# Energy levels, charge injection, charge recombination and dye regeneration dynamics for Donor-Acceptor π-conjugated organic dyes in mesoscopic $TiO_2$ sensitzed solar cells.

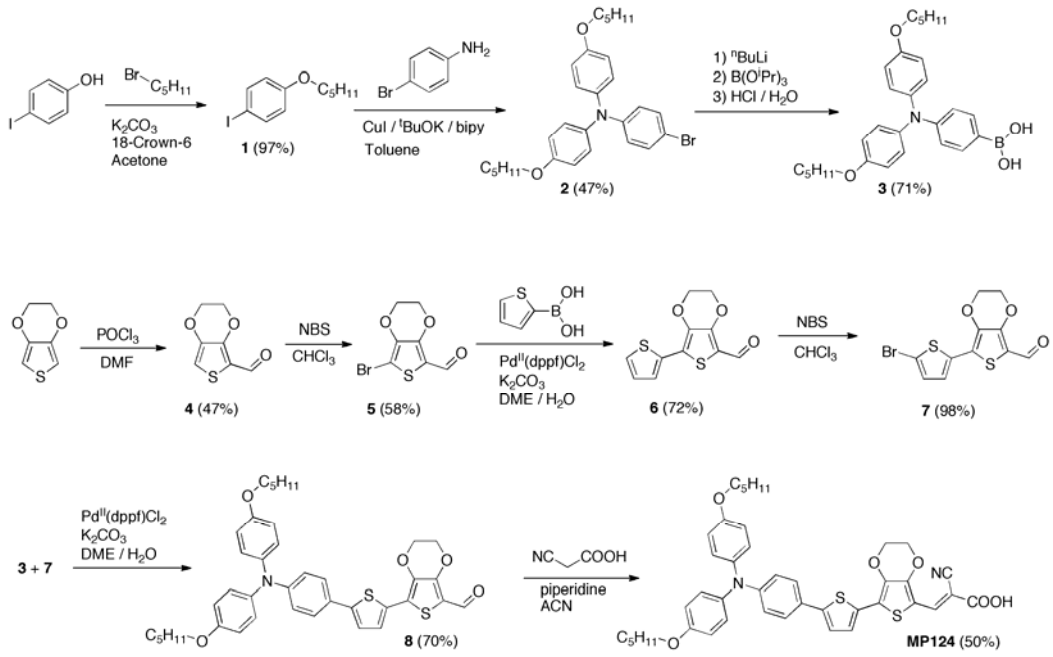
**Miquel Planells[a], Laia Pellejà[a], John N. Clifford[a], Mariachiara Pastore[b], Filippo De Angelis[b]*, Núria López[a], Seth R. Marder[c], and Emilio Palomares[a,d]*.**

# Supporting Information

## Detailed synthetic procedure

**Materials and reagents**. All reagents were purchased from either Sigma-Aldrich or Alfa Aesar and they were used as received without further purification unless otherwise stated.

### Synthesis of MP124




*Synthesis of 4-pentoxy-iodobenzene (**1**).* 4-iodophenol (5 g, 22.7 mmol), potassium carbonate (4.39 g, 31.8 mmol) and 18-crown-6 (1.2 g, 4.5 mmol) were placed in a round bottom flask with 250 mL of acetone (1 mL/mmol). The mixture was stirred and then bromopentane (4 mL, 31.8 mmol) was added. The reaction was stirred under reflux overnight. After cooling to room temperature (r.t.) the crude product was filtered off and the solvent removed. The crude product was extracted with $Et_2O$ and washed with $H_2O$. The organic layer was dried over $Na_2SO_4$ and the solvent removed. The crude product was then purified by column chromatography ($SiO_2$, $CH_2Cl_2$ / Hexane 1:1) to afford a colorless oil as the final product (6.4 g, 97% yield). NMR spectra are in agreement with those reported in the literature.[1] $^1$H-NMR (400 MHz, $CDCl_3$) $\delta_H$: 7.54 (d, $J$ = 8.8 Hz, 2H); 6.67 (d, $J$ = 8.8 Hz, 2H); 3.91 (t, $J$ = 6.6 Hz, 2H); 1.77 (m, 2H); 1.39 (m, 4H); 0.93 (t, $J$ = 7.1 Hz, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta_C$: 159.2; 138.3; 117.4; 82.6; 68.3; 29.1; 28.3; 22.6; 14.2.

*Synthesis of 4-bromo-N,N-bis(4-(pentyloxy)phenyl)aniline (**2**).* 4-bromoaniline (237 mg, 1.3 mmol), $^{t}$BuOK (464 mg, 4.1 mmol); CuI (10 mg, 0.05 mmol) and 2,2'-bipyridine (9 mg, 0.05 mmol) were added to a Schlenck flask and dried under high vacuum for 20 minutes. **1** (1 g, 3.4 mmol) was then added to 5 mL of toluene (4 mL/mmol) and the reaction was heated to 120 ºC. The reaction was stirred at this temperature overnight under argon. After cooling to r.t. the crude product was filtered over celite eluding with $CH_2Cl_2$. Finally, the crude product was purified by column chromatography ($SiO_2$, $CH_2Cl_2$ / Hexane 1:3) to afford the product as a yellow oil (471 mg, 47%). $^{1}$H-NMR (400 MHz, $CDCl_3$) $\delta_H$: 7.22 (d, $J$ = 8.9 Hz, 2H); 7.01 (d, $J$ = 8.9 Hz, 4H); 6.81 (d, $J$ = 9.0 Hz, 2H); 6.78 (d, $J$ = 9.0 Hz, 4H); 6. 3.92 (t, $J$ = 6.6 Hz, 4H); 1.77 (m, 4H); 1.39 (m, 8H); 0.93 (t, $J$ = 7.1 Hz, 6H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta_C$: 155.8; 148.2; 140.5; 131.9; 126.8; 122.1; 115.5; 112.3; 68.4; 29.2; 28.4; 22.7; 14.2. MS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{28}H_{35}NO_2Br$: 496.1851; found: 496.1848. Anal. Calcd for $C_{28}H_{34}NO_2Br$: C, 67.74; H, 6.90; N, 2.82; Found: C, 65.41; H, 6.97; N, 2.68.

*Synthesis of (4-(bis(4-(pentyloxy)phenyl)amino)phenyl)boronic acid (**3**).* **2** (165 mg, 0.33 mmol) was added to a round bottom flask with 2 mL of dry THF (6 mL/mmol) and was stirred under nitrogen atmosphere at -78 ºC. $^{n}$BuLi 1.6M in hexane (300 µL, 0.5 mmol) was added dropwise and the mixture was stirred for 1 hour at -78 ºC. Following this, $B(O^{i}Pr)_3$ was added in a single portion using a syringe and the reaction was stirred again for 1 hour at -78 ºC. The crude product was warmed to r.t. and 1 mL of $H_2O$ was added dropwise. $Et_2O$ was added and the mixture was then washed with water. The organic layer was dried over $Na_2SO_4$ and the solvent removed. Column chromatography ($SiO_2$, $CH_2Cl_2$ / EtOAc 1:1) was used to purify the product, which was obtained as a yellow oil (100 mg, 71% yield). The product was used immediately in the next step.

*Synthesis of 2,3-dihydrothieno[3,4-b][1,4]dioxine-5-carbaldehyde (**4**).* Freshly distilled 3,4-ethylenedioxythiophene (7 g, 49 mmol) was placed in a two neck round bottom flask with 75 mL of dimethylformamide (DMF) (1.5 mL/mmol). The mixture was cooled down to -10 ºC and $POCl_3$ (4.6 mL, 50 mmol) was added dropwise for 5 minutes, and stirred for 1 hour at -10 ºC. 200 mL of $H_2O$ then was added and the reaction was stirred overnight at r.t. The cake formed was filtered off and washed with $H_2O$. Column chromatography ($SiO_2$, $CH_2Cl_2$) was used to purify the product, which was obtained as white solid (4 g, 47 %). NMR spectra are in agreement with those reported in the literature.[35] $^{1}$H-NMR (400 MHz, $CDCl_3$) $\delta_H$: 9.91 (s, 1H); 6.79 (s, 1H); 4.36 (m, 2H); 4.27 (m, 2H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta_C$: 180.3; 148.6; 142.0; 118.7; 110.9; 65.5; 64.5.

*Synthesis of 7-bromo-2,3-dihydrothieno[3,4-b][1,4]dioxine-5-carbaldehyde (**5**).* **4** (1.2 g, 7 mmol) was added to a round bottom flask with 40 mL of $CHCl_3$ (6 mL/mmol) and was stirred at 0 ºC. N-Bromosuccinimide (NBS) (1.4 g, 7.7 mmol) was then added in one portion and the mixture was stirred overnight at r.t. The crude product was washed with a saturated solution of $NaHCO_3$ and $H_2O$. The organic layer was dried over $Na_2SO_4$ and the solvent removed. Column chromatography ($SiO_2$, $CH_2Cl_2$) was used to purify the product, which was obtained as a brown solid (1 g, 58% yield). NMR spectra are in agreement with those reported in the literature.[2] $^{1}$H-NMR (400 MHz, $CDCl_3$) $\delta_H$: 9.83 (s, 1H); 4.36 (m, 4H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta_C$: 179.0; 1404; 1142.0; 118.7; 110.9; 65.5; 64.5.

*Synthesis of 7-(thiophen-2-yl)-2,3-dihydrothieno[3,4-b][1,4]dioxine-5-carbaldehyde (**6**).* **5** (60 mg, 0.24 mmol), 2-thiophene boronic acid (47 mg, 0.36 mmol) and $Pd^{II}(dppf)Cl_2$ (5 mg, 0.007 mmol) were added to a Schlenck flask and dried under vacuum for 15 minutes. 2.5 mL of degassed solution of dimethoxyethane (10 mL/mmol) was then added and the mixture was degassed again. After stirring at r.t. for 30 minutes, 0.6 mL of degassed aqueous solution of $K_2CO_3$ 1M was added. The reaction was heated up to 90 ºC and stirred for 1.5 hours. After cooling to r.t. the solvent was removed under vacuum. Column chromatography ($SiO_2$, $CH_2Cl_2$) was used to purify the product, which was obtained as a yellow solid (42 mg, 68% yield). NMR spectra are in agreement with those reported in the literature.[3] $^{1}$H-NMR (400 MHz, $CDCl_3$) $\delta_H$: 9.91 (s, 1H); 7.44 (dd, $J$ = 3.7 Hz, 1.1 Hz, 1H) 7.38 (dd, $J$ = 5.2Hz, 1.1 Hz, 1H); 7.08 (dd, $J$ = 5.1 Hz, 3.7 Hz, 1H); 4.42 (m, 4H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta_C$: 179.6; 148.8; 137.0; 133.6; 127.7;

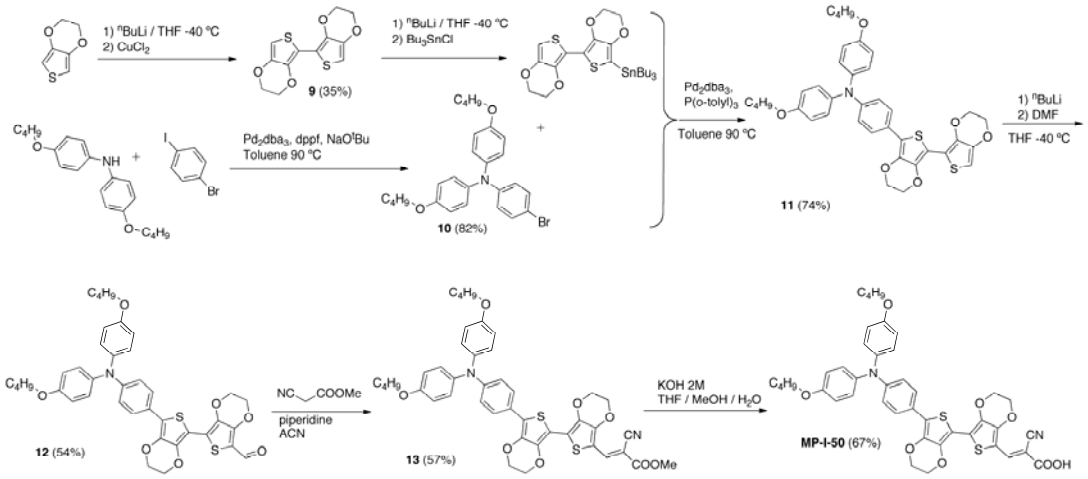
127.1; 126.1; 123.5; 115.0; 65.5; 65.0.

*Synthesis of 7-(5-bromothiophen-2-yl)-2,3-dihydrothieno[3,4-b][1,4]dioxine-5-carbaldehyde (**7**).* **6** (278 mg, 1.1 mmol) was added to a round bottom flask with 20 mL of $CHCl_3$ (18 mL/mmol). The mixture was stirred at 0 ºC and NBS (215 mg, 1.2 mmol) was added in one portion. The reaction was stirred at r.t. for 3 hours. The crude was washed with a saturated solution of $NaHCO_3$ and $H_2O$. The organic layer was dried over $Na_2SO_4$ and the solvent removed. Column chromatography ($SiO_2$, $CH_2Cl_2$) was used to purify the product, which was obtained as yellow solid (357 mg, 98% yield). $^1$H-NMR (400 MHz, $CDCl_3$) $\delta_H$: 9.91 (s, 1H); 7.15 (d, *J* = 4.0 Hz, 1H); 7.02 (d, *J* = 4.0 Hz, 1H); 4.41 (m, 4H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta_C$: 179.6; 148.6; 148.1; 137.2; 130.4; 125.7; 122.3; 115.3; 114.6; 65.5; 65.1. MS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{11}H_8O_3S_2Br$: 330.9098; found: 330.9109. Anal. Calcd for $C_{11}H_7BrO_3S_2$: C, 39.89; H, 2.13; Found: C, 39.69; H, 2.16.

*Synthesis of 7-(5-(4-(bis(4-(pentyloxy)phenyl)amino)phenyl)thiophen-2-yl)-2,3-dihydrothieno[3,4-b][1,4]dioxine-5-carbaldehyde (**8**).* **7** (36 mg, 0.11 mmol) and 1,1'-bis(diphenylphosphino)ferrocene]palladium(II) dichloride, $Pd^{II}$(dppf)$Cl_2$, (4 mg, 0.005 mmol) were added to a Schlenck flask and dried under vacuum for 15 minutes. 1.2 mL of degassed solution of dimethoxyethane (5 mL/mmol) containing **3** (70 mg, 0.16 mmol) was then added and the mixture was degassed again. After stirring at r.t. for 30 minutes, 0.3 mL of degassed aqueous solution of $K_2CO_3$ 1M was added. The reaction was heated to 90 ºC and stirred for 2 hours. After cooling at r.t. the solvent was removed under vacuum. Column chromatography ($SiO_2$, $CH_2Cl_2$) was used to purify the product, which was obtained as an orange solid (51 mg, 70% yield). $^1$H-NMR (400 MHz, $CDCl_3$) $\delta_H$: 9.89 (s, 1H); 7.40 (d, *J* = 8.9 Hz, 2H); 7.38 (d, *J* = 3.9 Hz, 1H); 7.13 (d, *J* = 4.0 Hz, 1H); 7.06 (d, *J* = 8.9 Hz, 4H); 6.90 (d, *J* = 8.8 Hz, 2H); 6.83 (d, *J* = 9.0 Hz, 4H); 4.42 (m, 4H); 3.94 (t, *J* = 6.4 Hz, 4H); 1.74 (m, 4H); 1.41 (m, 8H); 0.93 (m, 6H). $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta_C$: 179.4, 155.9, 149.0, 148.8, 146.6, 143.5, 140.3, 136.6, 131.2, 127.3, 127.0, 126.6, 125.5, 122.2, 120.2, 115.5, 114.5, 68.4, 65.5, 65.0, 29.2, 28.4, 22.6, 14.2. MS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{39}H_{41}NO_5S_2Na$: 690.2324; found: 690.2305. Anal. Calcd for $C_{39}H_{41}NO_5S_2$: C, 70.14; H, 6.19; N, 2.10; Found: C, 70.76; H, 6.52; N, 2.12.

*Synthesis of (E)-3-(7-(5-(4-(bis(4-(pentyloxy)phenyl)amino)phenyl)thiophen-2-yl)-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2-cyanoacrylic acid (**MP124**).* **8** (119 mg, 0.18 mmol) and cyanoacetic acid (23 mg, 0.27 mmol) were added to a Schlenck flask with 1 mL of acetonitrile (ACN) (5 mL/mmol). Piperidine (365 μL, 3.7 mmol) was then added and the reaction was stirred at reflux for 3 hours. After cooling to r.t. the solvent was removed and the crude was extracted with $CHCl_3$ and washed with diluted HCl (0.1% v/v) and brine. The organic layer was dried over $Na_2SO_4$ and the solvent removed. Size exclusion chromatography (Bio-beads S-X1, THF) was used in order to purify the product, which was obtained as a purple solid (67 mg, 50% yield). $^1$H-NMR (500 MHz, $CDCl_3$/THF-$d_8$ 3:1) $\delta_H$: 8.15 (s, 1H); 7.21 (d, *J* = 4.1 Hz, 1H); 7.19 (d, *J* = 8.5 Hz, 2H); 6.95 (d, *J* = 4.0 Hz, 1H); 6.83 (d, *J* = 8.7 Hz, 4H); 6.67 (d, *J* = 8.6 Hz, 2H); 6.61 (d, *J* = 8.7 Hz, 4H); 4.21 (m, 4H); 3.72 (t, *J* = 6.5 Hz, 4H); 1.57 (m, 4H); 1.19 (m, 8H); 0.73 (t, *J* = 7.1 Hz, 6H). $^{13}$C-NMR (125 MHz, $CDCl_3$/THF-$d_8$ 3:1) $\delta_c$: 155.6; 148.7; 148.1; 146.7; 140.6; 139.9; 130.6; 127.3; 126.6; 126.1; 125.7; 125.0; 123.5; 121.8; 119.6; 115.0; 109.1; 99.8; 93.2; 67.8; 65.3; 64.6; 30.3; 28.8; 22.2; 13.6. MS-ESI (*m/z*): $[M-H]^-$ calcd for $C_{42}H_{41}N_2O_6S_2$: 733.2406; found: 733.2396. Anal. Calcd for $C_{42}H_{42}N_2O_6S_2 \cdot 1.5H_2O$: C, 66.21; H, 5.95; N, 3.68; Found: C, 66.05; H, 6.06; N, 3.29.

**Synthesis of MP-I-50**




*Synthesis of 2,2'-bis(3,4-ethylenedioxythiophene) (**9**).* Freshly distilled 3,4-ethylenedioxythiophene (2 mL, 18.6 mmol) was placed in a two neck round bottom flask with 20 mL of freshly distilled THF (1 mL/mmol) and it was stirred under nitrogen atmosphere at -40 ºC (ACN/dry ice bath). $^{n}$BuLi 2.5M in hexane (8 mL, 20 mmol) was added dropwise and the mixture was stirred for 1 hour at -40 ºC. Then, $CuCl_2$ anhydrous (2.5 g, 18.6 mmol) was added in one portion and the reaction was allowed to reach r.t. The mixture was stirred overnight. 200 mL of $H_2O$ was added to the crude mixture and green precipitate appeared. The cake was filtered off and washed with 50 mL of $H_2O$ and 100 mL of hexane. The filtered cake was digested with $CH_2Cl_2$ (3 x 100 mL) and the crude was dried under vacuum and purified by column chromatography ($SiO_2$, $CH_2Cl_2$ / Hexane 1:1, then $CH_2Cl_2$ / Hexane 2:1) to afford the product as a white solid (930 mg, 35% yield). $^{1}$H-NMR (300 MHz, $CDCl_3$) $\delta_H$: 6.27 (s, 2H); 4.32 (m, 4H); 4.24 (m, 4H). $^{13}$C-NMR (75 MHz, $CDCl_3$) $\delta_C$: 141.4; 137.2; 110.1; 97.7; 65.2; 64.8. MS-EI (*m/z*): $[M]^+$ calcd for $C_{12}H_{10}O_4S_2$: 282.0021; found: 282.0011. Anal. Calcd for $C_{12}H_{10}O_4S_2$: C, 51.05; H, 3.57; Found: C, 50.90; H, 3.49.

*Synthesis of 4-bromo-N,N–(bis(4-butoxyphenyl)aniline (**10**).* Tris(dibenzylideneacetone)dipalladium(0), $Pd_2dba_3$, (29 mg, 0.032 mmol), dppf (26 mg, 0.048 mmol) and 4-bromoiodobencene (1.3 g, 4.8 mmol) were added to a Schlenck tube and dried under high vacuum for 30 minutes. 8 mL of dry toluene (2.5 mL/mmol) was added to the mixture and was stirred for 15 minutes under nitrogen atmosphere. Bis(4-butoxyphenhyl)amine (1 g, 3.2 mmol) and NaO$^{t}$Bu (430 mg, 4.5 mmol) were added and the reaction was heated to 90 ºC and stirred overnight. After cooling to r.t., the crude material was washed with water (50 mL) and extracted with diethyl ether (50 mL). The organic layer was dried over $MgSO_4$ and the solvent was removed. Column chromatography ($SiO_2$, Hexane / $CH_2Cl_2$ 4:1) was used to purify the product, which was obtained as pale brown liquid (1.22 g, 82% yield). $^{1}$H-NMR (300 MHz, $CDCl_3$) $\delta_H$: 7.23 (d, $J$ = 9.0 Hz, 2H); 7.02 (d, $J$ = 8.9 Hz, 4H); 6.81 (m, 6H); 3.94 (t, $J$ = 6.5 Hz, 4H); 1.77 (m, 4H); 1.50 (m, 4H); 0.99 (t, $J$ = 7.4 Hz, 6H). $^{13}$C-NMR (75 MHz, $CDCl_3$) $\delta_C$: 155.8; 148.2; 140.5; 131.9; 126.7; 122.0; 115.5; 112.3; 68.1; 31.6; 19.5; 14.1. MS-EI (*m/z*): $[M]^+$ calcd for $C_{26}H_{30}NO_2$: 467.1448; found: 467.1460.[4, 5]

*Synthesis of 4-butoxy-N-(4-butoxyphenyl)-N-(4-(2,2',3,3'-tetrahydro-5,5'-bithieno[3,4-b][1,4]dioxin-7-yl)phenyl)aniline (**11**).* **9** (700 mg, 2.5 mmol) was placed in a two neck round bottom flask with 25 mL of freshly distilled THF (10 mL/mmol) and was stirred under nitrogen atmosphere at -40 ºC (ACN/dry ice bath). $^{n}$BuLi 2.5M in hexane (1.1 mL, 2.75 mmol) was added dropwise and the mixture was stirred for 1 hour at -40 ºC. Tributyltinchloride (678 µL, 2.5 mmol) was then added dropwise and the mixture was allowed to reach r.t. and stirred overnight. The crude product was washed with brine (30 mL) and the organic layer was dried over $MgSO_4$, filtrated and the solvent removed. The formation of the tin

compound was checked by $^1$H-NMR. $Pd_2dba_3$ (45 mg, 0.05 mmol) and tri(o-tolyl)phosphine (30 mg, 0.1 mmol) were added to a Schlenck tube and dried under high vacuum for 30 minutes. A degassed solution of the tin compound and **10** (1.17 g, 2.5 mmol) in 10 mL of toluene (2 mL/ mmol) was then added via cannula. The mixture was degassed again by pump/freeze technique and stirred overnight under nitrogen atmosphere at 90 ºC. The mixture was poured into a KF aqueous solution and stirred vigorously for 1 hour (a white precipitate appears – tin side product). The mixture was filtered off and extracted with $CH_2Cl_2$ (150 mL) and washed twice with KF aqueous solution. The organic layer was dried over $MgSO_4$ and the solvent removed. The crude was purified by column chromatography ($SiO_2$, $CHCl_3$ / Hexane 3:1) to afford the product as a yellow solid (1.19 g, 74% yield). $^1$H-NMR (400 MHz, DMSO-$d_6$) $\delta_H$: 7.46 (d, *J* = 8.5 Hz, 2H); 6.98 (d, *J* = 8.6 Hz, 4H); 6.88 (d, *J* = 9.0 Hz, 2H), 6.78 (d, *J* = 8.5 Hz, 4H); 6.54 (s, 1H); 4.31 (m, 8H); 3.92 (t, *J* = 6.4 Hz, 4H); 1.68 (m, 4H); 1.43 (m, 4H); 0.93 (t, *J* = 7.4 Hz, 6H). $^{13}$C-NMR (100 MHz, DMSO-$d_6$) $\delta_C$: 155.1; 146.8; 141.0; 139.8; 137.3; 136.8; 136.7; 126.4; 126.2; 124.4; 119.7; 115.4; 113.7; 108.8; 105.9; 97.7; 67.3; 65.0; 64.8; 64.5; 64.2; 30.8; 18.7; 13.7. MS-ESI (*m/z*): [M+Na$^+$] calcd for $C_{38}H_{39}NO_6S_2Na$: 692.2117; found: 692.2105. Anal. Calcd for $C_{38}H_{39}NO_6S_2$: C, 68.14; H, 5.87; N, 2.09; Found: C, 68.42; H, 5.90; N, 2.19.

*Synthesis of 7'-(4-(bis(4-butoxyphenyl)amino)phenyl)-2,2',3,3'-tetrahydro-5,5'-bithieno[3,4-b][1,4]dioxine-7-carbaldehyde (**12**).* **11** (1 g, 1.5 mmol) was placed in a two neck round bottom flask with 9 mL of freshly distilled THF (6 mL/mmol) and was stirred under nitrogen atmosphere at -40 ºC (ACN/dry ice bath). $^n$BuLi 2.5 M in hexane (0.72 mL, 1.8 mmol) was added dropwise and the mixture was stirred for 1 hour at -40 ºC. DMF (210 µL, 2.7 mmol) was then added dropwise and the reaction mixture was allowed to reach r.t. and was then stirred for 2 hours. The crude product was poured into 1% HCl aqueous solution (150 mL) and the precipitate was filtered off. Size Exclusion chromatography (Bio-beads S-X1 in $CH_2Cl_2$) was used in order to obtain pure a orange solid (454 mg, 44%). $^1$H-NMR (300 MHz, $CDCl_3$) $\delta_H$: 9.88 (s, 1H); 7.54 (d, *J* = 8.9 Hz, 2H); 7.05 (d, *J* = 8.9 Hz, 4H); 6.90 (d, *J* = 8.9 Hz, 2H); 6.82 (d, *J* = 9.0 Hz, 4H); 4.41 (m, 8H); 3.94 (t, *J* = 6.5 Hz, 4H); 1.76 (m, 4H); 1.51 (m, 4H); 0.98 (t, *J* = 7.4 Hz, 6H). $^{13}$C-NMR (75 MHz, $CDCl_3$) $\delta_C$: 179.6; 155.8; 148.4; 148.3; 148.1; 141.0; 140.5; 136.9; 135.9; 127.1; 126.9; 124.4; 120.3; 115.4; 114.9; 105.9; 85.4; 68.2; 65.5; 65.3; 65.1; 64.8; 31.6; 19.5; 14.1. MS-ESI (*m/z*): [M+Na$^+$] calcd for $C_{39}H_{39}NO_7S_2Na$: 720.2066; found: 720.2085. Anal. Calcd for $C_{39}H_{39}NO_7S_2$: C, 67.12; H, 5.63; N, 2.01; Found: C, 67.28; H, 5.53; N, 2.04.

*Synthesis of (E)-methyl 3-(7'-(4-(bis(4-butoxyphenyl)amino)phenyl)-2,2',3,3'-tetrahydro-5,5'-bithieno[3,4-b][1,4]dioxin-7-yl)-2-cyanoacrylate (**13**).* **12** (101 mg, 0.145 mmol) was added to a Schlenk flask with 6 mL of ACN (40 mL/mmol). Piperidine (150 µL, 1.45 mmol) and methyl cyanoacetate (25 µL, 0.29 mmol) were then added and the mixture was heated to 75 ºC for 2.5 hours under nitrogen atmosphere. After this, the solvent was removed under vacuum and the crude product was purified by column chromatography ($SiO_2$, $CHCl_3$ up to $CHCl_3$ / 2% AcOEt) followed by size exclusion column chromatography (Bio-beads S-X1 in $CH_2Cl_2$) to afford the product as a purple solid (65 mg, 57 % yield). $^1$H-NMR (300 MHz, $CDCl_3$) $\delta_H$: 8.34 (s, 1H); 7.54 (d, *J* = 8.9 Hz, 2H); 7.05 (d, *J* = 8.9 Hz, 4H); 6.89 (d, *J* = 8.9 Hz, 2H); 6.82 (d, *J* = 8.9 Hz, 4H); 4.40 (m, 8H); 3.94 (t, *J* = 6.5 Hz, 4H); 3.85 (s, 3H); 1.76 (m, 4H); 1.49 (m, 4H); 0.98 (t, *J* = 7.4 Hz, 6H). $^{13}$C-NMR (75 MHz, $CDCl_3$) $\delta_C$: 164.9; 155.9; 151.5; 148.4; 148.3; 141.6; 141.5; 140.4; 137.0; 135.8; 127.2; 127.0; 124.3; 124.0; 121.7; 120.1; 117.8; 115.4; 110.4; 90.2; 68.1; 65.7; 65.6; 65.0; 64.8; 52.9; 31.6; 19.5; 14.1. MS-ESI (*m/z*): [M+Na]$^+$ calcd for $C_{43}H_{42}N_2O_8S_2Na$: 801.2280; found: 801.2280. Anal. Calcd for $C_{43}H_{42}N_2O_8S_2$: C, 66.30; H, 5.43; N, 3.60; Found: C, 66.33; H, 5.36; N, 3.64.

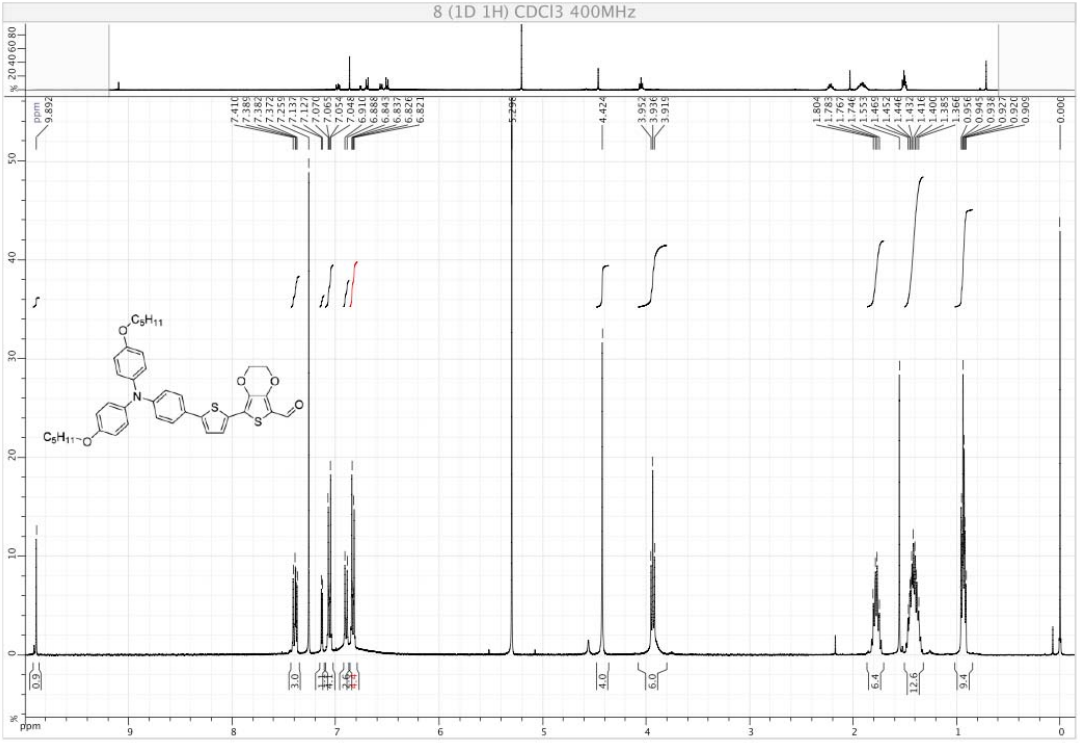
*Synthesis of (E)-3-(7'-(4-(bis(4-butoxyphenyl)amino)phenyl)-2,2',3,3'-tetrahydro-5,5'-bithieno[3,4-b][1,4]dioxin-7-yl)-2-cyanoacrylic acid (**MP-I-50**).* **13** (53 mg, 0.068 mmol) was added to a Schlenk flask with 10 mL of THF, 3 mL of MeOH and 2 mL of KOH 2M aqueous solution. The mixture was stirred overnight at r.t. The organic solvent was removed under vacuum and the crude product was extracted with $CH_2Cl_2$ (50 mL) and washed with 1% HCl (50 mL) and $H_2O$ (2 x 50 mL). The organic layer was dried over $MgSO_4$ and the solvent removed. The crude was purified by size exclusion column chromatography (Bio-beads S-X1 in $CH_2Cl_2$) to afford the product as a purple solid (35 mg, 67 % yield).

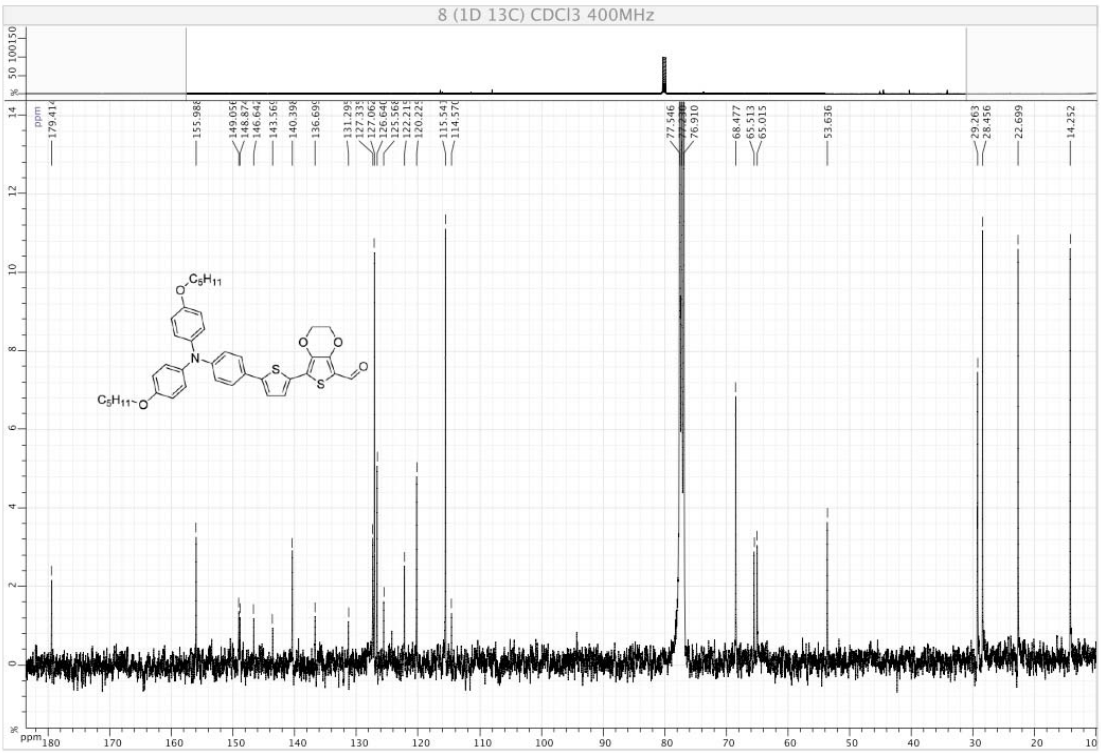
$^{1}$H-NMR (400 MHz, THF-$d_8$) $\delta_H$: 11.44 (br s, 1H); 8.28 (s, 1H); 7.54 (d, $J$ = 8.6 Hz, 2H); 7.01 (d, $J$ = 8.6 Hz, 4H); 6.85 (d, $J$ = 8.8 Hz, 2H); 6.82 (d, $J$ = 8.8 Hz, 4H); 4.41 (m, 8H); 3.93 (t, $J$ = 6.4 Hz, 4H); 1.72 (m, 4H); 1.50 (m, 4H); 0.97 (t, $J$ = 7.4 Hz, 6H). $^{13}$C-NMR (125 MHz, THF-$d_8$) $\delta_C$: 163.1; 154.8; 146.9; 146.7; 140.1; 139.2; 138.8; 136.1; 134.9; 125.6; 125.4; 123.5; 120.9; 119.2; 118.7; 115.5; 113.9; 108.7; 104.6; 90.9; 66.4; 64.7; 64.3; 63.9; 63.6; 30.3; 18.1; 12.2. MS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{42}H_{40}N_2O_8S_2Na$: 787.2124; found: 787.2114. Anal. Calcd for $C_{42}H_{40}N_2O_8S_2 \cdot 1/2H_2O$: C, 65.18; H, 5.34; N, 3.62 Found: C, 65.43; H, 5.53; N, 3.33.

**Characterization techniques**. $^{1}$H and $^{13}$C NMR spectra were recorded on both a Bruker Avance 400 (400 MHz for $^{1}$H and 100 MHz for $^{13}$C) and a Mercury Varian 300 (300 MHz for $^{1}$H and 75 MHz for $^{13}$C) spectrometer. The deuterated solvents used are indicated; chemical shifts, δ, are given in ppm, referenced to the solvent residual signal ($^{1}$H, $^{13}$C). Coupling constants, $J$, are given in Hz. MS spectra were recorded on both Waters LCT Premier and VG Instruments 70-SE, using electron impact (EI), electrospray ionization (ESI) and matrix-assisted laser desorption/ionization (MALDI) modes depending on the sample. Elemental analyses were carried out by both Atlantic Microlabs and Santiago de Compostela University using a LECO 932 CHNS elemental analyzer.

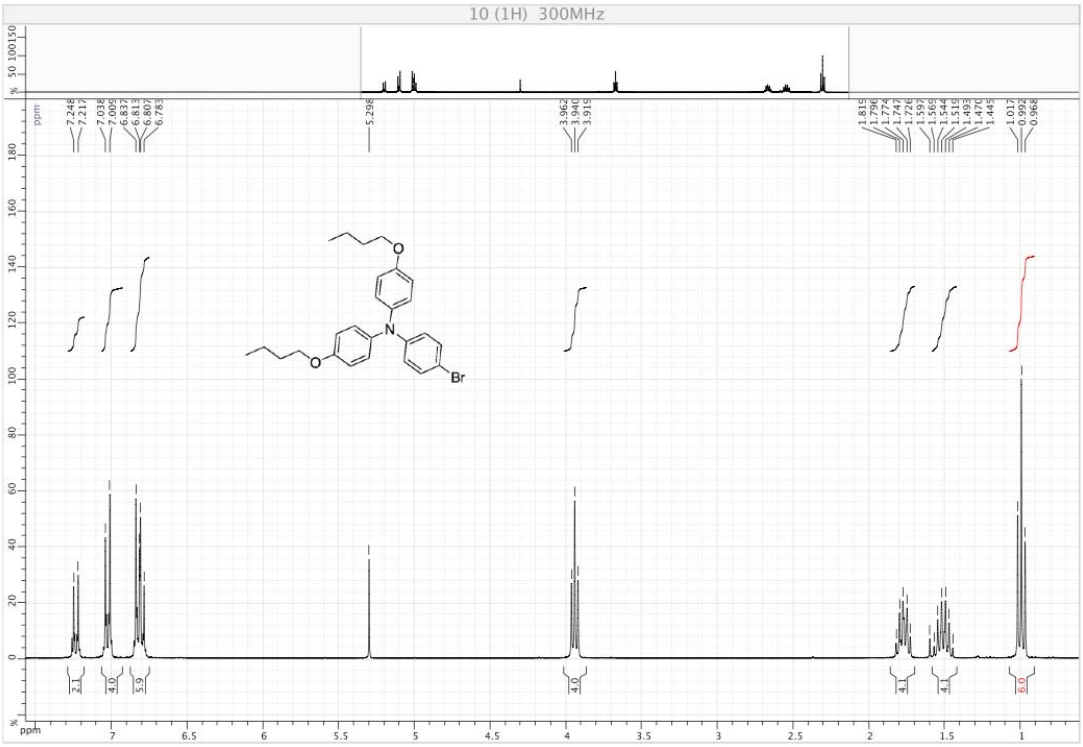
**$^{1}$H-NMR and $^{13}$C-NMR spectra of compounds that exceed 0.4% in elemental analysis**

7-(5-(4-(bis(4-(pentyloxy)phenyl)amino)phenyl)thiophen-2-yl)-2,3-dihydrothieno[3,4-b][1,4]dioxine-5-carbaldehyde (**8**)




4-bromo-N,N–(bis(4-butoxyphenyl)aniline (**10**)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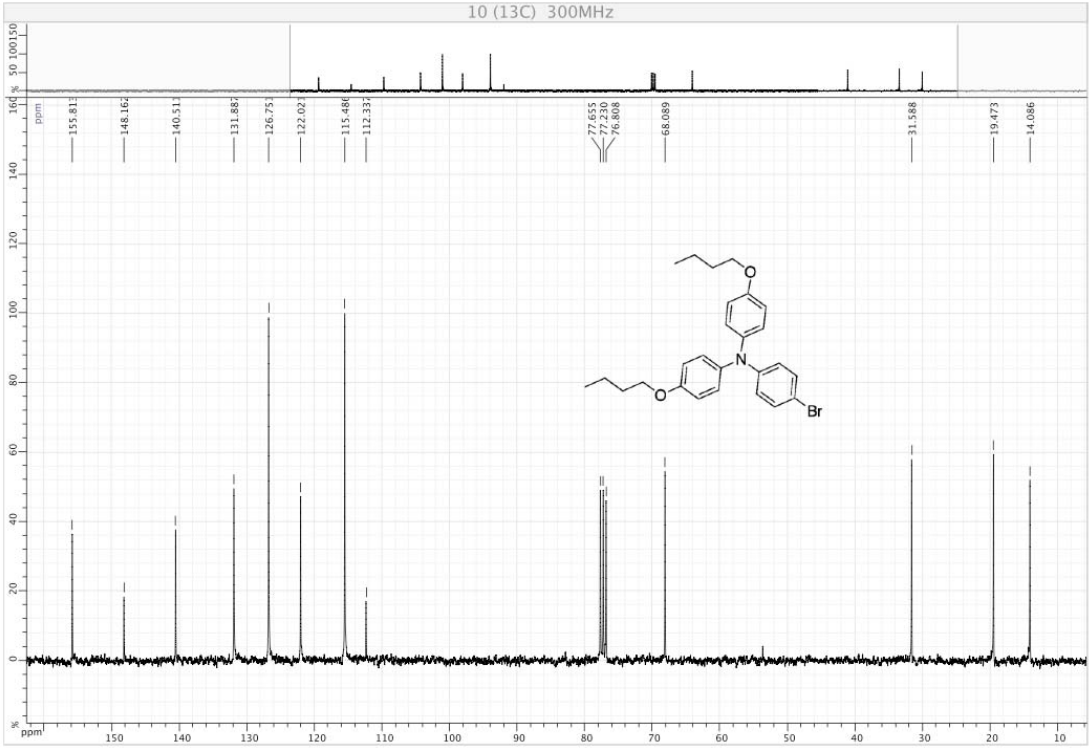
7.217
7.038
7.009
6.837
6.817
6.807
6.783
5.298
3.962
3.940
3.915
1.815
1.796
1.774
1.747
1.726
1.697
1.565
1.544
1.519
1.493
1.470
1.445
1.017
0.992
0.968
O
N
Br
2.1
4.0
5.9
4.0
4.1
4.1
6.0
ppm


10 (13C) 300MHz
155.813
148.162
140.514
131.887
126.751
122.023
115.486
112.337
77.655
77.230
76.808
68.089
31.588
19.473
14.086
O
N
Br
ppm

## Supporting Information Figures

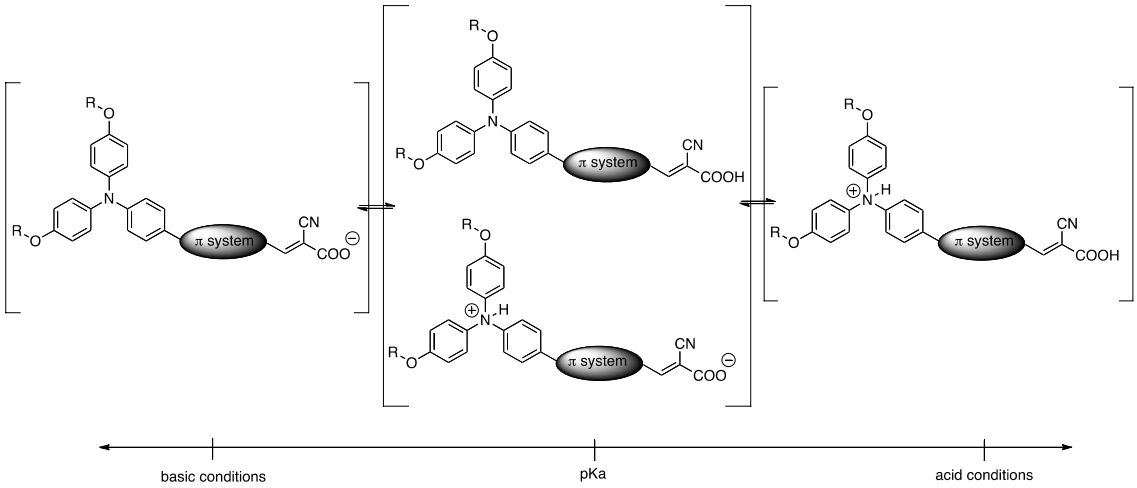



**Figure S1**. Schematic representation of the D - π - A dyes upon basic and acid conditions.

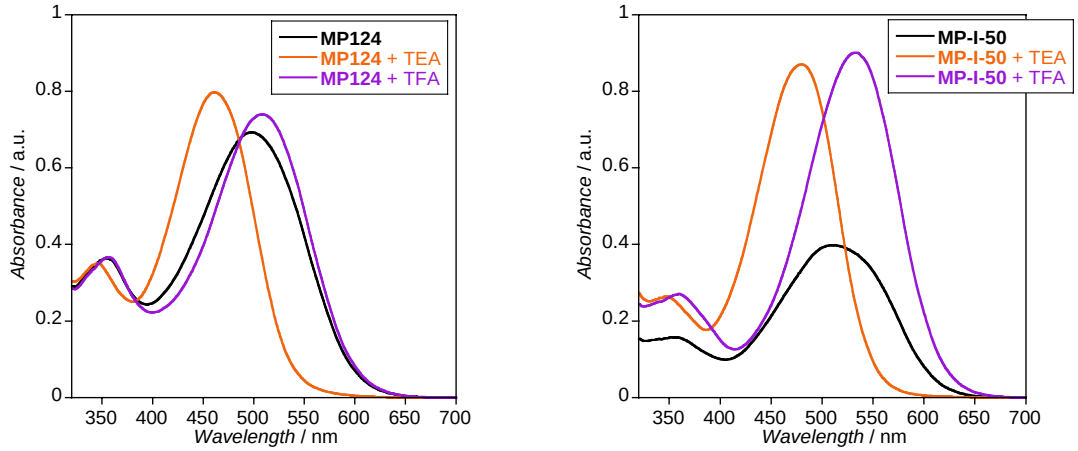



**Figure S2**. UV-Visible spectra in no modified (black line), basic (orange line) and acid (purple line) conditions for **MP124** (left) and **MP-I-50** (right) dyes in ACN/$^{t}$BuOH (1:1). Basic and acid conditions were obtained by adding 50 μL of triethylamine (TEA) and tryfluoroacetic acid (TFA), respectively.

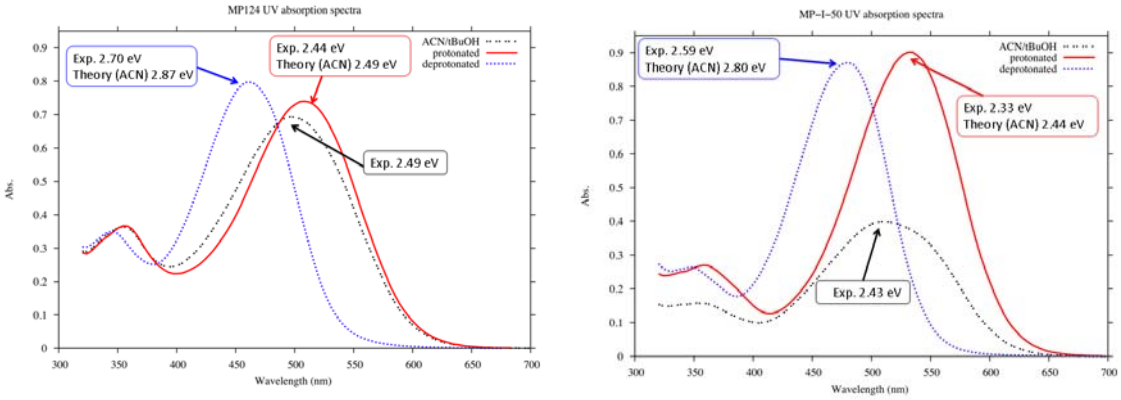



**Figure S3**. Experimental versus calculated normalized UV-Visible spectra of **MP124** and **MP-I-50** in ACN/tBuOH together with the calculated values for the hydrogenated and dehydrogenated dyes.

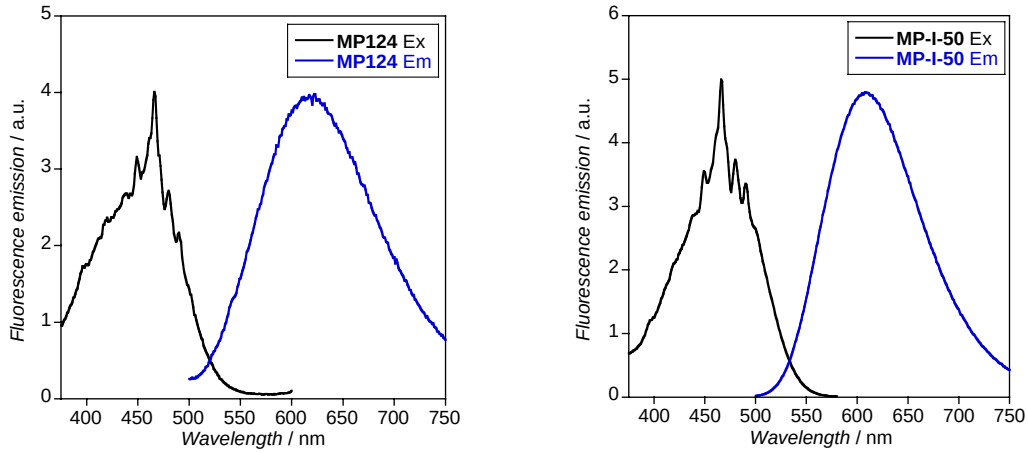



**Figure S4**. Excitation (black line) and fluorescence spectra (blue line) for **MP124** (left) and **MP-I-50** (right) dyes in ACN/$^{t}$BuOH (1:1). Both spectra were acquired under basic conditions described above.

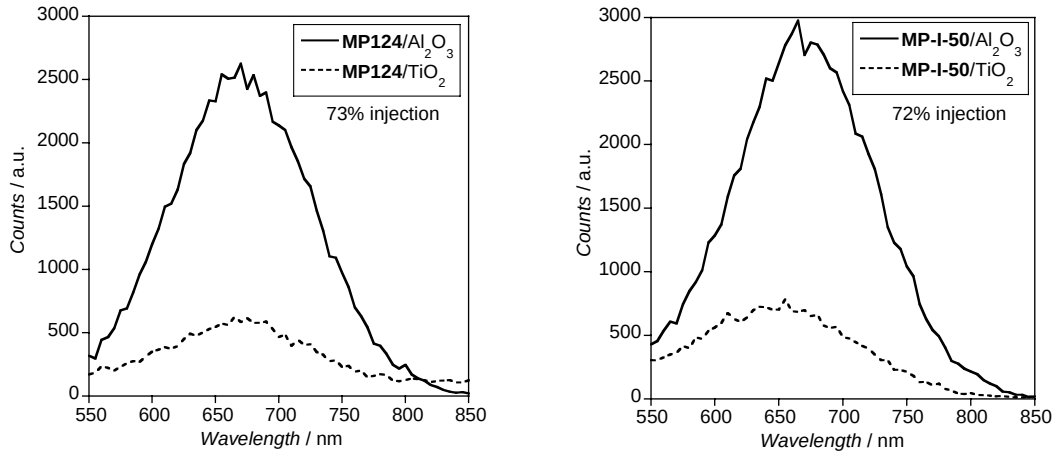



**Figure S5**. Emission spectra on $Al_2O_3$ (straight line) and $TiO_2$ (dash line) films for **MP124** (left) and **MP-I-50** (right) dyes. The emission spectra were measured using single photon counting apparatus under nanosecond laser irradiation at 405 nm for 15 minutes.

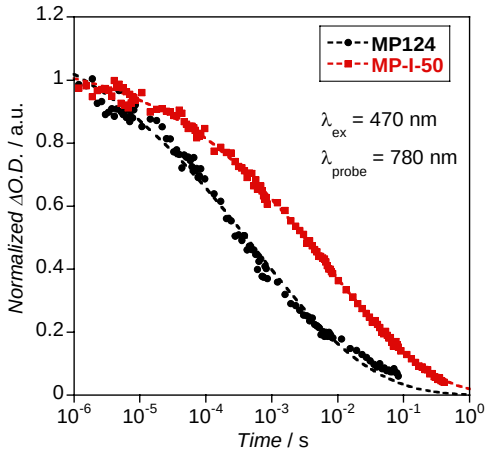



**Figure S6**. Transient absorption spectroscopy for sensitized 4 μm $TiO_2$ films sensitized **MP124** (black circles) and **MP-I-50** (red squares) with no triethylamine treatment. The data was fitted to eqn. 1. (dashed lines).

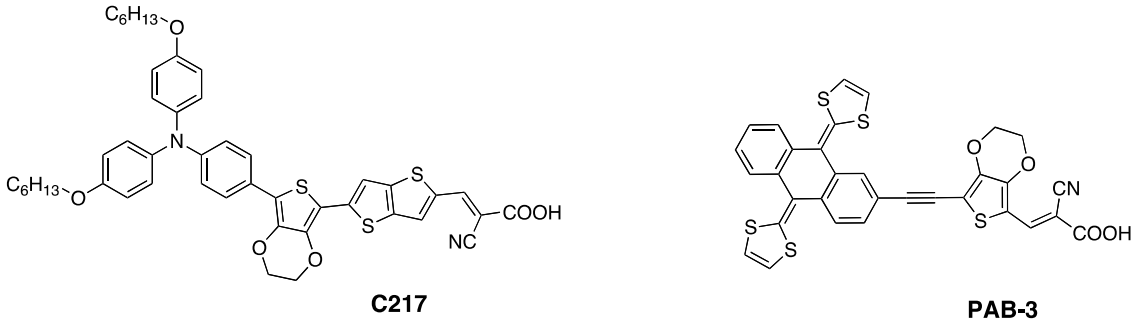



**Figure S7**. Molecular structures of organic dyes **C217** and **PAB-3**.

## Complete reference 38:

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