Photochromic Spiro-Indoline Naphthoxazines and Naphthopyrans

in Dye-Sensitized Solar Cells.

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General information

Electrochemical characterization

Cyclic voltammetry measurements were carried out in a three-electrode electrochemical cell equipped with a flat platinum working electrode (7 mm²), a platinum-made counter electrode and an Ag/AgNO₃ reference electrode. The potentials were calibrated using the Fc⁺/Fc couple as an internal standard before and after each measurement, assuming this value to be -5.1 eV. The electrolyte consisted of a 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) solution in anhydrous and degassed dichloromethane using a dye concentration of 10^{-3} M. The scanning rate was 100 mV/s.

Theoretical calculations

The geometry optimization was carried out using the ADF modeling suite 2016 software with a revPBE GGA functional corrected for dispersion using Grimme 3 methodology with TZ2P sets. The orbital simulation was eventually carried out using a single-point modeling with a B3LYP hybrid functional + dispersion and TZ2P sets in a COSMO model for dichloromethane on the previously optimized geometries.

Solar cells fabrication and characterization

TiO₂ thin films with a specific thickness and a total area of 0.36 cm² were screen printed in Solaronix (Switzerland) using a TiO₂ nanoparticle paste (Ti-Nanoxide HT/SP). Throughout the manuscript, opaque device refers to a device that includes an additional TiO₂ layer of about $3-4 \,\mu\text{m}$ in thickness above the mesoporous TiO₂ (Solaronix; Ti-Nanoxide R/SP). The active area of the solar cells (0.36 cm2) was estimated from the printing masks and re-measured with a caliper. Beforehand, the electrodes were cleaned with absolute ethanol and dried under an argon flux. These photoanodes were then treated by immersion into a freshly prepared 4.1 mmol.I⁻¹ TiO₂ aqueous suspension at 70 °C for 20 min. The electrodes were then cooled to room temperature and rinsed with distilled water then absolute ethanol, followed by drying under an argon flux. The electrodes were then sintered under air at 500 °C for 20 min, following the heating procedure reported in Figure S1. The photoanodes were then cooled down to 80 °C and sensitized through immersion in the dyeing solution for 16 h at room temperature in the dark ([Dye] = 0.5 mM; Dye/chenodeoxycholic acid in a 1:10 ratio; $CHCl_3/^tBuOH = 1/1$ (vol/vol)). The drilled counter electrodes were coated with a thin layer of platisol (Solaronix) and charred under air at 500 °C using the same heating procedure as presented in Figure S. The sensitized photoanode was rinsed with dichloromethane and absolute ethanol and dried with an argon flux. Both electrodes were then sealed together using a Surlyn thermoglueing polymer (60 μ m thick) using a heating press at 105 °C for 16 s. The cell was then filled with either our home-made electrolyte (90 mM of I₂ and 0.5 M Lil in acetonitrile) or the commercial lodolyte (Solaronix) via the pre-drilled hole using a vacuum pump. The electrolyte injection hole on the counter electrode was then sealed with the aid of Surlyn underneath the thin glass cover using heat. A contact along the cell edges was created.



Figure S1: heating procedure for electrode sintering

Before measurements, the AM 1.5 G simulator (Newport class AAA) was calibrated using a reference silicon photodiode equipped with an infrared-cut-off filter (KG3; Schott). This reference photodiode consisted of a readout device and a 2 cm × 2 cm calibrated solar cell made from monocrystalline silicon with a KG3 window. The cell was also equipped with a thermocouple assembled in accordance with IEC 60904-2. The certification is accredited by the National Institute of Standards and Technology to the ISO-17025 standard and is traceable to the National Renewable Energy Laboratory. The currentvoltage characteristics of the cells were measured under dark and under the AM 1.5 G (1,000 W m⁻²) irradiation condition, which was achieved by applying an external potential bias to the cell while measuring the generated photocurrent with a Keithley model 2400 digital source meter. Measurement for the cells was from +0.7 to -0.2 V, divided into 45 points, with a speed of 20 mV s⁻¹. The devices were masked before the measurements to attain an illuminated active area of 0.36 cm². The IPCE measurements were recorded with a Xenon lamp equipped with a monochromator from 350 to 800 nm. The impedance measurements were performed under different illumination conditions (i.e. in the dark and under white irradiation) using an Autolab PGSTAT30 FRA2 potentiostat in the $10^5 - 10^{-1}$ Hz frequency range. For dark conditions, the applied DC potential ranged from 0V to the OCV reached under 1-sun illumination using the AM1.5G solar simulator. The measurements under white illumination were performed by applying a potential equal to the observed OCV under constant illumination over a wide range of DC light intensities. The NOVA 2.1. software was used to control the potentiostat and generate the data while the resulting spectra were fit using the ZView software (Scribner).

Synthetic details

Synthesis of compounds **2** and **3** was adapted from an established procedure. The obtained spectroscopic properties were in agreement with those previously reported in the literature.¹

4-formyl-3-methoxynaphthalen-1-yl trifluoromethanesulfonate (4)



To a solution of dicholoromethyl methyl ether (0.19 mL, 2.1 mmol) and titanium tetrachloride (0.23 mL, 2.1 mmol) in anhydrous CH_2Cl_2 (20 mL) at 0 °C was added dropwise a solution of **3** (300 mg, 0.98 mmol) in anhydrous CH_2Cl_2 (6 mL). The solution was left to react at rt during 16 h and then it was quenched with a 1M solution of HCl for 15 minutes. Then, the organic phase was extracted with CH_2Cl_2 , dried over Na_2SO_4 and concentrated under reduced pressure. The crude was purified by column chromatography on silica gel (eluent: hexane/ CH_2Cl_2 55:45). Yield: yellowish solid (240 mg, 76%).

M.p: 82 - 84 °C. ¹H NMR (400 MHz, CDCl₃) δ 10.84 (s, 1H), 9.31 (d, *J* = 8.6 Hz, 1H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.72 (ddd, *J* = 8.6, 7.0, 1.3 Hz, 1H), 7.56 (ddd, *J* = 8.3, 7.0, 1.0 Hz, 1H), 7.32 (s, 1H), 4.08 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 190.8, 163.0, 150.8, 133.0, 131.4, 126.5, 125.5, 121.5, 121.0, 118.8 (q, *J*_{C-F} = 320.7 Hz), 116.9, 105.5, 57.2. ¹⁹F NMR (376 MHz, CDCl₃) δ -72.99. Elemental Analysis (calcd, found for C₁₃H₉F₃O₅S): C (46.71, 46.70), H (2.71, 2.68), S (9.59, 9.27).

4-formyl-3-hydroxynaphthalen-1-yl trifluoromethanesulfonate (5)



To a solution of **4** (1.04 g, 3.11 mmol) in chloroform (100 mL) at 0 °C was added dropwise BBr₃ (1 M in CH_2Cl_2 , 7.78 mL, 7.78 mmol). The solution was left to react at rt during 16 h and then it was quenched with a saturated solution of NaHCO₃ for 15 minutes. Then, the organic phase was extracted with CH_2Cl_2 , dried over Na_2SO_4 and concentrated under reduced pressure. The crude was purified by column chromatography on silica gel (eluent: hexane/CH₂Cl₂ 7:3). Yield: white solid (840 mg, 84%).

M.p: 81 - 83 °C. ¹H NMR (400 MHz, CDCl₃) δ 13.20 (s, 1H), 10.77 (s, 1H), 8.36 (d, *J* = 8.6 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.73 (t, *J* = 7.8 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.18 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 192.9, 164.6, 151.7, 134.2, 130.8, 126.0, 122.5, 121.3, 119.3, 118.8 (q, J_{C-F} = 320.6 Hz), 111.4, 111.3. ¹⁹F NMR (376 MHz, CDCl₃) δ -73.08. Elemental Analysis (calcd, found for C₁₂H₇F₃O₅S): C (45.01, 45.03), H (2.20, 2.13), S (10.01, 9.87).

1,3,3-trimethyl-2-methylene-N,N-bis(4-octylphenyl)indolin-5-amine (6)



To a solution of 5-bromo-1,3,3-trimethyl-2-methyleneindoline (2.44 g, 9.81 mmol) in anhydrous and degassed toluene (50 mL) were added diphenylamine (4.12 g, 10.4 mmol), potassium *tert*-butoxide (1.41 g, 12.5 mmol), $Pd_2(dba)_3$ (174 mg, 0.19 mmol) and tri*-tert*-butylphosphonium tetrafluoroborate (221 mg, 0.76 mmol) and the solution was stirred at 100 °C during 18 h. Then, the reaction was quenched with water and then the organic phase was extracted with CH_2Cl_2 , dried with Na_2SO_4 and concentrated under reduced pressure. The resulting crude was purified by column on silica gel (eluent: pure petroleum ether to petroleum ether/ethyl acetate 85:15). Yield: yellow oil (3.44 g, 63%).

M.p: 170 - 172 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.20 – 7.16 (m, 4H), 6.96 – 6.86 (m, 6H), 6.44 (d, *J* = 8.2 Hz, 1H), 3.81 (s, 2H), 3.03 (s, 3H), 1.69 (s, 4H), 1.35 (s, 12H), 1.27 (s, 6H), 0.75 (s, 18H). ¹³C NMR (100 MHz, CDCl₃) δ 163.1, 146.0, 142.9, 142.8, 139.8, 138.9, 126.8, 125.6, 121.9, 120.9, 105.1, 73.1, 57.4, 44.3, 38.2, 32.5, 31.9, 31.7, 30.0, 29.0. Elemental Analysis (calcd, found for C₄₀H₅₆N₂): C (85.05, 83.89), H (9.99, 9.81), N (4.96, 4.86).

6'-bromo-1,3,3-trimethylspiro[indoline-2,3'-naphtho[2,1-b][1,4]oxazine] (7)



To a solution of 4-bromonaphthalen-2-ol (2.12 g, 9.50 mmol) in acetic acid (60 mL) and water (10 mL), is added dropwise at 0 °C a solution of NaNO₂ (1.13 mg, 16.3 mmol) in water (20 mL). The reaction is stirred at the same temperature for 1 h. Then, the orange solid that precipitated was filtered off, washed with water and dried. Then, without further purification, it was dissolved in anhydrous toluene (30 mL) and the solution was heated at 70 °C, when a solution of 1,3,3-trimethyl-2-methyleneindoline (1.57 g, 9.06 mmol) in toluene (20 mL) was added dropwise. After stirring the mixture for 1.5 h at this temperature, the solvent was removed under reduced pressure and the crude was purified by column chromatography on silica gel (eluent: from petroleum ether/CH₂Cl₂ 7:3 to 6:4). Final purification was achieved by trituration in methanol. Yield: colorless solid (1.6 g, 65%).

M.p: 154 - 156 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.60 (ddd, *J* = 8.4, 1.3, 0.6 Hz, 1H), 8.12 (ddd, *J* = 8.4, 1.3, 0.6 Hz, 1H), 7.78 (s, 1H), 7.62 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 1H), 7.50 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 1H), 7.39 (s, 1H), 7.22 (td, *J* = 7.6, 1.3 Hz, 1H), 7.09 (dd, *J* = 7.6, 0.9 Hz, 1H), 6.91 (td, *J* = 7.6, 0.9 Hz, 1H), 6.58 (d, *J* = 7.6 Hz, 1H), 2.76 (s, 3H), 1.36 (s, 3H), 1.36 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 151.3, 147.6, 143.9, 135.8, 131.6, 128.2, 127.9, 127.9, 127.2, 125.6, 123.9, 122.9, 122.1, 121.6, 121.0, 120.2, 107.3, 99.2,

52.0, 29.8, 25.6, 20.9. Elemental Analysis (calcd, found for C₂₂H₁₉BrN₂O): C (64.87, 65.38), H (4.70, 4.62), N (6.88, 6.75).

6'-bromo-1,3,3-trimethyl-*N*,*N*-bis(4-octylphenyl)spiro[indoline-2,3'-naphtho[2,1-*b*][1,4]oxazin]-5-amine (8)



To a solution of 4-bromonaphthalen-2-ol (1.30 g, 5.83 mmol) in acetic acid (40 mL) and water (5 mL), is added dropwise at 0 °C a solution of NaNO₂ (680 mg, 9.91 mmol) in water (12 mL). The reaction is stirred at the same temperature for 1 h. Then, the orange solid that precipitated was filtered off, washed with water and dried. Then, without further purification, it was dissolved in anhydrous toluene (30 mL) and the solution was heated at 70 °C, when a solution of **6** (3.13 g, 5.54 mmol) in toluene (20 mL) was added dropwise. After stirring the mixture for 3 h at this temperature, the solvent was removed under reduced pressure and the crude was purified by column chromatography on silica gel (eluent: from petroleum ether/CH₂Cl₂ 7:3 to 6:4). Eventually, a second column chromatography was required to obtain the pure product (eluent: from petroleum ether/toluene 9:1 to 7:3). Yield: yellow solid (1.0 g, 22%).

M.p: 124 - 126 °C. ¹H NMR (400 MHz, CD₂Cl₂) δ 8.60 (d, *J* = 8.4 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 7.78 (s, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.46 (s, 1H), 7.23 (d, *J* = 8.6 Hz, 4H), 6.98 - 6.90 (m, 5H), 6.85 (d, *J* = 2.0 Hz, 1H), 6.49 (d, *J* = 8.2 Hz, 1H), 2.74 (s, 3H), 1.71 (s, 4H), 1.36 (s, 12H), 1.32 (s, 3H), 1.23 (s, 3H), 0.75 (s, 18H). ¹³C NMR (100 MHz, CDCl₃) δ 151.1, 145.9, 143.9, 143.6, 143.1, 141.4, 137.0, 131.7, 129.2, 128.4, 127.9, 127.9, 127.2, 126.9, 125.6, 125.5, 125.5, 123.9, 122.9, 122.3, 122.2, 121.0, 120.0, 107.7, 99.3, 57.4, 52.0, 38.2, 32.5, 31.9, 31.7, 29.9, 25.6, 21.6, 20.8. Elemental Analysis (calcd, found for C₅₀H₆₀BrN₃O): C (75.17, 75.15), H (7.57, 7.31), N (5.26, 5.47).

1',3',3'-trimethylspiro[benzo[f]chromene-3,2'-indolin]-6-yl trifluoromethanesulfonate (9)



A solution of **5** (190 mg, 0.59 mmol) and 1,3,3-trimethyl-2-methyleneindoline (0.11 mL, 0.59 mmol) in ethanol (15 mL) was stirred at 70 °C for 6 h. Then, the solvent was removed under reduced pressure and the crude was purified by column chromatography on silica gel (eluent: from pure hexane to hexane/ethyl acetate 95:5). Yield: pinkish solid (273 mg, 97%).

M.p: 123 - 125 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, *J* = 8.6 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.61 – 7.52 (m, 2H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 7.2 Hz, 1H), 7.05 (s, 1H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.56 (d, *J* = 7.7 Hz, 1H), 5.87 (d, *J* = 10.5 Hz, 1H), 2.75 (s, 3H), 1.35 (s, 3H), 1.22 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 152.0, 147.9, 145.9, 136.4, 130.7, 128.3, 127.9, 125.1, 124.3, 121.9, 121.7, 121.6, 121.2, 119.7, 119.3, 118.8 (q, J_{C-F} = 320.5 Hz), 111.6, 110.2, 107.1, 105.4, 52.0, 29.0, 25.9, 20.3. ¹⁹F NMR (376 MHz, CDCl₃) δ -73.29. Elemental Analysis (calcd, found for C₂₄H₂₀F₃NO₄S): C (60.63, 60.51), H (4.24, 4.60), N (2.95, 2.78), S (6.74, 6.30).

5'-(bis(4-octylphenyl)amino)-1',3',3'-trimethylspiro[benzo[*f*]chromene-3,2'-indolin]-6-yl trifluoromethanesulfonate (10)



A solution of **5** (130 mg, 0.41 mmol) and **6** (230 mg, 0.41 mmol) in ethanol (15 mL) was stirred at 70 °C for 6 h. Then, the solvent was removed under reduced pressure and the crude was purified by column chromatography on silica gel (eluent: from pure hexane to hexane/ethyl acetate 98:2). Yield: greenish solid (324 mg, 92%).

M.p: 111 - 113 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.11 (d, *J* = 8.6 Hz, 1H), 8.04 (d, *J* = 8.3 Hz, 1H), 7.66 – 7.61 (m, 1H), 7.59 (d, *J* = 10.6 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.28 (d, *J* = 8.7 Hz, 4H), 7.19 (s, 1H), 7.07 (d, *J* = 8.7 Hz, 4H), 7.03 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.95 (d, *J* = 2.1 Hz, 1H), 6.51 (d, *J* = 8.2 Hz, 1H), 5.91 (d, *J* = 10.5 Hz, 1H), 2.80 (s, 3H), 1.77 (s, 4H), 1.43 (s, 12H), 1.29 (s, 3H), 1.24 (s, 3H), 0.83 (s, 18H). ¹³C NMR (100 MHz, CDCl₃) δ 152.1, 146.0, 145.9, 144.0, 143.0, 140.9, 137.6, 130.7, 128.3, 126.9, 125.3, 125.1, 124.2, 122.2, 121.8, 121.6, 121.2, 120.3, 119.4, 118.9 (q, J_{C-F} = 320.5 Hz), 111.6, 110.2, 107.3, 105.5, 57.4, 52.1, 38.2, 32.5, 31.9, 31.6, 29.1, 26.0, 22.8, 20.3, 14.3. ¹⁹F NMR (376 MHz, CDCl₃) δ -73.19. Elemental Analysis (calcd, found for C₅₂H₆₁F₃N₂O₄S): C (72.03, 71.48), H (7.09, 7.00), N (3.23, 3.03), S (3.70, 3.33).

4-(1,3,3-trimethylspiro[indoline-2,3'-naphtho[2,1-b][1,4]oxazin]-6'-yl)benzoic acid (SINO-1)



A solution of **7** (210 mg, 0.52 mmol), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic acid (122 mg, 0.49 mmol), potassium acetate (152 mg, 1.5 mmol) in a mixture of 1,4-dioxane/water (20 and 1.5 mL respectively) was degassed for 30 minutes. Then, Pd(dppf)Cl₂ (21 mg, 0.03 mmol) was added and the mixture was left to react at 80 °C during 16 h. Water and diethyl ether were added and then the organic layer was extracted with ether, dried with Na₂SO₄ and concentrated under reduced pressure. The resulting crude was purified by column on silica gel (eluent: from CH₂Cl₂ to CH₂Cl₂/methanol 96:4). The resulting solid was dissolved in CH₂Cl₂, then precipitated with hexane affording the expected compound by filtration as a whitish solid (82 mg, 38%).

M.p: 221 - 223 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.72 (d, *J* = 8.5 Hz, 1H), 8.26 (d, *J* = 8.2 Hz, 2H), 7.86 (s, 1H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.67 – 7.56 (m, 3H), 7.40 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.26 – 7.20 (m, 1H), 7.11 (d, *J* = 7.0 Hz, 1H), 7.06 (s, 1H), 6.92 (t, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 7.8 Hz, 1H), 2.82 (s, 3H), 1.42 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 172.0, 151.4, 147.6, 145.6, 143.6, 141.6, 135.9, 131.4, 130.4, 130.2, 128.7, 128.2, 127.4, 127.3, 125.8, 124.7, 123.0, 122.1, 121.6, 120.1, 117.9, 107.3, 98.9, 52.0, 29.8, 25.6, 21.0. HRMS (MALDI): calcd. for C₂₉H₂₃N₂O₃ [M-H]⁺, 447.17032; found 447.170.

(*E*)-3-(4-(5-(bis(4-octylphenyl)amino)-1,3,3-trimethylspiro[indoline-2,3'-naphtho[2,1-*b*][1,4]oxazin]-6'-yl)phenyl)-2-cyanoacrylic acid (SINO-2)



A solution of **8** (184 mg, 0.23 mmol), (E)-2-cyano-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)phenyl)acrylic acid (69 mg, 0.23 mmol), potassium acetate (68 mg, 0.69 mmol) in a mixture of 1,4dioxane/water (20 and 1 mL respectively) was degassed for 30 minutes. Then, Pd(dppf)Cl₂ (9 mg, 0.01 mmol) was added and the mixture was left to react at 80 °C during 16 h. At that point, to increase the conversion of the starting material, additional amounts of Pd(dppf)Cl₂ (9 mg, 0.01 mmol) and boronic ester (69 mg, 0.23 mmol) were added prior to degassing the solution and stirring again the mixture at the same temperature for 32 h. Then, water and ethyl acetate were added and then the organic layer was extracted with ethyl acetate, dried with Na₂SO₄ and concentrated under reduced pressure. The resulting crude was purified by column on silica gel (eluent: from pure CH₂Cl₂ to CH₂Cl₂/methanol 9:1). Yield: greenish solid (98 mg, 47%).

M.p: 203 - 205 °C. ¹H NMR (400 MHz, THF-bis) δ 8.70 (d, *J* = 8.5 Hz, 1H), 8.33 (s, 1H), 8.17 (d, *J* = 7.3 Hz, 2H), 7.85 - 7.78 (m, 2H), 7.66 (d, *J* = 7.8 Hz, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 8.6 Hz, 4H), 7.14 (s, 1H), 6.94 - 6.86 (m, 6H), 6.52 (d, *J* = 8.8 Hz, 1H), 2.75 (s, 3H), 1.73 (s, 4H), 1.34 (s, 15H), 1.27 (s, 3H), 0.76 (s, 18H). ¹³C NMR (100 MHz, THF-bis) δ 151.9, 147.1, 145.2, 144.5, 143.7, 142.4, 142.0, 138.4, 132.7, 131.6, 128.3, 127.9, 127.7, 126.7, 126.5, 125.5, 124.2, 123.2, 123.0, 121.0, 118.8, 108.7, 99.9, 58.0, 52.7, 38.9, 33.2, 32.4, 32.2, 30.1, 26.0, 21.1. HRMS (MALDI): calcd. for C₆₀H₆₆N₄O₃, 890.51294; found 890.512.

4-(1',3',3'-trimethylspiro[benzo[f]chromene-3,2'-indolin]-6-yl)benzoic acid (NIPS-1)



A solution of **9** (100 mg, 0.21 mmol), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic acid (55 mg, 0.22 mmol), sodium acetate (52 mg, 0.63 mmol) in a mixture of 1,4-dioxane/water (20 and 2 mL respectively) was degassed for 30 minutes. Then, Pd(dppf)Cl₂ (8 mg, 0.01 mmol) was added and the mixture was left to react at 80 °C during 16 h. Water and CH_2Cl_2 were added and then the organic layer was extracted with CH_2Cl_2 , dried with Na_2SO_4 and concentrated under reduced pressure. The resulting crude was purified by column on silica gel (eluent: from hexane/ethyl acetate 3:1 to 2:3 with 5% methanol). Yield: pinkish solid (56 mg, 59%).

M.p: 249 - 251 °C. ¹H NMR (400 MHz, THF) δ 8.20 (d, *J* = 8.5 Hz, 1H), 8.10 (d, *J* = 8.2 Hz, 2H), 7.85 – 7.74 (m, 2H), 7.55 – 7.46 (m, 3H), 7.27 (t, *J* = 7.6 Hz, 1H), 7.12 – 7.04 (m, 2H), 7.00 (s, 1H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.51 (d, *J* = 7.7 Hz, 1H), 5.91 (d, *J* = 10.5 Hz, 1H), 2.74 (s, 3H), 1.35 (s, 3H), 1.22 (s, 3H). ¹³C NMR (100 MHz, THF) δ 167.6, 153.0, 149.3, 145.6, 142.6, 137.7, 132.7, 131.7, 131.2, 130.8, 130.6, 128.4, 127.9, 127.7, 127.2, 126.0, 124.5, 122.3, 122.2, 120.1, 119.2, 119.0, 115.8, 112.0, 107.7, 105.5, 52.5, 29.3, 26.3, 20.7. HRMS (MALDI): calcd. for C₃₀H₂₅NO₃, 447.18289; found 447.184.

(Z)-3-(4-(5'-(bis(4-octylphenyl)amino)-1',3',3'-trimethylspiro[benzo[f]chromene-3,2'-indolin]-6yl)phenyl)-2-cyanoacrylic acid (NIPS-2)



A solution of **10** (100 mg, 0.12 mmol), (E)-2-cyano-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)phenyl)acrylic acid (36 mg, 0.12 mmol), sodium acetate (28 mg, 0.35 mmol) in a mixture of 1,4dioxane/water (20 and 2 mL respectively) was degassed for 30 minutes. Then, Pd(dppf)Cl₂ (4 mg, 6 µmol) was added and the mixture was left to react at 80 °C during 16 h. Water and CH₂Cl₂ were added and then the organic layer was extracted with CH₂Cl₂, dried with Na₂SO₄ and concentrated under reduced pressure. The resulting crude was purified by column on silica gel (eluent: from hexane/ethyl acetate 3:7 to ethyl acetate/methanol 9:1). Yield: greenish solid (29 mg, 28%). M.p: 240 - 242 °C. ¹H NMR (400 MHz, THF) δ 8.42 (s, 1H), 8.16 – 7.81 (m, 4H), 7.77 – 7.68 (m, 2H), 7.50 – 7.32 (m, 4H), 7.17 (d, *J* = 8.5 Hz, 4H), 6.91 (d, *J* = 8.5 Hz, 4H), 6.88 – 6.79 (m, 2H), 6.41 (d, *J* = 8.1 Hz, 1H), 5.87 (d, *J* = 10.4 Hz, 1H), 2.70 (s, 3H), 1.69 (s, 4H), 1.31 (s, 12H), 1.22 – 1.14 (m, 6H), 0.73 (s, 18H). ¹³C NMR (100 MHz, THF) δ 153.0, 147.2, 145.8, 144.1, 143.4, 142.6, 141.4, 139.0, 133.6, 132.8, 132.7, 131.6, 131.3, 131.2, 129.6, 129.5, 127.9, 127.6, 127.3, 126.5, 126.0, 124.6, 122.9, 122.2, 121.2, 119.1, 118.9, 111.9, 108.2, 105.5, 58.1, 52.5, 38.9, 33.2, 32.4, 32.2, 30.8, 29.4, 20.7. HRMS (MALDI): calcd. for C₆₁H₆₇N₃O₃, 889.51769; found 889.517.

NMR spectra



Figure S2. ¹H NMR (400 MHz) spectrum of 4 in CDCl₃.



Figure S3. ¹³C NMR (100 MHz) spectrum of 4 in CDCl₃.



Figure S4. ¹H NMR (400 MHz) spectrum of 5 in CDCl₃.



Figure S5. ¹³C NMR (100 MHz) spectrum of 5 in CDCl₃.



Figure S6. ¹H NMR (400 MHz) spectrum of 6 in CDCl₃.



Figure S7. ¹³C NMR (100 MHz) spectrum of 6 in CDCl₃.



Figure S8. ¹H NMR (400 MHz) spectrum of 7 in CDCl₃.



Figure S9. ¹³C NMR (100 MHz) spectrum of 7 in CDCl₃.



Figure S10. ¹H NMR (400 MHz) spectrum of 8 in CDCl₃.



Figure S11. ¹³C NMR (100 MHz) spectrum of 8 in CDCl₃.



Figure S12. ¹H NMR (400 MHz) spectrum of 9 in CD₂Cl₂.



Figure S13. $^{\rm 13}{\rm C}$ NMR (100 MHz) spectrum of 9 in CDCl₃.



Figure S14. ¹H NMR (400 MHz) spectrum of 10 in CDCl₃.



Figure S15. ¹³C NMR (100 MHz) spectrum of 10 in CDCl₃.



Figure S16. ¹H NMR (400 MHz) spectrum of SINO-1 in CDCl₃.



Figure S17. ¹³C NMR (100 MHz) spectrum of SINO-1 in CDCl₃.



Figure S18. ¹H NMR (400 MHz) spectrum of SINO-2 in THF-d8.



Figure S19. ¹³C NMR (100 MHz) spectrum of SINO-2 in THF-d8.



Figure S20. ¹H NMR (400 MHz) spectrum of NIPS-1 in THF-bis.



Figure S21. ¹³C NMR (100 MHz) spectrum of NIPS-1 in THF-bis.



Figure S22. ¹H NMR (400 MHz) spectrum of NIPS-2 in THF-d8.



Figure S23. ¹³C NMR (100 MHz) spectrum of NIPS-2 in THF-d8.

Additional Figures and Tables



Figure S24: Structures and HOMO (down) and LUMO (up) distributions and energy levels of the preliminary SINO8', SINO5 and SINO6', used to determine the most promising synthetic design. The potential of the I_3^-/I^- pair (ca. -4.95 eV) and the TiO₂ conduction band (ca. -4.10 eV) are shown in yellow and grey dashed lines respectively. As the arrows point out in the right part, the driving force for the electron injection in the TiO₂ anode (from the LUMOs) and for the dye regeneration from the redox mediator (towards the HOMO) is sufficient for the three dyes in CF and MC.



Figure S25. UV-vis absorption spectra of a) **SINO-1**, b) **SINO-2**, c) **NIPS-1** and d) **NIPS-2** in $2 \cdot 10^{-5}$ M DMF solutions at 25 °C in the dark (black), under the irradiation of a 200-600 nm/200 W xenon lamp (blue) and in the dark after the addition of 1 drop of HCl (red).



Figure S26. UV-vis absorption spectra of a) **SINO-1**, b) **SINO-2**, c) **NIPS-1** and d) **NIPS-2** in $2 \cdot 10^{-5}$ M THF solutions at 25 °C in the dark (black), under the irradiation of a 200-600 nm/200 W xenon lamp (blue) and in the dark after the addition of 1 drop of HCl (red).



Figure S27. UV-vis absorption spectra of a) **SINO-1**, b) **SINO-2**, c) **NIPS-1** and d) **NIPS-2** in $2 \cdot 10^{-5}$ M toluene solutions at 25 °C in the dark (black), under the irradiation of a 200-600 nm/200 W xenon lamp (blue) and in the dark after the addition of 1 drop of HCl (red).



Figure S28. Normalized discoloration curves of **SINO-1**, **SINO-2** and **NIPS-1** in a) THF and b) toluene $2 \cdot 10^{-5}$ M solutions at 25 °C in the dark after irradiation 60 s with a 200-600 nm/200 W xenon lamp.



Figure S29. UV-Vis spectra of **NIPS-1** (2·10⁻⁵ M in THF in the dark at 25 °C) in its close form (CF) and after the addition of 1 drop of acids of different strength.



Figure S30. Normalized discoloration curves of **SINO-1** in DMF $2 \cdot 10^{-5}$ M solutions at 25 °C in the dark after irradiation 60 s with a 200-600 nm/200 W xenon lamp with and without the addition of 1 drop of HCl.



Figure S31. Cyclic voltammogram (25 °C, in the dark) of **SINO-1**, **SINO-2**, **NIPS-1** and **NIPS-2** (1 mM) in 0.1 M Bu₄NPF₆ in CH₂Cl₂ using a 100 mV/s scan rate.



Figure S32. UV-vis absorption spectra of **SINO-1**, **SINO-2**, **NIPS-1** and **NIPS-2** adsorbed onto transparent 2 μ m TiO₂ electrodes in the absence of illumination.



Figure S33. Images of a 13 μ m DSSCs of a) **NIPS-1** and b) **NIPS-2** throughout the introduction of the homemade electrolyte showing the instantaneous coloration in the absence of illumination.



Figure S34. J-V curves of the fresh (black) and 5000 h aged (red) 13 μ m **NIPS-2**/Iodolyte-based DSSCs measured under standard irradiation conditions AM 1.5 G, 1000 W m⁻²; 25 °C (active area= 0.36 cm²).



Figure S35. IPCE spectra and integrated current of 13 μ m NIPS-2-based DSSCs devices using a) an opaque configuration and lodolyte/homebased electrolytes and b) transparent configuration using lodolyte.



Figure S36. Impedance spectroscopy characterizations of the 13 μ m **NIPS-2**-based 13 μ m DSSC using both electrolyte compositions: a-b) Nyquist plots, c-d) charge transfer resistances comparisons at the same quasi-Fermi level and e-f) chemical capacitance plots.



Figure S37. Capacitance extracted from Impedance spectroscopy characterizations of the 13 μ m **NIPS-2**-based 13 μ m DSSC using both electrolyte compositions at dark conditions (a) and under white illumination (b).



Figure S38. Nyquist plots of 13 μm DSSCs made of NIPS-2 under white light compared at the corrected voltage.

Equation S1.
$$C_{\mu} = C_{00} \exp\left(\frac{\alpha q V}{k_B T}\right)$$

where C_{00} is a constant, α is the trap distribution parameter, q is the elemental charge, V is the DC voltage applied to obtain each impedance, and k_BT is the thermal voltage.

Equation S2.
$$R_{CT} = R_{00} \exp\left(-\frac{\beta qV}{k_{PT}}\right)$$

where R_{00} is a constant and β is the transfer parameter or recombination parameter.

Table S1. α and β parameters obtained for 13 μ m E	<pre>DSSCs made of NIPS-2 after fitting the impedance</pre>
data to an equivalent circuit.	

Electrolyte	Dark		Light	
	α	β	α	β
Iodolyte	0.23	0.56	0.27	0.73
Homebased electrolyte	0.22	0.75	0.28	1.04



Figure S39. a) CRI chart and b) CIE color coordinate spectrum of transparent 13 μ m DSSCs made of NIPS-2 and lodolyte.

References

 de Azevedo, O. D. C. C.; Elliott, P. I. P.; Gabbutt, C. D.; Heron, B. M.; Lord, K. J.; Pullen, C. Synthesis and Photochromism of Novel Pyridyl-Substituted Naphthopyrans. *J. Org. Chem.* 2020, *85* (16), 10772–10796. https://doi.org/10.1021/acs.joc.0c01296.