Photochromic Spiro-Indoline Naphthoxazines and Naphthopyrans in Dye-Sensitized Solar Cells.

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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 Fe⁺/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 µm 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.l⁻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; CHCl₃/BuOH = 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 ther mgueing polymer (60 µm 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 LiI in acetonitrile) or the commercial Iodolyte (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 current–voltage 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 10⁵ – 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.  

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

To a solution of dichloromethyl methyl ether (0.19 mL, 2.1 mmol) and titanium tetrachloride (0.23 mL, 2.1 mmol) in anhydrous CH$_2$Cl$_2$ (20 mL) at 0 °C was added dropwise a solution of 3 (300 mg, 0.98 mmol) in anhydrous CH$_2$Cl$_2$ (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$_2$Cl$_2$, dried over Na$_2$SO$_4$ and concentrated under reduced pressure. The crude was purified by column chromatography on silica gel (eluent: hexane/CH$_2$Cl$_2$ 55:45). Yield: yellowish solid (240 mg, 76%).

M.p: 82 - 84 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 10.84 (s, 1H), 9.31 (d, $J$ = 8.6 Hz, 1H), 8.01 (d, $J$ = 8.3 Hz, 1H), 7.72 (dd, $J$ = 8.6, 7.0, 1.3 Hz, 1H), 7.56 (dd, $J$ = 8.3, 7.0, 1.0 Hz, 1H), 7.32 (s, 1H), 4.08 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) 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. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -72.99.

Elemental Analysis (calcd, found for C$_{13}$H$_9$F$_3$O$_5$S): 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 BBr$_3$ (1 M in CH$_2$Cl$_2$, 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 NaHCO$_3$ for 15 minutes. Then, the organic phase was extracted with CH$_2$Cl$_2$, dried over Na$_2$SO$_4$ and concentrated under reduced pressure. The crude was purified by column chromatography on silica gel (eluent: hexane/CH$_2$Cl$_2$ 7:3). Yield: white solid (840 mg, 84%).

M.p: 81 - 83 °C. $^1$H NMR (400 MHz, CDCl$_3$) 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). $^{13}$C NMR (100 MHz, CDCl$_3$) 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. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -73.08. Elemental Analysis (calcd, found for C$_{13}$H$_7$F$_3$O$_5$S): C (45.01, 45.03), H (2.71, 2.68), 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$_2$Cl$_2$, dried with Na$_2$SO$_4$ 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. $^1$H NMR (400 MHz, CDCl$_3$) 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). $^{13}$C NMR (100 MHz, CDCl$_3$) 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 C$_{40}$H$_{56}$N$_2$): 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 NaNO$_2$ (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/CH$_2$Cl$_2$ 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. $^1$H NMR (400 MHz, CDCl$_3$) 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). $^{13}$C NMR (100 MHz, CDCl$_3$) 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,
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 NaNO\(_2\) (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/\(\text{CH}_2\text{Cl}_2\) 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. \(^1\)H NMR (400 MHz, \(\text{CD}_2\text{Cl}_2\)) \(\delta\) 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). \(^{13}\)C NMR (100 MHz, \(\text{CDCl}_3\)) \(\delta\) 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, 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 \(\text{C}_{50}\text{H}_{60}\text{BrN}_{3}\text{O}\)): C (75.17, 75.15), H (7.57, 7.31), N (5.26, 5.47).

1',3',3'-trimethylspiro[benzo[j]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%).
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%).

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)Cl\(_2\) (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 Na\(_2\)SO\(_4\) and concentrated under reduced pressure. The resulting crude was purified by column on silica gel (eluent: from CH\(_2\)Cl\(_2\) to CH\(_2\)Cl\(_2\)/methanol 96:4). The resulting solid was dissolved in CH\(_2\)Cl\(_2\), 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, CDCl\(_3\)) \(\delta\) 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, CDCl\(_3\)) \(\delta\) 172.0, 151.4, 147.6, 145.6, 143.6, 141.6, 135.9, 131.4, 130.4, 128.7, 128.2, 127.4, 127.3, 125.8, 121.6, 121.0, 117.9, 107.3, 98.9, 52.0, 29.8, 25.6, 21.0. HRMS (MALDI): calcd. for C\(_{29}\)H\(_{23}\)N\(_2\)O\(_3\) [M-H]+, 447.17032; found 447.170.

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

![Diagram of SINO-2](image)

A solution of 8 (184 mg, 0.23 mmol), (E)-2-cyano-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylic acid (69 mg, 0.23 mmol), potassium acetate (68 mg, 0.69 mmol) in a mixture of 1,4-dioxane/water (20 and 1 mL respectively) was degassed for 30 minutes. Then, Pd(dppf)Cl\(_2\) (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)Cl\(_2\) (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 Na\(_2\)SO\(_4\) and concentrated under reduced pressure. The resulting crude was purified by column on silica gel (eluent: from pure CH\(_2\)Cl\(_2\) to CH\(_2\)Cl\(_2\)/methanol 9:1). Yield: greenish solid (98 mg, 47%).

M.p: 203 - 205 °C. ¹H NMR (400 MHz, THF-bis) \(\delta\) 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) \(\delta\) 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 C\(_{60}\)H\(_{60}\)N\(_4\)O\(_3\), 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 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 3:1 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]-6-yl}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-2-yl)phenyl)acrylic acid (36 mg, 0.12 mmol), sodium acetate (28 mg, 0.35 mmol) in a mixture of 1,4-dioxane/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. $^1$H 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).

$^{13}$C 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 C$_{61}$H$_{67}$N$_3$O$_3$, 889.51769; found 889.517.
**Figure S2.** $^1$H NMR (400 MHz) spectrum of 4 in CDCl$_3$.

**Figure S3.** $^{13}$C NMR (100 MHz) spectrum of 4 in CDCl$_3$. 
Figure S4. $^1$H NMR (400 MHz) spectrum of 5 in CDCl$_3$.

Figure S5. $^{13}$C NMR (100 MHz) spectrum of 5 in CDCl$_3$. 
Figure S6. $^1$H NMR (400 MHz) spectrum of 6 in CDCl$_3$.

Figure S7. $^{13}$C NMR (100 MHz) spectrum of 6 in CDCl$_3$. 
Figure S8. $^1$H NMR (400 MHz) spectrum of 7 in CDCl$_3$.

Figure S9. $^{13}$C NMR (100 MHz) spectrum of 7 in CDCl$_3$. 
Figure S10. $^1$H NMR (400 MHz) spectrum of 8 in CDCl$_3$.

Figure S11. $^{13}$C NMR (100 MHz) spectrum of 8 in CDCl$_3$. 
**Figure S12.** $^1$H NMR (400 MHz) spectrum of 9 in CD$_2$Cl$_2$.

**Figure S13.** $^{13}$C NMR (100 MHz) spectrum of 9 in CDCl$_3$. 
Figure S14. $^1$H NMR (400 MHz) spectrum of 10 in CDCl$_3$.

Figure S15. $^{13}$C NMR (100 MHz) spectrum of 10 in CDCl$_3$. 
Figure S16. $^1$H NMR (400 MHz) spectrum of SINO-1 in CDCl$_3$.

Figure S17. $^{13}$C NMR (100 MHz) spectrum of SINO-1 in CDCl$_3$. 
Figure S18. $^1$H NMR (400 MHz) spectrum of SINO-2 in THF-d8.

Figure S19. $^{13}$C NMR (100 MHz) spectrum of SINO-2 in THF-d8.
Figure S20. $^1$H NMR (400 MHz) spectrum of NIPS-1 in THF-bis.

Figure S21. $^{13}$C NMR (100 MHz) spectrum of NIPS-1 in THF-bis.
Figure S22. $^1$H NMR (400 MHz) spectrum of NIPS-2 in THF-d8.

Figure S23. $^{13}$C 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 TiO_2 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 TiO_2 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.]

|        | CF     | MC     | CF     | MC     | CF     | MC     |
|--------|--------|--------|--------|--------|--------|--------|
| Δ e^- injection |       |        |        |        |        |        |
| CB TiO_2 |       |        |        |        |        |        |
| Δ dye regeneration |       |        |        |        |        |        |
| E(eV)   | -5.40  | -5.71  | -5.61  | -5.71  | -5.70  | -5.40  |
|         | -5.71  | -5.37  | -5.61  | -5.37  | -5.71  | -5.37  |
|         | -5.37  | -5.33  | -5.61  | -5.33  | -5.71  | -5.33  |
|         | -5.33  |        | -5.61  |        | -5.71  |        |
|         | -5.61  |        | -5.61  |        | -5.71  |        |
|         | -5.71  |        | -5.71  |        | -5.71  |        |
|         | -5.71  |        | -5.71  |        | -5.71  |        |
|         | -5.71  |        | -5.71  |        | -5.71  |        |
|         | -5.71  |        | -5.71  |        | -5.71  |        |
|         | -5.71  |        | -5.71  |        | -5.71  |        |
|         | -5.71  |        | -5.71  |        | -5.71  |        |
|         | -5.71  |        | -5.71  |        | -5.71  |        |
|         | -5.71  |        | -5.71  |        | -5.71  |        |
|         | -5.71  |        | -5.71  |        | -5.71  |        |
|         | -5.71  |        | -5.71  |        | -5.71  |        |
|         | -5.71  |        | -5.71  |        | -5.71  |        |
|         | -5.71  |        | -5.71  |        | -5.71  |        |
|         | -5.71  |        | -5.71  |        | -5.71  |        |
|         | -5.71  |        | -5.71  |        | -5.71  |        |
|         | -5.71  |        | -5.71  |        | -5.71  |        |
Figure S25. UV-vis absorption spectra of a) SINO-1, b) SINO-2, c) NIPS-1 and d) NIPS-2 in 2·10⁻⁵ 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 2·10⁻⁵ 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 2·10^{-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 Bu$_4$NPF$_6$ in CH$_2$Cl$_2$ 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 μm TiO$_2$ electrodes in the absence of illumination.
Figure S33. Images of a 13 μm 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 μm 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 μm NIPS-2-based DSSCs devices using a) an opaque configuration and iodolyte/homebased electrolytes and b) transparent configuration using iodolyte.
Figure S36. Impedance spectroscopy characterizations of the 13 µm NIPS-2-based 13 µm 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 µm NIPS-2-based 13 µm 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.**

\[ C_\mu = C_{00} \exp \left( \frac{\alpha qV}{k_B T} \right) \]

where \( C_{00} \) is a constant, \( \alpha \) is the trap distribution parameter, \( q \) is the elemental charge, \( V \) is the DC voltage applied to obtain each impedance, and \( k_B T \) is the thermal voltage.

**Equation S2.**

\[ R_{CT} = R_{00} \exp \left( \frac{-R qV}{k_B T} \right) \]

where \( R_{00} \) is a constant and \( \beta \) is the transfer parameter or recombination parameter.

**Table S1.** \( \alpha \) and \( \beta \) parameters obtained for 13 μm DSSCs made of **NIPS-2** after fitting the impedance data to an equivalent circuit.

| Electrolyte                | Dark \( \alpha \) | Dark \( \beta \) | Light \( \alpha \) | Light \( \beta \) |
|---------------------------|-------------------|------------------|-------------------|------------------|
| 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 µm DSSCs made of NIPS-2 and Iodolyte.

References

(1) 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.