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Small-Molecule Azomethines: Organic Photovoltaics via Schiff Base Condensation Chemistry


Conjugated small molecule azomethines for photovoltaic applications were prepared via Schiff base condensation chemistry. Bulk heterojunction devices exhibit efficiencies of 1.2% with MoO$_x$ as the hole-transporting layer. The versatility and simplicity of the chemistry is illustrated by preparing a photovoltaic device directly from the reaction mixture without any form of workup.

Most of the conjugated materials used in organic electronics are synthesized using time-consuming Suzuki-, Wittig-, or Heck-type coupling reactions. These chemistries often make use of expensive transition metal catalysts, require stringent reaction conditions, and extensive product purification.

In order to offer a more economic route towards organic photovoltaic materials we are currently exploring azomethines (-CH=N-) as the conjugated linker unit. The azomethine bond is isoelectronic to the vinyl bond and possesses similar optoelectronic and thermal properties. Besides that, azomethines offer significant advantages over vinylenes as they can be prepared using Schiff-base condensation chemistry under near ambient reaction conditions. Expensive catalysts are not required and water is the only by-product.

The first photovoltaic devices based on poly(azomethine)s were published by Hindson et al. ($\text{PCE} \sim 0.12\%$) and Iwan et al. ($\text{PCE} \sim 0.31\%$). The reported conjugated poly(azomethine)s are only moderately soluble and therefore difficult to process. Small molecules, on the other hand, have the advantage of having a higher solubility, a well-defined molecular structure and no batch-to-batch variations. Recent results have shown that conjugated small molecules can compete successfully with their polymeric counterparts.

For this study we have synthesized two azomethine-based small molecules via a simple condensation reaction (Figure 1).

![Figure 1. Synthesis and molecular structures of the small-molecule azomethines](image)

4-Aminotriphenylamine (TPA, 1) was reacted with two conjugated dialdehydes. 2,5-Thiophenedicarbaldehyde (Th, 2a) was used since thiophenes have been studied extensively and possess good charge transport properties. Besides that, both materials are readily available from commercial sources. 4,7-Bis(5-formylthiophen-2-yl)-2,1,3-benzothiadiazole (TBT, 2b) was used because it is a strong electron-accepting moiety and this yields a bipolar donor-acceptor-donor molecule with a small bandgap and thus a larger overlap with the solar spectrum. In addition TBT is known to possess high mobilities and good film-forming abilities. The reaction was performed in chloroform and p-toluenesulfonic acid was used as a catalyst. The products (3a-b) were precipitated, and treated with diluted triethylamine to neutralize the protonated azomethine bond. The small molecules were obtained in good yields (>80%) and characterized using $^1$H and $^{13}$C NMR, FTIR, and mass spectrometry where possible. Detailed synthetic procedures and characterization of the small molecules and their intermediates are available in the supporting information.

The thermal properties of the new molecules were assessed using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Both small molecules show excellent thermal stabilities with degradation temperatures ($T_d$) above 350 °C (Supplementary Figure S1, Table S1). Comparing TPA-Th-TPA to its vinyl analogue, we found that the degradation temperature is approximately 40 °C higher, confirming the superior thermal stability of azomethines. DSC experiments showed that both TPA-Th-TPA and TPA-TBT-TPA exhibit a glass transition temperature ($T_g$) at 86 and 114 °C, respectively (Supplementary Figure S2, Table S1).
TPA also showed a cold crystallization exotherm during the second heating at 143 °C. Both small molecules melt above 200 °C and form isotropic melts, as was confirmed by hot-stage optical second heating at 143 °C. Both small molecules melt above 200 °C and molecules.

Table 1. Summary of the optoelectronic properties of TPA-X-TPA small molecules

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \lambda_{\text{max}} ) ([\text{nm}])</th>
<th>( \varepsilon ) ([10^4\text{M}^{-1}\text{cm}^{-1}])</th>
<th>( \lambda_{\text{onset}} ) ([\text{nm}])</th>
<th>( E_g ) ([\text{eV}])</th>
<th>( E_{\text{onset}} ) ([\text{eV}])</th>
<th>HOMO ([\text{eV}])</th>
<th>LUMO ([\text{eV}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPA-Th-TPA</td>
<td>306, 467</td>
<td>3.6</td>
<td>314, 463</td>
<td>2.19</td>
<td>0.85</td>
<td>-5.32</td>
<td>-3.13</td>
</tr>
<tr>
<td>TPA-TBT-TPA</td>
<td>306, 389, 520</td>
<td>5.6</td>
<td>310, 400, 538</td>
<td>1.88</td>
<td>0.79</td>
<td>-5.26</td>
<td>-3.36</td>
</tr>
</tbody>
</table>

*Measured in dichloromethane. b) Spincoated from chloroform. c) Estimated from the onset of the absorption spectrum of the film, 1240/\( \lambda_{\text{onset}} \). d) Determined by cyclic voltammetry, with Fe/FeCl₃ at 4.8 eV below vacuum. e) Estimated by subtracting the bandgaps from the HOMO energy levels.

**Figure 2. UV-Vis absorption spectrum and computational study of the small molecules.** a) Normalized UV-Vis absorption spectrum of TPA-X-TPA small molecules in the solid state. b and c, DFT-calculated (CAM-B3LYP/6-31G*) Kohn-Sham HOMO level for the TPA-Th-TPA molecule; b) Shows the small molecule in the neutral state where the HOMO is delocalized over the entire molecule. c) Protonation of the azomethine nitrogen-atom interrupts conjugation and enforces localization of the HOMO to the non-protonated part of the molecule.

The molecular extinction coefficients at the most red-shifted absorption maxima were calculated to be on the order of \( 10^5 \text{M}^{-1}\text{cm}^{-1} \) TPA-TBT-TPA displays the highest molar extinction coefficient (Table 1). The absorption spectra of the small molecules in the solid state show no large shifts as compared to the solution spectra (Table 1). The bandgap of the small molecules could be estimated from the onset of the absorption spectra. Comparing the absorption maxima with those of their vinyl analogues, a redshift for TPA-Th-TPA was observed (21 nm), while TPA-TBT-TPA shows a 22 nm blue shift. Halochromatic behaviour was observed when the azomethine solutions were acidified and is described in the supplementary information.

The calculations indicate that protonation breaks the symmetry and enforces localization of the HOMO to the non-protonated part of the molecule. This can be detrimental for hole extraction and can also lead to energy recombination.

As a result of protonation, the azomethine linker and are described in the supporting information. The calculations indicate that protonation breaks the symmetry and enforces localization of the HOMO, which results in a lowering of the HOMO energy by approximately ~2 eV (Figure 2 and Supplementary Figure S9-S12) while the LUMO level shows a downward shift in energy by more than 3 eV. This suggests that upon protonation of the azomethine linker at the PEDOT:PSS interface, energy barrier states for holes and well states for electrons are formed. This can be detrimental for hole extraction and can also lead to energy recombination.

The photocatalytic performance of the conventional device (ITO/PEDOT:PSS/TPA-Th-TPA/[60]PCBM/LiF/Al) with a device where the acidic PEDOT:PSS was replaced by neutral molybdenum oxide (MoO₃) (Supplementary Table S3), Replacing PEDOT:PSS with MoO₃ increases the efficiency from 0.35% to 0.42%, which could be attributed to an increase in voltage from 0.45 V to 0.68 V (Supplementary Table S3). Also the lower work function of MoO₃, between 5.3 and 5.7 eV while PEDOT:PSS is approximately 5.0 eV could explain the higher voltage as a result of better energy alignment and higher driving force. As the voltage at 100 °C or higher destroyed the devices, the use of [70]PCBM resulted in an additional increase in efficiency (Supplementary Table S5, S6 and Figure S14), which is ascribed to the absorption of [70]PCBM, resulting in higher currents. The influence of the hole-blocking layer, annealing temperature and time, and type of fullerene were investigated for TPA-Th-TPA and the optimal conditions were also used to prepare the TPA-Th-TPA devices (Table 2, Figure 3a).

**Table 2. Summary of the characteristics of photovoltaic devices with ITO/MoO₃/TPA-X-TPA/[70]PCBM (1:2)/LiF/Al configuration after annealing at 70 °C.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>( J_{SC} ) ([\text{mA cm}^{-2}])</th>
<th>( \text{V}_{OC} ) ([\text{V}])</th>
<th>FF</th>
<th>PCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPA-Th-TPA</td>
<td>3.73</td>
<td>0.83</td>
<td>0.70</td>
<td>0.41</td>
</tr>
<tr>
<td>TPA-TBT-TPA</td>
<td>4.50</td>
<td>0.75</td>
<td>0.75</td>
<td>1.15</td>
</tr>
<tr>
<td>TPA-Th-TPA (one-pot)</td>
<td>2.60</td>
<td>0.75</td>
<td>0.75</td>
<td>0.60</td>
</tr>
</tbody>
</table>

\( J_{SC} \) was calculated by integrating the EQE spectrum with the AM1.5G spectrum under bias. a) After annealing for 30 minutes. b) After annealing for 5 minutes.
As expected from the absorption spectra, TPA-TBT-TPA, which has the smallest bandgap and thus the best overlap with the solar spectrum, shows a higher current. However, because of the slightly higher open-circuit voltage and fill factor TPA-Th-TPA shows the best power conversion efficiency (PCE). The high open-circuit voltages up to 0.83 V are in agreement with the fairly low-lying HOMO energy levels. All devices show a strong voltage dependence, i.e. significantly higher currents were obtained under reverse bias. This indicates that charge carrier generation is high, but are not extracted under working conditions, which can be explained by a low charge carrier mobility and/or a poor morphology. The poor fill factors also hint towards unbalanced charge transport, which is likely attributed to the limited mobility of azomethines when processed under these conditions. The vinyl analogues of TPA-Th-TPA and TPA-TBT-TPA have been published by other groups and show PCEs of 0.34% and 0.26%, respectively after extensive device optimization using [70]PCBM as the electron acceptor.

Figure 3. Device performance of small molecule BHJ solar cells. a, J–V characteristics and b, EQE spectra of small molecule bulk heterojunction solar cells based on TPA-X-TPA:[70]PCBM using MoOx as hole blocking layer after annealing.

In conclusion, two small-molecule azomethines were synthesized via Schiff base condensation chemistry. The small molecules both exhibit reversible oxidation behaviour, a fairly deep lying HOMO energy level, and a bandgap between 1.9 to 2.2 eV. Photovoltaic devices based on MoOx as the hole-transporting layer performed better when compared to PEDOT:PSS, which is mainly attributed to an increased voltage. Both small molecules showed efficiencies around 1.2% with [70]PCBM as the electron acceptor. TPA-Th-TPA performed slightly better (PCE of 1.21% with a Jsc of 3.7 mA cm⁻², Voc of 0.83 V, and FF of 39%) after post annealing. Both azomethine-based devices outperform their vinyl analogues, indicating that azomethines are promising candidates for organic photovoltaic applications. We also demonstrated that this chemistry enables the fabrication of OPV devices directly from the reaction mixture without any product workup. These devices showed a PCE of 0.6%. Because azomethine chemistry is easy, clean and proceeds under near ambient conditions we believe that this approach has the ability to reduce materials and production costs of organic photovoltaic devices.

Acknowledgements

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Notes and references


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Small molecule donor materials can be prepared in one step using simple condensation chemistry.

1- stir 24 h at 25 °C
2- [70]PCBM
3- spincoating
4- thermal annealing

Current density (mA cm⁻²) vs Voltage (V)
PCE = 0.6%