New organic dyes with high IPCE values containing two triphenylamine units as co-donors for efficient dye-sensitized solar cells†

Carlos A. Echeverry,a Robert Cotta,b Edison Castro,b Alejandro Ortiz,a Luis Echegoyenb and Braulio Insuasty*a

Here we report the synthetic routes as well as the structural and electronic properties of five new triphenylamine-based organic dyes and their application in dye-sensitized solar cells. In the designed dyes, two triphenylamine groups act as the electron donor units and the electron acceptor is a cyanoacrylic acid, and these units are linked by different π-conjugated spacers including thiophene, diocetyfluorene, ethylcarbazole, and benzo-dithiophene. Density functional theory was employed to study the electron distribution and the intramolecular charge transfer (HOMO–LUMO) of the dyes. Extending the π-conjugation of the dyes broaden and red-shift the bands and improves the light-harvesting ability, however, a device made with triphenylamine maximizer-based dye TPAM-1 without a π-conjugated spacer exhibited the best photovoltaic performance with a short-circuit photocurrent density ($J_{sc}$) of 11.37 mA cm$^{-2}$, an open-circuit voltage ($V_{oc}$) of 0.836 V, and a fill factor (FF) of 0.603, corresponding to an overall power conversion efficiency of 5.67% under AM 1.5 irradiation (100 mW cm$^{-2}$).

Introduction

Since the first paper by O’Regan and Grätzel,1 dye-sensitized solar cells (DSSCs) have attracted much attention because they present a highly promising alternative to conventional photovoltaic devices. In a typical DSSC, light is absorbed by the dye molecules anchored to the titanium dioxide (TiO2) surface, exciting the dye, which then injects electrons from the dye’s excited state into the conduction band of the TiO2, generating an electric current.12 The dye is then restored to its neutral state by electron donation from the electrolyte. So far, DSSCs show photocurrent efficiencies of up to 13.0% which have been observed with polypyridyl ruthenium complexes and zinc porphyrin dyes.5,6 Interest in metal-free organic sensitizers has grown in recent years because they offer several advantages over other sensitizers: (1) higher molar absorption coefficients due to intramolecular π–π* transitions; (2) easy modification due to relatively short synthetic routes, and (3) tunable electrochemical properties through suitable design.6

In these new dyes a covalently linked donor–π-spacer–acceptor (D–π–A)$^6$–$^{10}$ structure is used, more specifically, a co-donor system (D–D–π–A)$^{12}$–$^{13}$ The bulkiness of a co-donor system hinders the ability of the electrolyte to reach the semiconductor surface and also inhibits dye aggregation that would otherwise lead to self-quenching and poor electron injection.14 The role of the co-donor is fulfilled by the bis-triphenylamine (bis-TPA), which is well-known for its easy oxidation and stability. In order to have strong electronic interaction between the TiO2 and the dye, the choice of the electron acceptor is important; electron acceptors that have been studied are pyrindine,15–16 3-acetic-rhodanine acid,17,18 2-(1,1-dicyanomethylene) rhodanine,19,20 and cyanoacrylic acid,21,22 all of which have shown good performance in DSSCs. In this paper, we have studied the changes in the optical and electrochemical properties upon incorporation of different

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π-conjugated spacers into the bis-TPA skeleton, and their further application as sensitizers in DSSCs. The structures of the bis-TPA based dyes, terminated with the cyanocrylic acid, are shown in Fig. 1 with the different π-conjugated spacers of thiophene, dioctylfluorene, ethylcarbazole, or benzo-dithiophene.

Results and discussion

Synthesis

In this paper we describe a straightforward synthesis of new dyes using a bis-TPA co-donor system modified with different π-conjugated spacers. The co-donor system (2) was prepared by a Horner–Wadsworth–Emmons reaction of compound 1 with 4,4′-diformalytriphenylamine followed by purification, giving rise to the desired product in moderate yields (53%). Compounds 5a–d were also prepared by a Horner–Wadsworth–Emmons reaction of compound 3 with the corresponding spacer followed by purification, yielding the desired products in moderate yields (45–85%) (see ESI†). The target molecules, TPAM-(1–5), were also prepared in moderate yields (41–71%) through Knoevenagel condensation of cyanoacetic acid and 2, 5a–d in glacial acetic acid under reflux. The synthetic procedures followed for the preparation of the TPA-based dyes are shown in Scheme 1. The structures of the new compounds were supported by their analytical and spectroscopic data.

Absorption and emission properties

The absorption spectra of TPAM-1 recorded in different solvents are shown in Fig. 2. Specifically, TPAM-1 exhibits two bands around 385 and 450 nm, which can be assigned to the presence of the two TPA groups, the prominent red-shifted band appearing in the range of 400–500 nm is assigned to a charge transfer transition between the electron donor and the cyanacrylic segment.23

Fig. 2a shows that there is a blue shift of the second band when the polarity of the solvent increases in the order CHCl₃ < AcOEt < THF < EtOH < DMSO, showing only one band in DMSO and EtOH. The blue shift observed for TPAM-1 in polar solvents could be attributed to the protonation or deprotonation of the dye, probably due to the more efficient solvation of the dye in these solvents. Deprotonation would occur on the carboxylic acid, diminishing the electron-accepting ability of the

![Scheme 1](image-url)
cyanocrylic acid, which in turn may substantially decrease the donor–acceptor interaction of the dye.24

The presence of acid-base equilibria in solution could be confirmed by addition of trifluoroacetic acid (TFA) to the dyes in DMSO. Addition of TFA to the DMSO solution of the dye resulted in a red shift of the charge-transfer band and the appearance of a second band. Since, addition of triethyamine (TEA) to the dye solution did not change the position of the principal band, this leads us to believe that the dye exists in the completely deprotonated form in the ground state (Fig. 2b).

Fig. 3 shows the absorption and emission spectra of the dyes TPAM-(1–5) in THF at a concentration of 1 × 10⁻⁵ M, with the corresponding data summarized in Table 1. The absorption spectrum for both the thiophene (TPAM-2) and benzdithiophene (TPAM-5) in solution exhibit similar behavior to that of TPAM-1, showing similar bands around 392 and 485 nm but red-shifted by approximately 60 nm. It can be seen that the maximum absorptions of TPAM-4, which contains the ethylcarbazole spacer, show a blue shift in comparison with its analogue, TPAM-3. This blue shift shown for TPAM-4 may be attributed to the stabilization of the HOMO orbital and destabilization of the LUMO orbital, which increases the band gap.25

The emission spectrum for TPAM-1 contains a band at 453 nm, corresponding to the maximum emission and a shoulder at 538 nm, corresponding to the second TPA of the bis-TPA. The emission spectra of TPAM-(2–5) exhibit a longer bathochromic shift with increasing π-conjugation, especially in the case of TPAM-3 (Δλmax = 101 nm) and TPAM-5 (Δλmax = 97 nm). The absorption and emission properties of the new compounds both confirm that due to small variations in the π-conjugation length of the system, there are major changes to the photophysical properties of the dye molecules.

**Electronic structure quantum calculations**

Density functional theory (DFT) calculations were used to understand the electronic structures of TPAM-(1–5). It is interesting to note the trans orientation of the bis-TPA and π-conjugated spacers, where the dihedral angle is approximately 180°. Furthermore, the phenyls of the TPAs are not planar but are instead rotated, making it more difficult for the electrolyte to reach the semiconductor surface. The compounds show a quasi-planar π-conjugated spacer-acceptor union; this should facilitate the electronic coupling along the molecule through the spacers. In the case of TPAM-5, there is a decrease of the planarity and obviously in the aromaticity of the benzdithiophene spacer, with the dihedral angle between the spacer and bis-TPA at 3.3°, leading to an unfavorable donor–acceptor interaction.

We have also calculated the transition state energies by means a self-consistent field (SCF) method using the CAM-B3LYP functional and the conductor polarized continuum model (CPCM) in THF. The highest occupied molecular orbitals (HOMO–2, HOMO–1 and HOMO) and lowest unoccupied molecular orbitals (LUMO, LUMO+1) of TPAM-1 are shown in Fig. 4. The HOMO is localized primarily on the co-donor system, whereas the LUMO is mainly localized in the electron-acceptor unit of cyanocrylic acid with a bridge contribution. The topology of the molecular orbitals of TPAM-(1–5) (Fig. 5) is similar to that of TPAM-1.

To gain insight into the excited states of the dyes, TDDFT calculations were performed for the lowest six singlet–singlet excitations, and the transitions with oscillator strengths (f) are summarized in Table 2. The lowest transition for TPAM-1 was calculated to be 3.06 eV, corresponding to a charge-transfer excitation from the HOMO–2 to the LUMO and the HOMO–1 to the LUMO with an oscillator strength of 1.4431. The band experimentally found at 3.25 eV (381 nm) appears to correspond to the calculated value of 3.53 eV (351 nm), which is primarily composed of the CT from the HOMO–2 to the LUMO, the HOMO–1 to the LUMO, and the HOMO to the LUMO+1. The excitation characteristics of TPAM-(2–5) are similar to the behavior described here for TPAM-1; where the lowest transition states are calculated to be 2.60 eV (TPAM-2), 2.94 eV

Table 1 Maximum absorption and emission data of the TPAM-(1–5)  

<table>
<thead>
<tr>
<th>Dye</th>
<th>λmax (nm)</th>
<th>εmax (M⁻¹ cm⁻¹)</th>
<th>λem (nm)</th>
<th>εem (M⁻¹ cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPAM-1</td>
<td>421(45700), 381(43500)</td>
<td>453</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TPAM-2</td>
<td>482(28700), 395(39000)</td>
<td>452</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TPAM-3</td>
<td>397(90600)</td>
<td>554</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TPAM-4</td>
<td>394(86000), 353(66500)</td>
<td>457</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TPAM-5</td>
<td>474(66000), 401(75000)</td>
<td>550</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Absorption and emission spectra of the dyes measured in THF at a concentration of 1 × 10⁻⁵ M; ε is the extinction coefficient at the maximum absorption.*
(TPAM-3), 3.19 eV (TPAM-4), and 2.96 eV (TPAM-5). A bathochromic shift is observed when the $\pi$-conjugation length is increased across the spacer, except for TPAM-4, which agrees with the experimentally observed hypsochromic shift.

**Electrochemical properties**

The oxidation potential vs. NHE ($E_{\text{ox}}$) corresponds to the highest occupied molecular orbital (HOMO) and its energy was calculated using eqn (1). The excited state energy ($E_{\text{LUMO}}$) is important in determining the feasibility of an electron transferring from the dye into the conduction band of the TiO$_2$. An approximation of $E_{\text{LUMO}}$ can be calculated from the energy of the ground state oxidation ($E_{\text{HOMO}}$) and the zero–zero excitation energy ($E_{0-0}$) as follows:

$$E_{\text{HOMO}} = -(E_{\text{ox}} + 4.75) \text{ eV}$$  (1)

The $E_{\text{ox}}$ of the as-synthesized dyes were obtained from the cyclic voltammogram for each dye and the results are summarized in Table 3. The onset oxidative potentials ($E_{\text{ox}}$) of the dyes yield HOMO level energies in the range of $-5.58$ to $-5.47$ eV, lower than that of the electrolyte redox couple (4.90 eV), ensuring that there is efficient dye regeneration. The introduction of the $\pi$-conjugation promotes a decrease in the oxidation potentials, most likely due to the stabilization of the oxidized or reduced species across the entire molecule. Most significant is the addition of the benzo-dithiophene unit in TPAM-5 that leads to a decrease in the $E_{\text{ox}}$ of 0.112 V when compared with the value for TPAM-1, thus lowering the driving force resulting from the reduction of the oxidized dye by the electrolyte. The energy gap ($E_{\text{gap}}$) between the LUMO level of the dyes and the conduction band edge of the TiO$_2$ ($-3.90$ eV) should be at least 0.2 eV for efficient electron injection. The $E_{\text{gap}}$ ranges from...
0.82 to 1.27 eV for the bis-TPA dyes which are more than sufficient for electron injection into the conduction band of the TiO$_2$ (Fig. 6).

### Solar cells performance

Fig. 7a shows the incident photo-conversion efficiency (IPCE) for DSSCs composed of the dyes TPAM-1–5 and the standard N719. It can be seen that the photocurrent response of the TPAM-1 DSSC exceeds 90% in the range between 375 and 500 nm, which is higher than the response of the N719 DSSC (76% in the range of 516–531 nm, similar to the value reported in the literature).

The broadening of the IPCE spectra is desired for a larger photocurrent which explains the higher efficiency observed for N719. Generally, an increase of the π-conjugation in the dyes extends the spectral absorption towards longer wavelengths, leading to a broadening of the spectral region, which is important for light harvesting. In the case of TPAM-2, the presence of the spacer based on thiophene enhanced the breadth of the IPCE curve with a maximum value of 81% at 427 nm, yielding the highest photocurrent response comparable to that of the device based on N719. TPAM-3 also showed a high IPCE of 91% at 450 nm and effective light harvesting up to about 550 nm, however, the presence of the dioctylfluorene did not lead to an increase in the breadth of the IPCE curve, yielding a lower photocurrent response when compared to TPAM-2. Fig. 7b shows the corresponding photocurrent density–voltage (J–V) curves of the fabricated DSSCs under AM 1.5 solar irradiation (100 mW cm$^{-2}$). The photovoltaic data are summarized in Table 4, and the photoconversion efficiencies (PCEs) from lowest to highest were TPAM-4 < TPAM-5 < TPAM-2 < TPAM-3 < TPAM-1. The DSSC based on TPAM-1 showed the best overall PCE at 5.67% with an open circuit voltage of 0.836 V, a short circuit photocurrent density of 11.37 mA cm$^{-2}$, and a fill factor of 0.603.

The dyes TPAM-1, TPAM-2 and TPAM-3 showed the highest efficiency values, indicating better electron injection which is also observed in Fig. 7b. TPAM-2 showed a $J_{sc}$ of 12.20 mA cm$^{-2}$, which can be attributed to the wider absorption spectrum observed and its higher IPCE values in a broad wavelength range.

### Table 2: Calculated TD-DFT excitation energies ($E_l$), oscillator strengths ($f$), and character (CT = charge transfer) $^a$

<table>
<thead>
<tr>
<th>Dye</th>
<th>$E_l$/eV (nm)</th>
<th>Composition</th>
<th>Character</th>
<th>$E_l$/eV (nm)</th>
<th>$f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPAM-1</td>
<td>2.94(421)</td>
<td>H–2 → L[0.12]</td>
<td>CT</td>
<td>3.06(405)</td>
<td>1.4431</td>
</tr>
<tr>
<td></td>
<td>3.25(381)</td>
<td>H–1 → L[0.46]</td>
<td>CT</td>
<td>3.53(351)</td>
<td>1.3163</td>
</tr>
<tr>
<td>TPAM-2</td>
<td>2.57(482)</td>
<td>H–1 → L[0.42]</td>
<td>CT</td>
<td>2.60(476)</td>
<td>1.8212</td>
</tr>
<tr>
<td></td>
<td>3.14(395)</td>
<td>H–1 → L[0.18]</td>
<td>CT</td>
<td>3.39(366)</td>
<td>1.5291</td>
</tr>
<tr>
<td>TPAM-3</td>
<td>3.12(397)</td>
<td>H–1 → L[0.33]</td>
<td>CT</td>
<td>2.94(422)</td>
<td>2.6710</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H + L[0.40]</td>
<td>π–π*</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H + L[0.49]</td>
<td>π–π*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TPAM-4</td>
<td>3.15(394)</td>
<td>H–2 → L[0.27]</td>
<td>CT</td>
<td>3.19(389)</td>
<td>1.4118</td>
</tr>
<tr>
<td></td>
<td>3.49(355)</td>
<td>H–1 → L[0.21]</td>
<td>CT</td>
<td>3.39(366)</td>
<td>1.9393</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H + L[0.47]</td>
<td>π–π*</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>H + L[0.18]</td>
<td>π–π*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TPAM-5</td>
<td>2.61(474)</td>
<td>H–1 → L[0.64]</td>
<td>CT</td>
<td>2.96(419)</td>
<td>0.3988</td>
</tr>
<tr>
<td></td>
<td>3.09(401)</td>
<td>H–3 → L[0.27]</td>
<td>CT</td>
<td>3.68(337)</td>
<td>1.6166</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H–2 → L[0.34]</td>
<td>CT</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ $E_l$ is the experimental value of energy calculated from the absorption spectra: $E_l = 1240/\lambda$ (Table 1).

### Table 3: Electrochemical data of the as-synthesized dyes

<table>
<thead>
<tr>
<th>Dye</th>
<th>$\lambda_{int}$(nm)</th>
<th>$E_{ox}^a$ (V)</th>
<th>$E_{red}^b$ (V)</th>
<th>$E_{HOMO}^c$(eV)</th>
<th>$E_{LUMO}^d$(eV)</th>
<th>$E_{gap}^e$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPAM-1</td>
<td>455</td>
<td>2.73</td>
<td>0.83</td>
<td>−5.58</td>
<td>−2.85</td>
<td>1.05</td>
</tr>
<tr>
<td>TPAM-2</td>
<td>515</td>
<td>2.41</td>
<td>0.74</td>
<td>−5.49</td>
<td>−3.08</td>
<td>0.82</td>
</tr>
<tr>
<td>TPAM-3</td>
<td>492</td>
<td>2.52</td>
<td>0.74</td>
<td>−5.49</td>
<td>−2.97</td>
<td>0.93</td>
</tr>
<tr>
<td>TPAM-4</td>
<td>433</td>
<td>2.86</td>
<td>0.74</td>
<td>−5.49</td>
<td>−2.63</td>
<td>1.27</td>
</tr>
<tr>
<td>TPAM-5</td>
<td>505</td>
<td>2.45</td>
<td>0.72</td>
<td>−5.47</td>
<td>−3.02</td>
<td>0.88</td>
</tr>
</tbody>
</table>

$^a$ $E_{ox}$ values were calculated from the intercept of the normalized absorption and the emission spectra ($\lambda_{int}$); $E_{ox} = 1240/\lambda_{int}$. $^b$ Potentials measured vs. the (Fe/Fe$^3+$) couple were converted to normal hydrogen electrode (NHE) by addition of +0.63 V. $^c$ Calculated with the formula $E_{HOMO} = -(E_{ox} + 4.75)$ eV. $^d$ Calculated with the formula $E_{LUMO} = (E_{HOMO} + E_{red})$ eV. $^e$ $E_{gap}$ is the energy gap between the $E_{LUMO}$ of dye and the conduction band level of TiO$_2$ (−3.90 eV).
It can also be seen that the introduction of the thiophene in TPAM-2 leads to a lower $V_{oc}$ and FF, which results in an overall decrease in efficiency. This behaviour have already been shown by similar systems, because the introduction of thiophene leads generally a poor regeneration of the oxidized dyes, which have been confirmed in a previous studies done for us, where the introduction of thiophene spacer also leads to a lower $V_{oc}$ and FF because of a poor regeneration of the oxidized dyes.

The lower photocurrent response of TPAM-4 can be attributed to the compression of the absorption spectrum due to the higher energy band-gap and the isolation of the HOMO from the LUMO. Frontier orbital analysis, it is evident that the HOMO is typically localized on the electron-donor moiety and the LUMO is localized on the electron-acceptor unit, where the different $\pi$-bridges influence the push–pull effect of the dyes. The increased $\pi$-conjugation of the dyes tends to broaden and red-shift the absorption bands to improve the light-harvesting effect, however, a device made with TPAM-1 (no $\pi$-conjugated spacer) exhibited the best photovoltaic results with a short-circuit photocurrent density ($J_{sc}$) of 11.37 mA cm$^{-2}$, an open-circuit voltage ($V_{oc}$) of 0.836 V, and a fill factor (FF) of 0.603, corresponding to an overall power conversion efficiency of 5.67%. This is most likely due to the effectiveness of the dye to inject electrons into the conduction band of the TiO$_2$, as exhibited in the calculations.

### Conclusions

We have prepared and fully characterized five new co-donor based dyes for DSSC applications. Using DFT calculations and frontier orbital analysis, it is evident that the HOMO is typically localized on the electron-donor moiety and the LUMO is localized on the electron-acceptor unit, where the different $\pi$-bridges influence the push–pull effect of the dyes. The increased $\pi$-conjugation of the dyes tends to broaden and red-shift the absorption bands to improve the light-harvesting effect, however, a device made with TPAM-1 (no $\pi$-conjugated spacer) exhibited the best photovoltaic results with a short-circuit photocurrent density ($J_{sc}$) of 11.37 mA cm$^{-2}$, an open-circuit voltage ($V_{oc}$) of 0.836 V, and a fill factor (FF) of 0.603, corresponding to an overall power conversion efficiency of 5.67%. This is most likely due to the effectiveness of the dye to inject electrons into the conduction band of the TiO$_2$, as exhibited in the calculations.

### Experimental section

#### Materials and reagents

Solvents were dried according to standard procedures and reagents were used as purchased unless otherwise noted. All air-sensitive reactions were carried out under argon. Flash chromatography was performed using silica gel (Merck, Kieselgel 60, 230–240 mesh or Scharlau 60, 230–240 mesh). Analytical thin layer chromatography (TLC) was performed on aluminum coated with Merck Kieselgel 60 F254. Melting points were determined on a Sanyo Gallenkamp melting point apparatus. NMR spectra were recorded on a Bruker Avance 400 (1H: 400 MHz; $^{13}$C: 100 MHz) spectrometer at 298 K using deuterated solvents as internal standards. Coupling constants ($J$) are reported in Hz and chemical shifts ($\delta$) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. FT-IR spectra were recorded on a Shimadzu FT-IR 8400 spectrometer. UV-Vis spectra were recorded on a Shimadzu 1700 spectrometer. Mass spectra were scanned on a Shimadzu MS-QP 2010 spectrometer operating at 70 eV and Matrix Assisted Laser Desorption Ionization Time-Of-Flight (MALDI-TOF) were recorded on a HP1100 MSD spectrometer and a Bruker REFLEX spectrometer.

#### Electrochemical measurements

The electrochemical properties of the dyes were studied with an AutolabPGStat 30 at a scan rate of 100 mV s$^{-1}$, using a glassy carbon working electrode, a platinum wire counter electrode, and a silver wire pseudo-reference electrode. Tetra-$n$-butylammonium hexafluorophosphate (TBAPF$_6$) (0.1 M) was used as the supporting electrolyte in dry dichloromethane (DCM) and samples were purged with argon prior to the measurements. All
potentials are reported versus a ferrocene/ferrocinium (Fc/Fc+) internal reference.

**Computation methods**

The geometric and electronic properties of the new dyes were calculated with Gaussian 09. The geometry was optimized for each dye by means of the B3LYP and a 6-31G(d,p) basis set and the excitation transitions were calculated using time dependent density functional theory (TDDFT) calculations with CAM-B3LYP/6-31G(d,p).\(^3\)

**Cell fabrication and testing**

Fluorine-doped tin oxide (FTO) coated glass (TEC7) was cleaned in detergent and ethanol before being treated with a 40 mM aqueous solution of titanium(IV) tetrachloride (TiCl₄) for 30 min at 70°C. Devices were structured with three layers that were doctor-bladed using transparent, semitransparent, and opaque 1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.1 M guanidinium thiocyanate, 0.03 M L₂, 0.5 M 4-tert-butylpyridine in dry acetonitrile) between the dye coated photoanode (approx. 0.25 cm²) and the Pt counter electrode. Photovoltaic measurements were then made using a Photo Emission Tech Solar Simulator SS100 at AM 1.5 conditions.

**Synthetic procedure for TPAM-(1–5) dyes**

As shown in Scheme 1, the corresponding aldehyde (2, 5a-d) (50 mg), 3-cyanooacic acid (4 eq.), ammonium acetate (100 mg) and glacial acetic acid (15 mL) were stirred and heated at 120°C for 10 h. The acetic acid was evaporated and the solid was washed with water and filtered. The solid obtained was purified further by recrystallization from ethanol and column chromatography (TPAM-3 and TPAM-5).

**TPAM-1.** Red solid, (40 mg, 71%), mp > 350°C. \(^1\)H-NMR (DMSO-d₆, 400 MHz) \(\delta\): 7.97 (s, 1H), 7.79 (d, \(J = 8\) Hz, 2H), 7.49 (d, \(J = 8\) Hz, 2H), 7.40 (d, \(J = 8\) Hz, 2H), 7.34–7.31 (m, 2H), 7.23–7.20 (m, 4H), 7.15–7.09 (m, 3H), 7.03 (br, 4H), 6.98–6.93 (m, 6H), 6.85 (br, 4H) ppm; \(^13\)C-NMR (DMSO-d₆, 100 MHz) \(\delta\): 169.7, 161.4, 146.9, 146.7, 145.0, 132.4, 131.4, 130.0, 129.6, 127.7, 127.6, 126.2, 126.0, 125.9, 124.1, 123.3, 123.0, 119.3, 99.5, 63.1 ppm; FTIR (KBr) \(\nu\): 3390 (O-H), 2218 (CN), 1718 (C=O), 1506, 1487 cm⁻¹; MS (MALDI-TOF): calcd for C₄₃H₃₁N₃O₂ 828.346; found 828.389 [M+].

**TPAM-2.** Black solid, (32 mg, 48%), mp > 350°C. \(^1\)H-NMR (DMSO-d₆, 400 MHz) \(\delta\): 8.45 (s, 1H), 7.94 (d, \(J = 4\) Hz, 1H), 7.59 (d, \(J = 8\) Hz, 2H), 7.54–7.47 (m, 4H), 7.43–7.41 (m, 2H), 7.37–7.31 (m, 6H), 7.24 (d, \(J = 16\) Hz, 1H), 7.16–7.10 (m, 6H), 7.07–7.03 (m, 7H), 6.99–6.95 (m, 4H) ppm; \(^13\)C-NMR (DMSO-d₆, 100 MHz) \(\delta\): 164.3, 153.2, 148.1, 147.5, 147.0, 146.9, 146.2, 134.0, 133.1, 132.8, 132.0, 130.3, 130.1, 128.9, 128.0, 127.9, 127.4, 126.7, 125.4, 125.0, 124.8, 124.6, 123.7, 123.6, 122.8, 122.2, 117.2, 100.0, 97.9, 79.3, 55.6 ppm; FTIR (KBr) \(\nu\): 3398 (O-H), 2230 (C=O), 1431 cm⁻¹; MS (MALDI-TOF): calcd for C₄₆H₁₃N₃O₂S 717.245; found 717.235 [M⁺].

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Notes and references