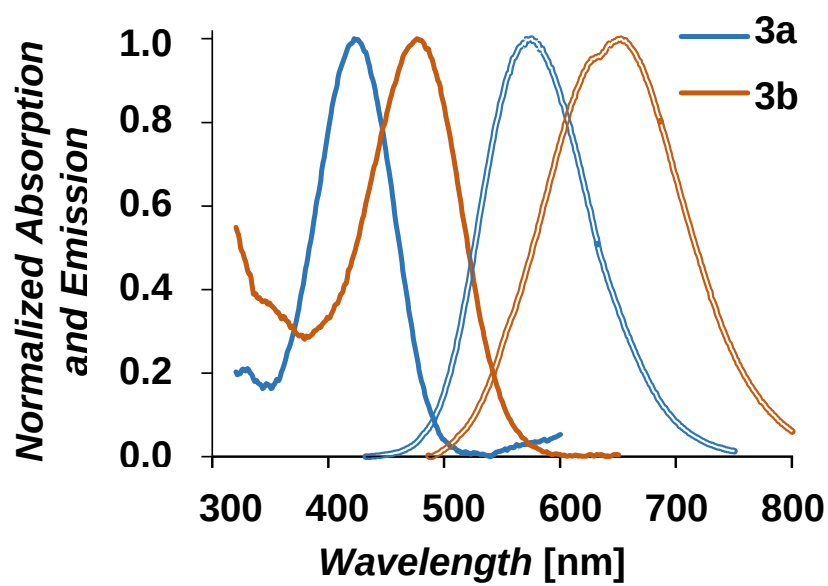


Figure S2. Normalized absorption (full lines) and emission (double lines) spectra for dyes **3a-b** in ethanol solution at 293 K.

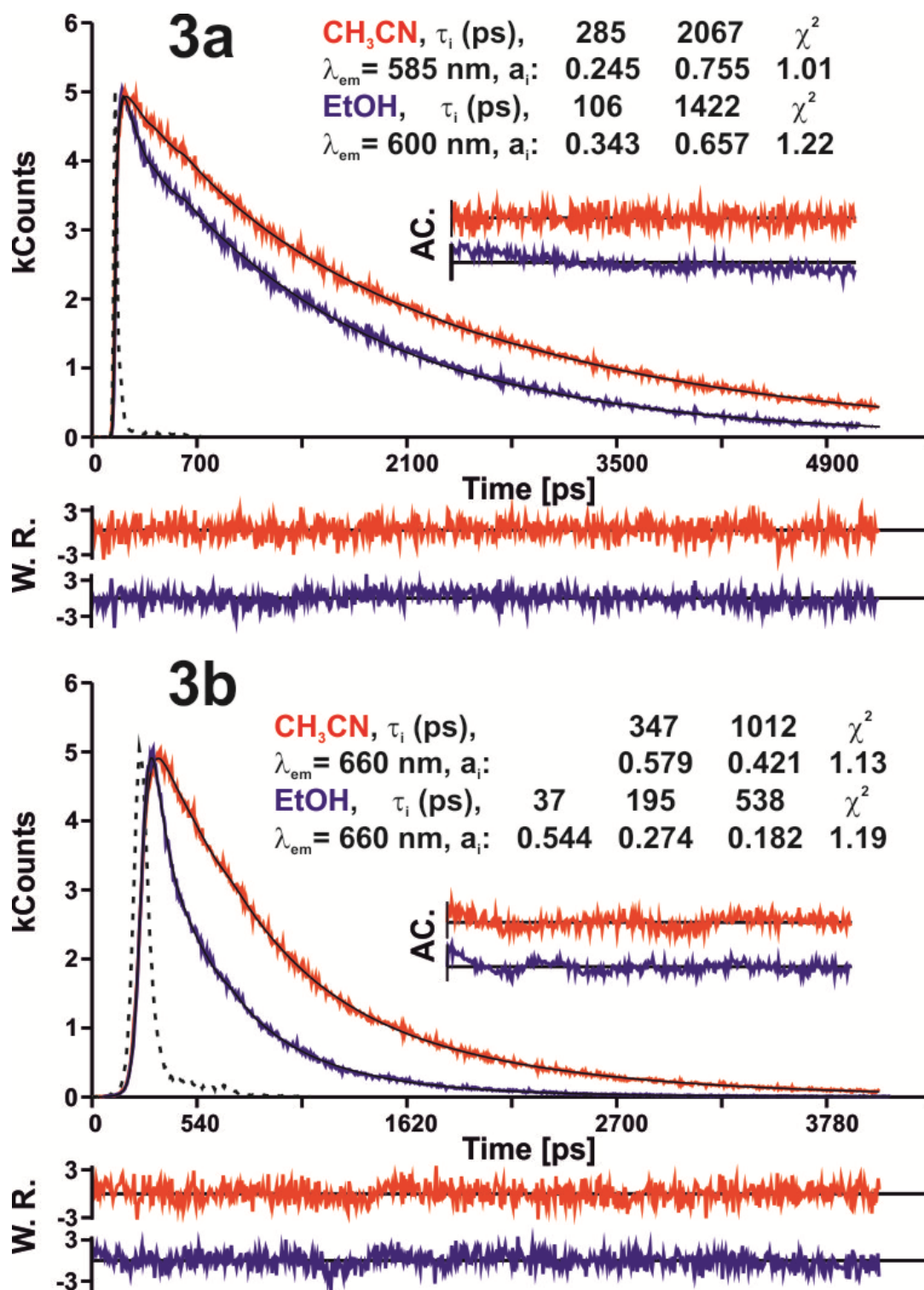


Figure S3. Room-temperature fluorescence decays for **3a** ($\lambda_{exc} = 445$ nm) and **3b** ($\lambda_{exc} = 451$ nm) in acetonitrile (CH₃CN) and ethanol solution. For a better judgment of the quality of the fit, weighted residuals (W.R.), autocorrelation function (AC.) and χ^2 values are also presented. The dashed lines in the decays are the instrumental response functions.

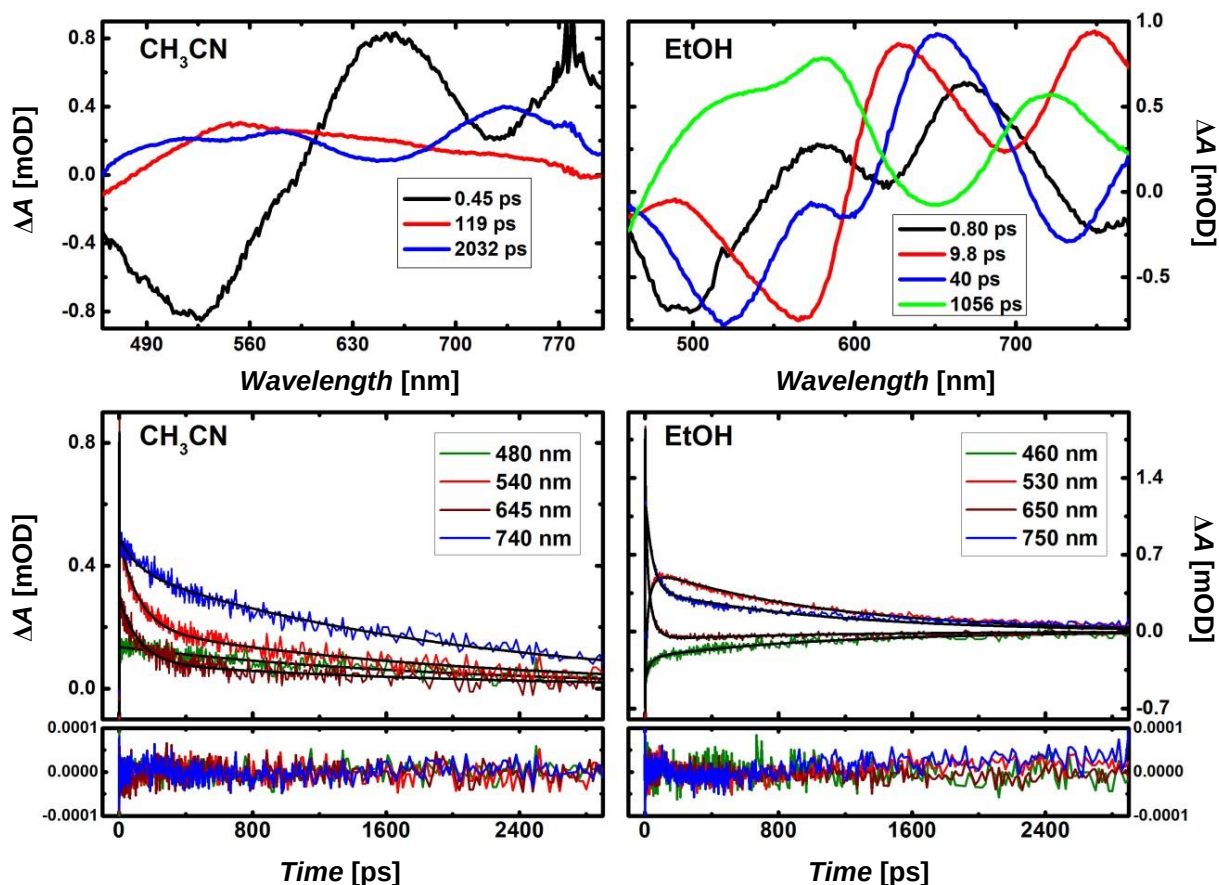


Figure S4. (Top) Decay associated spectra, DAS, of the time constants extracted from the time-resolved transient absorption data ($\lambda_{\text{exc}} = 455$ nm) after SVD/global analysis for **3a** in acetonitrile and ethanol solutions at 293 K; (bottom) together with representative kinetic traces with fits from the global analysis of the transient absorption data. The residuals are also presented for a better judgment of the quality of the fits.

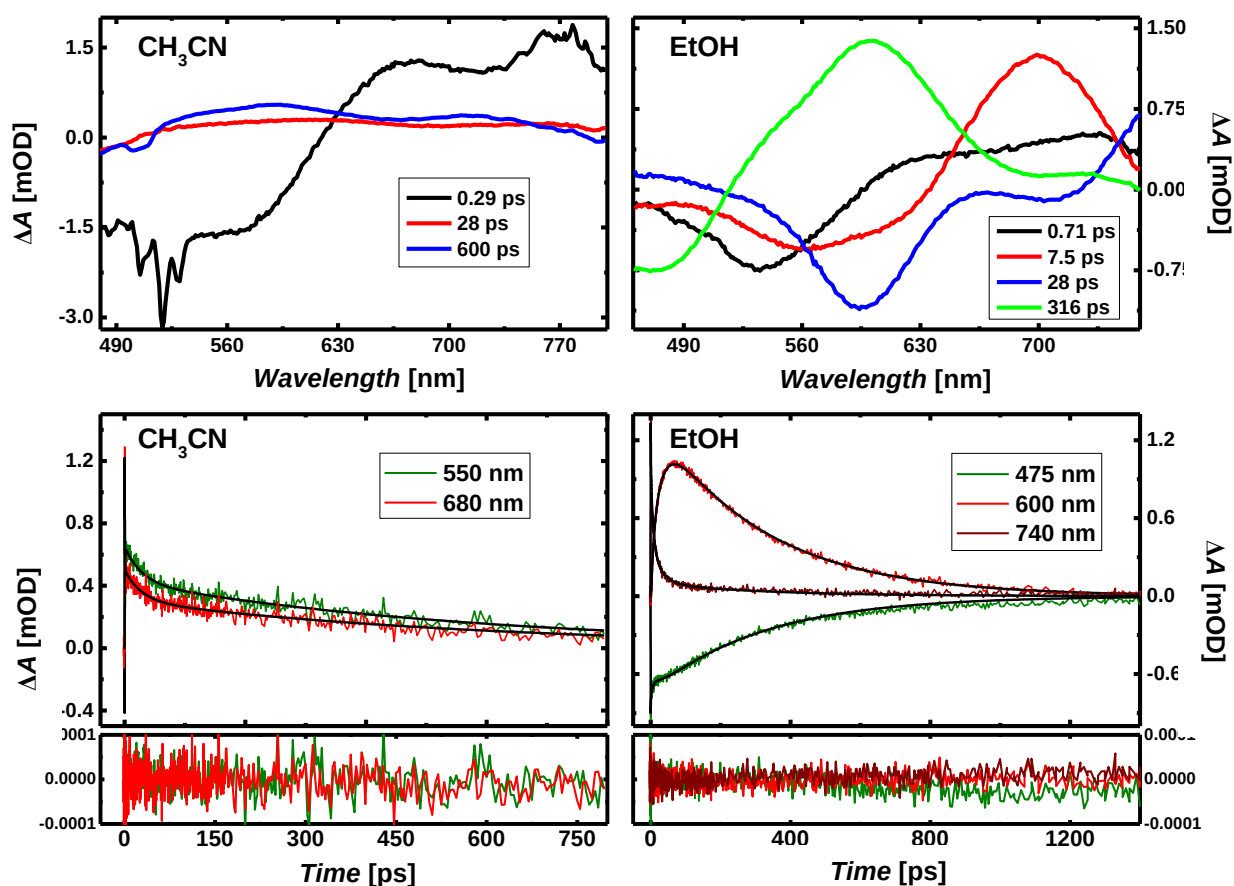


Figure S5. (Top) Decay associated spectra, DAS, of the time constants extracted from the time-resolved transient absorption data ($\lambda_{\text{exc}} = 455$ nm) after SVD/global analysis for **3b** in acetonitrile and ethanol solutions at 293 K; (bottom) together with representative kinetic traces with fits from the global analysis of the transient absorption data. The residuals are also presented for a better judgment of the quality of the fits.

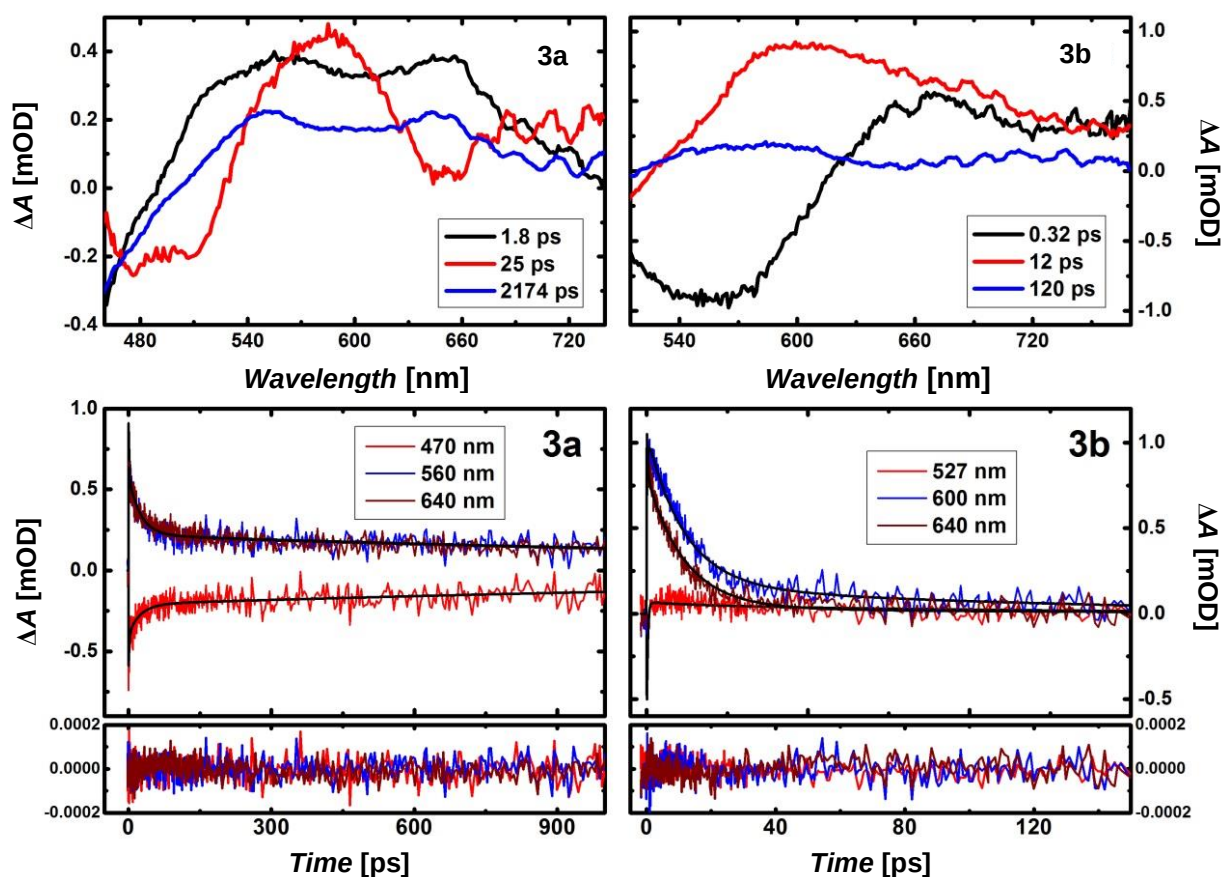


Figure S6. (Top) Decay associated spectra, DAS, of the time constants extracted from the time-resolved transient absorption data after SVD/global analysis for the investigated samples adsorbed in TiO₂ films; (bottom) together with representative kinetic traces with fits from the global analysis of the transient absorption data. The residuals are also presented for a better judgment of the quality of the fits.

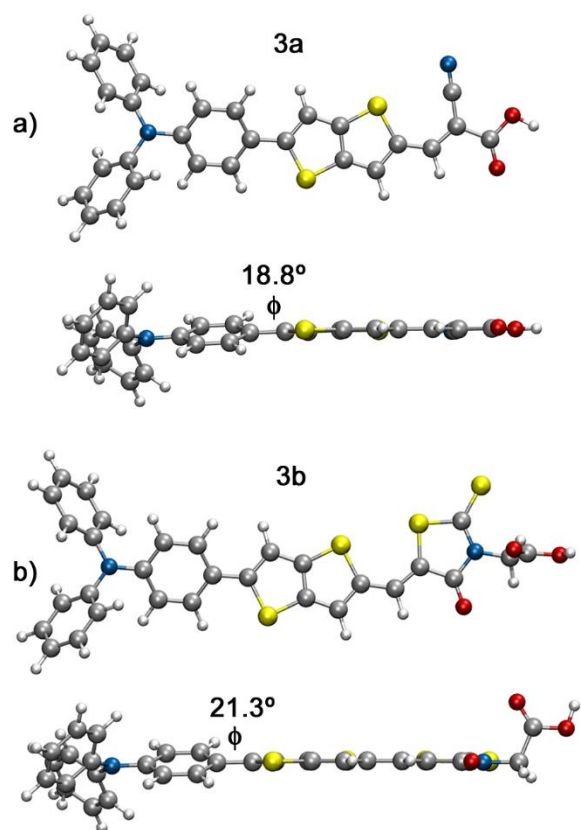


Figure S7. DFT B3LYP/6-31G(d,p) optimized geometries of the most stable conformers of dyes a) **3a** ((*E*)-**3a-I**) and b) **3b** ((*Z*)-**3b-I**). The bulk solvent effects of chloroform were considered using the PCM model.

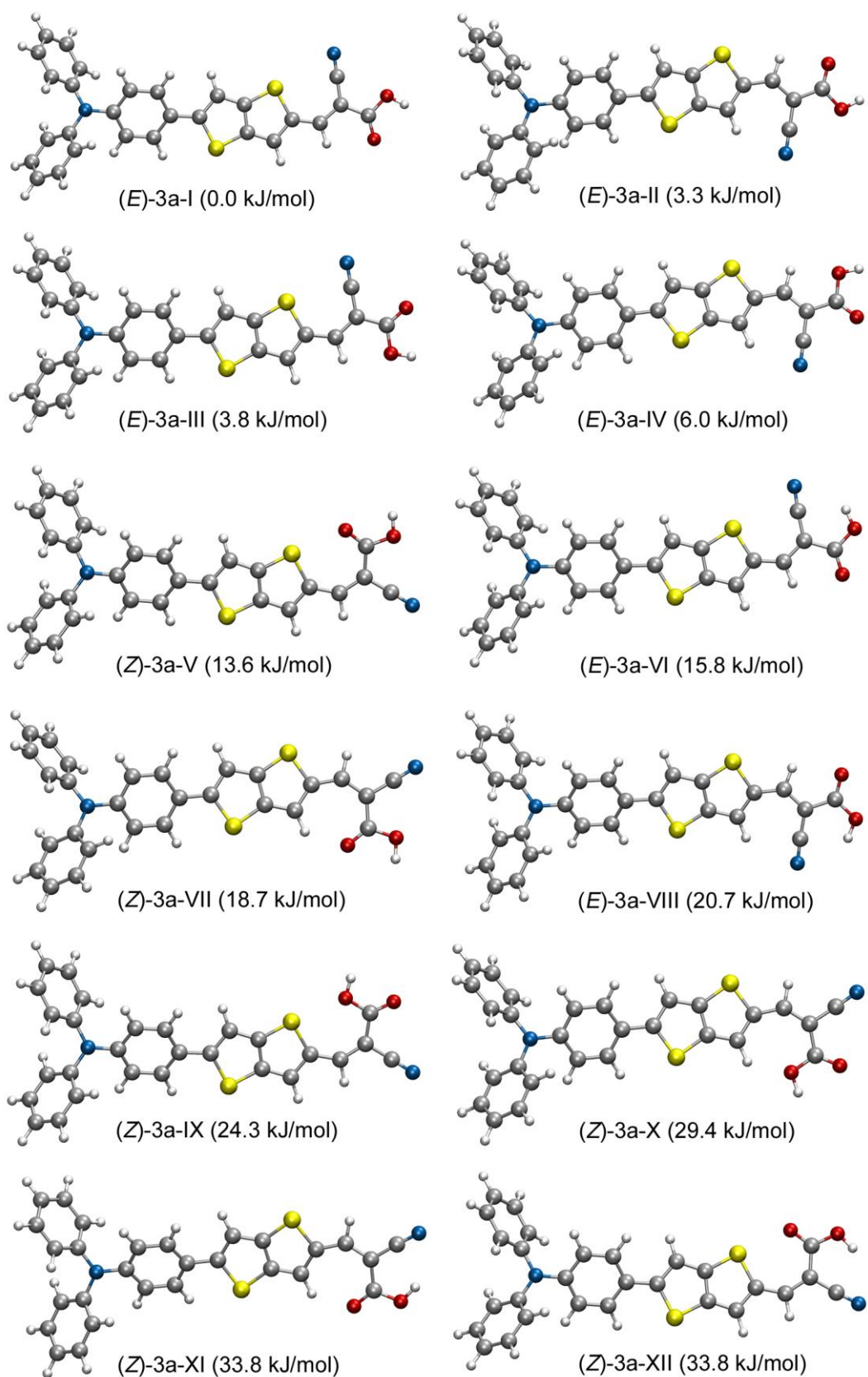


Figure S8. DFT B3LYP/6-31G(d,p) optimized geometries of the isomers of dye **3a** considered in this study. The bulk solvent effects of chloroform were considered using the PCM model.¹⁻²

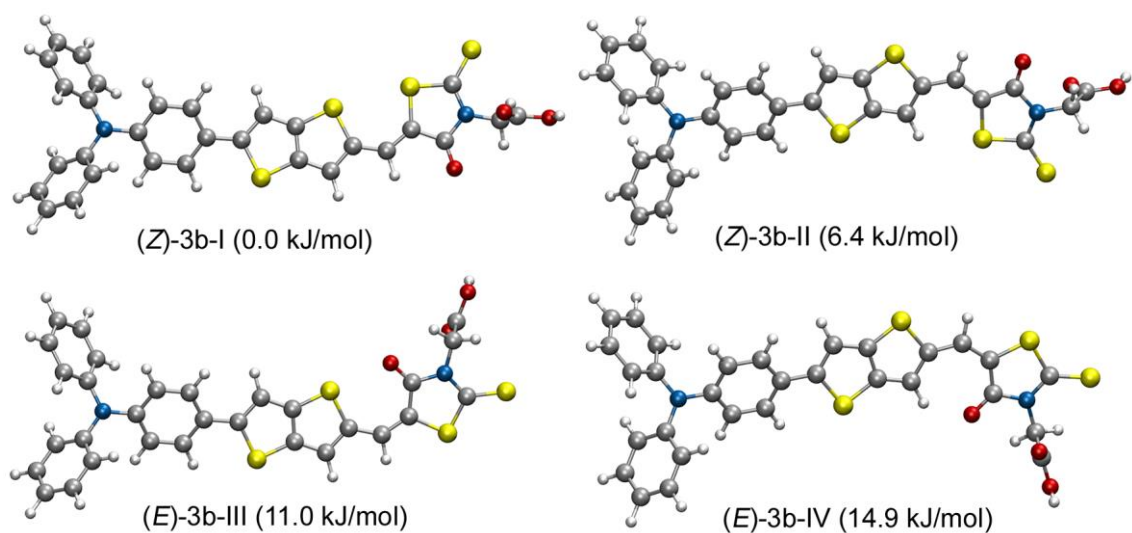


Figure S9. DFT B3LYP/6-31G(d,p) optimized geometries of the isomers of dye **3b** considered in this study. The bulk solvent effects of chloroform were considered using the PCM model.¹⁻²

Table S2. Calculated relative free energy (ΔG) and approximate population at 298 K (P_{298}) of the isomers of dyes **3a** and **3b** considered in this study.

Isomer	ΔG [kJ mol ⁻¹]	P_{298} [%]
(E)-3a-I	0.00	64
(E)-3a-II	3.31	17
(E)-3a-III	3.81	14
(E)-3a-IV	6.00	5.6
(Z)-3a-V	13.64	0.3
(E)-3a-VI	15.81	0.1
(Z)-3a-VII	18.72	0.0
(E)-3a-VIII	20.68	0.0
(Z)-3a-IX	24.29	0.0
(Z)-3a-X	29.38	0.0
(Z)-3a-XI	33.78	0.0
(Z)-3a-XII	33.81	0.0
(Z)-3b-I	0.00	92
(Z)-3b-II	6.42	6.9
(E)-3b-III	11.03	1.1
(E)-3b-IV	14.89	0.2

Table S3. Calculated relative free energy (ΔG) and approximate population of the major isomers at 298 K (P_{298}), wavelength of the absorption maxima ($\lambda_{\max}$), energy of the frontier molecular orbitals and HOMO-LUMO gap (E_g), compared with the experimental UV-vis and cyclic voltammetry results for dyes **3a** and **3b**.

Cpds	ΔG [kJ mol ⁻¹]	P_{298} [%]	$\lambda_{\max}$ (TDDFT) ^{a)} [nm]	$\lambda_{\max}$ (UV-Vis) [nm]	E_{HOMO} (DFT) ^{b)} [eV]	E_{HOMO} (CV) [eV]	E_{LUMO} (DFT) ^{b)} [eV]	E_{LUMO} (CV) [eV]	E_g (DFT) ^{b)} [eV]	E_g (CV) [eV]
(E)-3a-I	0	64	435	422	-5.05	-5.07	-2.64	-2.69	2.41	2.38
(E)-3a-II	3.31	17	437	422	-5.05	-5.07	-2.67	-2.69	2.37	2.38
(E)-3a-III	3.81	14	434	422	-5.05	-5.07	-2.65	-2.69	2.40	2.38
(Z)-3b-I	0	92	451	476	-5.00	-5.03	-2.71	-2.88	2.29	2.15
(Z)-3b-II	6.42	7	452	476	-4.99	-5.03	-2.73	-2.88	2.26	2.15

a) Results from TD-DFT calculations at the CAM-B3LYP/6-311G(d,p) level of theory. b) Results from ground state calculations on the neutral molecules at the B3LYP/6-31G(d,p) level of theory.

Experimental Section

Synthetic procedures

Procedure for the synthesis of 5-(4'-(diphenylamino)phenyl)thieno[3,2-*b*]thiophene-2-carbaldehyde, **2**, through Suzuki coupling

5-Bromothieno[3,2-*b*]thiophene-2-carbaldehyde **1**³ (0.5 mmol, 125 mg) was coupled to 4-(diphenylamino)phenylboronic acid pinacol ester (0.6 mmol, 223 mg) in a mixture of DME (8 mL), ethanol (2 mL), aqueous 2 M Na₂CO₃ (1 mL) and Pd(PPh₃)₄ (5 mol %) at 80 °C, under nitrogen. The reaction was monitored by TLC, from which the reaction time was determined (24 h). After cooling, the mixture was extracted with chloroform (3×20 mL), a saturated solution of NaCl was added (20 mL), and the phases were separated. The organic phase was washed with water (3×10 mL) and with 10 mL of a solution of NaOH (10 %). The organic phase was dried (MgSO₄), filtered, and the solvent removed to give a crude mixture. The crude product was purified using column

chromatography (silica gel, mixtures of chloroform and light petroleum of increasing polarity) to afford the coupled product **2**. Recrystallization from n-hexane/dichloromethane gave the pure compound as a yellow solid (95 %). Mp. 151-153 °C; ^1H NMR (DMSO- d_6 , 400 MHz, δ) 6.98 (d, J = 8.8 Hz, 2H; H3' and H5'), 7.07-7.13 (m, 6H; 2xH2'', 2xH6'', 2xH4''), 7.33-7.37 (m, 4H; 2xH3'', 2xH5''), 7.64 (d, J = 8.8 Hz, 2H; H2' and H6'), 7.87 (s, 1H; H6), 8.36 (s, 1H; H3), 9.94 (s, 1H; CHO) ppm; ^{13}C NMR (DMSO- d_6 , 100.6 MHz, δ) 114.5 (C6), 122.6 (C3' and C5'), 123.8 (C4''), 125.1 (C2'' and C6''), 126.9 (C1'), 127.0 (C2' and C6'), 129.3 (C3), 129.5 (C3'' and C5''), 137.5 (C3a or C6a), 144.0 (C2), 147.1 (C1''), 147.2 (C3a or C6a), 148.8 (C4'), 153.2 (C5), 183.0 (CHO) ppm; IR (Nujol): ν = 1657 (C=O) cm^{-1} ; UV-vis (ethanol): λ_{max} (ϵ) = 406 nm (34788); MS (ESI) m/z (%): 411 (100) M^{+} , 245 (12) $[\text{C}_{18}\text{H}_{15}\text{N}]^{+}$; HRMS (ESI) m/z : M^{+} calcd for $\text{C}_{25}\text{H}_{17}\text{NOS}_2$, 411.0752; found, 411.0759.

General procedure for the synthesis of push-pull thieno[3,2-*b*]thiophene derivatives **3a-b** from aldehyde precursor **2** through Knoevenagel condensation

To a solution of 5-(4'-(diphenylamino)phenyl)thieno[3,2-*b*]thiophene-2-carbaldehyde **2** (0.2 mmol, 80 mg) and 2-cyanoacetic acid (0.3 mmol, 26 mg) or rhodanine-3-acetic acid (0.3 mmol, 57 mg) in ethanol (15 mL), 2 drops of piperidine was added. The mixture was stirred at reflux temperature for 6 h and then cooled to room temperature. The mixture was evaporated to dryness, the organic layer extracted with chloroform (200 mL), and dried over anhydrous MgSO_4 . Evaporation of the solvent under reduced pressure gave the crude product, which was crystallized with hexane to give the pure product.

*2-Cyano-3-(2'-(4''-(diphenylamino)phenyl)thieno[3,2-*b*]thiophen-5'-yl)acrylic acid 3a.* Red solid (55 %). Mp. 161-163 °C; ^1H NMR (DMSO- d_6 , 400 MHz, δ) 6.97 (d, J = 8.8 Hz, 2H; H3'' and H5''), 7.08-7.13 (m, 6H; 2x (H2''', H4''' and H6''')), 7.33-7.37 (m, 4H; 2x H3''' and H5'''), 7.63 (d, J = 8.8 Hz, 2H; H2'' and H6''), 7.89 (s, 1H, H3'), 8.25 (s, 1H, H6'), 8.45 (s, 1H; H3) ppm; ^{13}C

NMR (DMSO-*d*₆, 100.6 MHz, δ) 115.6 (C3'), 116.9 (CN), 122.0 (C3'' and C5''), 123.9 (C4''), 124.8 (C2''' and C6'''), 126.5 (C1''), 127.0 (C2'' and C6''), 129.7 (C3''' and C5'''), 131.9 (C6'), 136.6 (C5'), 137.2 (C3a' or C6a'), 146.5 (C1'''), 146.8 (C3), 147.1 (C3a' or C6a'), 148.2 (C4''), 151.9 (C2'), 163.6 (C=O) ppm; IR (Nujol): ν = 3360 (O-H), 2204 (C $\equiv$ N), 1584 (C=O), cm⁻¹; UV-vis (ethanol): $\lambda_{\max}$ (ϵ) = 422 nm (22079); MS (ESI) *m/z* (%): 479 (13) [M+H]⁺, 478 (18) M⁺, 412 (37) [M⁺-66], 339 (100) [M⁺-139], 279 (7) [M⁺-199]; HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₈H₁₉N₂O₂S₂, 479.0888; found, 479.0883.

*2-(5'-((2''-(4'''-(Diphenylamino)phenyl)thieno[3,2-*b*]thiophen-5''-yl)methylene)-4'-oxo-2'-thioxothiazolidin-3'-yl)acetic acid 3b*. Red solid (82 %). Mp. with decomposition > 300 °C; ¹H NMR (DMSO-*d*₆, 400 MHz, δ) 4.49 (s, 2H; CH₂), 6.96 (d, *J* = 8.8 Hz; 2H; H3''' and H5'''), 7.06-7.15 (m, 6H; 2x (H2''', H4''' and H6''')), 7.33-7.35 (m, 4H; 2x (H3''' and H5''')), 7.58 (d, *J* = 8.4 Hz, 2H; H2''' and H6'''), 7.85 (s, 1H; H3''), 8.06 (s, 1H, CH_α), 8.08 (s, 1H, H6'') ppm; ¹³C NMR (DMSO-*d*₆, 100.6 MHz, δ) 47.6 (CH₂), 115.4 (C3''), 118.9 (C5'), 122.1 (C3''' and C5'''), 123.9 (C4'''), 124.7 (C1'''), 124.8 (C2''' and C6'''), 126.4 (C6''), 126.7 (C3a'' or C6a''), 126.8 (C2''' and C6'''), 128.4 (C_α), 129.7 (C3''' and C5'''), 138.2 (C5''), 138.3 (C3a'' or C6a''), 145.9 (C4''), 146.5 (C1'''), 147.9 (C2''), 149.9 (C4'), 166.4 (C1), 191.7 (C2') ppm; IR (Nujol): ν = 3362 (O-H), 1581 (C=O), 1279 (C=S) cm⁻¹. UV (ethanol): $\lambda_{\max}$ (ϵ) = 476 nm (13627). MS (ESI) *m/z* (%): 584 (52) M⁺, 412 (15) [M⁺-66], 339 (100) [M⁺-245], 279 (47) [M⁺-305]; HRMS (ESI) *m/z*: M⁺ calcd for C₃₀H₂₀N₂O₃S₄, 584.0357; found, 584.0351.

¹H and ¹³C NMR characterization

Peak assignments were made by comparison of chemical shifts, peak multiplicities and *J* values, and were supported by spin decoupling-double resonance and bidimensional heteronuclear HMBC (heteronuclear multiple bond coherence) and HMQC (heteronuclear multiple quantum coherence)

techniques. The solvents are indicated in parenthesis before the chemical shift values (δ relative to TMS).

The most characteristic signals in the ^1H NMR spectra of aldehyde **2** is that corresponding to the CHO proton at $\delta = 9.94$ ppm. A singlet at $\delta \sim 8.06$ or 8.45 ppm can also be observed for the rhodanine-3-acetic acid **3b** and cyanoacetic acid **3a**, respectively, which corresponds to the vinylic proton of the ethylenic bridge ($\text{C}=\text{CH}$) linked to the rhodanine or cyanoacetic acid acceptor moieties. Moreover, a downfield shift of the vinylic proton is observed due to the stronger electron withdrawing ability of the cyanoacetic acid group for compound **3a** ($\delta = 8.45$ ppm), meaning that this group withdraws the electron density more effectively than rhodanine-3-acetic acid group ($\delta = 8.06$ ppm). IR spectroscopy was also used to identify the typical absorption bands: the carbonyl group in aldehyde **2** (1657 cm^{-1}) and in carboxylic acid **3** ($1581\text{--}1584\text{ cm}^{-1}$); the nitrile (2204 cm^{-1}) and hydroxyl (3360 cm^{-1}) groups in cyanoacetic acid **3a**; and the thiocarbonyl (1279 cm^{-1}) and hydroxyl (3362 cm^{-1}) groups in rhodanine-3-acetic acid **3b**.

Femtosecond Transient Absorption Studies

The experimental setup for ultrafast spectroscopic and kinetic measurements consists of a broadband (350-1600 nm) HELIOS pump-probe femtosecond transient absorption spectrometer from Ultrafast Systems, equipped with an amplified femtosecond Spectra-Physics Solstice-100F laser (displaying a pulse width of 128 fs and 1 kHz repetition rate) coupled with a Spectra-Physics TOPAS Prime F optical parametric amplifier (195-22000 nm) for pump pulse generation. Probe light in the VIS range was generated by passing a small portion of the 800 nm light from the Solstice-100F laser through a computerized optical delay (with a time window up to 8 ns) and focusing in a sapphire plate to generate white-light continuum (450-800 nm). Solution phase measurements were obtained in a 2 mm quartz cuvette with absorptions less than 0.3 at the pump excitation wavelength. The instrumental response function of the system was assumed to be equal to that of the pump-probe cross correlation determined from the measurement of the instantaneous

stimulated Raman signal from the pure solvent (in a 2 mm cuvette). Typical values for the IRF of the system were found to be better than 250 fs. To avoid photodegradation either the solutions were stirred during the experiments or the laser pulse excitation area was changed using a motorized translating sample holder. Transient absorption data were analyzed using the Surface Xplorer PRO program from Ultrafast Systems and the global analysis of the data (from which the lifetimes and decay associated spectra, DAS, of the observed transients were obtained) was performed using Glotaran software.

Dye-sensitized solar cell preparation

A dye-sensitized solar cell typically consists of: i) TiO_2 photoelectrode where the dye molecules are adsorbed, both comprising the working electrode; ii) platinum counter-electrode; and iii) electrolyte containing the iodide/triiodide redox couple. To prepare the working electrodes, FTO glasses (TCO22-7, 2.2 mm thickness, $7 \text{ } \Omega/\text{square}$, Solaronix, Switzerland) were cleaned in a detergent solution using an ultrasonic bath, rinsed with water, and dried at $60 \text{ }^\circ\text{C}$. After treatment in a UV- O_3 system for 15 min, the FTO substrates were immersed in a 40 mM aqueous TiCl_4 solution at $70 \text{ }^\circ\text{C}$ for 20 min, washed with ethanol and dried with N_2 . A layer of TiO_2 paste (Ti-Nanoxide T/SP, Solaronix, Switzerland) was coated onto the FTO glass by screen-printing, kept at room temperature for 20 min, and then dried for 5 min at $120 \text{ }^\circ\text{C}$. The screen-printing procedure was repeated 2 times, to give 3 layers of TiO_2 paste (0.2 cm^2 circular active area, $12 \text{ } \mu\text{m}$ thickness). After drying the photoelectrode at $120 \text{ }^\circ\text{C}$, it was gradually heated ($10 \text{ }^\circ\text{C min}^{-1}$) up to $475 \text{ }^\circ\text{C}$ for 30 min. The TiO_2 electrode was then immersed into a 0.5 mM dye solution in ethanol and kept at room temperature for 12 h. To prepare the counter electrodes, two holes were made in the FTO glass using a drill with a diamond tip. The FTO substrates were then washed as described above. Pt catalyst (Platisol T/SP, Solaronix, Switzerland) was deposited on the FTO side of the glass by screen-printing and the system then heated to $450 \text{ }^\circ\text{C}$ for 10 min. The dye-covered TiO_2 electrode and the Pt counter-electrode were assembled into a sandwich type cell, and sealed with a $25 \text{ } \mu\text{m}$

thick hot-melt gasket-Surlyn (Meltonix 1170-25, Solaronix, Switzerland) by hot-pressing. The electrolyte (Iodolyte AN-50, Solaronix, Switzerland) was injected into the cell through the holes made in the counter-electrode side. These holes were then sealed by Surlyn® and a cover glass using a soldering iron.

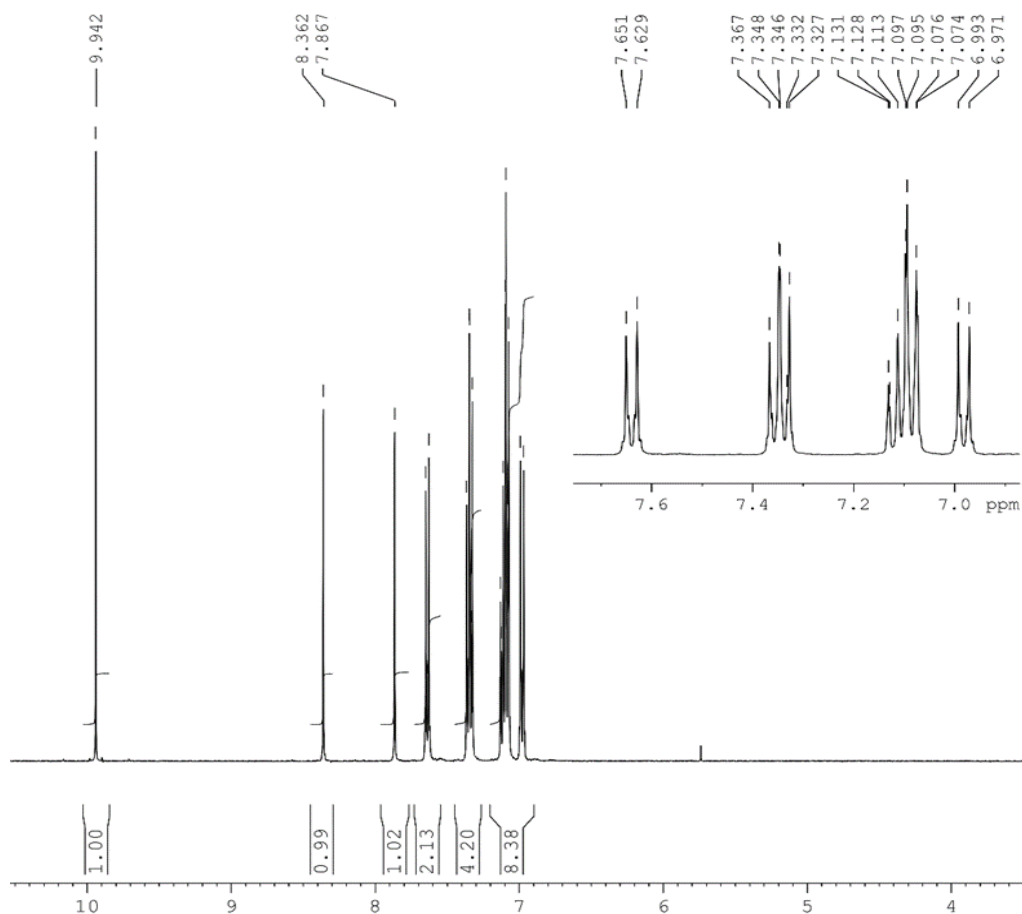


Figure S10. ^1H NMR spectra of compound **2**, in $\text{DMSO}-d_6$, at 400 MHz.

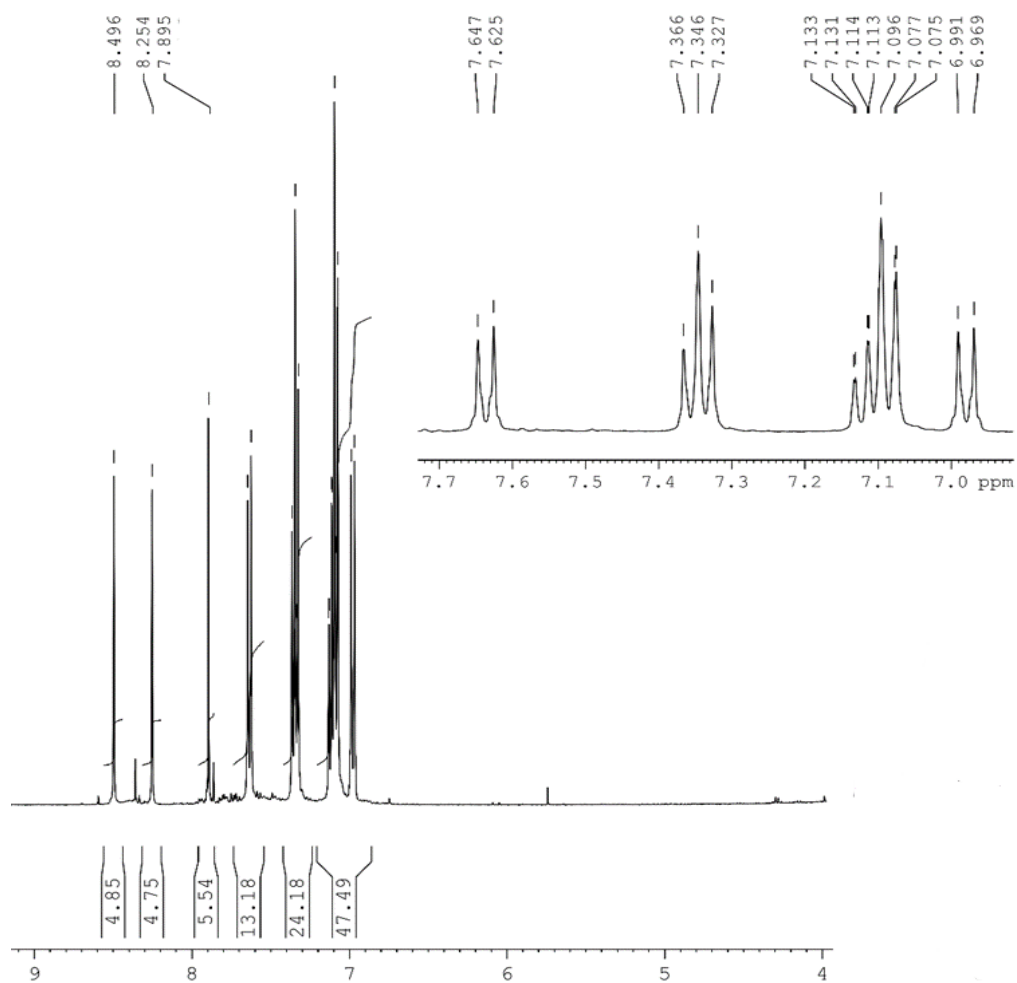


Figure S11. ^1H NMR spectra of dye **3a**, in $\text{DMSO-}d_6$, at 400 MHz.

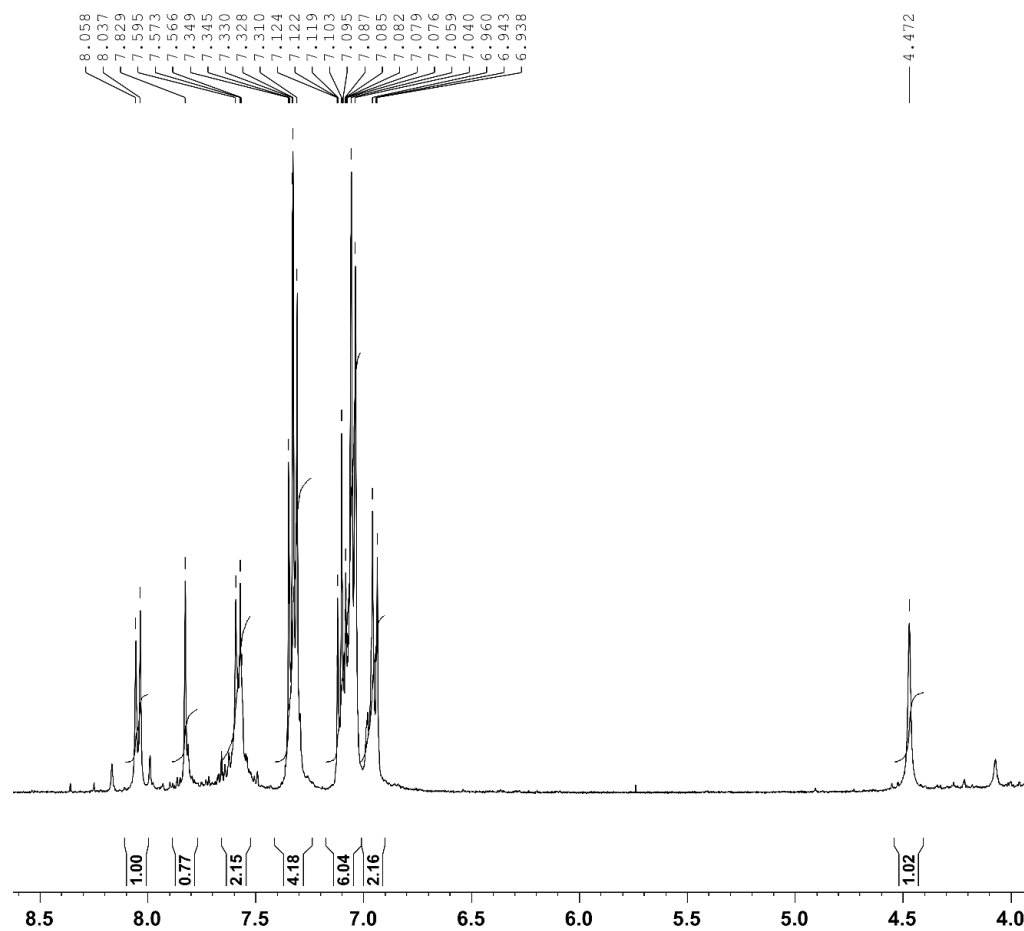


Figure S12. ^1H NMR spectra of dye **3b**, in $\text{DMSO-}d_6$, at 400 MHz.

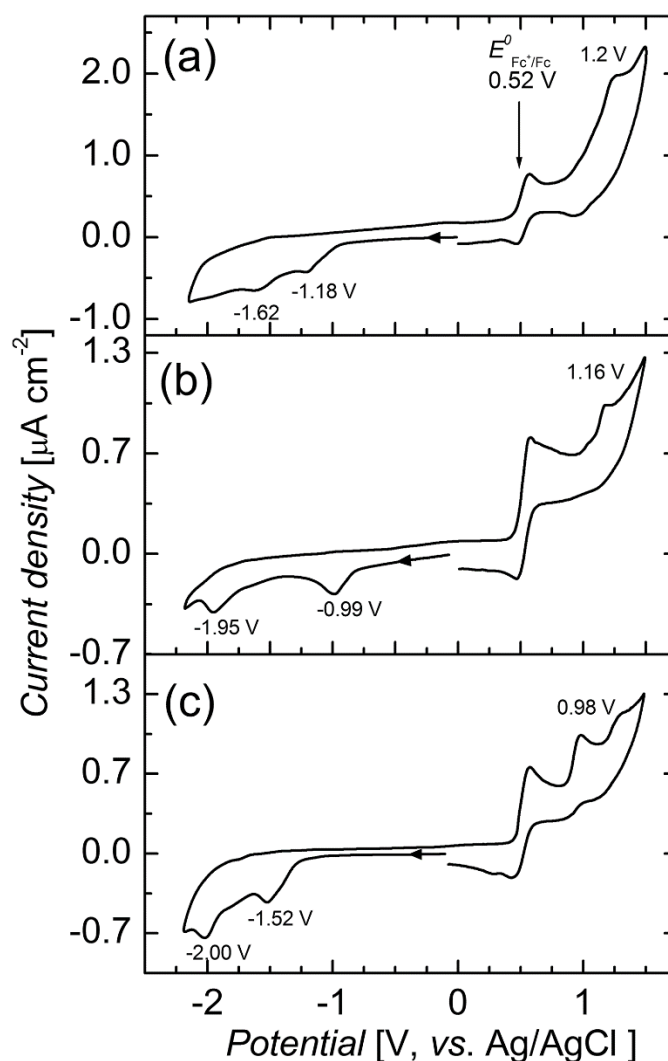


Figure S13. Cyclic voltammograms of glassy carbon electrode in dry DMF containing 0.1 M [NBu₄][BF₄] and 1.0 mM of dyes **3a** (a); **3b** (b) and N719 (c). Scan rate of potential 0.1 V s⁻¹.

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