COMMUNICATION

Highly Fluorescent Pyridinium Betaines for Light Harvesting: An Experimental and Computational Investigation


Abstract: We report the findings of our experimental and theoretical investigation into the properties of pyridinium enolates and their potential utility in light harvesting applications such as luminescent solar concentrators (LSCs). The synthesis, structures, photophysical characterization and quantum-chemical study of the five cyclo betaines as well as their suitability and performance in as the emissive component in LSCs is presented.

Molecules and materials with strong absorption and intense emission profiles find utility in a wide range of applications including light harvesting for energy related applications and as optical tags for imaging in biology.[1–3] Consequently, the design and synthesis of new chromophores and fluorophores,[4] as well as an understanding regarding the origin of their molecular spectral properties are required.[5] Betaine dyes are an important class of chromophore characterized by their dipolar electronic ground state, that can’t be represented by a neutral mesomeric form.[5–8] One of the most intensely studied groups of molecules in this class are the pyridinium N-phenolates with Riechardt’s dye being the most well-known.[9] Intramolecular charge transfer on excitation of the π – π* transition from the phenolate donor to the pyridinium acceptor results in the perichromism observed for these dyes making them important polarity sensors.[10,11] Unfortunately, the pyridinium N-phenolates are typically not fluorescent in solution due to rapid non-radiative relaxation processes such as large-amplitude intramolecular rearrangement, intramolecular electron transfer and back-electron transfer to the S₂ state.[12] There are however limited reports of emissive behavior at low temperature and in thin polymer films although this research area remains relatively unexplored.[13] Encouragingly, coumarin pyridinium cyclobetaines recently developed by Hell et al. display a marked increase in quantum efficiency on conjugation to antibodies and subsequent protein binding while maintaining their large Stokes shifts. This ultimately led to their utility as the large Stokes shift fluorophore in stimulated emission depletion (STED) microscopy.[14,15] The spectral properties of fluorophores for use as the large Stokes shift component in STED microscopy are similar to that of dyes for use as the light harvesting component in LSCs.[16,17] A typical LSC device consists of a transparent planar waveguide integrated with a fluorescent/phosphorescent compound dispersed in a polymer matrix.[18] The incorporated chromophore harvests light through absorption, meanwhile subsequent emission is focused to the edges of the waveguide by total internal reflection, where a photovoltaic cell is coupled to the LSC to generate electricity.[19] This form of device construct has led to technology aimed at harvesting solar energy from a myriad of surfaces as an alternative to direct capture and conversion by solar panels.[20] Two key photophysical properties of the chromophore affect the performance of LSC devices – photoluminescence quantum yield (PLQY) and Stokes shift.[20] PLQY near unity and large Stokes shifts with negligible overlap of the absorption and emission profiles are ideal parameters for LSC dyes.[21,22] While chromophores with such properties have been reported in the literature,[22] they are relatively rare especially at higher dye concentrations that are required for light harvesting.[23,24] Therefore, the design and facile preparation of

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new photo-stable organic chromophores with large Stokes shifts and achieving quantum efficiency therefore remains a significant fundamental challenge. In this communication, we demonstrate that appropriately designed zwitterionic pyridinium enolates can be engineered to meet the stringent requirements for utility in organic LSCs while also reporting theoretical findings that support the experimental observations and indicate the potential for predicting structure-property relationships. Indeed, our findings demonstrate that an LSC incorporating 1e performs comparably to the state-of-the-art. Herein we report the synthesis, single crystal X-ray structures, photophysical properties and highly accurate quantum-chemical calculations of five pyridinium enolate cyclobetaines as well as the performance of 1e as the active component in an LSC device. Compounds 1a-1e were prepared by addition of octafluorocyclopentene to an appropriate amount of the desired pyridyl precursor in a chilled THF-water solvent system. The reaction is proposed to proceed via the mechanism shown in Fig. 1 whereby two hydrolysis steps follow an initial nucleophilic substitution with the products purified chromatographically. Crystallization from ethyl acetate yields single crystals suitable for diffraction studies and structure determination of all five compounds. Structural analysis of compounds 1a-1e revealed typical bond lengths for resonance-stabilized enolates (C-O; 1.214 – 1.240 Å, C-C; 1.403 – 1.424 Å). Deviation of the heterocyclic enolate and pyridinium moieties from coplanar range from the almost co-planar 1c to the notably twisted 1a with a torsion angle of 52.2°. Additional crystallographic details can be found in the Electronic Supporting Information (ESI) (ESI - S28).

<table>
<thead>
<tr>
<th>Compound</th>
<th>λ_{max} (nm)</th>
<th>λ_{em} (nm)</th>
<th>ε_{max} (M⁻¹ cm⁻¹)</th>
<th>[a] Dk</th>
<th>[%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>360</td>
<td>448</td>
<td>9149</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>1b</td>
<td>330</td>
<td>409</td>
<td>22240</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>1c</td>
<td>386</td>
<td>480</td>
<td>15360</td>
<td>23.6</td>
<td></td>
</tr>
<tr>
<td>1d</td>
<td>407</td>
<td>480</td>
<td>28829</td>
<td>85.2</td>
<td></td>
</tr>
<tr>
<td>1e</td>
<td>403</td>
<td>473</td>
<td>34121</td>
<td>80.4</td>
<td></td>
</tr>
</tbody>
</table>

[a] Emission efficiencies relative to 9,10-diphenylanthracene.

Absorption spectra of freshly dissolved crystalline samples of 1a-1e in toluene display maxima ranging from 338 – 407 nm, with 1b being the only derivative where the absorption maximum is hypsochromically shifted with respect to parent 1a (Fig. 2 and Table 1). The molar extinction coefficients of 1a-1e vary significantly with thiophenyl derivatives 1d and 1e being the strongest absorbers (Table 1), while also being efficient fluorophores with an approximate 40-fold increase in quantum efficiency observed from 1a to 1e in toluene. As stated earlier, all compounds show large emission Stokes shifts, which in combination with the relatively high quantum efficiencies of 1d and 1e in toluene was intriguing. To further investigate the properties of 1a-1e, the absolute photo-luminescent quantum yield (PLQY) of the betaine dyes dispersed in a polymethyl methacrylate (PMMA) matrix (5mM) were measured using an integrating sphere (ESI - S1). The PLQY values of the dyes in PMMA were higher than the corresponding toluene samples (Fig. 3). As with the dyes in toluene, there was a large variation in PLQY across the five betaine dyes, with 1e having a quantum yield of 100%. These spectroscopic properties, in addition to the thermal stability > 310 °C of 1e (ESI - S20-S21) make it an excellent candidate for LSC applications that are discussed later.

<table>
<thead>
<tr>
<th>Compound</th>
<th>λ_{abs} (nm)</th>
<th>f</th>
<th>λ_{em} (nm)</th>
<th>f</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>343</td>
<td>0.361</td>
<td>454</td>
<td>0.179</td>
</tr>
<tr>
<td>1b</td>
<td>329</td>
<td>0.609</td>
<td>438</td>
<td>0.500</td>
</tr>
<tr>
<td>1c</td>
<td>371</td>
<td>0.862</td>
<td>509</td>
<td>0.420</td>
</tr>
<tr>
<td>1d</td>
<td>380</td>
<td>0.854</td>
<td>492</td>
<td>0.687</td>
</tr>
<tr>
<td>1e</td>
<td>383</td>
<td>0.348</td>
<td>452</td>
<td>0.679</td>
</tr>
<tr>
<td>1f</td>
<td>346</td>
<td>0.764</td>
<td>452</td>
<td>0.728</td>
</tr>
</tbody>
</table>

[a] SCS-CC2/def2-TZVP/SCS-CC2/def2-TZVP level of theory.

To understand the origin of the observed absorption and emission properties, quantum-chemical calculations were undertaken. While it is common to base such studies on linear-response time-dependent density functional theory (TD-DFT) methods, we...
report herein that compounds 1a-e posed a challenge for these routine approaches. Conventional TD-DFT methods gave chemically unreasonable geometries of the first excited states with the central N atoms being in pyramidal configurations. Subsequent single-point calculations resulted in strongly red-shifted emission energies to above 510 nm with nearly zero oscillator strengths, thus making the reliable computational analysis of the emission energies challenging (ESI-S33). As a remedy, we decided to conduct all geometry optimizations of the electronic ground and first excited states, as well as all single-point calculations of absorption and emission properties using the resource-intensive spin-component-scaled coupled-cluster singles with approximate doubles approach (SCS-CC2).[26] Note that CC2-type approaches are often regarded as the "gold standard" for large organic compounds, which makes our results particularly valuable.

Simulation of UV/Vis spectra reveal that the observed lowest-lying absorption bands are caused solely by single S0→S1 transitions without the presence of any other transitions in that energy regime (ESI - S34-S35). The calculated absorption wavelengths range from 320 nm for 1b to 390 nm for 1d (Table 2). All excitations are blue-shifted by 0.13-0.2 eV compared to experiment, an expected result as the calculations did not consider solvent effects. Moreover, the observed differences are well within the expected average accuracy of 0.17-0.2 eV for CC2-type approaches.[27] Indeed, our SCS-CC2 calculations reproduced the various substituent effects correctly. The emission wavelengths were reproduced to within 0.04 - 0.14 eV accuracy, meaning that the trends observed for the Stokes shifts are also correctly represented, with 1a-c having Stokes shifts around 0.2 eV larger than 1d-e (Table 2). The oscillator strengths for the absorption (Table 2) and the resulting simulated band intensities (ESI – S36-S37) support the experimental finding that 1d and 1e exhibit the largest intensities, while 1a is the weakest absorber. The calculated emission intensities also verify that 1d and 1e should have the brightest emissions. However, the relative intensities for 1a and 1b are notably overestimated. While an overestimation for calculated oscillator strengths is a known problem, it is also conceivable that solvent or aggregation effects quench the emission intensities in the experiment.

Molecular orbital analysis shows that the S0→S1 transitions can be described as transitions from the respective highest-occupied molecular orbital (HOMO) to the corresponding lowest...
unoccupied molecular orbital (LUMO). While the HOMO is predominantly localized in the enolate, the LUMO extends into the pyridinium acceptor unit (ESI - S39). While TD-DFT methods were inadequate for geometry optimization of the first excited states, TD-DFT single point calculations on the SCS-CC2 optimized structures revealed similar trends as calculated with SCS-CC2. This also allowed us to qualitatively assess the charge-transfer (CT) character of each relevant transition by comparing the results between the global hybrid functional PBE38[27] which cannot describe CT transitions, and the range-separated hybrid CAM-B3LYP which does. As outlined in (ESI - S38), the absorption energy differences between both functionalities are marginal and increase from 0.03 eV for 1a to a slightly larger value of 0.08 and 0.07 eV for 1d and 1e respectively. This allows the conclusion that the S2→S1 transitions in these systems have negligible CT character. Having established this computational approach, we are confident that we can implement it for the prediction of absorption and emissive properties of similar compounds in future studies such as 1f (Table 2, ESI - S40-S41). As indicated earlier, the promising properties of 1e led us to investigate this fluorophore in more detail regarding its applicability in LSC devices. The PLQY of 1e was examined at a range of concentrations in PMMA matrix, where increasing the concentration of 1e from 5 mM to 80 mM resulted in a steady decrease in quantum yield, however, the PLQY value was still greater than 90% at 30 mM (Fig. 3b). On incorporation of 1e in a LSC device, we determined its experimental external quantum efficiency (EQE) that perfectly matched its absorption spectrum thus indicating light harvesting was achieved through the absorption of light by 1e (Fig. 4a, see ESI - S2 for experimental details). Monte-Carlo ray tracing simulation28–30 was also performed to predict the performance of the LSC device containing 1e in different concentrations (5 mM and 50 mM) (ESI - S3). According to the simulation result, the re-absorption fraction of the LSC device increased with increasing geometric gain (G), with the slightly higher re-absorption fraction of the 5 mM device attributed to its higher PLQY compared to the 50 mM sample. The optical quantum efficiency (OQE) of each device decreased slowly against the geometrical gain, suggesting that the re-absorption effect was small in 1e based LSCs (Fig. 4b), while the OQE of the 5 mM LSC maintained at around 63% for G = 75 which is similar in performance to reported transparent LSC devices.31,32 Furthermore, the calculated flux gain increased almost linearly against the geometric gain up to G = 75 (ESI - S32) while at G = 45, the flux gain was 7.2 for the 5 mM LSC, with these results being comparable with reported benchmark devices.33

In conclusion, we have prepared and characterized several new pyridinium enolates while also investigating their photophysical properties in toluene and PMMA. Quantum-chemical calculations conducted to support the experimentally observed spectroscopic properties resulted in the development of a method that will enable us to predict the properties of similar molecules prior to synthesis thus enabling the identification of target compounds for a variety of future applications. Finally, we demonstrated that 1e is a very promising molecule for utility in LSCs with performance of our devices being comparable to state of the art LSC systems.

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**Keywords:** Betaines, Fluorophores, Energy Transfer, Luminescent solar concentrator

**References**

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