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# Enhanced $H_2$ production in carbazole based dyes in dye-sensitized photocatalysis

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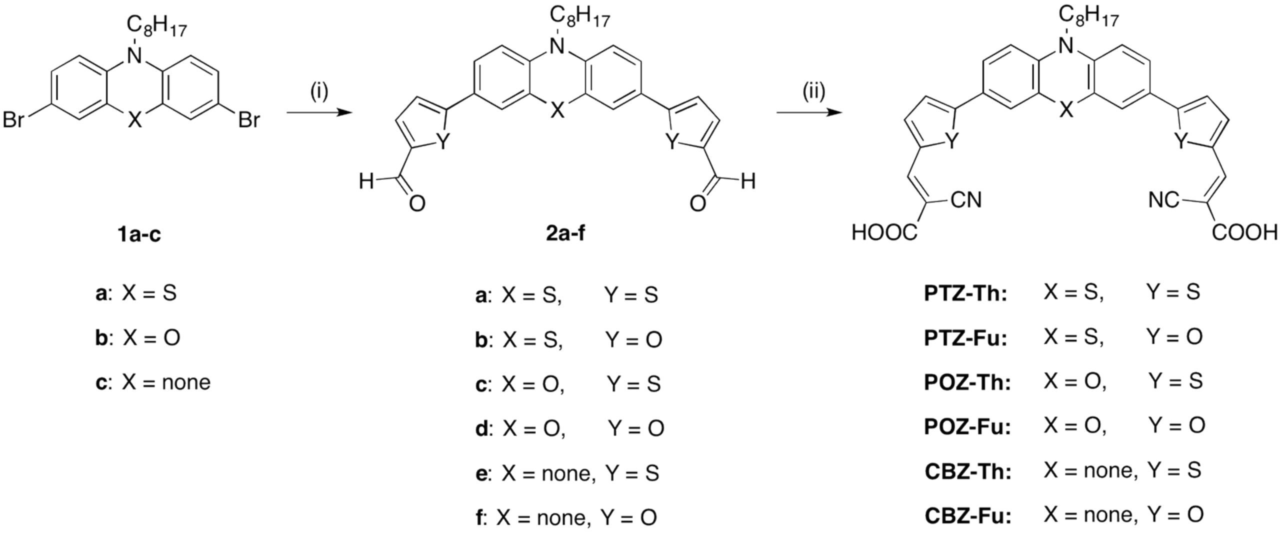
## Electronic Supplementary Material

## General information

NMR spectra were recorded with a Bruker AMX-500 spectrometer operating at 500.13 MHz ($^1$H) and 125.77 MHz ($^{13}$C). Coupling constants are given in Hz. Absorption spectra were recorded with a V-570 Jasco spectrophotometer. Infrared spectra (IR) were recorded with an ATR-FTIR Perkin–Elmer Spectrum100 spectrometer. Flash chromatography was performed with Merck grade 9385 silica gel 230–400 mesh (60 Å). Reactions performed under inert atmosphere were done in oven-dried glassware and a nitrogen atmosphere was generated with Schlenk technique. Conversion was monitored by thin-layer chromatography by using UV light (254 and 365 nm) as a visualizing agent. All reagents were obtained from commercial suppliers at the highest purity grade and used without further purification. Anhydrous solvents were purchased from Sigma-Aldrich and used without further purification. Extracts were dried with $Na_2SO_4$ and filtered before removal of the solvent by evaporation. Compounds **1a-c, 2a** and **PTZ-Th** have been prepared according to literature.[1-3]

**Scheme S1:** General synthetic procedure for dyes **PTZs**, **POZs**, **CBZs**.



**Reagents and conditions:** (i) 5-Formyl-2-aryl-boronic acid, $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ [dppf = 1,1′-bis(diphenylphosphino)ferrocene], $K_2CO_3$, DME/MeOH, microwave 100 °C, 90 min; (ii) cyanoacetic acid, piperidine, $CHCl_3$, reflux, 5 h.

## Synthetic procedures

**General Procedure for Suzuki-Miyaura Cross-Coupling:** Product **1** (1 eq.) and $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (10 % eq.) were dissolved in dimethoxyethane (0.1 M) and stirred for 15 minutes under nitrogen atmosphere. Then boronic acid derivative (2.4 eq.) and $K_2CO_3$ (10 eq.) were added as suspension in methanol (0.1 M). The reaction was performed with microwave irradiation (100 °C, 200 watt, 90 minutes) and then quenched by pouring into a saturated solution of $NH_4Cl$ (50 mL). Filtration on Celite and extractions with organic solvent allowed to isolate the crude product, then purified through column chromatography on silica gel.

**General Procedure for Knoevenagel Condensation:** Aldehyde precursor (1 eq.), cyanoacetic acid (10 eq.) and piperidine (10 eq. + catalytic) were dissolved in $CHCl_3$ (0.02 M) and warmed to reflux for 5 h. After having the solvent evaporated, a solution of HCl 1 M (~50 mL) was added and the mixture was left under magnetic stirring for 5 h at rt. The dark red solid that precipitated was filtered and washed with water (3x30 mL), PE (2x30 mL) and $Et_2O$ (1x10 mL).

**5,5'-(10-octyl-10*H*-phenothiazine-3,7-diyl)difuran-2-carbaldehyde (2b)**. Product **2b** was synthetized according to general procedure for Suzuki-Miyaura cross-coupling, using product **1a** (330 mg, 0.71 mmol), $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (57 mg, 0.071 mmol), (5-formylfuran-2-yl)boronic acid (240 mg, 1.7 mmol), $K_2CO_3$ (980 mg, 7.1 mmol), DME (3 mL) and methanol (3 mL). Extractions were performed with $CH_2Cl_2$ (3 x 50 mL) and a mixture of PE:AcOEt – 7:3 was used as eluent for purification. The desired product was isolated as a red solid (160 mg) with a 45% of yield. $^1$H NMR (500 MHz, $CDCl_3$) δ 9.60 (s, 2H), 7.58 (dd, *J* = 8.5, 1.9 Hz, 2H), 7.52 (d, *J* = 1.9 Hz, 2H), 7.28 (d, *J* = 3.7 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.71 (d, *J* = 3.7 Hz, 2H), 3.86 (t, *J* = 7.2 Hz, 2H), 1.86 – 1.74 (m, 2H), 1.50 – 1.37 (m, 2H), 1.36 – 1.18 (m, 8H), 0.86 (t, *J* = 6.9 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ.76, 158.67, 151.82, 145.39, 124.75, 124.59, 124.06, 123.78, 115.55, 106.77, 47.90, 31.65, 29.11, 29.08, 26.75, 26.71, 22.53, 13.98.

**5,5'-(10-octyl-10*H*-phenooxazine-3,7-diyl)dithiophene-2-carbaldehyde (2c)**. Product **2c** was synthetized according to general procedure for Suzuki-Miyaura cross-coupling, using product **1b** (300 mg, 0.66 mmol), Pd(dppf)$Cl_2$·$CH_2Cl_2$ (54 mg, 0.066 mmol), (5-formylthiophen-2-yl)boronic acid (247 mg, 1.58 mmol), $K_2CO_3$ (910 mg, 6.6 mmol), DME (3 mL) and methanol (3 mL). Extractions were performed with AcOEt (3 x 50 mL) and a mixture of PE:AcOEt - 3:1 was used as eluent for purification. The desired product was isolated as a red-orange solid (50 mg) with a 15% of yield. $^1$H-NMR ($CDCl_3$, 500 MHz): δ 9.84 (s, 2H), 7.68 (d, 2H, *J* = 4.0 Hz), 7.24 (d, 2H, *J* = 4.0 Hz), 7.14 (dd, 2H, *J* = 8.4, 2.0 Hz), 6.93 (d, 2H, *J* = 2.0 Hz), 6.49 (d, 2H, *J* = 8.4 Hz), 3.50 (t, 2H, *J* = 8.0 Hz), 1.67 (q, 2H, *J* = 8.0 Hz), 1.45-1.20 (m, 10H), 0.89 (t, 3H, *J* = 6.8 Hz). $^{13}$C-NMR ($CDCl_3$, 126 MHz): δ 182.48, 153.48, 144.78, 141.26, 137.57, 133.51, 126.37, 122.76, 122.31, 113.06, 111.80, 44.24, 31.75, 29.68, 29.31, 29. 23, 26.86, 25.10, 22.60, 14.06.

**5,5'-(10-octyl-10*H*-phenooxazine-3,7-diyl)furan-2-carbaldehyde (2d)**. Product **2d** was synthetized according to general procedure for Suzuki-Miyaura cross-coupling, using product **1** (300 mg, 0.66 mmol), Pd(dppf)$Cl_2$·$CH_2Cl_2$ (54 mg, 0.066 mmol), (5-formylfuran-2-yl)boronic acid (221 mg, 1.58 mmol), $K_2CO_3$ (910 mg, 6.6 mmol), DME (3 mL) and methanol (3 mL). Extractions were performed with AcOEt (3 x 50 mL) and a mixture of $CH_2Cl_2$/PE - 97:3 was used as eluent for purification. The desired product was isolated as a dark red solid (200 mg) with a 63% of yield. $^1$H-NMR ($CDCl_3$, 500 MHz): δ 9.55 (s, 2H), 7.26 (d, 2H, *J* = 3.7 Hz), 7.24 (dd, 2H, *J* = 8.4, 2.0 H), 6.98 (d, 2H, *J* = 2.0 Hz), 6.62 (d, 2H, *J* = 3.7 Hz), 6.45 (d, 2H, *J* = 8.4 Hz), 3.45 (t, 2H, *J* = 7.8 Hz), 1.63 (q, 2H, *J* = 7.6 Hz), 1.45-1.20 (m, 10H), 0.89 (t, 3H, *J* = 6.7 Hz). $^{13}$C-NMR ($CDCl_3$, 126 MHz): δ 176.64, 158.85, 151.51, 144.73, 133.66, 122.24, 121.46, 112.08, 111.63, 106.46, 44.21, 31.74, 29.28, 29.22, 26.81, 25.07, 22.60, 14.06.

**5,5’-(9-Octyl-9H-carbazole-3,6-diyl)dithiophene-2-carbaldehyde (2e).** Product **2e** was synthetized according to general procedure for Suzuki-Miyaura cross-coupling, using product **1c** (253 mg, 0.58 mmol), Pd(dppf)$Cl_2$·$CH_2Cl_2$ (48 mg, 0.059 mmol), (5-formylthiophen-2-yl)boronic acid (225 mg, 1.44 mmol), $K_2CO_3$ (790 mg, 5.75 mmol), DME (3 mL) and methanol (3 mL). Extractions were performed with AcOEt (3 x 50 mL) and a mixture of $CH_2Cl_2$/$Et_2O$ - 95:5 was used as eluent for purification. The desired product was isolated as a red solid (210 mg) with a 72% of yield. $^1$H NMR (500 MHz, $CDCl_3$): δ 9.89 (s, 2H), 8.40 (d, *J* = 1.7 Hz, 2H), 7.80 (dd, *J* = 8.6 Hz, 1.8 Hz, 2H), 7.77 (d, *J* = 4.0 Hz, 2H), 7.47 (d, *J* = 3.9 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H), 4.30 (t, *J* = 7.3 Hz, 2H), 1.88 (q, *J* = 7.3Hz, 2H), 1.41-1.19 (m, 10H), 0.87 (t, *J* = 6.8 Hz, 3H).

**5,5’-(9-Octyl-9H-carbazole-3,6-diyl)difuran-2-carbaldehyde (2f).** Product **2f** was synthetized according to general procedure for Suzuki-Miyaura cross-coupling, using product **1c** (253 mg, 0.58 mmol), Pd(dppf)$Cl_2$·$CH_2Cl_2$ (49 mg, 0.059 mmol), (5-formylfuran-2-yl)boronic acid (193 mg, 1.38 mmol), $K_2CO_3$ (788 mg, 5.71 mmol), DME (3 mL) and methanol (3 mL). Extractions were performed with $CH_2Cl_2$ (3 x 50 mL) and a mixture of $CH_2Cl_2$:AcOEt - 9:1 was used as eluent for purification. The desired product was isolated as a red solid (159 mg) with a 59% of yield. $^1$H NMR (500 MHz, $CDCl_3$): δ 9.65 (s, 2H), 8.60 (d, *J* = 1.4 Hz, 2H), 7.94 (dd, *J* = 8.6 Hz, 1.7 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 3.8 Hz, 2H), 6.88 (d, *J* = 3.7 Hz, 2H), 4.28 (t, *J* = 7.3 Hz, 2H), 1.87 (q, *J* = 7.4 Hz, 2H), 1.42-1.18 (m, 10H), 0.86 (t, *J*= 7.0 Hz, 3H). $^{13}$C-NMR ($CDCl_3$, 126 MHz): δ 176.76,160.76, 151.63, 141.57, 123.90, 123.14, 120.76, 118.11, 109.53, 106.39, 43.46, 31.73, 29.28, 29.12, 28.97, 27.23, 22.57, 14.04.

**3,3'-(5,5'-(10-octyl-10*H*-phenothiazine-3,7-diyl)bis(furan-5,2-diyl))bis(2-cyanoacrylic acid) (PTZ-Fu)**. **PTZ-Fu** was synthetized according to general procedure for Knoevenagel condensation using product **2b** (160 mg, 0.32 mmol), cyanoacetic acid (272 mg, 3.2 mmol), piperidine (290 mg, 3.4 mmol) and $CHCl_3$ (10 mL). A dark red solid (185 mg) has been isolated as the product with 91 % of yield. $^1$H NMR (500 MHz, DMSO-*d*$_6$) δ 8.03 (s, 2H), 7.75 (dd, *J* = 8.5, 2.0 Hz, 2H), 7.72 (d, *J* = 2.0 Hz, 2H), 7.52 (d, *J* = 3.8 Hz, 2H), 7.31 (d, *J* = 3.7 Hz, 2H), 7.19 (d, *J* = 8.8 Hz, 2H), 3.97 (t, *J* = 6.9 Hz, 2H), 1.70 (quint, *J* = 7.0 Hz, 2H), 1.39 (quint, *J* = 7.0 Hz, 2H), 1.31 – 1.15 (m, 8H), 0.81 (t, *J* = 6.8 Hz, 3H). $^{13}$C NMR (126 MHz, DMSO-*d*$_6$) δ 164.43, 158.54, 147.78, 145.30, 137.89, 125.28, 123.99, 123.78, 123.67, 117.20, 116.99, 31.54, 29.05, 28.89, 26.52, 26.35, 22.46, 14.35. Anal. Calcd. For : C, 68.23; H, 4.93; N,6.63. Found: C,68.11; H,5.31; N,6.69.

**3,3'-(5,5'-(10-octyl-10*H*-phenooxazine-3,7-diyl)bis(thiophene-5,2-diyl))bis(2-cyanoacrylic acid) (POZ-Th)**. **POZ-Th** was synthetized according to general procedure for Knoevenagel condensation using product **2c** (50 mg, 0.097 mmol), cyanoacetic acid (82 mg, 0.97 mmol), piperidine (103 mg, 1.16 mmol) and $CHCl_3$ (5 mL). A dark red solid (58 mg) has been isolated as the product with quantitative yield. $^1$H-NMR (DMSO-*d*$_6$, 500 MHz): δ 8.35 (s, 2H), 7.87 (d, 2H, *J* = 4.2 Hz), 7.53 (d, 2H, *J* = 4.0 Hz), 7.16 (dd, 2H, *J* = 8.2, 1.8 Hz), 6.93 (d, 2H, *J* = 1.9 Hz), 6.65 (d, 2H, *J* = 8.7 Hz), 3.48 (broad s, 2H), 1.51 (broad s, 2H), 1.40-1.10 (m, 10H), 0.85 (t, 3H, *J* = 6.7 Hz). $^{13}$C-NMR (DMSO-*d*$_6$, 126 MHz): δ164.21, 152.76, 146.77, 144.40, 141.81, 133.73, 133.41, 125.92, 124.27, 122.96, 117.04, 113.07, 112.61, 97.56, 31.70, 29.26, 29.22, 26.53, 25.10, 22.56, 14.40. Anal. Calcd. For : C, 66.54; H, 4.81; N, 6.47. Found: C, 66.64; H, 4.64; N 6.17.

**3,3'-(5,5'-(10-octyl-10*H*-phenooxazine-3,7-diyl)bis(furanen-5,2-diyl))bis(2-cyanoacrylic acid) (POZ-Fu)**. **POZ-Fu** was synthetized according to general procedure for Knoevenagel condensation using product **2d** (200 mg, 0.41 mmol), cyanoacetic acid (349 mg, 4.1 mmol), piperidine (431 mg, 4.92 mmol) and $CHCl_3$ (5 mL). A dark red solid (190 mg) has been isolated as the product with 75 % of yield. $^1H$ NMR (500 MHz, DMSO-$d_6$): δ 7.89 (s, 2H), 7.38 (d, 2H, *J* = 3.5 Hz), 7.36 (d, 2H, *J* = 8.9 Hz), 7.16 (d, 2H, *J* = 3.4 Hz), 7.14 (s, 2H), 6.76 (d, 2H, *J* = 8.6 Hz), 3.56 (broad s, 2H), 1.54 (broad s, 2H), 1.45-1.15 (m, 10H), 0.85 (t, 3H, *J* = 6.2 Hz). $^{13}C$-NMR (DMSO-$d_6$, 125 MHz): δ 164.64, 158.27, 147.69, 144.46, 136.73, 133.49, 122.31, 121.99, 117.76, 113.15, 111.62, 109.13, 43.75, 31.69, 29.23, 26.45, 25.11, 22.54, 14.39. Anal. Calcd. For : C, 70.01; H, 5.06; N, 6.80. Found: C, 70.04; H, 5.39; N,6.73.

**5,5’-(9-Octyl-9H-carbazole-3,6-diyl)bis(thiophene-5,2-diyl))bis(2-cyanoacrylic acid) (CBZ-Th)**. **CBZ-Th** was synthetized according to general procedure for Knoevenagel condensation using product **2e** (210 mg, 0.42 mmol), cyanoacetic acid (370 mg, 4.35 mmol), piperidine (384 mg, 4.5 mmol) and $CHCl_3$ (5 mL). A dark red solid (187 mg) has been isolated as the product with 71 % of yield. $^1H$ NMR (500 MHz, DMSO-$d_6$): δ 8.80 (d, *J* = 1.8 Hz, 2H), 8.51 (s, 2H), 8.06 (d, *J* = 4.2 Hz, 2H), 7.93 (dd, *J* = 8.6 Hz, 1.9 Hz, 2H), 7.84 (d, *J* = 4.1 Hz, 2H), 7.74 (d, *J* = 8.7 Hz, 2H), 4.45 (t, *J* = 6.7 Hz, 2H), 1.80 (q, *J* = 7.2 Hz, 2H), 1.33-1.12 (m, 10H), 0.80 (t, *J* = 6.9 Hz, 3H). Anal. Calcd. For : C, 68.22; H, 4.93; N,6.63. Found: C, 68.07; H, 5.09; N, 7.03.

**5,5’-(9-Octyl-9H-carbazole-3,6-diyl)bis(furanen-5,2-diyl))bis(2-cyanoacrylic acid) (CBZ-Fu)**. **CBZ-Fu** was synthetized according to general procedure for Knoevenagel condensation using product **2f** (159 mg, 0.34 mmol), cyanoacetic acid (275 mg, 3.23 mmol), piperidine (300 mg, 3.5 mmol) and $CHCl_3$ (5 mL). A dark red solid (110 mg) has been isolated as the product with 53 % of yield. $^1H$ NMR (500 MHz, DMSO-$d_6$): δ 8.67 (s, 2H), 8.02 (d, *J* = 8.5 Hz, 2H), 7.94 (s, 2H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 3.2 Hz, 2H), 7.21 (d, *J* = 3.2 Hz, 2H), 4.41 (s, 2H), 1.77 (d, *J* = 6.0 Hz, 2H), 1.31-1.10 (m, 10H), 0.80 (t, *J* = 7.0 Hz, 3H). $^{13}C$ NMR (126 MHz, DMSO-$d_6$) δ 158.60, 148.22, 141.41, 123.68, 122.90, 121.18, 119.08, 117.55, 110.97, 43.12, 31.58, 29.12, 29.02, 28.97, 26.85, 22.43, 14.32. Anal. Calcd. For : C, 71.87; H, 5.19; N, 6.98. Found: C, 71.47; H, 5.48; N,6.60.

## Electrochemical characterization

Pulsed Voltammetry (DPV) and Cyclic Voltammetry (CV) were carried out at scan rate of 20 and 50 mV/s, respectively, using a PARSTA2273 potentiostat in a two compartments, three electrode electrochemical cell in a glove box filled with $N_2$ ($[O_2]$ and $[H_2O] \leq 0.1$ ppm). The working, counter, and the pseudo-reference electrodes were a glassy carbon pin, a Pt flag and an Ag/AgCl wire, respectively. The working electrodes discs were well polished with alumina 0.1 μm suspension, sonicated for 15 min in deionized water, washed with 2-propanol, and cycled for 50 times in 0.5 M $H_2SO_4$ before use. The Ag/AgCl pseudo-reference electrode was calibrated, by adding ferrocene ($10^{-3}$ M) to the test solution after each measurement.

## Preparation of Pt/TiO$_2$ nanopowder

Platinization of $TiO_2$ Degussa P25 was done through a photodeposition method known in literature.[4-7] $TiO_2$ Degussa P25 (2.0 g) was suspended in a solution of $H_2O$ (200 mL) and EtOH (200 mL) containing 32.7 mg of $Pt(NO_3)_2$, in order to reach a final metal loading of 1.0 wt%. After stirring for 1 h in the dark, the suspension was irradiated with a 450 W medium pressure lamp for 4 h. Nanopowders were recovered through centrifugation, washed with EtOH 3 times, and dried under vacuum at 50 °C overnight.

## Characterization of Pt/TiO$_2$ nanopowder

Phase composition has been analysed by Powder X-ray Diffraction (PXRD) using a Philips X’Pert diffractometer using a Cu Kα ($\lambda = 0.154$ nm) X-ray source in the range $10° < 2\theta < 100°$ and data were analyzed by using the PowderCell 2.0 software. Mean crystallite sizes were calculated applying the Scherrer’s equation to the principal reflection of each phase [(101) for anatase and (110) for rutile].

Textural properties of the catalyst has been analyzed by $N_2$ physisorption at the liquid nitrogen temperature using a Micromeritics ASAP 2020 automatic analyzer. The samples were previously degassed under vacuum at 200°C overnight. Specific surface area has been determined applying the BET method to the adsorption isotherm in the range $0.10 < p/p^0 < 0.35$. Pore size distribution has been evaluated applying the BJH theory to the desorption branch of the isotherm.[8]

The morphology of the composite materials and the distribution of the supported Pt nanoparticles were evaluated by High Resolution Transmission Electron Microscopy (HR-TEM) and High Angle Annular Dark Field-Scanning Transmission Electron Microscopy (HAADF-STEM) images recorded by a JEOL 2010-FEG microscope operating at the acceleration voltage of 200 kV. The microscope has 0.19 nm spatial resolution at Scherzer defocus conditions in HR-TEM mode and a probe of 0.5 nm was used in HAADF-STEM mode.

## Adsorption of PTZs, POZs, CBZs dyes on $Pt/TiO_2$

Dye staining was done by suspending 200 mg of $Pt/TiO_2$ nanopowders in 20 mL of dye solution (0.3 mM in ethanol) for 24 h in the dark. Then nanopowders were separated through centrifugation, washed twice with ethanol, and dried under vacuum at room temperature overnight. After adsorption, the concentration of the dyes in the solution was measured by UV-vis spectroscopy, confirming that the loading of dyes on the $Pt/TiO_2$ material is quantitative.

## Hydrogen production through water splitting

The dye-functionalized $Pt/TiO_2$ nanomaterials have been tested for $H_2$ production following a procedure previously described.[1] 50 mg of the dye-functionalized $Pt/TiO_2$ catalyst was suspended into 60 mL of 10 % v/v aqueous solution of triethanolamine (TEOA) previously neutralized with HCl. After purging with Ar (15 mL $min^{-1}$) for 30 min, the suspension was irradiated using a 150 W Xe lamp with a cut-off filter at 420 nm. Irradiance was ~ 6 x $10^{-3}$ W $m^{-2}$ in the UV-A range and ~ 1080 W $m^{-2}$ in the visible range (400 – 1000 nm). The concentration of $H_2$ in gas stream coming from the reactor has been quantified using a Agilent 7890 gaschromatograph equipped with a TCD detector, connected to a Carboxen 1010 column (Supelco, 30 m x 0.53 mm ID, 30 μm film) using Ar as carrier.

The performances of the sensitized photocatalysts have been reported in terms of $H_2$ production rate and overall $H_2$ productivity. Turn-Over Numbers (TON) were calculated as:

$$TON = \frac{2\,x\; overall\; H_2\; amount\; (\mu mol\; g^{-1})}{dye\; loading\; (\mu mol\; g^{-1})}$$

Light-to-Fuel Efficiency (LFE) was calculated as:

$$LFE = \frac{F_{H_2} \times \Delta H^0_{H_2}}{S \times A_{irr}}$$

where $F_{H2}$ is the flow of $H_2$ produced (expressed in mol $s^{-1}$), $\Delta H^0_{H2}$ is the enthalpy associated with $H_2$ combustion (285.8 kJ $mol^{-1}$), S is the total incident light irradiance, as measured by adequate radiometers in 400 – 1000 nm ranges (expressed in W $cm^{-2}$) and $A_{irr}$ is the irradiated area (expressed in $cm^2$). UV-vis spectra of the aqueous solutions recovered at the end of the photocatalytic runs highlighted that no desorption of the dyes took place during the experiments.

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**Table S1.** Main optical and electrochemical characterization of the **PTZs**, **CBZs** and **POZs** dyes.

| Sample | $\lambda_{max}$[a] (nm) | ε ($M^{-1}cm^{-1}$) | $V_{ox}$ (V vs. Fc) ± 10 mV | HOMO[b] (eV) ± 0.05 eV | $E_{gap}^{opt}$ (eV) | LUMO$_b$ eV ± 0.05 eV |
|---|---|---|---|---|---|---|
| PTZ-Th[c] | 470 | 34000 ± 1000 | 0.15 | -5.38 | 2.05 | -3.33 |
| PTZ-Fu | 481 | 30200 ± 700 | 0.36 | -5.59 | 1.98 | -3.61 |
| POZ-Th | 534 | 31800 ± 1500 | 0.41 | -5.64 | 1.87 | -3.77 |
| POZ-Fu | 524 | 27200 ± 200 | 0.38 | -5.61 | 1.90 | -3.71 |
| CBZ-Th | 414 | 35800 ± 100 | 0.41 | -5.64 | 2.26 | -3.38 |
| CBZ-Fu | 409 | 41800 ± 600 | 0.43 | -5.66 | 2.28 | -3.38 |

[a] Dye solution $10^{-5}$ M in THF. [b] Vacuum potential = Fc/Fc$^+$ + 5.23 V. [c] Values from Ref 1; CV and DPV plots are reported in Ref 1.

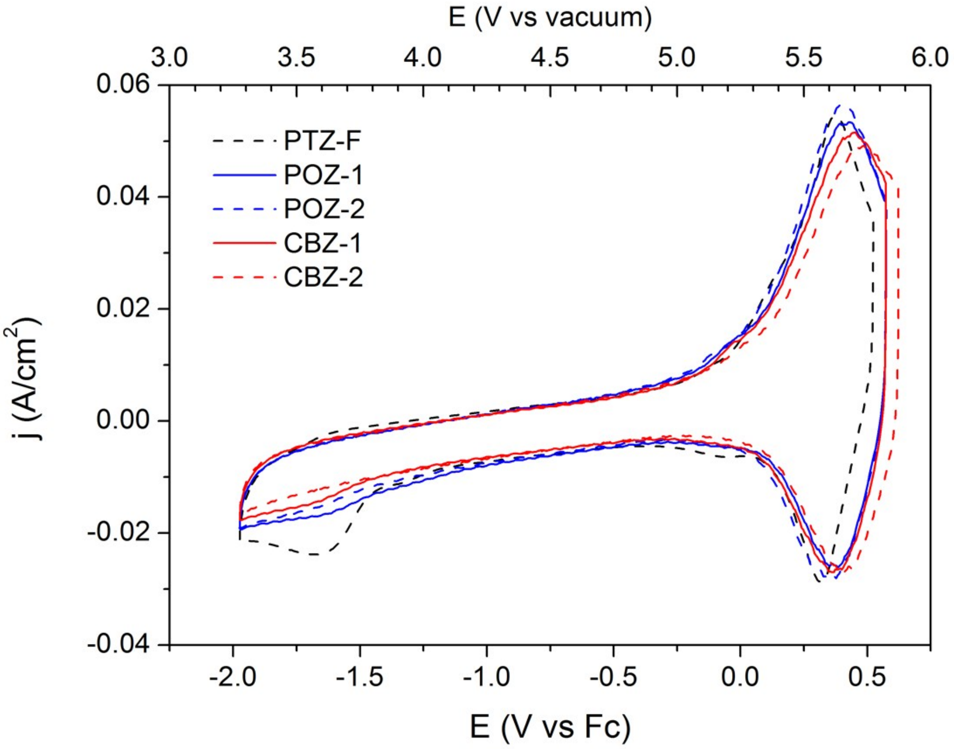


**Figure S1.** Ciclic voltammetry (CV) of the **PTZs**, **CBZs** and **POZs** dyes recorded in ACN:$CH_2Cl_2$ 3:1 $TBAClO_4$ 0.075M solution.

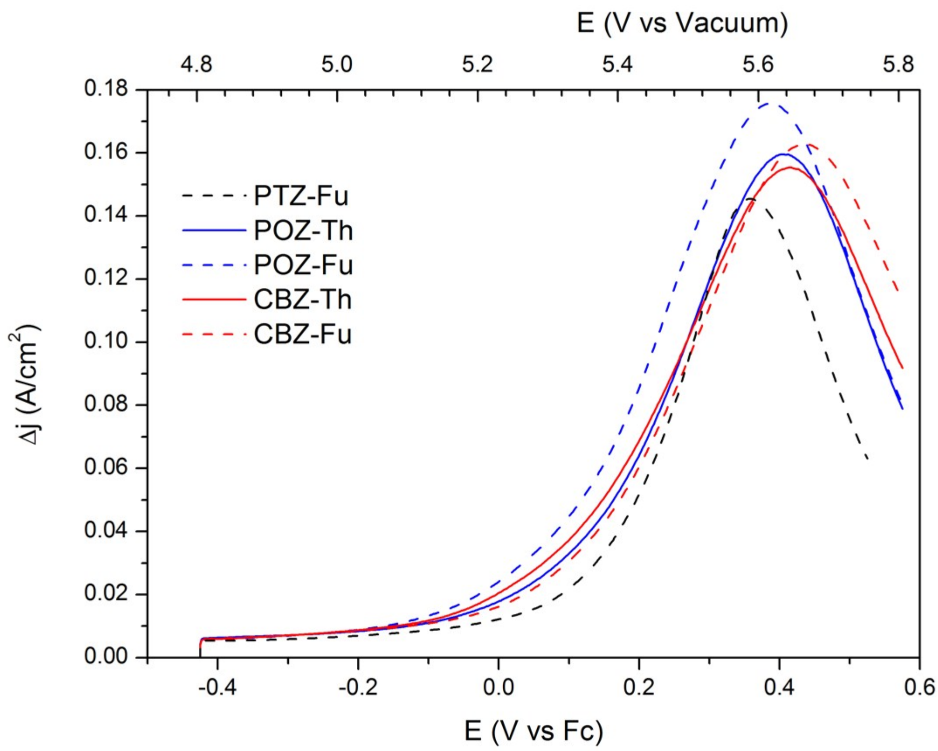


**Figure S2.** Differential pulse voltammetry (DPV) of the **PTZs**, **CBZs** and **POZs** dyes recorded in ACN:$CH_2Cl_2$ 3:1 $TBAClO_4$ 0.075M solution.

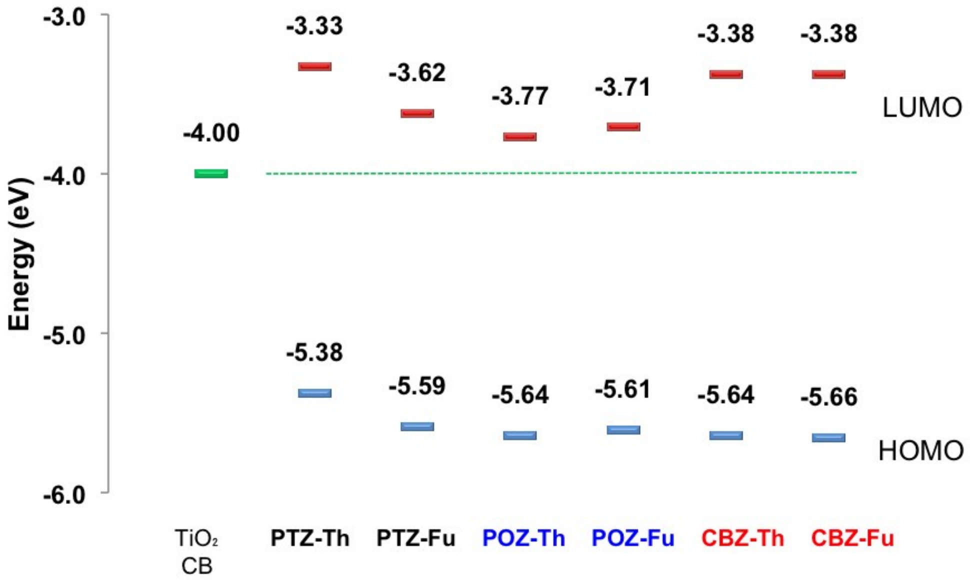


**Figure S3.** Experimental HOMO/LUMO energy levels for the dyes investigated in this work (CB level of $TiO_2$ is included as a reference for electron injection from the dye to the semiconductor).

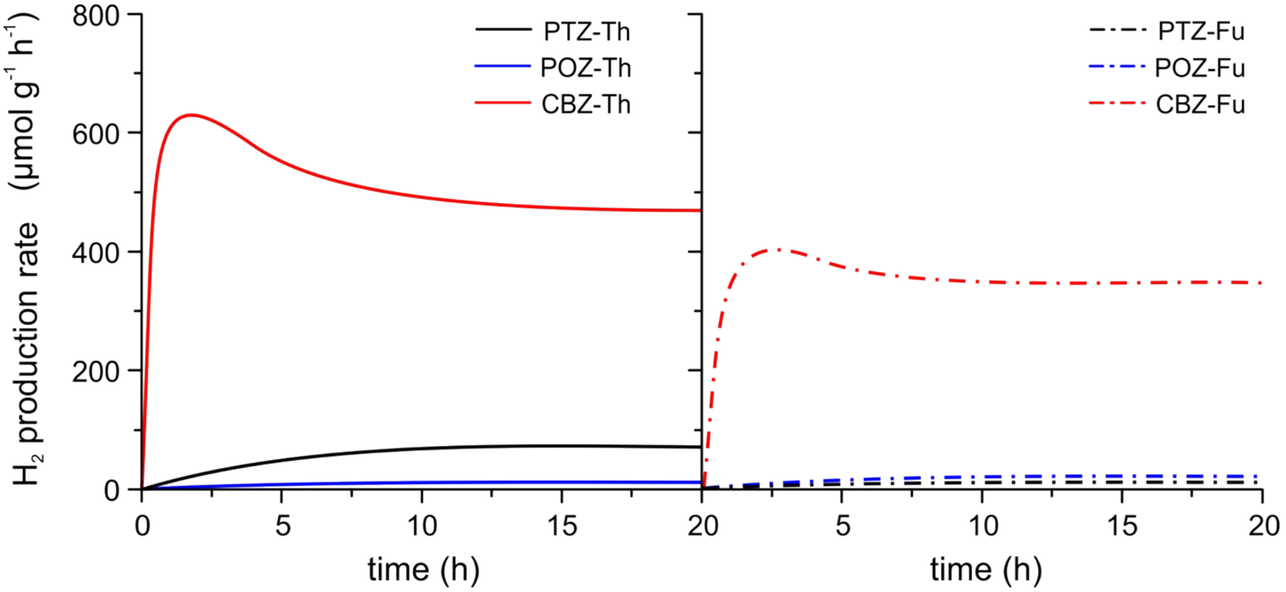


**Figure S4.** $H_2$ production rate from TEOA 10% v/v solution at pH = 7.0 under irradiation with visible light (λ > 420 nm) over Pt/TiO$_2$ materials sensitized with **PTZs**, **POZs** and **CBZs** dyes.

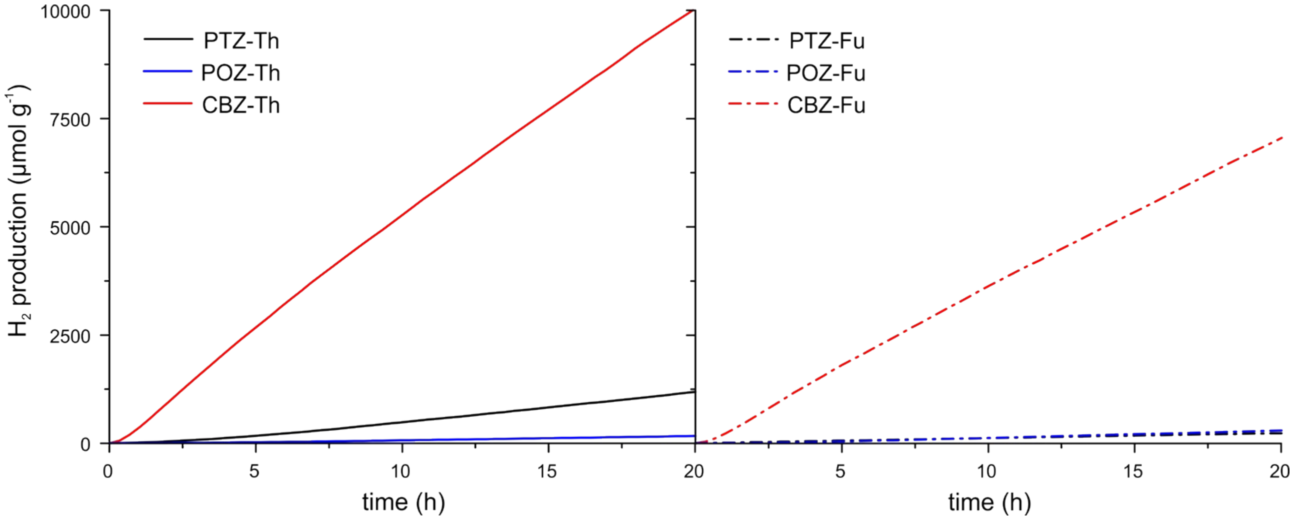


**Figure S5.** $H_2$ production from TEOA 10% v/v solution at pH = 7.0 under irradiation with visible light (λ > 420 nm) over Pt/TiO$_2$ materials sensitized with **PTZs**, **POZs** and **CBZs** dyes.

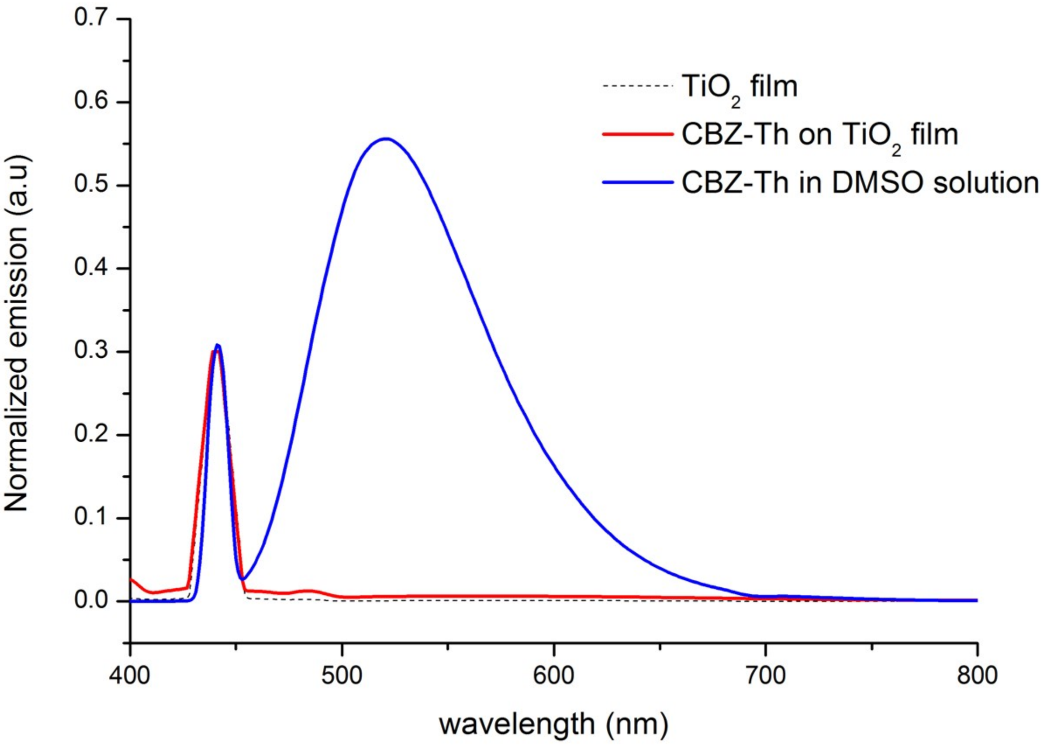


**Figure S6.** Normalized emission spectra of **CBZ-Th** on 5 μm transparent $TiO_2$ films (red line) in comparison with emission spectra **CBZ-Th** dye in solution ($3 \times 10^{-6}$ M DMSO) (blue line), and 3 μm transparent $TiO_2$ films. (black dashed line).

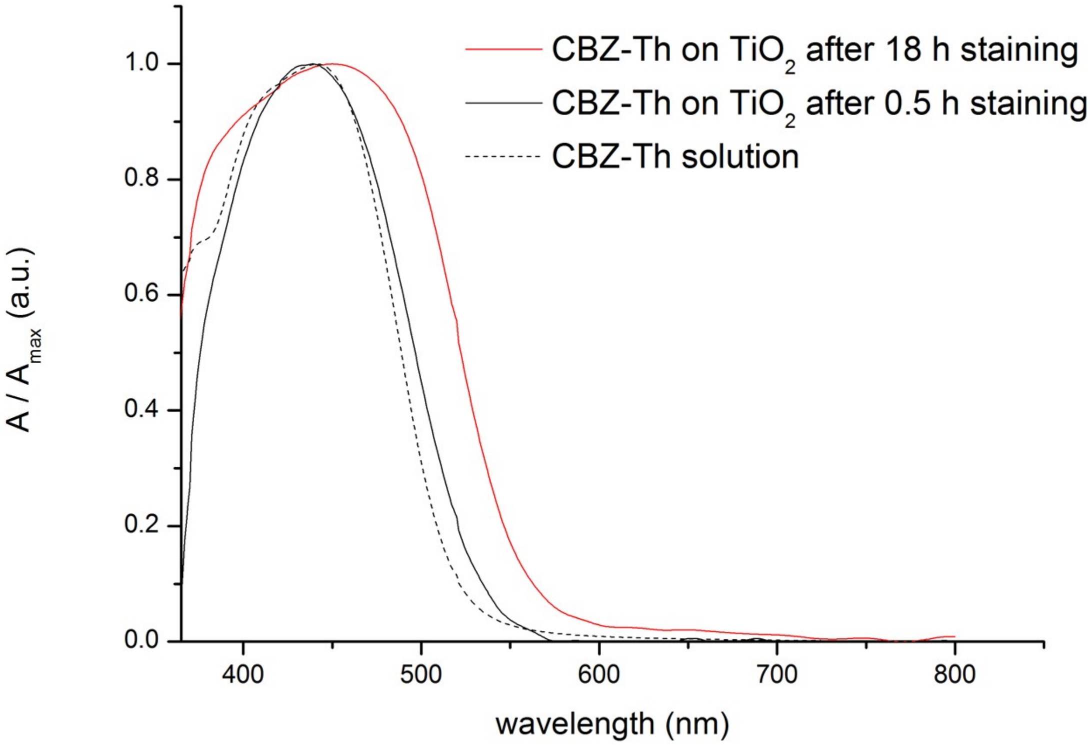


**Figure S7.** Normalized absorption spectra of **CBZ-Th** on 3 μm transparent $TiO_2$ films at different staining times and comparison with absorption spectra as a DMSO solution.

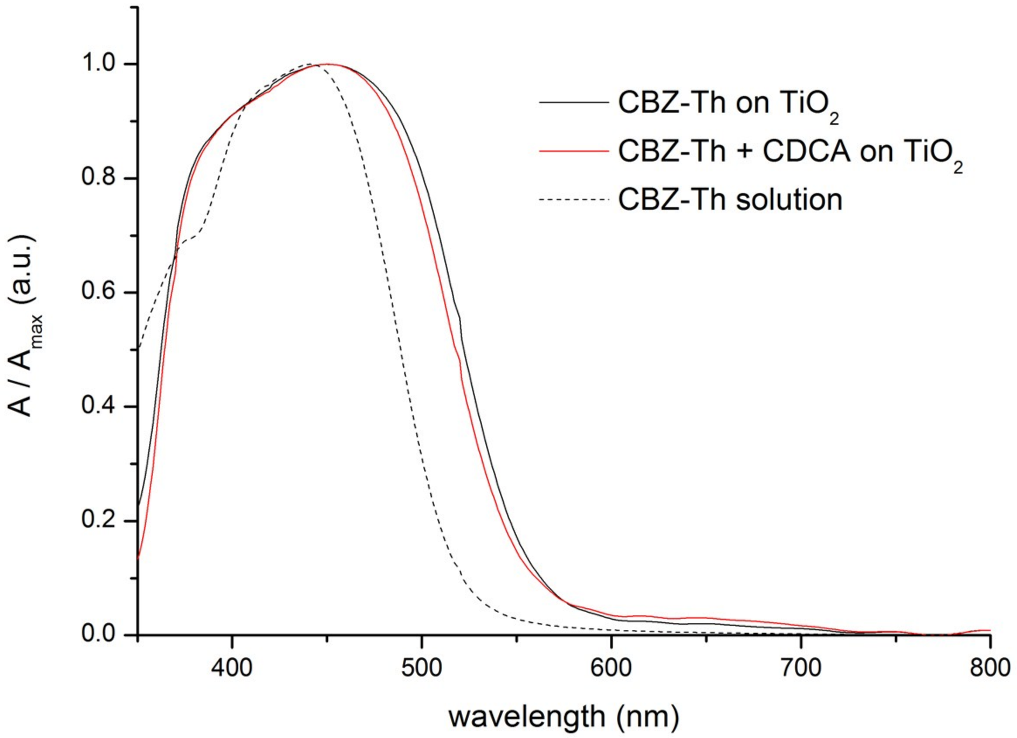


**Figure S8.** Normalized absorption spectra of **CBZ-Th** on 3 μm transparent $TiO_2$ films (black line), in presence of 100:1 CDCA (red line), and comparison with absorption spectra as a DMSO solution. (black dashed line).

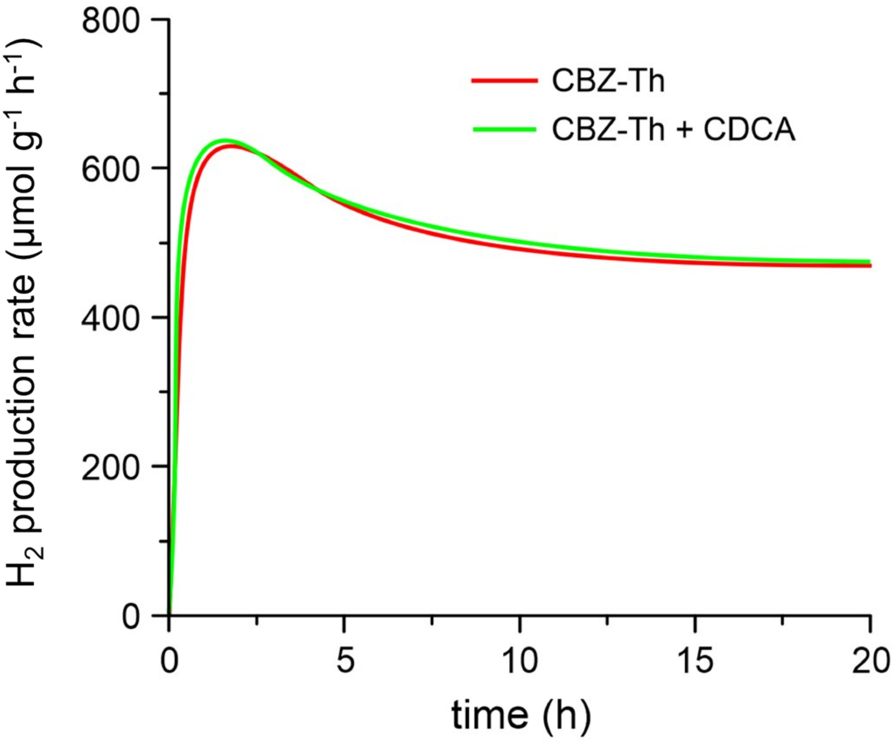


**Figure S9.** $H_2$ production rates from TEOA 10% v/v solution at pH = 7.0 under irradiation with visible light ($\lambda > 420$ nm) over $Pt/TiO_2$ materials sensitized with the **CBZ-Th** dye (red) and with **CBZ-Th**+CDCA 1:1 mol (green)

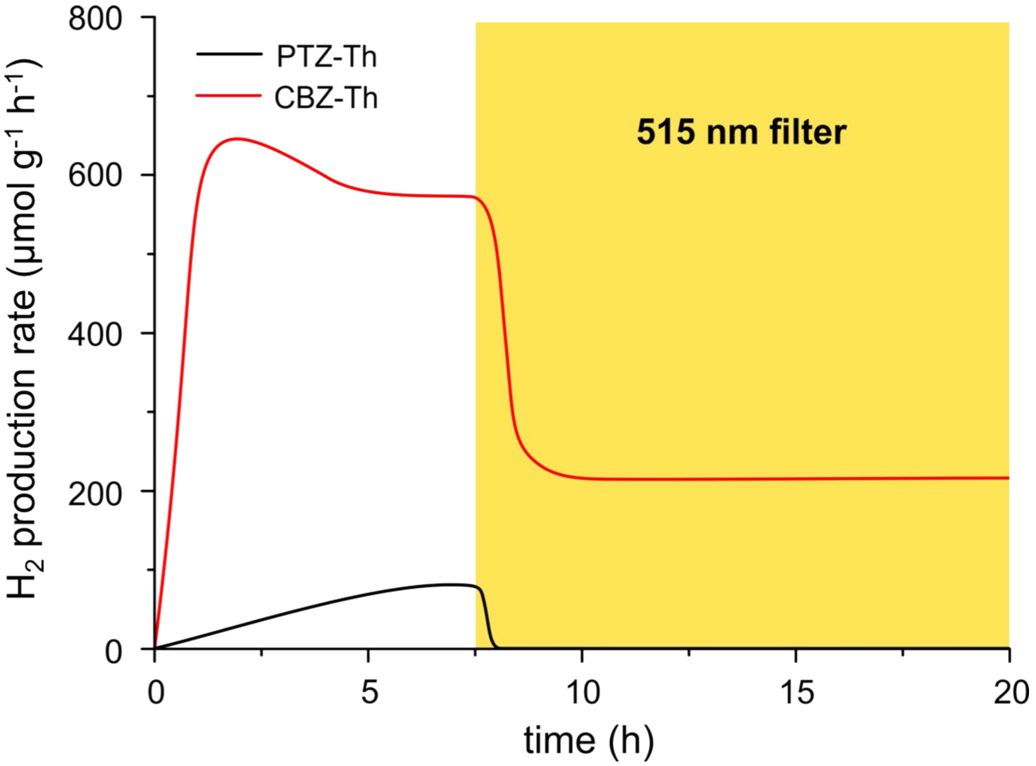


**Figure S10.** $H_2$ production rate from TEOA 10% v/v solution at pH = 7.0 over Pt/$TiO_2$ materials sensitized with **PTZ-Th** and **CBZ-Th** dyes: after activation under irradiation with visible light (λ > 420 nm) for 8 h, the photocatalytic activity under irradiation with photons with λ > 515 nm is presented.

**Table S2.** TON values and $LFE_{20}$ for **PTZs**, **POZs**, and **CBZs** sensitized catalysts.

| Dye sensitizer | $H_2$ amount (µmol $g^{-1}$ at 20 h) | TON (µmol($H_2$) µmol(dye)$^{-1}$ at 20 h) | $LFE_{20}$ (%) |
|---|---|---|---|
| **PTZ-Th** | 1178 | 236 | 0.032% |
| **PTZ-Fu** | 227 | 45 | 0.006% |
| **POZ-Th** | 163 | 33 | 0.004% |
| **POZ-Fu** | 294 | 59 | 0.008% |
| **CBZ-Th** | 10083 | 2017 | 0.272% |
| **CBZ-Fu** | 7064 | 1413 | 0.190% |

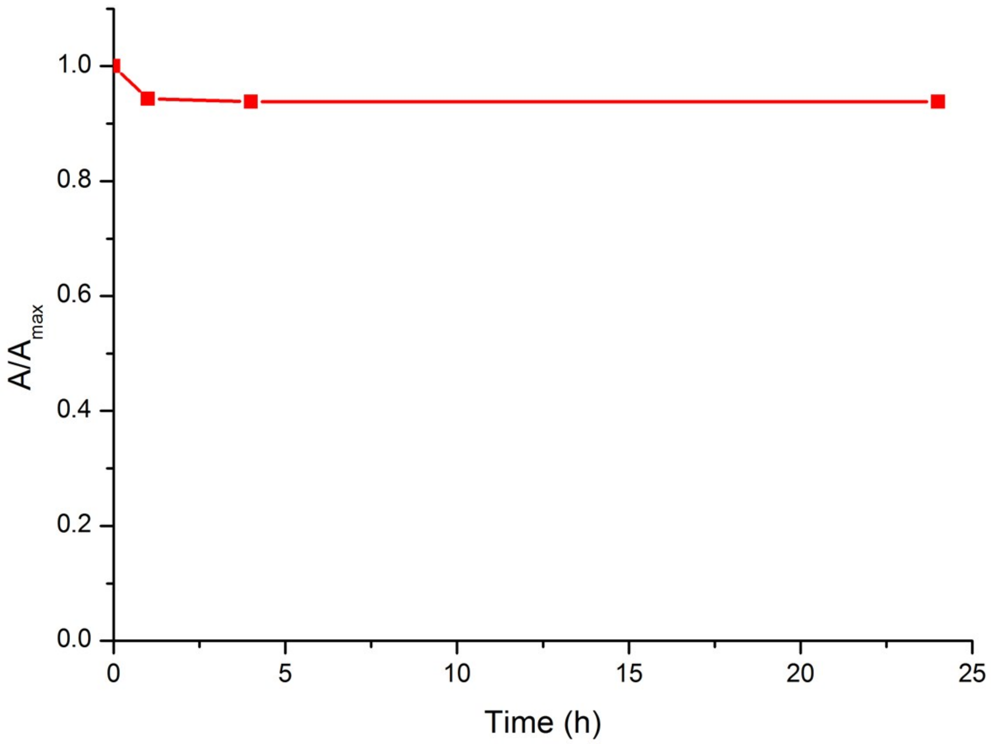
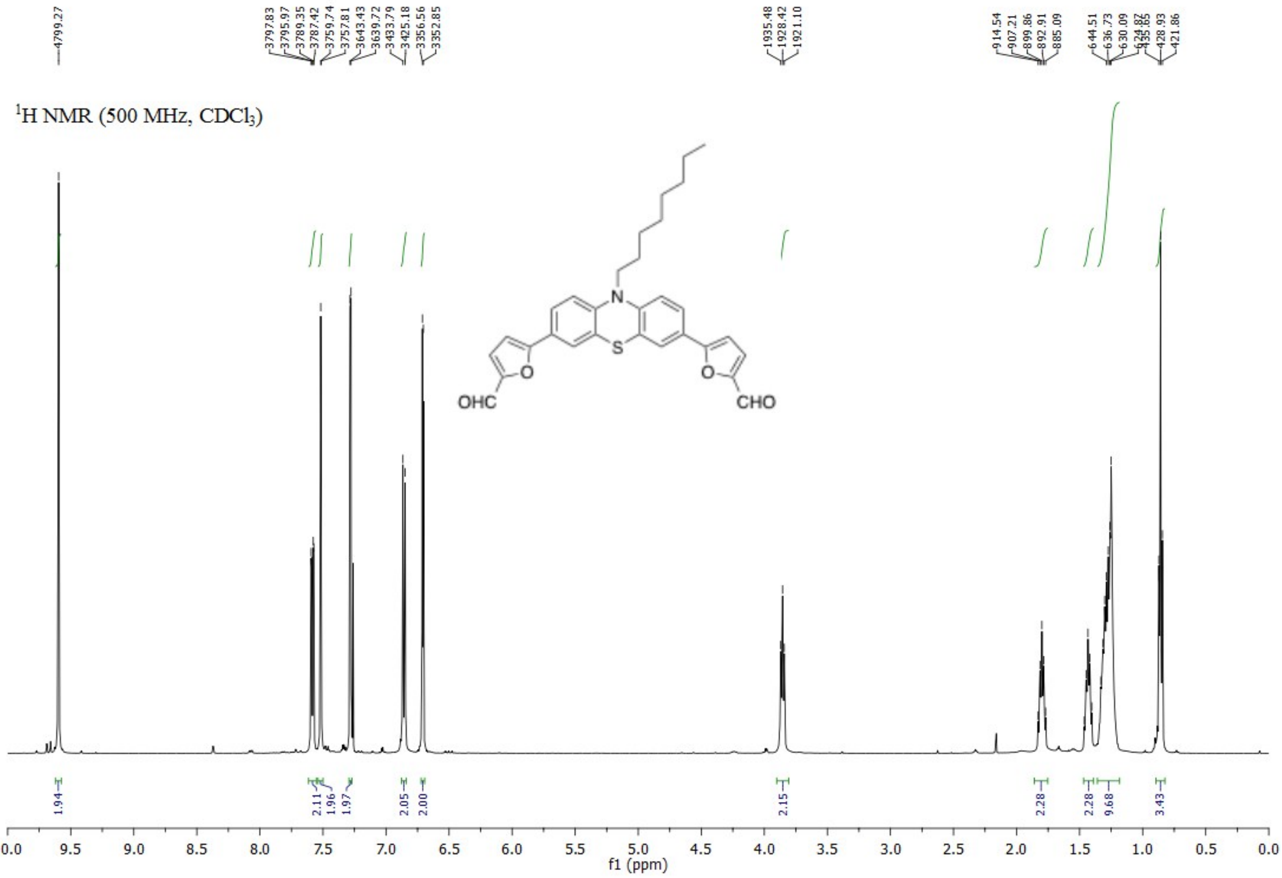
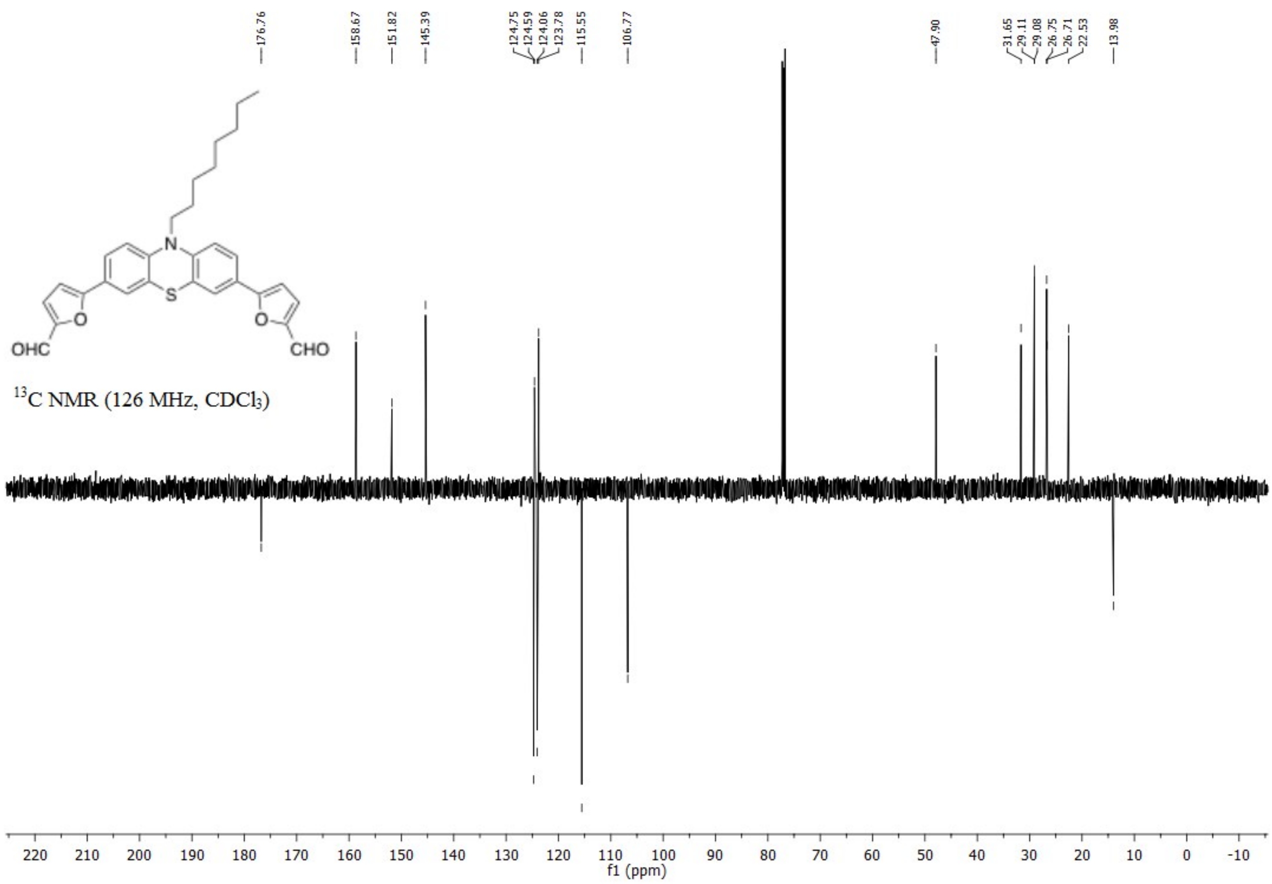
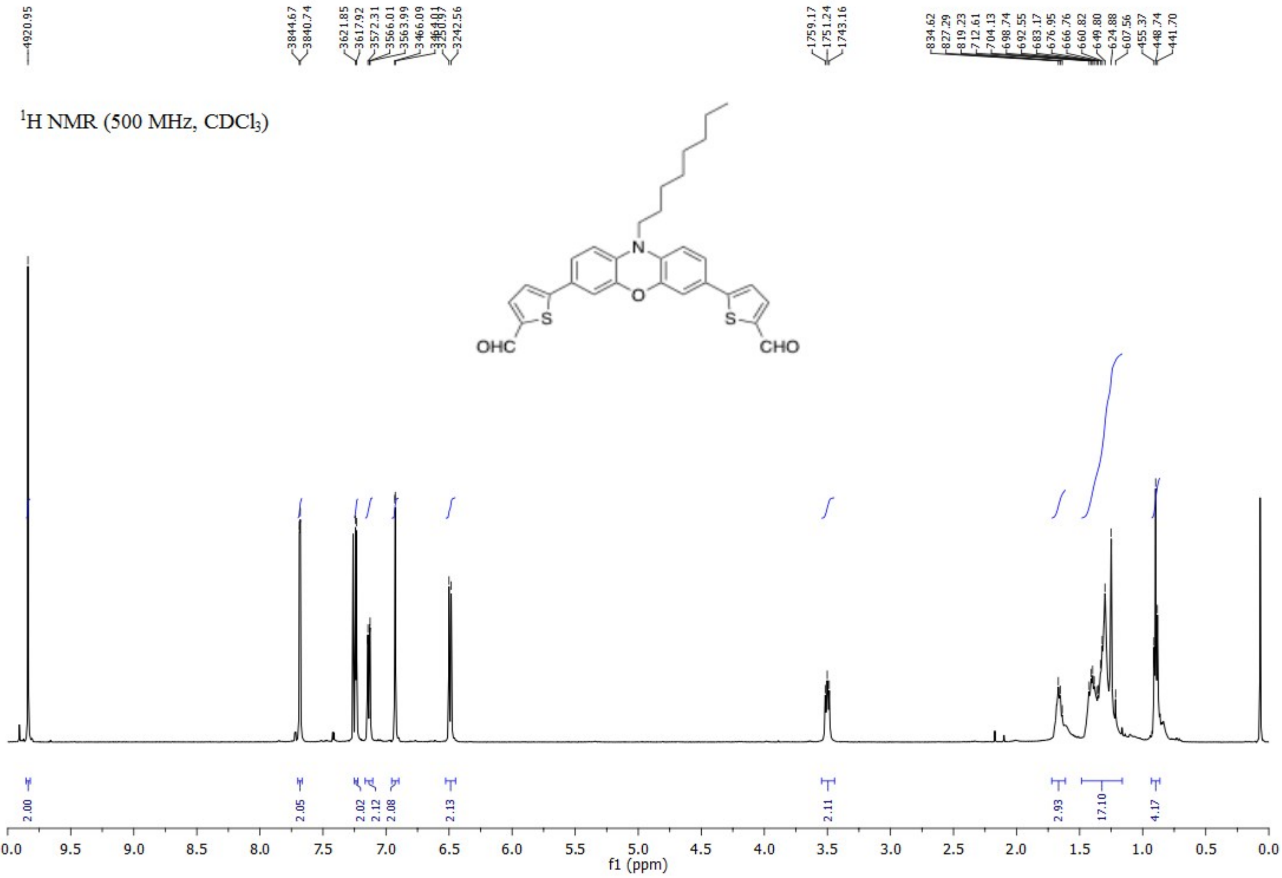


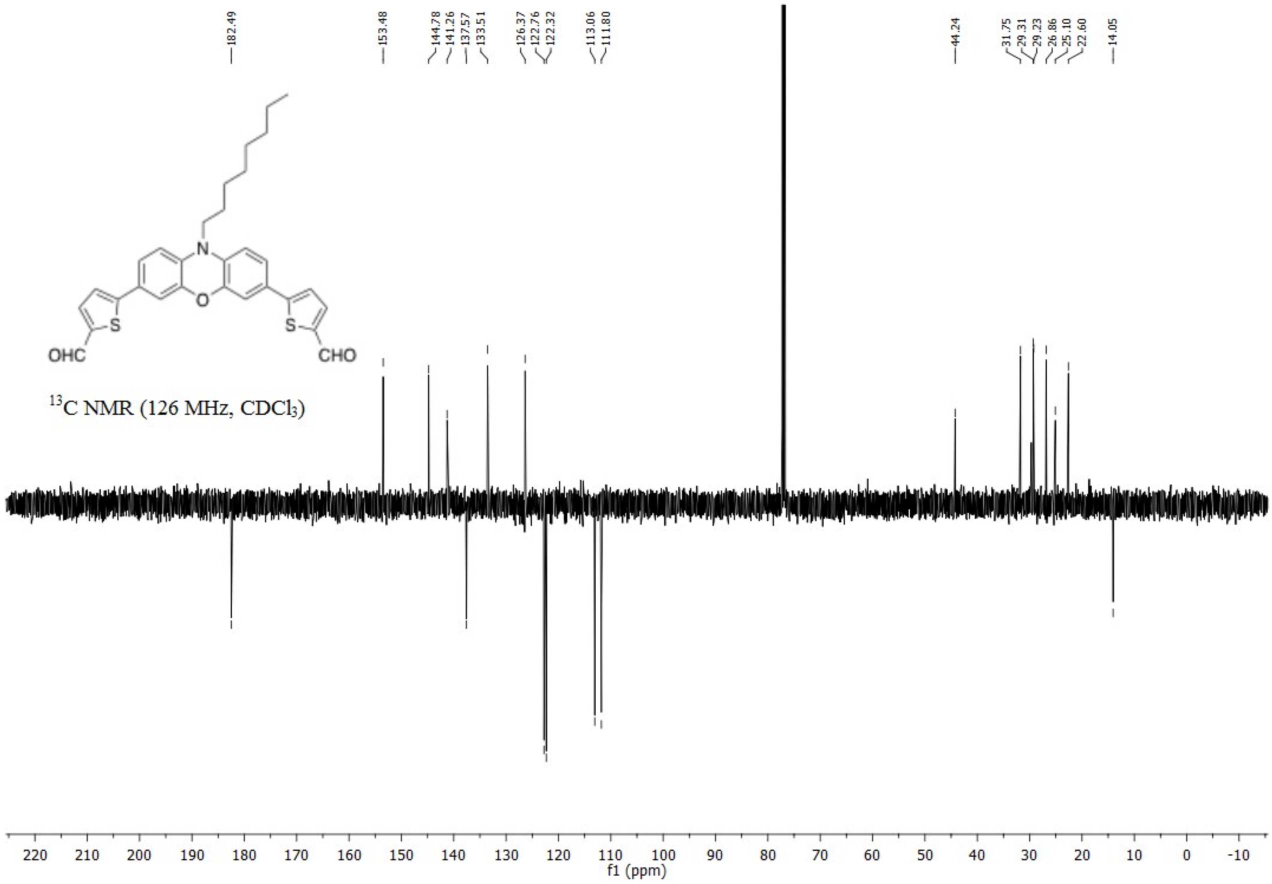
**Figure S11.** Normalized absorption values of **CBZ-Th** on 5 µm transparent $TiO_2$ films under irradiation with $\lambda > 420$ nm (500 $W/m^2$ at 50 °C) for 24 h.

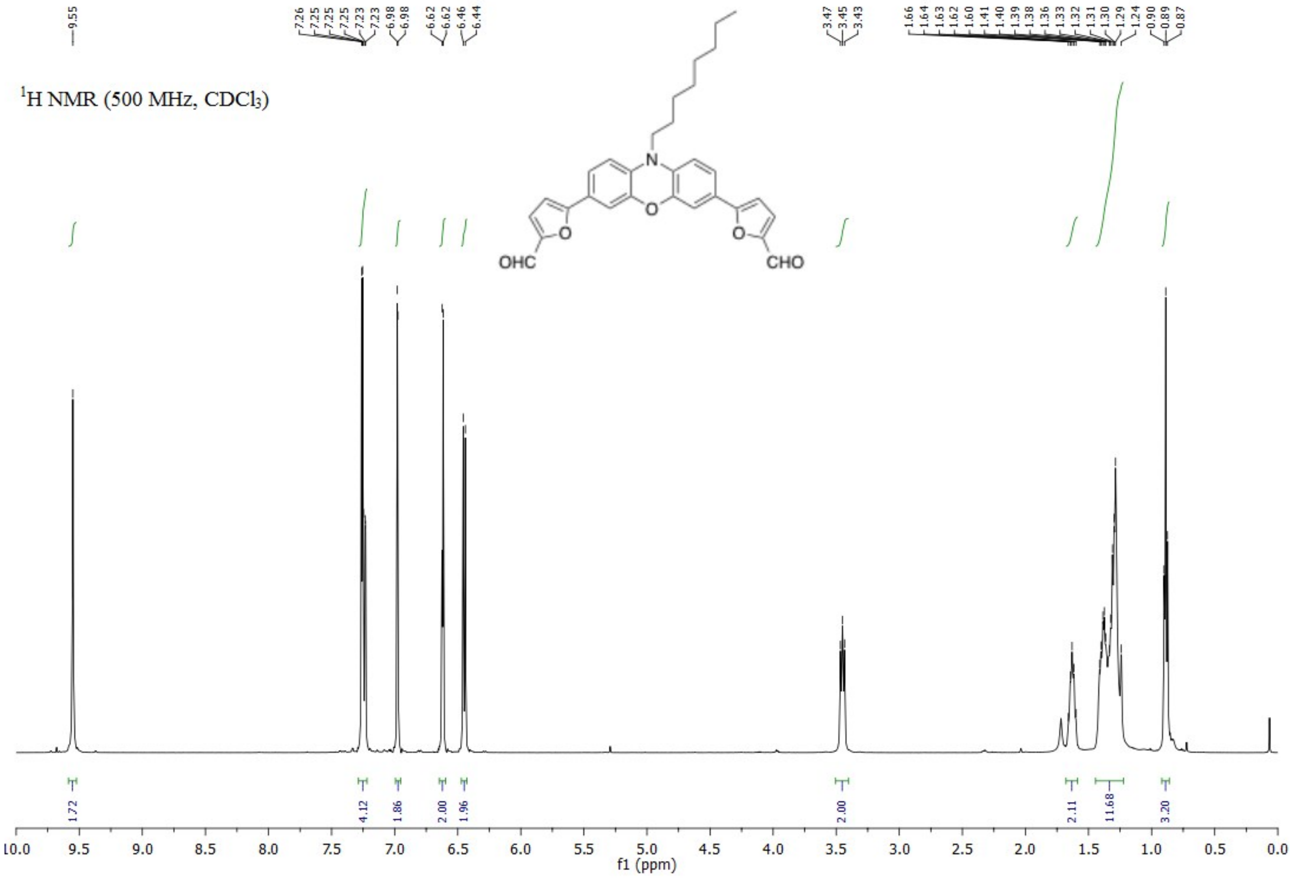
### $^1$H-NMR and $^{13}$C-NMR spectra

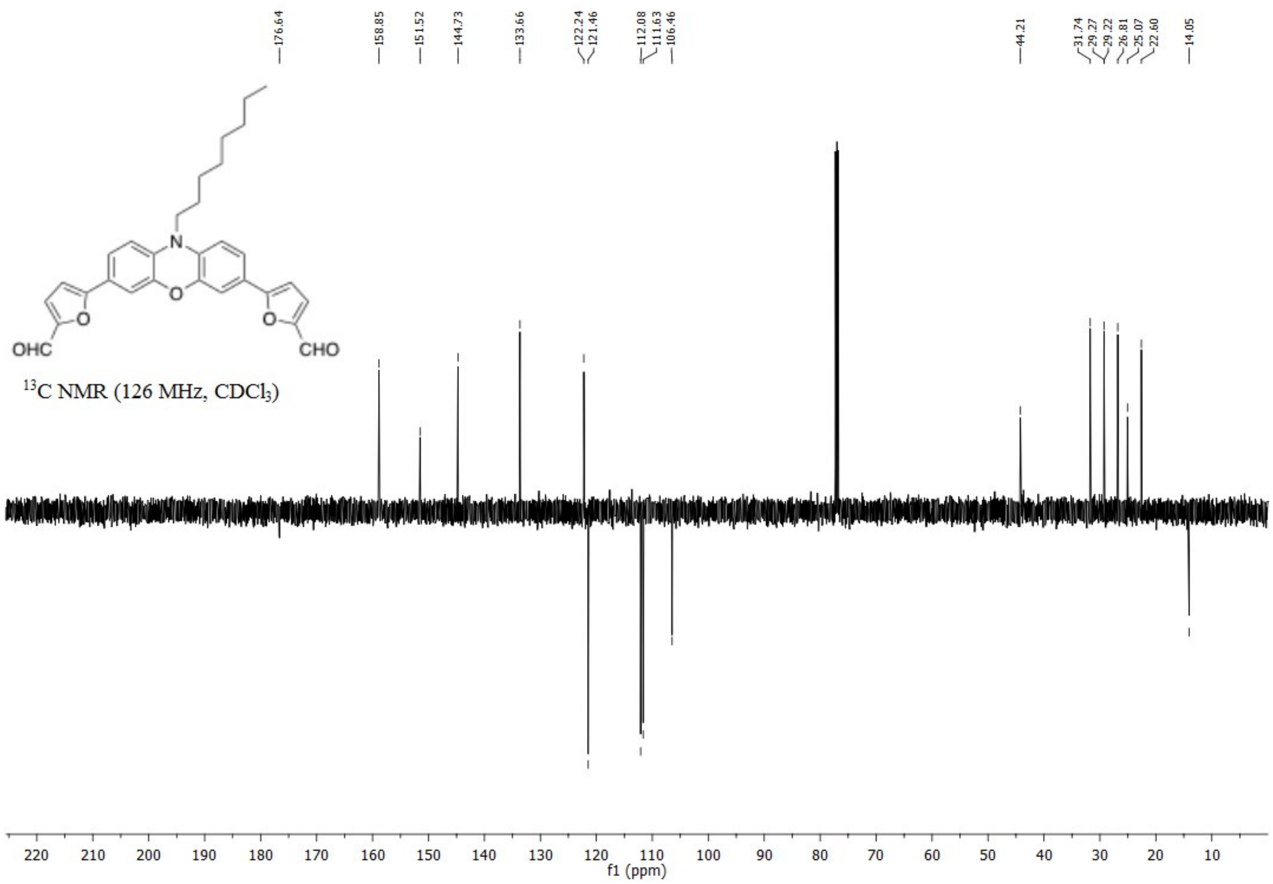



176.76
158.67
151.82
145.39
124.75
124.59
124.06
123.78
115.55
106.77
47.90
31.65
29.11
29.08
26.75
26.71
22.53
13.98
N
S
O
OHC
CHO
$^{13}$C NMR (126 MHz, CDCl$_3$)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

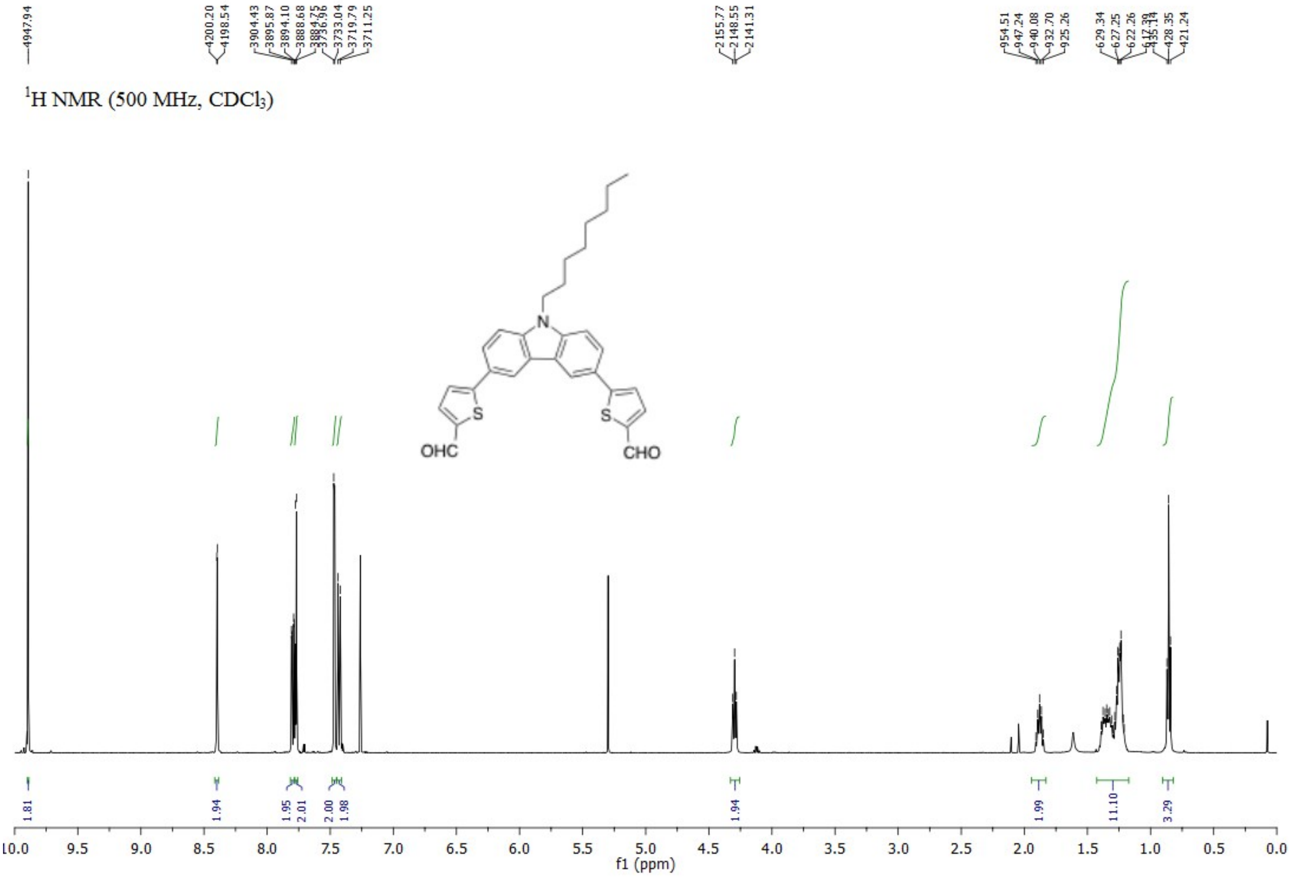

4920.95
3844.67
3840.74
3621.85
3617.92
3572.31
3566.01
3563.99
3466.09
3464.01
3250.97
3242.56
1759.17
1751.24
1743.16
834.62
827.29
819.23
712.61
704.13
698.74
692.55
683.17
676.95
666.76
660.82
649.80
624.88
607.56
455.37
448.74
441.70
$^1$H NMR (500 MHz, CDCl$_3$)
N
O
S
OHC
CHO
2.00
2.05
2.02
2.12
2.08
2.13
2.11
2.93
17.10
4.17
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


$^{13}$C NMR (126 MHz, CDCl$_3$)

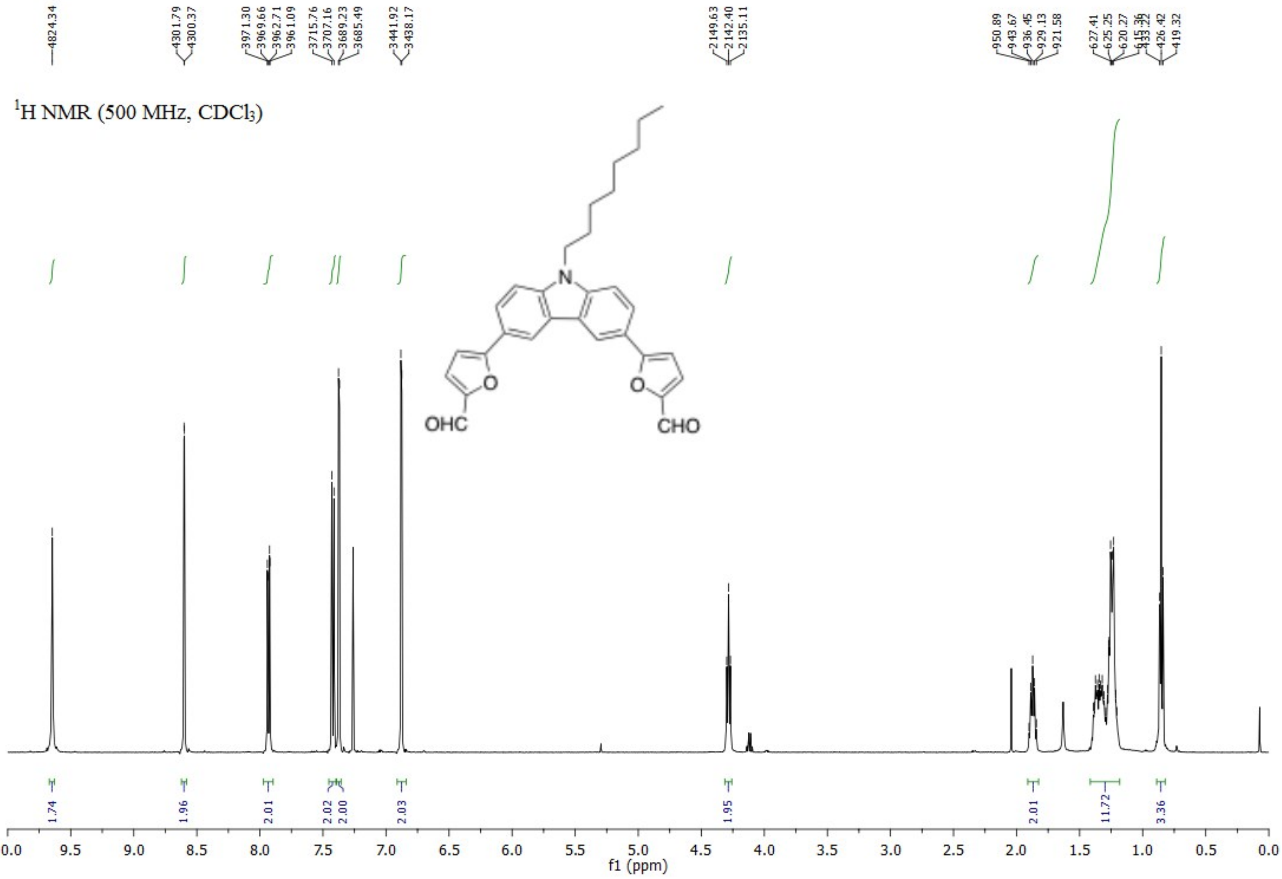

$^{1}$H NMR (500 MHz, CDCl$_3$)

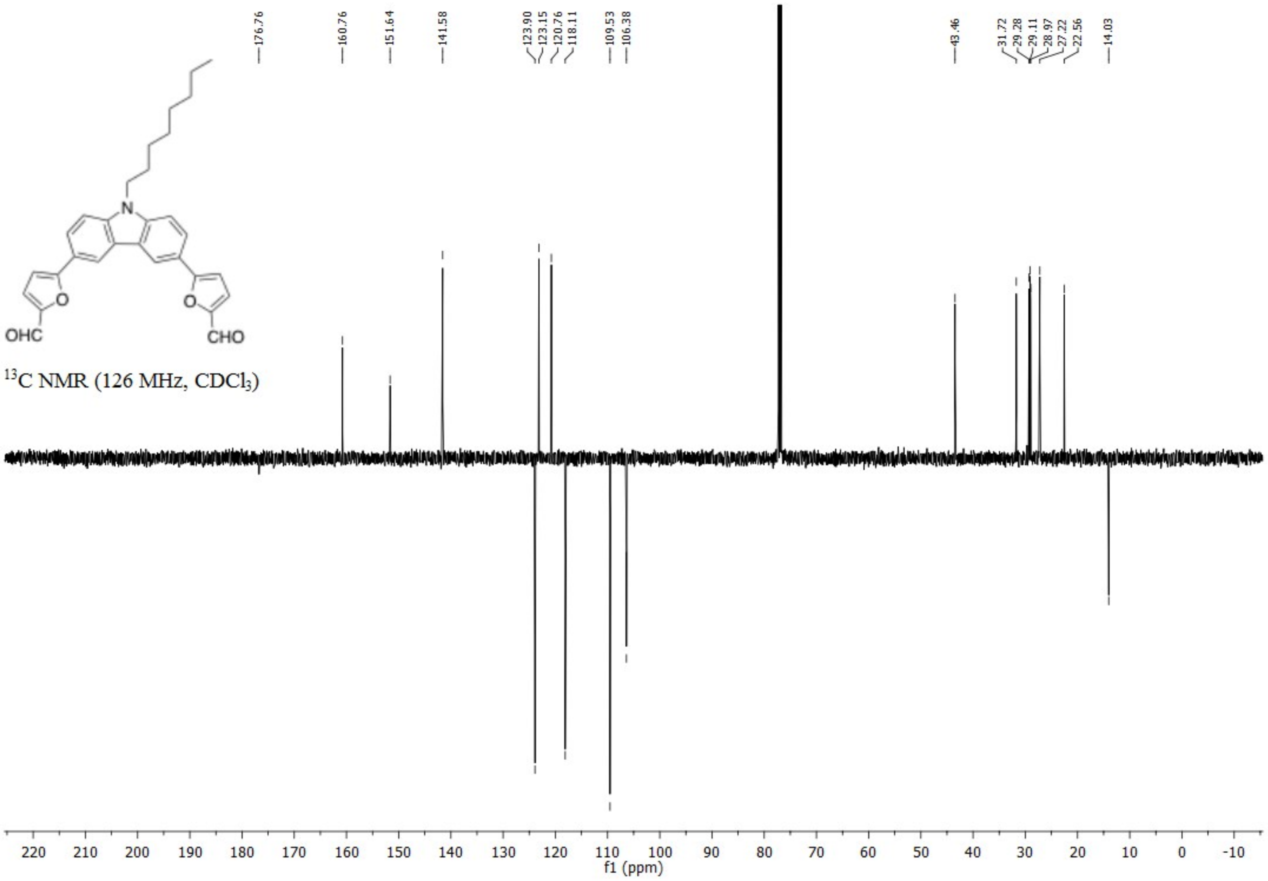


$^{13}$C NMR (126 MHz, CDCl$_3$)



$^{1}$H NMR (500 MHz, CDCl$_3$)


$^1$H NMR (500 MHz, CDCl$_3$)


$^{13}$C NMR (126 MHz, CDCl$_3$)