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## Heteroatom-Mediated Performance of Dye-Sensitized Solar Cells based on T-Shaped Molecules

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#### Abstract

Two novel "sister" organic dyes featuring a T-shape molecular pattern based on phenothiazine/phenoxazine and triphenylamine framework as electron donor core and cyanoacrylic acid as acceptor and anchoring group were designed, synthesized and thoroughly characterized. Both dyes were functionalized at the nitrogen atom of phenoxazine/phenothiazine with the triphenylamine unit containing two hexyloxy substituents to obtain a T-shape configuration. The photo-optical and electrochemical data corroborated with time-dependent density functional theory computations and photovoltaic features were discussed in correlation with the structural architecture of each dye. Their performances in dye-sensitized solar cells (DSSCs) were comparatively surveyed with a special concern on the influence of the heteroatom variation on the most important DSSCs characteristics. In spite of its more favorable optical performance, the cells realized with phenoxazine-based dye are less efficient than those fabricated with phenothiazine ones. The cause is the stronger electron interception by the electrolyte in the case of phenoxazine dye which consistently degrades the open-circuit voltage, corroborated with a better regeneration of the phenothiazine by the iodine/iodide redox couple. In fact, to the best of our knowledge, this is one of the first studies which highlights how a single heteroatom in a T-shape dye structure can affect the dye interaction with the electrolyte and its regeneration, consequently the photovoltaic performances and brings out new opportunities for developing novel dyes for efficient DSSCs.

Keywords: phenoxazine, phenothiazine, T-shape structure, dye-sensitized solar cells, heteroatom-dependent dark current

## **1. INTRODUCTION**

Dye-sensitized solar cells (DSSCs) as the most viable alternatives to crystalline Si-based photovoltaics for converting clean, unlimited sunlight to electricity have attracted significant research interest due to their low fabrication cost and relatively high power conversion efficiency (PCE) since the first cell reported by Grätzel in 1991.<sup>1</sup> In almost three decades this type of solar cell has shown much promise in the solar energy sector, the most glaring benefit being the ability to overcome the so-called Shockley-Queisser limit<sup>2,3</sup> through applying a smart design. The advantageous traits are not limited to the potential efficiency, but also include the facility of large-scale manufacture and low impurity sensitivity, besides the aesthetically pleasing. Two of the most important physical parameters that contribute to the overall efficiency of a DSSC are the open circuit voltage ( $V_{oc}$ ) and short circuit current ( $I_{sc}$ ). In separately p- and n-type DSSCs, since  $V_{oc}$  is the difference between the Fermi-level of the semiconducting oxide and the redox potential of the electrolyte, its value can be modulated be using various electrolytes and/or different semiconductors.<sup>4</sup> On the other hand, the maximum current delivered by a DSSC is limited by the transport resistance and various recombination pathways; all these can be prevented via intelligent dye design approach to address the intermolecular quenching due to aggregation on the semiconductor surface and photo-current limitations through device optimization fabrication.

DSSCs are typically composed of a mesoporous semiconductor metal oxide film, a dye, an electrolyte as hole transporter, and a counter electrode.<sup>5</sup> The sensitizer is crucial in the DSSCs structure, because it absorbs sunlight and injects the electron into the  $TiO_2$  semiconductor. Most organic sensitizers have a rod-shape structure, which tend to aggregate on the semiconductor surface, lessening the photovoltaic effect due to the intermolecular quenching: the molecules are not functionally attached to the  $TiO_2$  surface and thus behave as filters.<sup>6</sup> It is worth knowing that a phenoxazine or phenothiazine-based dye contains electron-

rich nitrogen and oxygen/sulphur heteroatoms in the heterocyclic structure, with high electron-donating ability. The nonplanar butterfly conformation of phenoxazine/phenothiazine with two phenyl rings arranged in a small torsion angle related to N(10) and O/S(9) atoms can lead to a sufficiently inhibition of molecular aggregation and formation of intermolecular excimers.<sup>7,8</sup> Numerous attempts have been made to molecularly engineer phenoxazine or phenothiazine dyes in order to broaden the absorption band and increase the efficiency. When designing the dye, high molar extinction coefficients are of particular importance, because they reduce parasitic light absorption. One of the strategies to achieve better performances is to introduce an additional electron donor group into the core of phenoxazine or phenothiazine sensitizer to form a D-D- $\pi$ -A structure. In this way, the  $\pi$ - delocalization can be extended and the molar absorptivity of the materials significantly enhanced.<sup>9,10</sup> Arylamine derivatives (carbazole, triphenylamine, indoline and their derivatives) are well known electron-rich structures that are widely incorporated in phenoxazine- or phenothiazine-based dyes as additional electron donor moiety. For example, the insertion of thiophene and triphenylamine units into some phenothiazine sensitizers extended the  $\pi$ -conjugation leading to a larger molar absorptivity. Meanwhile, this design makes the whole molecule to expand on larger surface area compared to a molecule of linear shape, leading to the reduction of the dye loading capacity.<sup>11</sup> Besides, the red-shift of their absorption spectra and an enhanced efficiency were achieved.<sup>12</sup> This strategy avoids the charge recombination process of injected electrons with the triiodide in the electrolyte and also minimizes the formation of aggregates between dye molecules. A thorough literature survey evidenced that the vast majority of developed phenoxazine/phenothiazine sensitizers having a D-D- $\pi$ -A topology contains the second donor group connected in most cases to the (C)7 position of these cores (rod-like dyes), and only few studies are reported so far in which the second donor is directly linked to the (N)10 atom of phenoxazine/phenothiazine (T-shape dyes).<sup>13</sup> The optical features indicated that rod-like

dyes displayed broader and red-shifted absorption waves compared to the T-shaped dyes due to longer conjugation. But T-shaped dyes were superior because of higher recombination resistance, lower charge transport resistance, better electron lifetime, and good electron injection which led to high efficiency due to the favorable  $V_{OC}$  and  $J_{SC}$  values.

Following the issues outlined above, it appeared challenging to us to design and synthesize two novel DD- $\pi$ -A structurally related phenoxazine/phenothiazine- and triphenylamine-based dyes and to survey comparatively their physico-chemical properties and performances as sensitizers in DSSCs. The conceptual design consists in the direct bonding of triphenylamine core to the (N)10 position and of the cyanoacrylate moiety to the C(3) position of phenoxazine/phenothiazine, resulting in a T-shaped structural motif. Two additional hexyloxy chains were attached in the *para* position of triphenylamine unit in order to improve its donating capability, suppress the dyes aggregation and minimize the recombination. It is expected this molecular architecture to provide a satisfied relay for the electron migration from donor to acceptor and better photovoltaic performances when compared to the rod-shaped dyes.

#### 2. EXPERIMENTAL SECTION

Details about starting materials and 1-(hexyloxy)-4-iodobenzene synthesis<sup>14,15</sup> are available in the *Supporting Information (SI)*.

#### 2.1. Synthesis

The synthetic pathway to phenoxazine/phenothiazine-triphenylamine based dyes (PTH-TPA and PHX-TPA) is outlined in Scheme 1 and the details are described as follows. All reactions were performed under nitrogen atmosphere with the use of standard Schlenk technique.



Scheme 1. Synthetic route to the T-shaped dyes based on phenothiazine or phenoxazine

*N*-(4-nitrophenyl)phenoxazine (1a). In a 100 mL three-necked round-bottomed flask equipped with a magnetic stirring bar, nitrogen inlet and outlet and condenser, 4-fluoronitrobenzene (2.3 g, 16.4 mmol), 10*H*-phenoxazine (2 g, 10.1 mmol), potassium carbonate (2.26 g, 16.4 mmol) and DMSO (30 mL) were placed. The reaction mixture was refluxed at 120°C overnight (21 h) when the solution became dark-red. The reaction evolution was monitored by thin layer chromatography (TLC) using hexane/ethyl acetate, 30/1, v/v. When 10*H*-phenoxazine was no longer present, the reaction mixture was allowed to cool to room temperature and slowly poured into 150 mL of stirred methanol when an orange-red solid started to precipitate. It was collected by filtration and washed thoroughly with methanol/water. The resulting nitro compound **1a** was dried under vacuum to obtain 2.15 g of orange-red powder (70% yield).

<sup>1</sup>H-NMR (DMSO, 400 MHz), d (ppm): 8.49–8.47 (d, 2H), 7.77–7.75 (d, 2H), 6.83–6.70 (m, 6H), 6.05–6.05 (d, 2H).

<sup>13</sup>C-NMR (DMSO, 400 MHz), δ (ppm): 146.71, 144.97, 143.52, 132.82, 131.37, 126.51, 123.76, 122.38, 115.66, 113.94.

*N*-(4-nitrophenyl)phenothiazine (1b) was synthesized according to the procedure reported for 1a to afford 2.3 g of yellow powder (73% yield).

<sup>1</sup>H-NMR (DMSO, 400 MHz), d (ppm): 8.14–8.12 (d, 2H), 7.65–7.63 (d, 2H), 7.60–7.58 (d, 2H), 7.52–7.48 (t, 2H) 7.39–7.35 (t, 2H), 7.07–7.05 (d, 2H).

<sup>13</sup>C-NMR (DMSO, 400 MHz), δ (ppm): 150.87, 140.66, 140.18, 133.35, 129.82, 129.32, 128.37, 127.348, 127.24, 126.04.

*N*-(4-aminophenyl)phenoxazine (2a). In a 250 mL three-necked round-bottomed flask equipped with a magnetic stirring bar, nitrogen inlet and outlet and condenser was added the dinitro-derivative **1a** (1.8 g, 6 mmol) and a mixture of ethanol and water (120 mL), EtOH/H<sub>2</sub>O, 20/1, v/v. To the resulting suspension, iron powder (1 mg, 18 mmol) and CaCl<sub>2</sub> (0.66 g, 6 mmol) were added and stirred at 78°C for 24 h. The reaction evolution was monitored by TLC using hexane/ethylacetate, 10/1, v/v. After completion, the reaction mixture was filtered on celite to remove the iron residues, and to the alcoholic solution ice flakes were added when a white-grey solid started to precipitate. The solid was collected by filtration and washed thoroughly with water. The resulting amine **2a** was dried under vacuum to obtain 1.40 g of white-grey powder (86% yield).

<sup>1</sup>H-NMR (DMSO, 400 MHz), d (ppm): 6.89–6.96 (d, 2H), 6.78–6.76 (d, 2H), 6.69–6.61 (m, 6H), 5.93–5.91 (d, 2H), 5.44 (s, 2H).

<sup>13</sup>C-NMR (DMSO, 400 MHz), δ (ppm): 148.90, 143.16, 134.71, 130.44, 125.44, 123.56, 120.85, 115.67, 114.94, 113.06.

*N*-(4-aminophenyl)phenothiazine (2b) was synthesized following a reported procedure,<sup>16</sup> using Pd/C and hydrazine monohydrate in ethanol at reflux. Accordingly, 3.8 g of white-grey

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solid (90% yield) were obtained when starting from 2.3 g (14.5 mmol) of N-(4-nitrophenyl)phenothiazine.

<sup>1</sup>H-NMR (DMSO, 400 MHz), d (ppm): 7.01–6.99 (m, 4H), 6.93–6.88 (t, 2H), 6.82–6.77 (m, 4H), 6.22–6.20 (d, 2H), 5.43 (s, 2H).

<sup>13</sup>C-NMR (DMSO, 400 MHz), δ (ppm): 148.81, 144.42, 130.91, 127.58, 127.04, 126.24, 122.045, 118.37, 115.43, 115.37.

**Bis(4-hexyloxy-phenyl)-(4-phenoxazin-10-yl-phenyl)-amine** (**3a**). In a 100 mL threenecked round-bottomed flask equipped with a magnetic stirring bar, nitrogen inlet and outlet and condenser was added potassium hydroxide (1.93 g, 34.56 mmol) and copper (I) iodide (0.17 g, 0.86 mmol) to a stirred solution of amine **2a** (1.2 g, 4.32 mmol), 1-(hexyloxy)-4iodobenzene (3.95 g, 12.96 mmol), and 1,10-phenanthroline (0.16 g, 0.86 mmol) in toluene (50 ml). The reaction mixture was heated under reflux for 24 h at 120°C, when the solution became dark red. After that, the reaction mixture was allowed to cool to room temperature and filtered to remove the insoluble solids. The resulting mixture was poured into 250 mL water. The crude product was extracted three times with ethyl acetate, and the combined organic layer was washed with water and dried over anhydrous sodium sulphate. After removing the solvent under reduced pressure, the oil residue was purified by column chromatography using a mixture of hexane and ethyl acetate, 99/1, v/v to obtain 0.76 g of light-yellow oil (30% yield).

<sup>1</sup>H-NMR (DMSO, 400 MHz), d (ppm): 7.14–7.12 (m, 6H), 6.96–6.94 (d, 4H), 6.91–6.88 (d, 2H), 6.71–6.64 (m, 6H), 5.97–5.95 (d, 2H), 3.97–3.93 (t, 4H), 1.73–169 (m, 4H), 1.40–1.44 (m, 4H), 1.32–1.31 (m, 8H), 0.91–0.87 (t, 6H).

<sup>13</sup>C-NMR (DMSO, 400 MHz), δ (ppm): 155.83, 143.24, 139.48, 138.02, 134.39, 130.82, 127.56, 123.78, 121.32, 119.87, 117.37, 115.72, 115.23, 113.26, 67.75, 31.04, 28.75, 25.26, 22.12, 13.96.

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**Bis(4-hexyloxy-phenyl)-(4-phenothiazin-10-yl-phenyl)-amine** (**3b**) was synthesized according to the procedure described for **3a** to afford 0.81 g of light-yellow oil (34% yield).

<sup>1</sup>H-NMR (DMSO, 400 MHz), d (ppm): 7.18–7.16 (m, 6H), 7.04–6.92 (d, 2H), 6.97–6.90 (m, 8H), 6.85–6.82 (t, 2H), 6.26–6.24 (d, 2H), 3.97–3.94 (t, 4H), 1.73–169 (m, 4H), 1.44–1.40 (m, 4H), 1.33–1.31 (m, 8H), 0.90–0.87 (t, 6H).

<sup>13</sup>C-NMR (DMSO, 400 MHz), δ (ppm): 156.98, 145.38, 140.63, 131.98, 128.14, 127.67, 127.08, 123.02, 122.98, 120.73, 120.16, 116.40, 116.12, 68.53, 32.13, 29.65, 26.28, 23.10, 22.12, 14.13.

10-(4-(Bis(4-(hexyloxy)phenyl)amino)phenyl)phenoxazinyl-3-carbaldehyde (4a). А Schlenk tube equipped with a magnetic stirring bar, nitrogen inlet and outlet and condenser, containing anhydrous DMF (0.47 mL, 5.5 mmol) was cooled in an ice bath (0-5 °C). To this solution, phosphorous oxychloride (0.65 mL, 5.5 mmol) was added dropwise for 30 min, when a slightly opaque solid started to appear. 10 mL of 1,2-dichloroethane was added to the formed Vilsmeier reactive and the stirring was continued for 1 hour at 0–5 °C, when a white opalescent solution was obtained. The triphenylamine-substituted phenoxazine 3a (0.7 g, 1.1 mmol) in 10 mL of 1,2-dichloroethane was added to the above solution and heated to 90 °C for 24 h. The occurrence of the newly formed aldehyde was monitored by TLC using hexane:ethylacetate, 10/1, v/v. Upon completion, the reaction mixture was allowed to cool to room temperature, poured into ice water and neutralized to pH 6-7 by dropping saturated aqueous sodium hydroxide solution. The mixture was extracted with 250 mL ethyl acetate. The organic layer was washed three times with water and dried with anhydrous sodium sulphate, followed by concentration under reduced pressure. The aldehyde was purified by column chromatography to obtain 0.55 g of vellow-greenish solid (73% yield).

<sup>1</sup>H-NMR (DMSO, 400 MHz), δ (ppm): 9.64 (s, 1H,), 7.29–7.27 (d, 1H), 718–7.15 (m, 6H), 7.09 (s, 1H), 6.97–6.95 (d, 4H), 6.91–6.89 (d, 2H), 6.75–6.73 (m, 3H), 6.09–6.07 (d, 1H),

6.00–5.99 (d, 1H), 3.97–3.94 (t, 4H), 1.73–1.67 (m, 4H), 1.44–1.40 (m, 4H), 1.36–1.31 (m, 8H), 0.90–0.87 (t, 6H).

<sup>13</sup>C-NMR (DMSO, 400 MHz), δ (ppm): 189.99, 155.86, 148.92, 143.39, 142.93, 139.89,
139.11, 132.69, 130.27, 129.85, 128.22, 127.65, 127.39, 123.96, 122.67, 119.32, 115.59,
115.31, 113.96, 113.78, 112.74, 67.59, 30.96, 28.65, 25.17, 22.04, 13.88.

**10-(4-(Bis(4-(hexyloxy)phenyl)amino)phenyl)phenothiazinyl-3-carbaldehyde (4b)** was synthesized according with the procedure detailed for **4a** to obtain 0.53 g of yellow-greenish solid (72% yield).

<sup>1</sup>H-NMR (DMSO, 400 MHz), δ (ppm): 9.7 (s, 1H), 7.49 (s, 1H), 7.47–7.45 (d, 1H), 7.20–7.18 (d, 6H), 7.06–7.04 (d, 1H), 6.98–6.96 (m, 5H), 6.92–6.90 (m, 3H), 6.33–6.31 (d, 1H), 6.24–6.22 (d, 1H), 3.97–3.94 (t, 4H), 1.73–1.67 (m, 4H), 1.44–1.40 (m, 4H), 1.34–1.30 (m, 8H), 0.90–0.86/ (t, 6H).

<sup>13</sup>C-NMR (DMSO, 400 MHz), δ (ppm): 190.70, 156.44, 149.34, 149.30, 142.94, 139.64,
131.27, 130.97, 130.38, 130.29, 128.27, 128.07, 127.71, 127.20, 127.05, 124.14, 119.51,
119.36, 118.46, 116.91, 116.16, 115.67, 68.16, 31.47, 29.17, 25.68, 22.55, 14.38.

3-(10-(4-(Bis-(4-hexyloxy-phenyl)-amino)-phenyl)-10H-phenoxazin-3-yl)-2-cyanoacrylic

acid (PHX-TPA). In a Schlenk tube, **4a** (0.5 g, 0.76 mmol) dissolved in 4 mL chloroform and cyanoacetic acid (0.12 g, 2.25 mmol) were placed. This mixture was stirred for 10 minutes under nitrogen stream, and then piperidine (0.45 g 5.33 mmol) dissolved in 2 mL chloroform was added dropwise to the mixture. The reaction mixture was kept under stirring and gentle reflux (65 °C) for 12 h. The reaction was quenched with 60 mL HCl 2 M, when the colour turned from orange-red to dark-red. The organic phase was extracted three times with DCM and washed three times with water as the last washing water to have pH = 5.5. After drying over sodium sulphate and solvent evaporation, the residue was purified by column

chromatography using successively DCM and DCM/methanol 10/1, v/v, to afford 0.33 g of dark-red powder (66 % yield).



<sup>1</sup>H-NMR (DMSO, 400 MHz),  $\delta$  (ppm): 13.14 (s, 1H, H–1), 7.89 (s, 1H, H–6), 7.46 (s, 1H, H–8), 7.30–7.28 (d, 1H, H–18), 7.19–7.15 (m, 6H, H–21,25), 6.97–6.94 (d, 4H, H–24), 6.91–6.89 (d, 2H, H–20), 6.81–6.79 (m, 1H, H–11), 6.75–6.72 (m, 2H, H–12,13), 6.04–6.02 (m, 2H, H–14,17), 3.97–3.93 (t, 4H, H–27), 1.74–1.67 (m, 4H, H–28), 1.44–1.40 (m, 4H, H–29), 1.32–1.30 (m, 8H, H–30,31), 0.90–0.87 (t, 6H, H–32).

<sup>13</sup>C-NMR (DMSO, 400 MHz), δ (ppm): 163.39 (C–2), 155.79 (C–26), 148.90 (C–5), 143.02 (C–23), 139.19 (C–19,22), 138.05 (C–9), 132.64 (C–10), 130.21(C–15,16), 129.37 (C–18), 127.52 (C–24), 127.40 (C–7), 125.03 (C–12), 123.91 (C–13), 122.54 (C–17), 119.51 (C–20,21), 117.99 (C–11), 115.58 (C–25), 115.34 (C–4), 114.55 (C–14), 113.85 (C–8), 112.85 (C–3), 67.59 (C–27), 30.92 (C–28), 28.63 (C–29), 25.13 (C–30), 21.99 (C–31), 13.83 (C–32). Elemental analysis calc. for C<sub>46</sub>H<sub>47</sub>N<sub>3</sub>O<sub>5</sub> (M = 721) (%): C 76.56; H 6.52; N 5.83. Found, %: C 76.50; H 6.58; N 5.75.

# **3-(10-(4-(Bis-(4-hexyloxy-phenyl)-amino)-phenyl)-10***H***-phenothiazin-3-yl)-2cyanoacrylic acid (PTH-TPA) was synthesized according to the procedure described for <b>5a** to obtain 0.39 g of red powder (69 % yield).



<sup>1</sup>H-NMR (DMSO, 400 MHz),  $\delta$  (ppm): 13.15 (s, 1H, H–1), 7.81 (s, 1H, H–6), 7.63 (s, 1H, H–8), 7.51–7.49 (d, 1H, H–18), 7.20–7.17 (d, 6H, H–21,25), 7.06–7.04 (d, 1H, H–11), 6.98–6.96 (m, 5H, H–12,24), 6.92–6.86 (m, 3H, H–13,20), 6.25–6.22 (m, 2H, H–14,17), 3.97–3.94 (t, 4H, H–27), 1.74–1.68 (m, 4H, H–28), 1.44-1.40 (m, 4H, H–29), 1.30–1.34 (m, 8H, H–30,31), 0.90–0.87 (t, 6H, H–32).

<sup>13</sup>C-NMR (DMSO, 400 MHz), δ (ppm): 163.38 (C–2), 156.38 (C–26), 149.25 (C–5), 143.16 (C–19,22), 139.72 (C–23), 131.30 (C–15,16), 130.66 (C–7), 130.38 (C–18), 128.20 (C–24), 128.01 (C–13), 127.68 (C–8), 127.33 (C–11), 127.06 (C–9), 123.80 (C–10), 119.67 (C–20,21), 119.21 (C–14), 118.40 (C–12), 116.61 (C–17), 116.03 (C–4), 116.15 (C–25), 115.79 (C–3), 68.15 (C–27), 31.47 (C–28), 29.17 (C–29), 25.68 (C–30), 22.55 (C–31), 14.38 (C–32). Elemental analysis calc. for C<sub>46</sub>H<sub>47</sub>N<sub>3</sub>O<sub>4</sub>S (M = 737) (%): C 74.90; H 6.38; N 5.70; S 4.34. Found, %: C 74.83; H 6.42; N 5.78; S 4.28.

## 2.2. Measurements

The <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were registered with a Bruker Avance III 400 spectrometer provided with a 5 mm multinuclear inverse detection probe, operating at 400.1 and 100.6 MHz for <sup>1</sup>H and <sup>13</sup>C nuclei, respectively. <sup>1</sup>H and <sup>13</sup>C chemical shifts are afforded in  $\delta$  units (ppm) relative to the residual peak of the solvent. All column chromatography purifications were performed with the use of silica gel 60 (0.063-0.2 mm) as the stationary phase in columns of different lengths and diameters. The infrared (FTIR) spectra were

recorded on a FTIR Bruker Vertex 70 Spectrophotometer in ATR mode by using samples in form of powder. Electronic absorption spectra were obtained on a Specord M42 UV-Visible spectrophotometer at room temperature using freshly prepared solutions at low concentration  $(\approx 10^{-5} \text{ M})$  in various solvents. The absorption spectra of the dye-loaded TiO<sub>2</sub> films were obtained by diffuse reflectance spectroscopy (DRS) using Eding. Inst. FLS920 spectrofluorometer. Photoluminescence (PL) spectra of dye solutions were acquired with a Perkin Elmer LS 55 instrument. The PL decay profiles were measured using time-correlated single-photon counting (TCSPC) and pulsed laser excitation (5 mW at 375nm). Cyclic voltammetric experiments were carried out at room temperature on a Potentiostat-Galvanostat (PG581, Uniscan Instruments) with a conventional three-electrode configuration consisting of ITO-coated glass covered with the dye or platinum as working electrode, a platinum wire auxiliary electrode, and a calomel (SCE) reference electrode. Tetrabutylammonium perchlorate (TBAP)/acetonitrile (CH<sub>3</sub>CN) was used as supporting electrolyte for the dye coating samples and TBAP/dichloromethane for solution samples having the concentration of  $1 \times 10^{-3}$  M. All potentials were reported with respect to SCE electrode at a scan rate of 50 mV/s. The potentials are quoted against the ferrocene internal standard (+0.45 vs SCE). The current-voltage (I-V) characteristics of the cells were measured with Keithley 4200-SCS semiconductor characterization system, under dark and illumination conditions, using a LED solar simulator, class ABA (model LSH 7320, Newport, USA). The measurement of incident photon to current conversion efficiency - IPCE ( $\lambda$ ) - spectra was performed by incrementing the F920 calibrated monocromator over the 300-900 nm wavelength range, and the shortcircuit photocurrent density (mA/cm<sup>2</sup>) was recorded with PGSTAT302N potentiostat. The electrochemical impedance spectroscopy (EIS) measurements of the cells were recorded with Autolab/PGSTAT302N electrochemical workstation, under 100 mW/cm<sup>2</sup> light illumination, in the frequency range from 50 mHz to 100 kHz, with logarithmic point spacing, at open

circuit potential (OCP) bias, using an alternating low signal with 10 mV amplitude. The impedance spectra were analyzed on the basis of the electrical equivalent circuit  $R_s(Q1R1)(Q2R2)(Q3R3)$ , using the ZSimpWin software, which takes into consideration the phenomena encountered at the Pt counterelectrode, sensitized TiO<sub>2</sub> photoanode and within the electrolyte, respectively. In order to compensate the non-ideal behavior, the constant phase elements (Q) replace the simple capacitances in the model. Accordingly, it allows the extraction of series resistance ( $R_s$ ), charge transfer resistance at Pt/electrolyte interface ( $R_1$ ,  $R_{ce}$ ) and at TiO<sub>2</sub>/dye/electrolyte interface ( $R_2$ ,  $R_r$ ), or chemical capacitance of the TiO<sub>2</sub> film ( $C_2$ ).

#### 2.3. Fabrication of DSSCs

A 10µm thick mesoporous TiO<sub>2</sub> layer, with a 4µm scattering layer deposited on it (Solaronix, Switzerland), both treated in a TiCl<sub>4</sub> atmosphere, was functionalized using a 0.3mM solution of the dye in dichlormethane (DCM), for an immersion time of 4 or 6 hours. Thereafter, the film, rinsed with ethanol and soaked in nitrogen flux, was encapsulated using a platinum counter electrode and a 60µm thick Surlyn sealant (Solaronix). The cells have been impregnated using two different electrolytes (HI-30 and AN-50, Solaronix). Both are based on  $I/I_3^-$  redox couple, but with different  $I_3^-$  concentrations, 30 mM (HI-30) and 50 mM (AN-50), with acetonitrile as solvent and ionic liquid, lithium salt and pyridine derivative as additives. The Surlyn sealant has been heated for two different times (2 and 3 minutes). After the TiO<sub>2</sub> film impregnation, the hole in the counter electrode was sealed by heating a Surlyn sheet covered by a glass cover. The device area was 0.36 cm<sup>2</sup>.

#### 2.4. Quantum chemical simulations

In order to avoid geometry optimization difficulties due to the floppiness of the long alkyl chains, slightly modified structural motifs of PTH-TPA and PHX-TPA were involved in simulations by replacing the hexyl unit with the less voluminous methyl group (PTH-TPAm and PHX-TPAm, *SI*, figure S1). The ground-state geometries of PTH-TPAm and PHX-TPAm were fully optimized without any symmetry constraints using the density functional theory (DFT) level with the B3LYP exchange-correlation functional<sup>17,18</sup> and 6-311++G\*\* basis set on all atoms<sup>19-21</sup>. This approach for geometry optimization has been noted to be robust.<sup>22</sup>

The UV-Vis absorption spectra of both dyes were simulated by computing the excited states and oscillator strengths for the lowest 30 singlet transitions using the time-dependent (TD) DFT with the B3LYP functional and the 6-311++G\*\* basis set using the B3LYP/6-311++G\*\* optimized geometry in the ground state. The simulated UV-Vis spectrum of PHX-TPAm in vacuo is in good qualitative/semi-quantitative agreement with the experimental one, while for PTH-TPAm the peak around 400nm is missing. UV-Vis absorption spectra of PHX-TPAm and PTH-TPAm were also simulated using CAM-B3LYP<sup>23</sup>, which is a range-separated hybrid functional and it has been found to successfully describe charge-transfer excited states.<sup>24,25</sup> However, for both molecules the whole simulated UV-Vis spectrum using CAM-B3LYP is blue-shifted by 0.5-0.6 eV. This behaviour has been previously reported for phenothiazine-based molecules.<sup>26</sup>

All computations DFT and TD-DFT were carried out with the Gaussian 09 program in a computer workstation;<sup>27</sup> molecular structures and HOMO-LUMO orbitals figures, along with UV-Vis spectra were attained with GaussView Version 5.<sup>28</sup>

#### **3. RESULTS AND DISCUSSIONS**

#### 3.1. Molecular design and synthesis

Novel DD-n-A type organic dyes (PTH-TPA and PHX-TPA) with a T shape configuration have been developed by inserting a subordinate donor unit in the conventional design of metal-free organic sensitizers with the aim to facilitate the electron migration, to improve photostability and to inhibit the dye aggregation. The developed sensitizer combines as structural features the triphenylamine containing two hexyloxy substituents and phenothiazine/phenoxazine as donor framework (DD), the vinylene bridge as  $\pi$ -linker ( $\pi$ ), and the cyanoacrylic acid as both anchoring group and electron acceptor (A). The long hexyl groups on the triphenylamine core were used aiming at increasing the *push* strength, suppressing the aggregation and minimizing the recombination.<sup>14</sup> Having in mind the proposed design a scenario of photovoltaic mechanism can be rationalized as follows. When the dyes harvest sunlight, the electrons move from the triphenylamine core under the pushing force of hexyloxy units to the phenothiazine/phenoxazine unit, being further driven through the  $\pi$ -conjugated vinyl bridge to the cyanoacrylic acid acceptor by means of dye photoexcitation. The generated photo-excited electrons are then injected into the conduction band of TiO<sub>2</sub> via the anchoring carboxyl group. Next, the dye captures an electron from the redox couple and comes back to the initial state (dye regeneration), leaving a positive charge (a hole) in the electrolyte. Since the mechanism of charge separation responsible for the generation of the photovoltaic effect is accomplished, the structural motif of our metal-free organic sensitizers suggests that they are suitable for use in DSSCs.

The developed structural pattern of PTH-TPA and PHX-TPA sensitizers was fully proved by spectral methods, as <sup>1</sup>H-, <sup>13</sup>C-NMR and FTIR. In the <sup>1</sup>H-NMR spectra (Figure 1) the most shielded signal at 7.82 ppm for PTH-TPA and 7.88 ppm for PHX-TPA was attributed to the vinyl proton H-6 of cyanoacrylic acid.



Figure 1. <sup>1</sup>H-NMR spectra of PTH-TPA and PHX-TPA sensitizers

The protons belonging to the phenothiazine/phenoxazine core gave splitted patterns that are partially overlapped with the signals corresponding to the aromatic protons of the triphenylamine unit. The protons belonging to phenothiazine/phenoxazine in the vicinal positions of vinylene linkage were evidence by a singlet (H-8) at 7.63 ppm for PTH-TPA and 7.46 ppm for PHX-TPA and a doublet (H-18) at 7.51-7.49 for PTH-TPA and 7.30-7.28 ppm for PHX-TPA. The less shifted signal in the aromatic region, at 6.26-6.23 and 6.04-6.02 ppm for PTH-TPA and PHX-TPA, respectively, was assigned to the protons H-14 and H-17 of the phenothiazine/phenoxazine rings. The protons belonging to the phenylene units of triphenylamine fall at 7.20-7.17 ppm (d, H-21, H-25), 6.98-6.95 ppm (m, H-24, overlapped signal) and 6.92-6.90 ppm (d, H-20, overlapped signal) for PTH-TPA and 7.19-7.15 ppm (m, H-21, H-25), 6.97-6.94 ppm (d, H-24) and 6.91-6.89 ppm (d, H-20) for PHX-TPA. The protons belonging to the hexyloxy groups were evidenced for both dyes at similar shielding. The triplet at 3.97–3.94 ppm was associated with the CH<sub>2</sub> protons linked to O of hexyloxy group (H-17). The other four methylene groups were grouped in three multiplets at 1.74–1.68 ppm (H-28), 1.44–1.40 ppm (H-29) and 1.32–1.31 ppm (H-30, H-31). Finally, the protons of the end-methyl group (H-32) appeared at 0.90–0.87 ppm as a triplet. The <sup>13</sup>C-NMR spectra evidenced the presence of carboxylic group in PTH-TPA and PHX-TPA dyes by the most shielded signal at 163.38-163-39 ppm, while the nitrile group appeared at 116.03 and 115.34 ppm for PTH-TPA and PHX-TPA, respectively (Figure S2, SI).

FTIR spectra of PTH-TPA and PHX-TPA sensitizers showed characteristic absorption bands of the newly formed vinylene linkage at 826-818 cm<sup>-1</sup>, whereas the FTIR bands due to the aldehyde (approx. 1700 cm<sup>-1</sup>) of the starting reagents completely disappeared, undeniable proving the formation of cyanoacrylic acid core under the Knoevenagel condensation conditions. The carboxylic functional group was found by the absorption bands at 3485-3465 cm<sup>-1</sup> (OH stretching, wide band) and 1718-1724 cm<sup>-1</sup> (C=O stretching), while CN groups was

evidenced by the absorption band at 2218-2221 cm<sup>-1</sup>. The IR bands at approx. 3061-3041 cm<sup>-1</sup> originate from the C–H stretching in phenylene units, while the system band at approx. 2954-2857 cm<sup>-1</sup> corresponds to the aliphatic C-H stretching of the hexyloxy groups. The -C=C- stretching in phenylene and phenothiazine/phenoxazine rings falls at 1585-1601 and 1504 cm<sup>-1</sup>, while C–O–C stretching in hexyloxy units can be identified at 1241-1244 cm<sup>-1</sup> as strong band. The absorption band at 801 cm<sup>-1</sup> in FTIR spectrum of PTH-TPA was associated with stretching vibrations of C-S bond in phenothiazine core, whereas the mediumstrong band at 1021 cm<sup>-1</sup> found in FTIR spectrum of PHX-TPA was attributed to the =C–O–C= vibration or heteroatom ring deformation of the phenoxazine ring. The FTIR spectra of PTH-TPA and PHX-TPA are provided in Figure S3, *SI*.

#### 3.2. Electrochemistry and electronic structure

Cyclic voltammetry (CV) was employed to survey the oxidation and reduction potentials of PTH-TPA and PHX-TPA sensitizers, and to further asses the HOMO and LUMO energy levels for an accurate evaluation of the electron transfer from the excited dye molecules into the conductive band of  $TiO_2$  and the dyes regeneration. The redox waves of the PTH-TPA and PHX-TPA in DCM/TBAP electrolyte system at a scan rate of 50 mV/s are shown in Figure 2. A small oxidation wave with an onset around + 0.67 V *vs* SCE, followed by other four peaks, could be observed in the CV curve of PTH-TPA upon positive potential sweep. This irreversible oxidation is assumed to occur at the free electron pair of the S atom of the phenothiazine core, as this oxidation process at the N atom of the phenothiazine at the same potential at which the oxidation takes place at the N atom of the phenoxazine in PHX-TPA. It was followed by the quasireversible oxidation of the triphenylamine unit. This oxidation wave shows a slight shift correlated with the electronic effect of the substituent on

the TPA moiety. It appears that phenothiazine has a better electron donating effect than phenoxazine since it leads to a lower oxidation potential of the TPA core in PTH-TPA (1.10V vs SCE) compared to PHX-TPA (1.13V vs SCE).

Figure 2. Redox waves of PTH-TPA and PHX-TPA in DCM/TBAP:

a) anodic waves; b) cathodic waves



By further scanning the potential in the anodic direction both dyes registered two irreversible oxidation processes which are most likely due the dimerization of the formed cationic radicals. These peaks disappeared on repeated cycling, being an indicative that the formed dimers are soluble oligomeric products. Instead, the oxidation processes at the lone electron pair of the N atoms of PHX-TPA, either from phenothiazine/phenoxazine or triphenylamine are maintained over at least 10 scans between 0 and 1.5 V, being accomplished by a small increase of the peaks intensity during the measurement, most probably due to the deposition of a material on the electrode (Figure S4b, *SI*). Different behavior was observed for PTH-TPA for which these oxidation processes appear completely irreversible, being accompanied by a visible decrease of current intensity (Fig. S3a, *SI*). We may assume that released electrons are well-captured by the electron-withdrawing

cyanoacrylic acid, and in the absence of an external electron donor the reduction of radical cations to neutral states became difficult.

Upon scanning in the negative direction to -2 V vs SCE, both dyes exhibited reduction waves in accord with the electron deficient nature of the electron acceptor units, indicating electron transport characteristics. The phenothiazine-based dye displays a large reduction wave centered at -1.39 V vs SCE, being attributed to the formation of radical anions of the electron-withdrawing cyanoacrylic acid unit (Figure 2b). A similar trend was noticed for PHX-TPA, but at slightly more positive potential value (centred at -1.17 V vs SCE). A further oxidation to neutral species of the formed radical anions was observed for both molecules at -1.27 V vs SCE.

Evaporation of a drop of dye solutions in DCM (0.5 % concentration) onto ITO electrodes resulted in thin dye layers with characteristic surface waves quite different from those recorded for solutions (Figure 3).

Figure 3. CV diagrams of a) PHX-TPA and b) PTH-TPA films during the positive potential



There are three oxidation peaks in the anodic region of PHX-TPA in the first oxidation cycle, at 0.89 V, 1.25 and 1.81 V *vs* SCE due to the formation of radical cations and dications

of triphenylamine and/or phenoxazine. In the reverse scan, a single reduction peak centered at 0.62 V was recorded. In the second oxidation cycle, the three oxidation processes were preserved, but shifted to 0.94, 1.19 and 1.54 V *vs.* SCE, being accompanied by drastically intensity decrease. We may assume that a migration of radical cations occurs up to full stabilization by resonant reactions since the dye is fully conjugated.<sup>29</sup> Starting with the 3<sup>rd</sup> scan, only two overlapped oxidation peaks remained prevalent. The oxidation processes in the following cycles could not be detected due to the total detachment of the dye film from the ITO electrode. Unlike PHX-TPA film, during first potential sweeping of PTH-TPA in the anodic region, two reduction bands with maximum at 0.95 and 0.77 V *vs* SCE appear after the dye oxidation at 0.92 V, 1.15 and 1.39 V *vs* SCE (Figure 3b). Moreover, the detachment of the film from the electrode did not occurred, and only instability of the oxidation processes peaked at 1.15 and 1.39 V *vs* SCE was observed.

The peak potential due to the reduction of cyanoacrilic acid units to the correspondic radical anions (-1.58 V *vs* SCE for PHX-TPA and -1.54 eV *vs* SCE for PTH-TPA) registered an important shift to more negative values in films compared to solutions, proving that the process of electron acceptance is much difficult in condensed phase. No subsequent oxidation peak was detected upon reverse scanning (Figure S5, *SI*). A very good electrochemical stability of both dye films in the cathodic area has been noted.

The energy of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of PHX-TPA and PTH-TPA sensitizers were calculated from the oxidation ( $E^{ox}_{onset}$ ) and reduction ( $E^{red}_{onset}$ ) onset potentials *vs* SCE. Different LUMO and HOMO energy values were found for PHX-TPA (-3.17 eV and -5.07 eV) compared to PTH-TPA (-3.2 eV and -5.18 eV), most probably due an increased electron delocalization between donor and acceptor as a result of a better planarity of the former in condensed phase. As a

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consequence, a lower energy bandgap (1.9 eV) was estimated for PHX-TPA compared to PTH-TPA (1.98 eV).

By comparing the edge of the conduction band of  $TiO_2$  and the potential of the redox couple  $(I/I_3)$  with HOMO and LUMO energy levels of sensitizers used in DSSCs, the energy barriers can be established. <sup>30-32</sup> The band structure of PHX-TPA and PTH-TPA is presented in Figure 4. It suggests that both dyes have more negative HOMO energy than the  $I/I_3$  redox couple, leading to dyes regeneration with the selected electrolyte. The more positive LUMO energy relative to the conduction band of  $TiO_2$  ensures an energetically favorable downhill electron injection.

Figure 4. Energy levels diagram of PHX-TPA and PTH-TPA sensitizers



#### 3.3. Photo-optical features

The photophysical properties of PHX-TPA and PTH-TPA were investigated by UV-Vis and photoluminescence (PL) spectroscopy, both in solution and solid state. UV-Vis absorption spectra of the two compounds measured in solvents of different polarities are shown in Figure S6, *SI*, and the pertaining data are listed in Table S1, *SI*. Figure 5 displays the absorption spectra of PHX-TPA and PTH-TPA dye in dichloromethane (DCM) and acetonitrile (ACN)

solutions in comparison with computed spectra of PHX-TPAm and PTH-TPAm with timedependent DFT using the B3LYP functional: excitation energies with their oscillator strengths (atomic units), and UV-Vis spectrum simulated by Gaussian broadening of excitation energies (with a broadening parameter of 0.33eV).

In DCM solutions two distinctive absorption bands were observed for PHX-TPA and three distinctive bands for PTH-TPA. The first band in the region of 280–330 nm is originating from the phenothiazine/phenoxazine and triphenylamine localized  $\pi$ - $\pi$ \* transitions that partially overlap with the absorption band associated with the localized  $\pi$ - $\pi$ \* transitions in the conjugated skeleton formed by donor-acceptor framework. Due to the Tshape configuration, this band registered a bathochromic shift compared to the analogous rigid-rod dyes, where the extension of conjugation takes place through the phenothiazine/phenoxazine ring via the C3 atom. The electronic coupling between phenothiazine/phenoxazine and the acceptor unit is poor in the T-shaped dyes due to the perpendicular orientation of the phenothiazine/phenoxazine and conjugation pathway.<sup>13</sup>





The band appearing at the longer wavelength region, 492 nm for PHX-TPA and 477 nm for PTH-TPA is mainly ascribed to the charge transfer from the donor comprising phenoxazine/phenothiazine - triphenylamine framework to the cyanoacryclic acid acceptor. The origin of this electronic absorption was confirmed by TD-DFT which proved that it originates intrinsically from the intramolecular charge-transfer (ICT) transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). Further discussion on this topic is carried out in Section 3.4. Interestingly, PHX-TPA and PTH-TPA display longer wavelength CT transition compared to the analogous fluorene-containing T-shaped dyes.<sup>13</sup> This clearly indicates that our T–shape DD- $\pi$ -A system generates improved donor – acceptor interactions and consequently the light harvesting properties.

Moreover, the CT absorption of dye possessing phenothiazine linker appeared 15 nm blue-shifted compared to phenoxazine-based dye attributable to the more twisted conformation of phenothiazine with respect to phenoxazine,<sup>33</sup> which hampers the donor–acceptor interaction. The most intriguing feature is the long wavelength band extending beyond 400 nm in the spectra of PTH-TPA. It may belong to a CT state or to localized  $\pi$ – $\pi$ \* transitions in the conjugated skeleton. The simulated UV-Vis spectrum for PTH-TPA predicted no excitations in this region. Therefore, it appeared reasonable to assume that this band is very likely due to the presence of the protonated form of PTH-TPA, as previously reported.<sup>26</sup> To prove this, the UV-Vis spectrum of PTH-TPAm protonated at the N atom in the thiazine cycle (H+ PTH-TPAm) was simulated (Figure S7, *SI*). The obtained spectrum qualitatively correlates with the experimental spectrum reported in ref. <sup>26</sup>, in which the low energy transition around 500 nm almost disappeared. The molecular orbitals of H+PTH-TPAm show a disruption of the conjugation in the thiazine ring due to the presence of the proton, and the orbitals are spatially separated on the two halves of the phenothiazine

fragment (Figure 6). It is apparent that LUMO becomes less and less delocalized as we go from PHX-TPAm to PTH-TPAm, and to H<sup>+</sup>·PTH-TPAm.



basis set (energies are in eV).



To gain further insight into the photo-physical processes of these donor-acceptor dyes, their absorption behaviour in different solvents was investigated (Figure S6, *SI*). Both dyes showed a negative solvatochromic behaviour (blue shift of the absorption maximum with solvent polarity increase), indicating a better stabilization by solvation of dye molecules in ground state with respect to the excited state with increasing solvent polarity. It is well-known that a larger absorption range is favorable to a good performance of DSSCs, as more photons can be harvested. According to the absorption maxima and molar extinction coefficients in different solvents, it is clear that DCM is the most suitable solvent for TiO<sub>2</sub> photoanode functionalization due to a better ability of both dyes to harvest light in this medium, which would lead to a higher photocurrent.

Due to the donor-acceptor arrangement, the photophysical features of PHX-TPA and PTH-TPA are predictably solvent dependent. Thus, the PL spectra were recorded in different polarity media by exciting at the ICT absorbance maxima. Figure 7 displays normalized fluorescence spectra of PHX-TPA and PTH-TPA dyes in the chosen solvents.



Figure 7. Normalized PL spectra of dyes in various solvents

By exciting at maximum ICT absorbance wavelength a single PL emission was registered, except PTH-TPA in THF solution that shows two PL maxima. It can be fully attributed to the

spin-singlet charge-transfer excited state ( ${}^{1}CT$ )  $\rightarrow$  S<sub>0</sub> transition from the intramolecular charge transfer (ICT) excited state. The splitting of the ICT band in THF solution in two peaks are probably due to the twisted conformations adopted by the PTH-TPA in this solvent that impart the conjugated core in two individual fluorophores. A new CT band appears, suggesting that the charge transfer process is considerable forbidden in this solvent. Such features indicate that the fluorescence behavior of the dyes is strongly depending on the relationship between molecular conformation and excited states. Maximum emission wavelength values of PHX-TPA and PTH-TPA in selected solvents and solid state are collected in Table S1, *SI*. The ICT band showed a negative solvatoflurochromism for both dyes, except ACN, when a strong bathochromic shift of the ICT band with increasing solvent polarities occurred. A large solvatochromic shift with polarity decreasing is generally determined by a material that holds a strong ICT character. Here, the strongest electron density accumulation on the acceptor unit was achieved in PHX-TPA along with the largest solvatochromic shift of 100 nm.

Fluorescence lifetime measurements were recorded for both dyes in DCM using a pulsed picosecond 375 nm diode laser. The fluorescence decay curves were convoluted with the instrument response and fitted to a bi-exponential function and the resulting decay time constants are presented in the Figure 8. The average lifetime of PHX-TPA (3.6 ns) is significantly longer than the PTH-TPA lifetime (2.6 ns) which indicates that the time spent by PHX-TPA in the excited states is longer than in the case of PTH-TPA, therefore the probability of electron injection into  $TiO_2$  appears to be higher for PHX-TPA. As a consequence, one would expect better performance for solar cells realized with PHX-TPA.

Figure 8. Fluorescence decay curves of PHX-TPA and PTH-TPA dyes excited at 375 nm with



the corresponding time constants

There is an important change observed between the DCM solutions and solid state absorptions of the dyes recorded on thin  $TiO_2$  films. The main difference is the broadening of  $TiO_2$  films spectra up to 700 nm with respect to the corresponding solutions. As shown in Figure 9, the maxima absorption peaks for PHX-TPA and PTH-TPA on the  $TiO_2$  film were found upon deconvolution at 503 and 532 nm, respectively.

Figure 9. Electronic absorption spectra of dyes on TiO<sub>2</sub> surface



The absorption maximum associated with CT state registered a significant red-shift for PTH-TPA (54 nm) with respect to the absorption of isolated molecules, and only 11 nm red shift for PHX-TPA. The red-shifted absorptions of dye thin films compared to corresponding dye solutions were commonly observed for conjugated systems due to the enhancement of intermolecular  $\pi$ - $\pi$  interactions and the packing of dye molecules in *J* aggregates. Specifically, the PTH-TPA dye showed larger red-shift compared to corresponding phenoxazine analogue. The molecules may adopt antiparallel arrangement due to the long alkyl chains linked to triphenylamine unit and arrange in slipped stacking motifs. On the other hand, an increased delocalization of the  $\pi^*$  orbital of the conjugated system could result from the interaction between the carboxylate unit and titanium ions.

The amount of dye loading on TiO<sub>2</sub> surface was measured by desorbing the dye from the films with 1 mM NaOH ethanol solution and measuring the UV–Vis absorption spectra. For the film made with PHX-TPA, the dye loading was found to be  $0.93 \times 10^{-7}$  mol/cm<sup>2</sup>, whereas for PTH-TPA, it was estimated at  $2.55 \times 10^{-7}$  mol/cm<sup>2</sup>. It was somehow expected taking into account that PHX-TPA display an extended  $\pi$ -conjugation and increased molar extinction coefficient (PHX-TPA:  $\varepsilon = 35500$  M<sup>-1</sup>cm<sup>-1</sup>; PTH-TPA:  $\varepsilon = 10990$  M<sup>-1</sup>cm<sup>-1</sup>). The more planar PHX-TPA molecules will expand on a larger surface compared to PTH-TPA molecules of less-planar or twisted shape, leading to the reduction of loading capacity. Therefore, the enhanced PTH-TPA loading compared to PHX-TPA cannot explain the better absorption on the film in the case of the latter one. Apparently it is predominantly due to an increased molar extinction coefficient in the case of PHX-TPA in comparison with the one of PTH-TPA.

The fluorescence spectra of the thin films spin-coated from DCM solution showed different behavior with regard to the emission wavelength and intensity, suggesting the fluorescence quenching. Direct excitation of ICT states resulted in one emission bands

centred at 600 nm for PTH-TPA and 623 nm for PHX-TPA (Figure S8, *SI*). The ICT fluorescence band of PHX-TPA film registered a 11 nm red shift compared to the DCM solution, accounting for a better planarization of the ICT excited state geometry. This was not the case of PTH-TPA for which a strong (32 nm) blue shift was observed in condensed phase compared to fluid state.

#### 3.4. Theoretical calculations

To get a further insight into the electronic structure of PTH-TPA and PHX-TPA dyes, their ground state geometries were optimized in *vacuo* until convergence by density functional theory (DFT) calculations at b3lyp/6-311++G\*\* level, optimum confirmed by frequency calculation, using the B3LYP functional. Since, due to the structural features, the length of the alkyl chain on the triphenylamine unit is not expected to have an influence on energies of the HOMO and LUMO levels, the simulations were carried out on PTH-TPAm and PHX-TPAm (Figure S1, *SI*), where the *n*-hexyl was replaced by the methyl group.

The optimized geometries of both dyes evidenced that the triphenylamine and phenothiazine/phenoxazine moieties are perpendicular to one another forming a non-coplanar arrangement in a T-shaped configuration. Between these dyes, the replacement of phenothiazine with phenoxazine significantly affects the adsorption geometries on the TiO<sub>2</sub> surface since the phenoxazine moiety is virtually planar, while the phenotiazine moiety has a butterfly shape, as previously reported in the literature.<sup>26,34</sup> Consequently, it appears that the phenoxazine-based dye generated a more extended structure compared to the phenothiazine analogue. According to the optimized geometry, the phenyl rings in the triphenylamine unit are non-planar, in a propeller shape, with the dihedral angles of  $\approx 50^{\circ}$ , this arrangement contributing to a diminished contact between molecules. The two hexyloxy substituents behave just like two umbrellas and may induce some distances between dyes molecules when

absorbed on  $TiO_2$ , thus suppressing the aggregation. Also, the hexyloxy groups may promote the dye self-assembling on the  $TiO_2$  surface that will definitely contribute to a better charge carrier transport.

The lowest simulated excitation  $S0 \rightarrow S1$  holds an excitation energy of 2.49 eV (498 nm) for PHX-TPAm and 2.43 eV (511 nm) for PTH-TPAm, being a HOMO $\rightarrow$ LUMO transition for both molecules. While for PHX-TPAm this transition has high oscillator strength and hence high absorbance in the UV-Vis spectrum, for PTH-TPAm the oscillator strength is very low. However, the  $S0 \rightarrow S2$  transition in PTH-TPAm, at 2.50 eV (495 nm), (HOMO–1 $\rightarrow$ LUMO) has a sizable oscillator strength, and is responsible for the long wavelength feature in the UV-Vis spectrum of PTH-TPA. The  $S0 \rightarrow S2$  transition in PTH-TPAm is the counterpart of the  $S0 \rightarrow S1$  transition in PHX-TPAm, as can be inferred from the shape of the molecular orbitals involved in the two transitions (Figure 6). In fact, the  $S0 \rightarrow S1$  and  $S0 \rightarrow S2$  transitions are interchanged in the two molecules, as will be discussed later. The next excitations with a sizable oscillator strength appear between 3.7 eV (350 nm) and 4.3 eV (288 nm), accounting for the second feature in the UV-Vis spectrum, for both molecules.

However, in both cases the lowest energy transition with high intensity is between two molecular orbitals delocalized on the heterocyclic fragment. The target molecular orbital is LUMO in both cases, and has significant density on the cyanoacrylic acid moiety. The source molecular orbital is delocalized mostly away from the cyanoacrylic acid. Even if fortuitous, it is interesting to note that the energy of LUMO+1 is the same for both molecules. The LUMO electron density distributions of both dyes are prevalently localized around the cyanoacrylic acid acceptor units, and spread up to the phenoxazine/phenothiazine core, thereby favoring an efficient electron transfer from the excited state of the dyes to the TiO<sub>2</sub> conduction band edge.

For PHX-TPAm, HOMO is localized predominantly on the PHX fragment, while for the PTH-TPAm, HOMO is localized predominantly on the TPA fragment. Since both

molecules are anchored with the cyanoacrylate end to the  $TiO_2$ , it is likely that the electron transfer from  $\Gamma$  to the molecular ion is more facile at the TPA end of the molecule. The access of  $\Gamma$  to the cyanoacrylate end of the molecule (anchored to  $TiO_2$ ) is impeded compared to the access of  $\Gamma$  to the TPA end, which points towards the bulk of the electrolyte. For the molecular ion of PTH-TPA, for which the HOMO (with the hole) is localized on TPA, the electron transfer is likely to be faster than for the molecular ion of PHX-TPA, for which the HOMO (with the hole) is localized on PHX (Figure 6). Consequently, the electron transfer for the PTH-TPA cell could be higher than that for the PHX-TPA and better photovoltaic performance are expected for PTH-TPA.

#### 3.5. Photovoltaic performance

Current-voltage (I-V) characteristics of six cells, realized with both PHX-TPA (C1, C24 and C32) and PTH-TPA (C9, C21 and C25) are shown in figure 10. Their complete electrical performance is presented in the Table 1.

All cells have been functionalized by immersing the TiO<sub>2</sub> film in a dye solution of the same concentration (300  $\mu$ M) in DCM. Two different functionalization times have been used: 4 hours (C1 and C9) and 6 hours for the other cells; C1, C9, C24 and C25 have been realized with HI30, while C21 and C32 with AN50. To reduce the I<sub>3</sub><sup>-</sup> transport length, some cells have been realized by increasing the gasquet polymerization time from 2 to 3 minutes. In this way, one would expect a higher concentration of  $\Gamma$  anions in the TiO<sub>2</sub> pores, therefore a possible faster regeneration of the dye cations.

Figure 10. I-V characteristics and IPCE spectra (blue – PHX-TPA dye; red – PTH-TPA dye) of six cells realized with the same dye concentration (0.3mM), same solvent (DCM), with two different immersion time (4 and 6 hours), two polymerization time (PT) and different

commercial electrolyte (HI-30 and AN-50, Solaronix).



Table 1. Electrical parameters of the DSSC prototypes fabricated

| Cell | Soaking | Dye     | Electrolyte | Time   | Jsc         | Voc   | FF    | η(%)  | $R_r(\Omega)$ |
|------|---------|---------|-------------|--------|-------------|-------|-------|-------|---------------|
|      | Time    |         | A Y         | (min.) | $(mA/cm^2)$ | (V)   |       |       |               |
|      | (hours) |         |             |        |             |       |       |       |               |
| 1    | 4       | PHX-TPA | HI30        | 2      | 6.02        | 0.689 | 0.68  | 2.83  | 16.36         |
| 9    | 4       | PTH-TPA | HI30        | 2      | 7.361       | 0.684 | 0.605 | 3.02  | 12.62         |
| 24   | 6       | PHX-TPA | HI30        | 3      | 8.02        | 0.675 | 0.664 | 3.597 | 9.85          |
| 25   | 6       | PTH-TPA | HI30        | 3      | 9.02        | 0.695 | 0.659 | 4.13  | 13.78         |
| 32   | 6       | PHX-TPA | AN50        | 3      | 6.93        | 0.625 | 0.694 | 3     | 15            |
| 21   | 6       | PTH-TPA | AN50        | 3      | 10.22       | 0.702 | 0.587 | 4.21  | 6.98          |

## with PTH-TPA and PHX-TPA

From Figure 10 a-c and Table 1, one can observe that for the cells with PTH-TPA, both short-circuit current (Isc) and open-circuit voltage (Voc) increases with the electrolyte concentration. By contrast, Voc consistently decreases in the case of the cells with PHX-TPA. The fill factor (FF) of all cells realized with the PHX-TPA dye is higher in comparison with theirs PTH-TPA counterparts. Almost generally, the open circuit voltages ( $V_{OC}$ ) of the cells fabricated with the phenothiazine-based dye are larger than the ones of the cells containing phenoxazine-based dye, the higher difference (77mV) being obtained between C21 and C32 (Figure 10c), both fabricated with AN50. Realized exactly by the same technology, but with a lower electrolyte concentration (HI30), the cells C1 and C9 exhibit almost the same Voc but the short circuit current (Isc) of the cell C9 (PTH-TPA) is about 22% higher than the one of the C1(PHX-TPA). It indicates that the intensity of the recombination mechanism is similar in the two dyes, while the difference in the short circuit current points to a better regeneration of the PTH-TPA.

The cells 24 and 25 (Figure 10b) manufactured with a higher dye loading (6h immersion time) and a longer polimerization time (3 min.) behave differently: while for the phenothiazine-based dye both Isc and Voc increases, for the phenoxazine-based dye the variation of the two parameters is opposite. Such a behavior indicates that although the electron injection is more efficient in both cells, a stronger recombination mechanism is at work in the phenoxazine-based dye. Increasing the concentration of the redox couple, as in the case of the cells 21 and 32 (Figure 10c), which differ from 24 and 25 only by electrolyte - AN50 instead of HI30, both Voc and Isc of the cell realized with PTH-TPA improves, while those of the cell manufactured with PHX-TPA decrease. The lower current observed in PHX-TPA – cells may be due to lower loading-related injection or to a less efficient regeneration, while for PTH-TPA-cells the higher currents can be ascribed either to a better injection or a better regeneration or both of them.

The Voc degradation is usually associated either with a mechanism of electron interception by electrolyte or dye recovery by capture of an electron from TiO<sub>2</sub> (back electron transfer). To qualitatively evaluate the recombination by back electron transfer in our cells, the absolute (Mulliken) electronegativity of both dyes was calculated with the formula (HOMO+LUMO)/2.<sup>35,36</sup> Using the HOMO and LUMO data of the dyes shown in figure 4, we get -4.12eV for the electronegativity of PHX-TPA, while for PTH-TPA the electronegativity is -4.19eV. For the cells realized with the PHX-TPA, the Fermi level in different cells is located between -4.11eV and -4.175eV, while for those with PTH-TPA this is between -4.095eV and -4.116eV. Comparing the position of the Fermi level with the dyes absolute electronegativity, one observes that the PHX-TPA dye is less prone to back electron transfer than the PTH-TPA dye. That because, as can be seen in the Table 1, the constant Voc degradation with the increase of electrolyte concentration of the cells realized with the dye containing the oxygen atom implies a more and more negative Fermi level, therefore back electron transfer is less and less probable. This indicates electron interception by electrolyte as the dominant mechanism of recombination in these cells. By contrast, the Voc of the cells realized with the dye containing the sulfur atom is less sensitive to electrolyte concentration, which is the signature of a weaker interception of electrons by electrolyte in these cells. An argument in favor of these considerations comes from the dark I-V characteristics of the cells presented in Figure 11.

Except for the cells C1 and C9 whose dark currents ( $I_d$ ) are very close, confirming the almost similar Voc values reported in Figure 10a, Figure 11 shows that the dark current of the cells realized with the dyes containing sulphur as heteroatom is considerably lower than the ones with the dye containing oxygen heteroatom, regardless of the electrolyte concentration. The difference in the dark currents between the two dyes increases with the electrolyte concentration (e.g.: cells C21-PTH-TPA and C32- PHX-TPA, both with AN50), the cells with

PHX-TPA dye containing oxygen as heteroatom being more sensitive to the electrolyte concentration than those containing sulphur in the dye.



Figure 11. Dark I-V characteristics of the cells realized with HI30 and AN50

Since the dye loading ratio is  $2.55 \times 10^{-7}/0.93 \times 10^{-7} = 2.74$  in favor of PTH-TPA, it would result that the dye scaffold on TiO<sub>2</sub> surface could be responsible for the lower dark current measured in the case of the dye containing sulfur. However, if one considers that the dark current would be roughly in an inverse relationship with the dye loading and calculate I<sub>d</sub> ratios at 0.8V, from Figure 10 one gets I<sub>d1</sub>/I<sub>d9</sub>=1.06, I<sub>d24</sub>/I<sub>d25</sub>=1.29 and I<sub>d32</sub>/I<sub>d22</sub>=1.96, respectively. All I<sub>d</sub> rations are consistently smaller than the loading ratio. Apparently, these values of the I<sub>d</sub> ratios merely mirror the effect of the electrolyte concentration on the recombination mechanism than that of the dye loading.

That different dye moieties influence the recombination of the electrons with the electrolyte is well known for long.<sup>37-39</sup> As for the structural differences of a single atom, there is a quite common view that the presence of the sulphur heteroatom in a dye is not favorable to some parameters of the cell. For instance, in Ru-based dyes, O'Regan and coworkers<sup>40</sup>

found that the effect of the iodide binding to an oxygen atom located on a hexyloxy chain tethered at a phenyl ring on the open circuit voltage is much less detrimental than the situation when the oxygen atom is replaced by a sulphur one. Similar experiments done by Hu et al.<sup>41</sup> showed that modifying the chalcogen atom "does not impact the regeneration of the oxidized dye by electrolyte", which "is not aligned" with the previous work of the same group but "leads to faster recombination rates". More recently, some authors<sup>42</sup> observed that for cyclometalated ruthenium sensitizers with different "thiophene units on the auxiliary ligands"<sup>42</sup> the lifetime of photooxidized dye depends on both recombination and regeneration and that, depending on the situation, the sulfur atom is able to catalyze both regeneration and recombination with iodide<sup>42</sup>. The authors concluded that due to this dual character "sulfur containing aromatic rings should be avoided...when  $I_3^{-}/I^{-}$  redox mediator is used"<sup>42</sup> because these act as recombination channels. However, for the organic dyes, Robson et al.<sup>43</sup> revealed that the oxygen on the hexyloxy chain at the donor site is a more efficient promoter for the recombination than the sulphur. It is to be mentioned that these observations are valid for the cobalt-based redox couple, but not for the standard  $I/I_3$  electrolyte. For organic dyes with large regeneration rate, Simon et al.<sup>44</sup> found that Voc tracked the dye regeneration rate. This observation has been assigned to "halogen-bonding interaction between the dye and the electrolyte",<sup>44</sup> which is capable to increase the cell photovoltage. Baumann *et al.*<sup>45</sup> compared the Raman spectra of thiophene with furan-based dyes, both with and without iodine  $(I^2)$ , and found that iodine interacts with both dyes but "sulfur halogen bonding with I<sup>2,,45</sup> is stronger. Consequently, the performance of the cells realized with thiophene-based dye is lower. Similar effects of the thiophene vs. furan have been reported for porphyrin based DSSCs.<sup>46</sup> Our results presented in Figure 10 feature the same behavior as those of Robson et al.<sup>43</sup> but for  $I/I_3$  couple. These similarities are the reason why we consider that the differences between the two dyes are attributable to the mechanism of regeneration, as in Ref.<sup>43</sup>. In fact,

in the case of sulfur-containing dye (Figure 10), the continuous improve of Isc with the increase of electrolyte concentration is the signature of a better dye regeneration.

The regeneration mechanism is well reflected by measurements of Incident Photons to Current Conversion Efficiency (IPCE) at different electrolyte concentrations.<sup>47</sup> Figures 10d-f show that all action spectra, with an onset at  $\approx 650$  nm, have a dominant maximum at about 460 nm and a smaller one located at about 338 nm and 335 nm for the phenothiazine-based dye and phenoxazine-based dye, respectively. Comparing the data from Figure 10a with corresponding IPCE (Figure 10d), the Isc difference between C1 (PHX-TPA) and C9 (PTH-TPA) can be explained by a more efficient regeneration of the phenothiazine-based dye, therefore a better charge collection. Figure 10b shows that although the Isc of the PHX-TPA improves, its Voc is 20mV lower than the one of C25 (PTH-TPA). Apparently, increasing  $\Gamma$ concentration in TiO<sub>2</sub> pores, both PTH-TPA and PHX-TPA are better regenerated, but, at the same time, in the case of PHX-TPA the interaction with the electrolyte becomes stronger, therefore a lower Voc in comparison with both C1 and C25. This is not the case of the PTH-TPA (C25), because both Isc and Voc improve, which is the signature of either a higher loading or better regeneration or both of them. The mechanism of charge collection in these cells seems to be more subtle, because the IPCE spectra (Figure 10e) show that the intensity of the small peaks increases for both dyes, while the dominant peaks located at about 460 nm are enlarged toward the shorter wavelengths (blue-shift). More important, especially in the case of PTH-TPA, while the intensity of the small peak increases, the one of the larger peak diminishes. As usually, the small peaks can be assigned to TiO<sub>2</sub> contribution. The position of the small peaks slightly shifts with the electrolyte concentration, which, in principle, can be explained by the oxide conduction band shift due to TiO<sub>2</sub>-electrolyte interaction. However, as observed from the Figure 10e, increasing the concentration of  $\Gamma$ , not only the position but also the intensity of both maxima modifies. In fact, especially in the case of the PTH-TPA, the

intensification of the small peak is accompanied by a decrease in the intensity of the larger one. According to Ardo et al.,<sup>48</sup> these are the symptoms of the Stark effect induced by an electric field in the TiO<sub>2</sub> generated by fast injection from a dye excited state. In this respect, it is interesting to observe that the positions of the small peaks correspond to the excitation energies found by simulation at 334.36 nm for the PHX-TPA and 338 nm for the PTH-TPA, respectively. Therefore, the small peaks can be alternatively associated with the electron transfer from the dye excited state. In the case of the cells C21 (PTH-TPA) and C32 (PHX-TPA) (Figure 10f), realized exactly as C25 (PTH-TPA) and C24 (PHX-TPA) but with AN50, one observes a consistent degradation of both Isc and Voc of the cell with PHX-TPA (C32). It tracks the IPCE degradation at both the smaller peak (25%) and the maximum one (about 15%). This performance decrease is due to higher electrolyte concentration which intensifies the recombination in the case of the PHX-TPA (C32), corroborated with a less efficient regeneration. By contrast, in the presence of higher electrolyte concentration, the PTH-TPA (C21) shows an increase of Isc which is the consequence of a better regeneration. It is nicely reflected in the IPCE spectrum (Figure 10f), where, this time, the interplay between the peaks is in the favour of the larger one which is boosted toward 90%, while the smaller one is reduced by about 10%. A slight broadening toward the longer wavelength is noted in the case of the higher peak.

To find a quantitative explanation of the differences between the two dyes, from the energy diagram presented in Figure 4 we found that the values of the free enthalpies or the driving forces at the dye-electrolyte interface are  $\Delta G_0$ =-0.27eV and  $\Delta G_s$ =-0.38eV for PHX-TPA and PTH-TPA, respectively. Since  $\Delta G_s$ =-0.38eV is better placed on the Marcus transfer curve, one would expect a better regeneration of the PTH-TPA cation. Moreover, if one assumes that the reorganization energy ( $\lambda$ ) for hole transfer in both dyes is the same (e.g.:  $\lambda$ =0.6eV) and the same coupling factor between the dyes and electron density of states in

TiO<sub>2</sub>, then from Marcus formula,<sup>49</sup> the ratio of the two rate factors is  $k_S/k_0 \sim \exp[-(\Delta G_S + \lambda)^2/4\lambda k_B T]/\exp[-(\Delta G_0 + \lambda)^2/4\lambda k_B T]$ , where  $k_B$  is the Boltzmann constant and T the absolute temperature. Therefore, at room temperature, we get  $k_S/k_0 \approx 2.7$ , which means that the regeneration of the PTH-TPA dye cations containing sulfur is almost three times faster than the oxygen-containing dye cations.

We have previously stated that, in comparison with PTH-TPA dye, the recombination by back electron transfer in the PHX-TPA dye should be weaker. Here we show that this observation is supported by the values of the total recombination resistance obtained by electrochemical impedance spectroscopy (EIS). As an example, Fig. 12 shows a comparison of the Nyquist diagrams of the cells C32 and C21 realized with PTH-TPA and PHX-TPA dye, respectively. The total recombination (charge transfer) resistance ( $R_r$ ) at the TiO<sub>2</sub>-dyeelectrolyte interface of each cell has been extracted, as usually, from the second semicircle of the corresponding Nyquist plot. Its values for all cells are presented in the Table 1.

Figure 12. Impedance spectra of the cells C32 and C21, realized with PHX-TPA and PTH-



From the Fig. 12, it is evident that the total recombination resistance of the cell C32 (15  $\Omega$ ) is larger than the one of C21 (6.98  $\Omega$ ). This observation is also valid for the C1-C9 pair, but not for C24-C25. Therefore, it is reasonable to consider that, while the electron interception by electrolyte is stronger for PHX-TPA dye, the contribution of back electron transfer to the total recombination is weaker, in comparison with PTH-TPA dye. Consequently, as stated previously, the back electron transfer is stronger in PTH-TPA dye and this is the factor responsible for the lower R<sub>r</sub> values observed in most of the cells realized with PTH-TPA dye. However, these differences do not explain the lower global performance of the cells realized with PHX-TPA dye. This situation may be due to specific dye-electrolyte interaction, which warrants further investigations.

Table 1 shows that all the fill factors (FF) of the cells with phenothiazine are lower than those of their phenoxazine analogues. This is observed for all cell pairs: 0.605<0.68 for C9-C1, 0.659<0.664 for C25-C24 and 0.587< 0694 for C21-C32, respectively, regardless of the electrolyte used in their fabrication. The fill factor depends on the shape of the I-V curve, which is modulated by both series and the recombination resistance.<sup>50</sup> From the Table 1, one can observe that the higher the short circuit current, the lower the fill factor is. Since Isc is higher in the phenothiazine based cells, their FF factor will be more affected by the series resistance than their phenoxazine counterparts. In the case of the recombination resistance of the phenothiazine based cells, one observes the following sequences:  $R_{r21}$ < $R_{r9}$ < $R_{r25}$ , while  $FF_{21}$ < $FF_{9}$ < $FF_{25}$ . It strongly supports the recombination as mechanism of fill factor degradation in phenothiazine based cells. Since  $R_r$  is generally higher in the phenoxazine based cells, its effect on FF degradation is lower than in the case of the cells with phenothiazine dye.

#### 4. CONCLUSIONS

Two novel sensitizers incorporating phenoxazine or phenothiazine in a DD- $\pi$ -A configuration and T-pattern have been designed, synthesized, and fully characterized for use in DSSCs. The relationship between the dyes structures, photo-physical behavior and redox activity were thoroughly investigated to predict their DSSC performance. The charge transfer band from the donor phenoxazine/phenothiazine-triphenylamine framework to the cyanoacryclic acid acceptor was registered at 492 nm for phenoxazine-based dye and 477 nm for phenothiazine-based dye, proving improved donor-acceptor interactions compared with other T-shape molecules. Time-dependent density functional theory evidenced that HOMO is localized predominantly on the phenoxazine fragment for phenoxazine-based dye, while for the phenothiazine-based dye, it is localized predominantly on the triphenylamine fragment, suggesting a faster electron transfer for the phenothiazine-based molecular ion, hence better photovoltaic characteristics. Solar cells have been fabricated with both kinds of dye. In cells fabricated in the same way but with different dye, it has been found that the open circuit voltage of those manufactured with phenoxazine-based dye is lower than those with phenothiazine in the dye structure. In phenoxazine dye-based cells, the Voc continuously degrades with the electrolyte concentration, while in the case of phenothiazine dye it remains quite stable. It was attributed to the stronger electron interception by electrolyte mediated by the phenoxazine dye. This observation was confirmed by the dark current measurements and it is also supported by both the recombination resistance at the  $TiO_2$ -electrolyte interface, determined by impedance spectroscopy, and the action spectra of the cells. The increase of the electrolyte concentration is beneficial in the case of the cells manufactured with phenothiazine-based dye, a result which was assigned to a better dye regeneration. A simple calculation quantitatively supporting this statement was presented. These results show that the presence of the oxygen heteroatom in the new dye structures promotes the interaction of the

electrons in TiO<sub>2</sub> with the iodine/iodide redox couple, while the sulphur is less detrimental to the cell performance. Though the best power conversion efficiency of a cell sensitized with the developed dyes was 4.21 % at the current stage, there is still room for further improvements either by incorporating a more extended  $\pi$ -linker between phenoxazine/phenothiazine and the anchoring group, or finding more appropriate functionalization conditions and cell engineering in order to promote a better photovoltaic effect.

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#### References

- O'Regan, B.; Grätzel, M., A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO<sub>2</sub> films. *Nature* 1991, 353, 737-740.
- Shockley, W.; Queisser, H. J. J, Detailed balance limit of efficiency of pn junction solar cells. J. Appl. Phys. 1961, 32, 510-519.
- 3. De Vos, A., Detailed balance limit of the efficiency of tandem solar cells. *J. Phys. D. Appl. Phys.* **1980**, *13*, 839–846.
- Powar, S.; Daeneke, T.; Ma, M. T.; Fu, D.; Duffy, N. W.; Götz, G.; Weidelener, M.; Mishra, A.; Bäuerle, P.; Spiccia, L.; Bach, U., Highly efficient p-type dye-sensitized solar cells based on tris(1,2-diaminoethane)cobalt(II)/(III) electrolytes. *Angew. Chem. Int. Ed. Engl.* 2013, 52, 602-605.
- Grätzel, M., Recent advances in sensitized mesoscopic solar cells. Acc. Chem. Res. 2009, 42, 1788-1798.

- 6. Ning, Z. J.; Fu, Y.; Tian, H., Improvement of dye-sensitized solar cells: what we know and what we need to know. *Energy Environ. Sci.* **2010**, 3, 1170-1181.
- Luo, J. S.; Wan, Z. Q.; Jia, C. Y., Recent advances in phenothiazine-based dyes for dyesensitized solar cells. *Chinese Chem. Lett.* 2016, 27, 1304–1318.
- 8. Li, P.; Cui, Y.; Song, C.; Zhang, H., A systematic study of phenoxazine-based organic sensitizers for solar cells, *Dyes Pigm.* **2017**, *137*, 12-23.
- Luo J.; Wan, Z.; Jia, C.; Wang, Y.; Wu, X.; Yao, X., Co-sensitization of dithiafulvenylphenothiazine based organic dyes with N719 for efficient dye-sensitized solar cells. *Electrochim. Acta* 2016, 211, 364-374.
- Bae, J. H.; Lim, S. J.; Choi, J.; Yuk, S. B.; Namgoong, J. W.; Ko, J. H.; Lee, W.; Kim,
   J. P., Effects of introducing functional groups on the performance of phenoxazine-based dye-sensitized solar cells, *Dyes Pigm.* 2019, *162*, 905-915.
- 11. Wu, W. J.; Yang, J. B.; Hua, J. L.; Tang, J.; Zhang, L.; Long, Y. T.; Tian, H., Efficient and stable dye-sensitized solar cells based on phenothiazine sensitizers with thiophene units. *J. Mater. Chem.* **2010**, *20*, 1772-1779.
- Hua, Y.; Chang, S.; Wang, H. D.; Huang, D.; Zhang, J.; Chen, T.; Wong, W. Y.; Wong,
   W. K.; Zhu X., New phenothiazine-based dyes for efficient dye-sensitized solar cells: positioning effect of a donor group on the cell performance. *J. Power Sources* 2013, *24*, 253–259.
- Baheti, A.; Thomas, K. R. J.; Li, C. T.; Lee, C. P.; Ho, K. C., Phenothiazine-sensitized organic solar cells: effect of dye anchor group positioning on the cell performance. ACS *Appl. Mater. Interfaces* 2015, 7, 2249–2262.
- Damaceanu, M. D.; Mihaila, M.; Constantin, C. P.; Chisca, S.; Serban, B. C.;
   Diaconu, C.; Buiu, O.; Pavelescu, E. M.; Kusko, M., A new sensitizer containing

dihexyloxy-substituted triphenylamine as donor and a binary conjugated spacer for dyesensitized solar cells. *RSC Adv.* **2015**, *5*, 53687-53699.

- Yamanishi, H.; Tomita, I.; Ohta K., Endo, T., Solid Dimorphism of tetra arylcyclobutadienecobalt derivatives bearing long aliphatic lateral groups. *Mol. Cryst. Liq. Cryst.*, 2001, 369, 47–61.
- 16. Yen, H. J.; Liou, G. S., Enhanced near-infrared electrochromism in triphenylaminebased aramids bearing phenothiazine redox centers. *J. Mat. Chem.* **2010**, *20*, 9886–9894.
- Becke, A. D., Density-functional thermochemistry. III. The role of exact exchange, J. Chem. Phys. 1993, 98, 5648–5652.
- Lee, C.; Yang, W.; Parr, R. G., Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B Condens Matter.* 1988, *37*, 785–789.
- Krishnan, R.; Binkley, J. S.; Seeger R.; Pople, J. A., Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions. *J. Chem. Phys.* 1980, 72, 650– 654.
- 20. McLean, A. D.; Chandler, G. S., Contracted Gaussian basis sets for molecular calculations. I. Second row atoms, Z=11–18. J. Chem. Phys. **1980**, 72, 5639–5648.
- Clark, T.; Chandrasekhar, J.; Spitznagel G. W.; von Ragué Schleyer, P., Efficient diffuse function-augmented basis sets for anion calculations. III. The 3-21+G basis set for first-row elements, Li–F. *J. Comp. Chem.* 1983, *4*, 294–301.
- Cramer, C. J. Essentials of computational chemistry: Theories and models, 2nd ed; John Wiley & Sons: Chichester, 2005.
- 23. Yanai, T.; Tew, D.; Handy, N., A new hybrid exchange-correlation functional using the Coulomb-attenuating method (CAM-B3LYP). *Chem. Phys. Lett.* **2004**, *393*, 51–57.

- 24. Ciofini, I.; le Bahers, T.; Adamo, C.; Odobel, F.; Jacquemin, D., Through-space charge transfer in rod-like molecules: lessons from theory. *J. Phys. Chem. C* **2012**, *116*, 11946–11955.
- 25. Adamo, C.; Jacquemin, D., The calculations of excited-state properties with Time-Dependent Density Functional Theory. *Chem. Soc. Rev.* **2013**, *42*, 845–856.
- 26. Agrawal, S.; Pastore, M.; Marotta, G.; Reddy, M. A.; Chandrasekharam, M.; De Angelis, F., Optical properties and aggregation of phenothiazine-based dye-sensitizers for solar cells applications: a combined experimental and computational investigation. *J. Phys. Chem. C* 2013, *117*, 9613–9622.
- Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009. *Gaussian 09 Revision D.01*, Gaussian Inc.: Wallingford, 2013.
- Dennington, R.; Keith, T.; Millam, J., *Gaussview Version 5*, Semichem Inc.: Shawnee Mission, 2009.

- Damaceanu, M. D.; Constantin, C. P.; Marin, L., Insights into the effect of donoracceptor strength modulation on physical properties of phenoxazine-based imine dyes. *Dyes Pigm.* 2016, 134, 382-396.
- Tigreros, A.; Dhas, V.; Ortiz, A.; Insuasty, B.; Martín, N.; Echegoyen, L., Influence of acetylene-linked π-spacers on triphenylamine–fluorene dye sensitized solar cells performance. *Sol. Energy Mater. Sol. Cells* 2014, *121*, 61–68.
- Buene, A. F.; Uggerud, N.; Economopoulos, S. P.; Gautun, O. R.; Hoff, B. H., Effect of π-linkers on phenothiazine sensitizers for dye-sensitized solar cells, *Dyes Pigm.* 2018, 151, 263–271.
- Sambathkumar, S.; Priyadharshini, S.; Fleisch, M.; Bahnemann, D. W.; Gnana Kumar G.; Senthilarasu, S.; Renganathan, R., Design and synthesis of imidazole-triphenylamine based organic materials for dye sensitized solar cells, *Mater. Lett.* 2019, 242, 28-31.
  - Freitas, V. L. S.; Gomes, J. R. B; Ribeiro da Silva, M. D. M. C., Structural, energetic and reactivity properties of phenoxazine and phenothiazine. *J. Chem. Thermodynamics* 2014, 73, 110–120.
- Hart, A. S.; Bikram K. C., C.; Subbaiyan, N. K.; Karr, P. A.; D'Souza, F., Phenothiazine-sensitized organic solar cells: effect of dye anchor group positioning on the cell performance. *ACS Appl. Mater. Interfaces* 2012, *4*, 5813–5820.
- 35. Mulliken, R. S., A new electroaffinity scale; together with data on valence states and on valence ionization potentials and electron affinities. *J. Chem. Phys.* **1934**, *2*, 782-793.
- 36. Parr, R. G.; Pearson, R. G., Absolute Hardness: Companion parameter to absolute electronegativity. J. Am. Chem. Soc. **1983**, 105, 7512-7516.
- 37. Reynal, A.; Forneli, A.; Martinez-Ferrero, E.; Sanchez-Diaz, A.; Vidal-Ferran, A.;
  O'Reagan B. C.; Palomares, E., Interfacial charge recombination between e<sup>-</sup>-TiO<sub>2</sub> and the

I / $I_3$  electrolyte in Ruthenium heteroleptic complexes: dye molecular structre-open circuit voltage relationship. *J. Am. Chem. Soc.* **2008**, *130*, 13558-13567.

- Clifford, J. N.; Martinez-Ferrero, E.; Palomares, E., Dye mediated charge recombination dynamics in nanocrystalline TiO<sub>2</sub> dye sensitized solar cells, *J. Mater. Chem.* 2012, 22, 12415-12422.
- Barea, E. M.; Bisquert, J., Properties of chromophores determining recombination at the TiO<sub>2</sub>-dye-electrolyte interface. *Langmuir* 2013, 29, 8773–8781.
- 40. O'Regan, B. C; Walley, K.; Juozapavicius, M.; Anderson, A.; Matar, F.; Ghaddar, T.; Zakeeruddin, S. M.; Klein, C.; Durrant, J. R., Structure/function relationships in dyes for solar energy conversion: a two-atom change in dye structure and the mechanism for its effect on cell voltage. *J. Am. Chem. Soc.* **2009**, *131*, 3541-3548.
- Hu, K.; Severin, H. A.; Koivisto, B. D.; Robson, K. C. D.; Schott, E.; Arratia-Perez, R.; Meyer, G. J.; Berlinguette, C. P., Direct spectroscopic evidence for constituent heteroatoms enhancing charge recombination at a TiO<sub>2</sub>-ruthenium dye interface. *J. Phys. Chem. C* 2014, *118*, 17079- 17089.
- 42. Aghazada, S.; Peng Gao, P.; Yella, A.; Moehl, T.; Teuscher, T.; Moser, J. E.; Gratzel, M.; Nazeeruddin, M. K., Unraveling the dual character of sulfur atoms on sensitizers in dye-sensitized solar cells, ACS Appl. Mater. Interfaces, 2016, 8, 26827-26833.
- 43. Robson, K. C. D.; Hu, K.; Meyer, G. J.; Berlinguette, C. P., Atomic level resolution of dye regeneration in the dye sensitized solar cell. *J. Am. Chem. Soc.* **2013**, *135*, 1961-1971.
- Simon, S. J. C.; Parlane, F. G. L.; Swords, W. B.; Kellett, C. W.; Du, C.; Lam, B.; Dean, R. K.; Hu, K.; Meyer, G. J.; Berlinguette, C. P., Halogen bonding promotes higher dye-sensitized solar cell photovoltages, *J. Am. Chem. Soc.* 2016, *138*,10406–10409.
- 45. Baumann, A.; Cheema, H; Sabuj, Md. A.; McNamara L.E.; Zhang, Y.; Peddapuram, A.; Nguyen, S. T.; Watkins, D.L.; Hammer, N. I.; Rai, N.; Delcamp, J. H., Iodine binding with

thiophene and furan based dyes for DSCs. Phys. Chem. Chem. Phys. 2018, 20, 17859-17870.

- 46. Cariello, M.; Abdalhadi, S. M.; Yadav, p.; Decoppet, J.-D.; Zakeeruddin, S. M.; Gratzel, M.; Hagfeldt, A.; Cooke, G., An investigation of the roles furan *versus* thiophene- $\pi$ -bridges play in donor- $\pi$ -acceptor porphyrin based DSSC. *Dalton Trans.* **2018**, *47*, 6549-6556.
- Barea, E. M.; Ortiz, J.; Paya, F. J.; Fernandez-Lazaro, F.; Fabregat-Santiago, F.; Sastre-Santos, A.; Bisquert, J., Energetic factors, governing injection, regeneration and recombination in dye solar cells with phtalocyanine sensitizers, *Energy Environ. Sci.* 2010, *3*, 1985-1994.
- 48. Ardo, S.; Sun, Y.; Staniszewski, A.; Castellano, F. N.; Mayer, G. J., Stark effect after excited-state interfacial electron transfer ar sensitized TiO2 nanocrystallites, *J. Am. Chem. Soc.* **2010**, *132*, 6696-6709.
- 49. Marcus, R. A., On the theory of oxidation-reduction involving electron transfer, J. Chem. Phys. 1956, 24, 966-978.
- Wang, Q.; Ito, S.; Gratzel, M.; Fabregat-Santiago, F.; Mora-Sero, I.; Bisquert, J.; Bessho, T.; Imai, H., Characteristics of High Efficiency Dye-Sensitized Solar Cells, J. Phys. Chem. B 2006, 110, 25210-25221.

- Two novel "sister" organic dyes featuring a T-shape molecular pattern were developed
- TD-DFT evidenced different localization of HOMO for phenothiazine/phenoxazine dyes
- Stronger electron interception by electrolyte mediated by the phenoxazine dye was found
- A better dye regeneration was proved when phenothiazine was used in the donor core
- The best power conversion efficiency of a cell sensitized with these dyes was 4.21 %