The Molecular Engineering of Organic Sensitizers for Solar-Cell Applications**

Jared H. Delcamp, Aswani Yella, Thomas W. Holcombe, Mohammad K. Nazeeruddin, and Michael Grätzel*

Organic materials with attractive electronic and optoelectronic properties for functional device applications are in high demand. Organic alternatives to inorganic counterparts are desirable because of the potential to decrease manufacturing costs and realize a more diverse set of devices, including lightweight, efficient low-light, and flexible solar cells. Substantial progress has been made toward functional organic materials for solar-to-electricity conversion. Among photovoltaics, dye-sensitized solar-cell (DSC) research has progressed toward becoming a significant contributor to the solar energy conversion market since the seminal work of O’Regan and Grätzel in 1991. DSCs are particularly attractive as light-harvesting devices because they allow for judicious control of device properties.

DSCs operate by photoexcitation of a sensitizer (dye) anchored to a semiconductor (such as TiO₂), enabling the transfer of an electron to the semiconductor conduction band followed by regeneration of the dye to the ground-state by a redox shuttle. Metal-based dyes currently yield the highest power conversion efficiencies (PCEs) in DSC devices. However, metal-free dyes have recently produced comparably efficient DSCs, often with much larger molar absorptivity and may be more cost effective considering the price of precious metals. Among organic dyes, the donor–acceptor systems have been particularly promising. Herein we report the synthesis, characterization, and DSC device performance of an electron-rich heterocycle with the common name ullazine (1).

Ullazine is a 16 π-electron nitrogen-containing heterocyclic system that is isoelectronic with pyrene. It was first reportedly synthesized in 1983 to study radical cation and anion persistence (Figure 1).

** This work was financially supported by the FP7-Energy-2010-FET project Molesol (contract No. 256617). M.G. thanks the European Research Council (ERC) for an advanced research grant (ARC) to support the Mesolight project. M.K.N. thanks the World Class University program funded by the Ministry of Education, Science and Technology through the National Research Foundation of Korea (R31-2011-000-10035-0), Department of Materials Chemistry, Korea University. A.Y. thanks the Balzan Foundation for partial financial support as part of the 2009 Balzan Prize awarded to M.G.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201205007.
stabilized ullazine core to maintain a concise synthesis. Installation of late-stage conjugated acceptor/anchor functionality to the ullazine core through electrophilic aromatic substitution (EAS) was examined. Based on the DFT studies, EAS will occur at the 4- and 5-positions of unsubstituted ullazine. Substitution at the 5-position is both preferential to maintain planarity for promotion of a strong ICT and favorable based on the steric influence of substituents at the 3- and 9-positions.

The Balli synthesis of 3,9-diphenyl ullazine (2) requires ten steps from present-day, commercially available materials, with an expected 19% overall yield (Scheme 1). This original route relies on a lengthy series of oxidation/reduction reactions (two steps) and functional-group manipulations (three steps), which install and remove oxygen and sulfur functionality not present in the final structure. Additionally, no regioselective reactions to generate the 4,8-unsubstituted ullazine were demonstrated by the Takahashi route (Scheme 1).[23] Alternate synthetic routes were examined. The stabilized 3,9-bisaryl-substituted ullazine core by a double Fürstner cyclization proceeded in four total steps from commercial starting materials on 5 g scale and in 55% overall yield.

The ground-state oxidation potential (\(E_{S^+/S}\)) and excited-state oxidation potential (\(E_{S^*/S^}\)) of ullazine 3 were determined for comparison to a commonly used donor motif in organic electronics, bis(4-hexyloxyphenyl)phenylamine (4; Supporting Information, Table 1).[26–28] Ullazine 3 demonstrates a slight decrease (20 mV) in \(E_{S^+/S}\) when compared with JD21. JD26 also experiences a significant increase in the high-energy spectral region. Although the major difference in the absorption spectra for the dyes 3, 4, and JD21 is a blue-shift of the max peak by 28000 L mol\(^{-1}\) cm\(^{-1}\) at 575 nm and a maximum molar absorptivity \(\varepsilon\) of 28000 L mol\(^{-1}\) cm\(^{-1}\) in dichloromethane (Supporting Information, Figure S1). The aldehyde 9 then smoothly underwent condensation with cyanacetic acid to give dye JD21 in 97% yield. The InCl\(_3\)-based double cyclization route was implemented for the synthesis of five additional dyes that vary the acceptor position or the donor groups on the ullazine core (Scheme 2).

The absorption properties of each of the ullazine-based dyes were examined to better understand the effects of substituents on the ICT band. JD21 has a strong absorbance in the range of 400–625 nm with a \(\lambda_{max}\) of 575 nm and a maximum molar absorptivity \(\varepsilon\) of 28000 L mol\(^{-1}\) cm\(^{-1}\). Dyes JD21, JD25, JD26, and JD29 differ in absorption spectrum shape by a significant increase in the high-energy spectral region. Although the \(\lambda_{max}\) of JD26 is blue-shifted by > 40 nm, the \(\lambda_{max}\) peak is significantly broadened and the onset is slightly red-shifted when compared with JD21. JD26 also experiences a signifi-

\[
\begin{array}{|c|c|c|c|c|}
\hline
\text{Compound} & \lambda_{max} [\text{nm}] & \varepsilon [\text{Lmol}^{-1}\text{cm}^{-1}] & E_{S^+/S\text{H}} [\text{eV}] & E_{S^*/S\text{H}} [\text{eV}] \\
\hline
3 & 393 & 19400 & 2.74 & 0.89 \\
4 & 299 & 20500 & 3.44 & 0.91 \\
\hline
\text{Ullazine sensitizers} & & & & \\
JD21 & 582 & 28000 & 2.03 & 1.09 \\
JD25 & 598 & 33000 & 1.99 & 1.03 \\
JD26 & 548 & 7500(1) & 2.06 & 1.06 \\
JD29 & 598 & 24000 & 2.00 & 1.09 \\
JD30 & 531 & 12000 & 2.05 & 1.09 \\
JD32 & 393 & 1600(1) & 2.08 & 1.04 \\
\hline
\end{array}
\]

*Table 1: Optical and electrochemical data.*

[a] \(E_{S^+/S\text{H}}\) and \(E_{S^*/S\text{H}}\) vs. NHE. [b] Measured in CH\(_2\)Cl\(_2\). [c] Measured at the intersection of the normalized absorbance and emission spectra. [d] Measured in CH\(_2\)Cl\(_2\), 0.1 M Bu\(_4\)NPF\(_6\), glassy carbon working electrode, Pt reference electrode, and Pt counter electrode with ferrocene as an internal standard. [e] Calculated from \(E_{S^*/S\text{H}} = (E_{S^+/S\text{H}} - E_{0/0})\). [f] Shoulder.
The application of the ullazine-based dyes as sensitizers for DSC devices was tested with liquid electrolytes (Table 2; Supporting Information, Table S2). Dye JD21 shows a broad incident photon-to-electron conversion efficiency (IPCE), from just before 400 nm to approximately 730 nm, with a maximum of 95% at 520 nm (Figure 2). The IPCE range is broadened by approximately 75 nm when compared to the solution absorption of JD21 in dichloromethane which may indicate favorable aggregation.[30,31] The integrated current under the IPCE curve is in good agreement with the short-circuit current density ($J_{SC}$) of $-15.4 \text{ mA cm}^{-2}$ measured under AM1.5 conditions. The measured $J_{SC}$ combined with an open-circuit voltage ($V_{OC}$) of 730 mV and fill factor (FF) of 0.75 gives an excellent power conversion efficiency (PCE) of 8.4% according to the equation $\eta = V_{OC}J_{SC}FF/I_0$, where $I_0$ is the solar intensity. The exceptional performance from low-molecular-weight JD21 (MW = 638 g mol$^{-1}$, PCE = 8.4%) is exemplified when compared with other low molecular weight dyes.[32] JD21 is a good organic sensitizer candidate for industrial applications based on the concise, scalable (5 g) synthesis (six steps, 43% yield) of JD21, given that several intermediates were well-behaved solids and high performance in DSC devices was achieved. Computationally, electron density contribution from the 3,9-bisalkoxyphenyl substituents of JD21 to the ground-state HOMO is minimal; however, upon cation generation, the alkoxyphenyl substituents contribute substantially to the HOMO orbital delocalization.

### Table 2: Photovoltaic device data with an iodide/triiodide redox shuttle.\textsuperscript{[b]}

<table>
<thead>
<tr>
<th>Sensitizer</th>
<th>$V_{OC}$ [mV]</th>
<th>$J_{SC}$ [mA cm$^{-2}$]</th>
<th>FF</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>JD21</td>
<td>730</td>
<td>$-15.4$</td>
<td>0.75</td>
<td>8.4</td>
</tr>
<tr>
<td>JD25</td>
<td>807</td>
<td>$-11.5$</td>
<td>0.72</td>
<td>6.7</td>
</tr>
<tr>
<td>JD29</td>
<td>716</td>
<td>$-13.3$</td>
<td>0.70</td>
<td>6.7</td>
</tr>
<tr>
<td>JD30</td>
<td>672</td>
<td>$-11.0$</td>
<td>0.70</td>
<td>5.2</td>
</tr>
<tr>
<td>JD32</td>
<td>553</td>
<td>$-3.7$</td>
<td>0.78</td>
<td>1.7</td>
</tr>
</tbody>
</table>

[a] For electrolyte compositions, film thickness discussion and N719 comparison, see the Supporting Information. Measured under AM1.5 with a 6 × 6 mm$^{2}$ black mask.

---

Scheme 2. Ullazine-based dyes for examining the donor and acceptor influence on ICT strength, cation stability, and surface coverage.

Cyclic voltammetry and absorption/emission spectra for each of the dyes were measured to determine the ground-state oxidation potential ($E_{(S_{0}/S_{1})}$) and HOMO–LUMO transition energy ($E_{(0/0)}$) values, respectively (Table 1 and Supporting Information). The $E_{(S_{0}/S_{1})}$ values were measured to be within a concise range for all the dyes, from 1.03–1.09 V vs. NHE (Table 1). These values are substantially more positive than the iodide/triiodide redox shuttle, which indicates that the ground-state sensitizer regeneration is energetically favorable for DSC applications. The $E_{(0/0)}$ values were found from the intersection of the absorption and emission spectra for each of the dyes (Supporting Information, Figure S11). The $E_{(S_{0}/S_{1})}$ values were calculated to be $-0.91$ to $-1.04$ V vs. NHE, which provides the free energy required to transfer an electron from the excited dye to the TiO$_2$ conduction band. Energetically, a functional DSC device fabricated with the ullazine-based sensitizers, iodide/triiodide redox shuttle and TiO$_2$ semiconductor is favorable based on the $E_{(S_{0}/S_{1})}$ and $E_{(S_{0}/S_{1})}$ values of the dyes.
ization (Supporting Information, Figure S9). Although substituents in the 3- and 9-positions do not dramatically shift the ICT band, they are valuable for controlling morphology and increasing cation stability. The dye cation is a critical intermediate species formed during DSC device operation after electron transfer from the dye to the semiconductor conduction band. Increasing the stability of this charged intermediate and increasing spatial separation of the cation from the semiconductor surface has a direct, positive impact on device performance. DFT calculations with all of the dyes synthesized indicate the LUMO is delocalized on the cyanoacrylic acid acceptor group, which is desirable for efficient charge injection to the TiO₂ conduction band upon dye photoexcitation.

As expected, an acceptor at the 4-position (JD26) proved to be a poor dye for DSC applications, as the dye readily desorbs from the TiO₂ surface, presumably because of the cumbersome steric environment near the anchor. Additionally, placing an acceptor in the 6-position of ullamazine dramatically decreased the device short-circuit current, as observed from the IPCE measurements and expected from the UV/Vis data (Supporting Information, Figure S11). Computationally and experimentally (UV, IPCE), the 6-dyes JD25, JD29, and JD30 focused on the donor moiety, towards modifying the titanium dioxide surface coverage. Addition of alkyl chains to d-π-A dyes is known to increase DSC device Vₜₚₚ by blocking access to the semiconductor surface, which retards the recombination of electrons in the semiconductor with the redox shuttle. Through the use of two additional hexyloxy chains, the Vₜₚₚ of JD25-based devices was improved by greater than 5 mV in comparison to JD21-based devices. With a Vₜₚₚ of > 800 mV (theoretical max. ca. 850 mV), DSC devices based on the TiO₂ semiconductor, I/V redox shuttle and sensitizer JD25 exhibit minimal loss owing to unfavorable recombination pathways. JD21-based devices have a broader IPCE that extends further into the blue region as expected based on the solution absorption spectrum; however, JD21-based devices demonstrated a larger red-shift of the IPCE spectrum when compared to the solution absorption spectrum than JD25 (75 nm vs. 50 nm). The additional alkyl moiety of JD25 rotates the phenyl substituent further out of plane with the ullamazine π-face and is likely to disrupt any productive aggregate formation.

In conclusion, we have developed a rapid, efficient synthesis of a novel heterocycle for organic electronic applications. The ullamazine core is available from simple commercial starting materials in four scalable steps by a double Fürstner cyclization as the key bond-forming reaction. The ullamazine core also offers an attractive number of π-conjugated sites for the molecular engineering of ullamazine-based functional materials. The unique resonance structure contributions to generate an electron-accepting center and an electron-donating aromatic periphery in part contribute to the remarkable performance exhibited in DSCs with this heterocycle. DSC devices sensitized with metal-free, low-molecular-weight ullamazine-based dye JD21 demonstrate an excellent visible absorption spectra resulting in a power conversion efficiency of 8.4%. Owing to the concise, scale-friendly synthesis, and high performance in DSCs, we expect the ullamazine core to find widespread use in electronic applications with possible industrial applications for the high-efficiency DSC organic dye JD21.

Received: June 26, 2012
Published online: August 24, 2012

Keywords: dyes/pigments · light harvesting · photonics · sensitizers · solar cells


[34] In agreement with a bulkier aryl substituent, dye-loading studies indicate a significantly lower dye adsorption onto the TiO$_2$ surface for JD25 when compared to JD21 (ca. 30% lower). The dye loading trend follows the same trend as substituent bulk at the 3- and 9-positions of ullaizine (SI, Table S3).