

## Supporting Information

# Push-pull *N,N*-Diphenylhydrazones Bearing Bithiophene or Thienothiophene Spacers as NLO Second Harmonic Generators and as Photosensitizers for Nanocrystalline TiO<sub>2</sub> DSSCs

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## 1-Experimental Section

### 1.1-Synthesis and Characterization

The structures of compounds **3-6** and **7c** were confirmed by standard procedures (Table S1). The most characteristic signals in the  $^1\text{H}$  NMR spectra of the aldehydes **4** are those corresponding to the *CHO* proton at  $\delta \sim 9.87\text{-}9.93$  ppm. A singlet at  $\delta 8.17\text{-}8.18$  or  $7.19\text{-}7.95$  ppm is observed for the cyanoacetic acid derivatives **5** and dicyanovinyl derivatives **6**, respectively, and corresponds to the vinylic proton of the ethylenic bridge ( $\text{C}=\text{CH}$ ) linked to the cyanoacetic acid or dicyanovinyl acceptor moieties. The following IR absorption bands were observed: the carbonyl group in aldehydes **4a-b** ( $1660\text{-}1663\text{ cm}^{-1}$ ), and cyanoacetic acids **5a-b** and carboxyl acid **7c** ( $1601\text{-}1657\text{ cm}^{-1}$ ); the nitrile group in cyanoacetic acids **5a-b** ( $2261\text{-}2265\text{ cm}^{-1}$ ), and dicyanovinyl derivatives **6a-b** ( $2208\text{-}2209\text{ cm}^{-1}$ ); and the hydroxyl group in the acids **5** and **7c** ( $3413\text{-}3417\text{ cm}^{-1}$ ).

**Table S1.** Experimental Spectral Data for *N,N*-Diphenylhydrazone Derivatives **3-7**.

Cpds	$\eta / \%$	IR <sup>a)</sup> $\nu / \text{cm}^{-1}$			$^1\text{H}$ NMR <sup>b,c)</sup> $\delta /$ ppm	
		C=O	C $\equiv$ N	O-H	<i>CHO</i>	<i>CH</i> =(CN) <sub>2</sub>
<b>3a</b>	66	-	-	-	-	-
<b>3b</b>	72	-	-	-	-	-
<b>4a</b>	58	1663	-	-	9.93 <sup>b)</sup>	-
<b>4b</b>	45	1660	-	-	9.87 <sup>b)</sup>	-
<b>5a</b>	58	1601	2265	3416	-	8.18 <sup>c)</sup>
<b>5b</b>	27	1613	2261	3417	-	8.17 <sup>b)</sup>
<b>6a</b>	29	-	2209	-	-	7.95 <sup>c)</sup>
<b>6b</b>	22	-	2208	-	-	7.19-7.24 <sup>b)</sup>
<b>7c</b>	55	1657	-	3413	-	-

<sup>a)</sup> IR spectra were performed in liquid film.

<sup>b)</sup>  $^1\text{H}$  NMR spectra were performed at 400 MHz, using  $\text{CDCl}_3$  as solvent.

<sup>c)</sup>  $^1\text{H}$  NMR spectra were performed at 400 MHz, using  $\text{DMSO-}d_6$  as solvent.

## 1.2- Synthetic procedures

### Procedure for the synthesis of precursor **2c** by Suzuki-Miyaura coupling.<sup>1</sup>

5-Bromothiophene-2-carboxylic acid (1 equiv.) was coupled to 5-formyl-2-thiopheneboronic acid (1.2 equiv.) in a mixture of DME (8 mL), ethanol (2 mL), aqueous 2 M Na<sub>2</sub>CO<sub>3</sub> (1 ml) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.05 equiv.) at 80 °C, in nitrogen atmosphere. The reaction time (48 h) was determinate by TLC. The reaction mixture was extracted, after cooling, with chloroform (3×20 ml) followed by extraction with a saturated solution of NaCl (20 mL). After separation of the phases, the aqueous layer was acidified with HCl until pH = 1. The suspension obtained was filtered, and washed with diethyl ether giving the pure 5-(5'-formylthiophen-2'-yl)thiophene-2-carboxylic acid, **2c** as a yellow solid (53 %). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.50 (d, 1H, 4'-H, *J* = 4.0 Hz), 7.61 (d, 1H, 3'-H, *J* = 4.0Hz), 7.71 (d, 1H, 4-H, *J* = 4.0 Hz), 8.02 (d, 1H, 3-H, *J* = 4.0 Hz), 9.91 (s, 1H, CHO) ppm. (CAS: 886508-47-0).

### General procedure for the synthesis of *N,N*-diphenylhydrazones **3a-b** and **7c** by condensation reaction.<sup>2</sup>

A solution of *N,N*-diphenylhydrazine hydrochloride **1** (1 equiv.) in ethanol (5 mL) was added dropwise into a solution of the corresponding aldehyde **2c** (1 equiv.) in ethanol (5 mL). The mixture was stirred during 5 h, at room temperature, then poured into water, and extracted with ethyl acetate (3 × 50 mL). Evaporation of the organic layer under reduced pressure, after being dried with anhydrous magnesium sulfate, originate the pure compounds.

2,2-Diphenyl-1-((thieno[3,2-*b*]thiophen-2''-yl)methylene)hydrazine, **3a**.<sup>3</sup> Yellow solid (66 %). Mp: 158-160 °C. UV (ethanol): λ<sub>max</sub> nm (ε, M<sup>-1</sup> cm<sup>-1</sup>) 368, (24,867). IR (liquid film) ν 3098, 2358, 1586, 1485, 1451, 1369, 1279, 1208, 1093, 1067, 1025, 944, 904, 820, 789, 766, 751, 713 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.05 (s, 1H, 3''-H), 7.20-7.24 (m, 7H, 5''-H, 2x 2'-H, 2x 6'-H, 2x 4'-H), 7.32 (s, 1H, H<sub>a</sub>), 7.42-7.42 (m, 4H, 2x 3'-H, 2x 5'-H) ppm. <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ 118.5,

119.8, 122.4, 124.7, 127.5, 129.8, 130.5, 139.1, 143.2, 144.2 ppm. HRMS:  $m/z$  (EI) for  $C_{19}H_{14}N_2S_2$ ; calcd 334.0598; found: 334.0597.

2,2-Diphenyl-1-((5''-(thiophen-2''-yl)thiophen-2''-yl)methylene)hydrazine, **3b**. Yellow oil (72 %). UV (ethanol):  $\lambda_{max}$  nm ( $\epsilon$ ,  $M^{-1} cm^{-1}$ ) 373, (26,060). IR (liquid film)  $\nu$  3438, 2964, 2921, 1644, 1590, 1492, 1367, 1302, 1260, 1207, 1171, 1093, 1069, 1021, 748  $cm^{-1}$ .  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  6.81 (d, 1H, 3''-H,  $J = 3.6$  Hz), 7.05-7.07 (m, 2H, 2x 4'-H), 7.22-7.28 (m, 9H,  $H_a$ , 2x 2'-H, 2x 6'-H, 2x 4''-H, 3'''-H, 4'''-H, 5'''-H), 7.45-7.49 (m, 4H, 5'-H, 3'-H).  $^{13}C$  NMR (100.6 MHz,  $CDCl_3$ )  $\delta$  122.4, 123.6, 123.8, 124.4, 124.6, 127.0, 127.9, 129.8, 130.1, 137.0, 137.6, 140.6, 143.2 ppm.

5-(5'-(*N,N*-Diphenylhydrazone)thiophen-2'yl)thiophene-2-carboxylic acid, **7c**. Yellow solid (55 %). UV (ethanol):  $\lambda_{max}$  nm ( $\epsilon$ ,  $M^{-1} cm^{-1}$ ) 416, (12,562). IR (liquid film)  $\nu$  3413 (O-H), 1657 (C=O)  $cm^{-1}$ .  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  6.82 (d, 1H, 4'-H,  $J = 4.0$  Hz), 7.16-7.26 (m, 8H, 2x 2''-H, 2x 6''-H, 2x 4''-H, 3'-H, 4-H), 7.42-7.46 (m, 4H, 2x 3''-H, 2x 5''-H), 7.77 (d, 1H, 3-H,  $J = 4.0$  Hz) ppm.  $^{13}C$  NMR (100.6 MHz,  $DMSO-d_6$ )  $\delta$  121.8, 122.0, 125.0, 125.3, 126.4, 129.4, 130.2, 132.7, 134.3, 134.7, 141.7, 142.6, 146.1, 162.5 ppm. HRMS:  $m/z$  (ESI)  $[M+H]^+$  found 405.0726;  $C_{22}H_{17}N_2O_2S_2$  requires 405.0731.

*General procedure for the synthesis of N,N-diphenylhydrazone formyl derivatives 4 by Vilsmeier formylation.*<sup>4-5</sup>

Precursors **3** (1 equiv.) were dissolved in dry DMF (1.5 equiv.) and 1,2-dichloroethane.  $POCl_3$  was added to the solution at 0 °C. The reaction mixture was stirred at room temperature during 6 h, after which the solution was then transferred gradually into 10 mL of a saturated aqueous sodium acetate solution and stirred during 30 min. The organic phase was diluted with diethyl ether (25 mL),

washed with a saturated NaHCO<sub>3</sub> aqueous solution (2 × 25 mL), and dried with anhydrous MgSO<sub>4</sub>. The crude aldehydes were obtained after evaporation of the organic layer under reduced pressure. The purification of the crude compounds was made using silica gel column chromatography, with mixtures of dichloromethane and light petroleum with increasing polarity giving the pure products.

5-(*N,N*-Diphenylhydrazone)thieno[3,2-*b*]thiophene-2-carbaldehyde, **4a**.<sup>3</sup> Yellow solid (58 %). Mp: 139-141 °C. UV (ethanol):  $\lambda_{\max}$  nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>) 420, (29,750). IR (liquid film)  $\nu$  1663 (C=O) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.06 (s, 1H, 6-H), 7.20-7.28 (m, 7H, 2x 2'-H, 2x 6'-H, 2x 4'-H, H<sub>a</sub>), 7.44-7.48 (m, 4H, 2x 3'-H, 2x 5'-H), 7.87 (s, 1H, 3-H), 9.93 (s, 1H, CHO) ppm. HRMS: m/z (EI) for C<sub>20</sub>H<sub>14</sub>N<sub>2</sub>OS<sub>2</sub>; calcd 362.0548; found: 362.0549.

5-(5'-(*N,N*-Diphenylhydrazone)thiophen-2'yl)thiophene-2-carbaldehyde, **4b**.<sup>3</sup> Yellow solid (45 %). UV (ethanol):  $\lambda_{\max}$  nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>) 440, (23,588). IR (liquid film)  $\nu$  1660 (C=O) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.83 (d, 1H, 4'-H, *J* = 4.0 Hz), 7.19-7.30 (m, 9H, 2x 2''-H, 2x 6''-H, 2x 4''-H, 3'-H, 4-H, H<sub>a</sub>), 7.43-7.47 (m, 4H, 2x 3''-H, 2x 5''-H), 7.68 (d, 1H, 3-H, *J* = 4.0 Hz), 9.87 (s, 1H, CHO) ppm. <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>)  $\delta$  122.4, 124.1, 125.0, 126.3, 126.9, 129.2, 129.86, 135.1, 137.4, 141.5, 143.0, 143.8, 147.3, 182.4 ppm. HRMS: m/z (EI) for C<sub>22</sub>H<sub>16</sub>N<sub>2</sub>OS<sub>2</sub>; calcd 388.0704; found: 388.0706.

*General procedure for the synthesis of push-pull N,N-diphenylhydrazone chromophores 5a-b by Knoevenagel condensation of aldehydes 4a-b with 2-cyanoacetic acid.*<sup>4</sup>

Two drops of piperidine were added to a solution of aldehydes **4a-b** (1 equiv.) and cyanoacetic acid (1.2 equiv.) in ethanol (10 mL). The solution was stirred at reflux during 6 h. After this time the cooled mixture was evaporated to dryness. Recrystallization using ethanol/diethyl ether gave the pure products.

2-Cyano-3-(5'-(*N,N*-diphenylhydrazone)thieno[3,2-*b*]thiophen-2'-yl)acrylic acid, **5a**. Yellow solid (58 %). Mp: 181-183 °C. UV (ethanol):  $\lambda_{\max}$  nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>) 435, (30,740). IR (liquid film)  $\nu$  3416 (O-H), 2265 (C≡N), 1601 (C=O) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  7.14 (m, 4H, 2x 2''-H, 2x 6''-H), 7.23-7.27 (m, 2H, 2x 4''-H), 7.35 (s, 1H, 6'-H), 7.43-7.53 (m, 5H, H<sub>a</sub>, 2x 3''-H, 2x 5''-H), 7.97 (s, 1H, 3'-H), 8.18 (s, 1H, 3-H) ppm. <sup>13</sup>C NMR (100.6 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  118.4, 119.0, 120.2, 122.0, 125.2, 127.7, 128.7, 130.2, 131.3, 137.8, 138.9, 139.2, 141.6, 142.4, 143.2, 147.2, 148.0 ppm. HRMS: m/z (ESI) [M+H]<sup>+</sup> found 430.0780; C<sub>23</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub>S<sub>2</sub> requires 430.0684.

2-Cyano-3-((5''-(*N,N*-diphenylhydrazone)thiophen-2''-yl)thiophen-2'-yl)acrylic acid, **5b**. Yellow solid (27 %). Mp: 143-145 °C. UV (ethanol):  $\lambda_{\max}$  nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>) 456, (20,141). IR (liquid film)  $\nu$  3417 (O-H), 2261 (C≡N), 1613 (C=O) cm<sup>-1</sup>. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>)  $\delta$  6.81 (d, 1H, 4''-H, *J* = 4.0 Hz), 7.18-7.24 (m, 9H, H<sub>a</sub>, 4'-H, 3''-H, 2x 2'''-H, 2x 6'''-H, 2x 4'''-H), 7.41-7.46 (m, 4H, 2x 3'''-H, 2x 5'''-H), 7.52 (d, 1H, 3'-H, *J* = 4.4 Hz), 8.17 (s, 1H, 3-H) ppm. <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>)  $\delta$  117.4, 119.2, 122.4, 124.0, 124.9, 125.7, 127.1, 129.4, 129.9, 135.4, 135.5, 136.4, 142.7, 143.0, 144.4, 167.6, 168.1 ppm. HRMS: m/z (ESI) [M+H]<sup>+</sup> found 456.0800; C<sub>25</sub>H<sub>18</sub>N<sub>3</sub>O<sub>2</sub>S<sub>2</sub> requires 456.0840.

*General procedure for the synthesis of push-pull N,N-diphenylhydrazone chromophores 6 by Knoevenagel reaction of aldehydes 4a-b with malononitrile.*<sup>1,4</sup>

Piperidine (2 drops) was added to a solution of the corresponding aldehydes **4** (1 equiv) and malononitrile (1.2 equiv) in ethanol (10 mL). This mixture was stirred under reflux for 6 h and after cooling till room temperature was evaporated to dryness. The pure compounds were obtained after recrystallization using ethanol/diethyl ether.

2-((5'-(*N,N*-Diphenylhydrazone)thieno[3,2-*b*]thiophen-2'-yl)methylene)malononitrile, **6a**.<sup>3</sup> Yellow solid (29 %). Mp: 132-134°C. UV (ethanol):  $\lambda_{\max}$  nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>) 420, (26,766). IR (liquid film)  $\nu$

2209 (C≡N)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  7.15-7.18 (m, 4H, 2x 2''-H, 2x 6''-H), 7.23-7.28 (m, 2H, 2x 4''-H), 7.37 (s, 1H, 6'-H), 7.46-7.51 (m, 5H, 2x 3''-H, 2x 5''-H,  $H_\alpha$ ), 7.54 (s, 1H, 3'-H), 7.95 (s, 1H, 2-H) ppm.  $^{13}\text{C}$  NMR (100.6 MHz, DMSO- $d_6$ )  $\delta$  116.6, 117.7, 119.9, 122.0, 125.2, 127.1, 129.9, 130.2, 133.4, 137.7, 142.4, 143.3, 147.2 ppm. HRMS:  $m/z$  (EI) for  $\text{C}_{23}\text{H}_{14}\text{N}_4\text{S}_2$ ; calcd 410.0660; found: 410.0659.

2-((5''-(*N,N*-Diphenylhydrazone)thiophen-2''-yl)thiophen-2'-yl)methylene)malononitrile, **6b**.<sup>3</sup>  
Yellow solid (22 %). UV (ethanol):  $\lambda_{\text{max}}$  nm ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ) 416, (19,221). IR (liquid film)  $\nu$  2208 (C≡N)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.79 (d, 1H, 4''-H,  $J = 3.6$  Hz), 7.02-7.05 (m, 2H, 3''-H, 4'-H), 7.19-7.24 (m, 9H, 2-H,  $H_\alpha$ , 3'-H, 2x 2'''-H, 2x 6'''-H, 2x 4'''-H) ppm. HRMS:  $m/z$  (EI) for  $\text{C}_{25}\text{H}_{16}\text{N}_4\text{S}_2$ ; calcd 436.0816; found: 436.0818.

### 1.3-Nonlinear optical measurements

The incident beam with a fundamental wavelength of 1064 nm is focused into the center of a long cuvette (1x5 cm) containing the solution. A combination of a half wave plate and Glan polarizer allows the incident laser pulse energy to be varied in order to avoid parasitic nonlinear effects such as self-focusing or continuum generation. A high numerical aperture lens collimated the hyper-Rayleigh signal at 532 nm. Before detection the light is filtered using a narrow bandpass interference filter with a full width at half maximum transmission of 3.3 nm centered on the second harmonic wavelength (532 nm). The resulting electronic signal from a photomultiplier (Hamamatsu model H9305-04) the photomultiplier were integrated using a Stanford Research Systems gated box-car integrator (model SR250). The signal from each pulse was normalized using the second harmonic signal generated by a 1 mm  $\text{KH}_2\text{PO}_4$  plate. This allows us to compensate for fluctuations in the temporal profile of the laser pulses. All compounds were dissolved in 1,4-Dioxane. A  $10^{-2}$  M solution of *p*NA in 1,4-dioxane was used to calibrated the detection efficiency

and obtain absolute estimates of the effective hyperpolarizability  $\beta$  values.<sup>6-7</sup> The concentrations of the solutions under study were adjusted so that the hyper-Rayleigh signals remained within the dynamic range of the photomultiplier and the box-car integrator. To avoid spurious signals from suspended impurities, all solutions were filtered using membranes with a 0.2  $\mu\text{m}$  porosity. To ascertain the extent of possible multi-photon induced fluorescence overlapping with the spectral band of the detecting Hyper-Rayleigh signal, measurements are carried out using interference filters with two different transmission pass bands. The transmission of each filter at the second harmonic wavelength was carefully determined using a crystalline quartz sample as a source of second harmonic light. The narrower passband was 1.66 nm (full width at half maximum) with a transmission of 47.6 %; the transmission band of the wider filter was 3.31 nm, with a 63.5 % transmission. By comparing the signals transmitted by the two filters, the ratio of the hyper-Rayleigh signal and that of overlapping fluorescence can be estimated.<sup>8</sup> Our effective hyperpolarizability measurements are reported using the so-called T (Taylor expansion) convention<sup>6</sup> in which the  $\beta_{333}$  of *p*NA in dioxane at 1064 nm is  $40 \times 10^{-30}$  esu. This includes a correction factor of 1.88 arising from a recent measurement of the  $\text{CCl}_4$  hyper-Rayleigh scattering signal employed as an absolute reference.<sup>9</sup> The associated static second-order hyperpolarizability  $\beta_0$ , was estimated using the conventional two-level model ignoring damping.<sup>10-12</sup> These values are only meant to be indicative of the effective intrinsic second order nonlinear response, their validity is limited by the simplicity of the model.

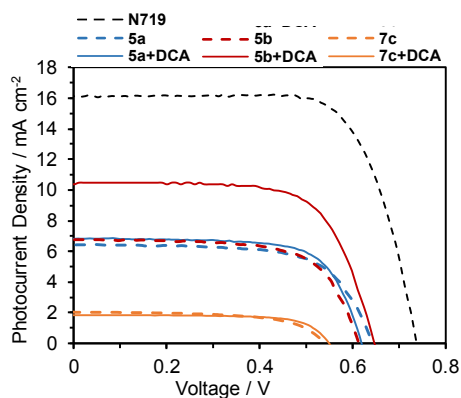
#### *1.4- Preparation and evaluation of the performance of DSSCs*

FTO-coated glasses (7  $\Omega/\text{square}$ , TCO22-7, Solaronix, Switzerland) were used for working electrodes. The photoanode was constructed from 15  $\mu\text{m}$  mesoporous transparent layer of  $\text{TiO}_2$  covered by 9  $\mu\text{m}$  of active opaque titania. The layers of titania were assembled by screen-printing of  $\text{TiO}_2$  pastes: 30 NR-D (transparent mesoporous) and 18NR-AO (opaque) both from Dyesol. The photoanodes have a circular shape with an area of 0.125  $\text{cm}^2$ . The titania electrodes were immersed

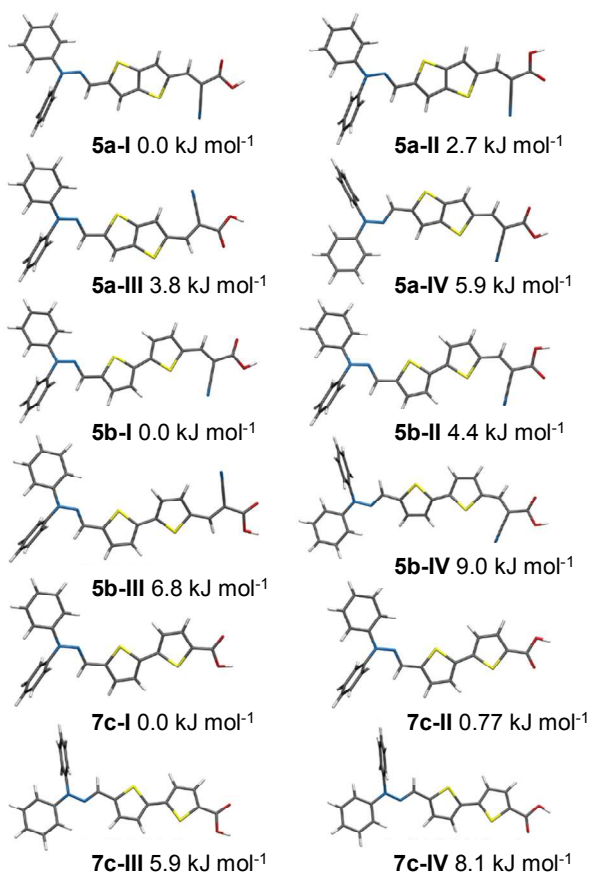


into a 0.5 mM dye solution in absolute C<sub>2</sub>H<sub>5</sub>OH and kept at 21±2 °C for 24 h. The TiO<sub>2</sub> electrodes for studies of co-adsorption were immersed during the same time in 0.5 mM solution of the dye with the addition of 50 mM of deoxycholic acid.<sup>13</sup> Counter electrodes were activated by Pt catalyst. For this screen-printable paste (T/SP, Solaronix) was applied on the FTO-glasses and then sintered for 20 min at 450 °C. Counter-electrode and dye-covered titania electrode were sandwiched and sealed with Surlyn® (Meltonix 1170-60) in a hot-press. High Performance iodine-based electrolyte (EL-HPE, Dyesol) was used in the cells. In each sensitizing condition, several cells were tested. Oriel class A solar simulator, (Newport, USA) was used to provide an irradiance equivalent to AM 1.5G. The irradiance was adjusted using calibrated silicon detector (Newport 70356). The current-voltage responses of the DSSCs were collected using ZENNIUM workstation (Ref. 2425-C, Zahner Elektrik, Germany). Mask with an aperture area of 0.25 cm<sup>2</sup> was used for measurements of the photocurrent-voltage response. The incident-photon-to-electron conversion efficiency (IPCE) spectra were collected using a PC-operated monochromator (Newport Cornerstone 74125) and a Lock-in amplifier (Newport Merlin 70104). Photon flux of incident light was calibrated using a Si photodiode (Newport 70356). The bias light with intensity of 30 mW cm<sup>-2</sup> was supplied by a 100 W halogen lamp.

## 2-Figures



**Figure S1.** Photocurrent–Voltage curves of the cells assembled using dye **N719** as a reference and synthesized dyes **5a-b**, **7c**. The sensitization was in 0.5 mM ethanol solutions of the corresponding dye (dashed lines) and with 50 mM DCA addition (solid lines).



**Figure S2.** DFT B3LYP/6-31G(d,p) optimized geometries and relative energies of the minima for dyes **5a**, **5b** and **7c**.

### 3- References

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