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Synthesis, characterization and \textit{ab initio} investigation of a panchromatic ullazine–porphyrin photosensitizer for dye-sensitized solar cells†

Simon Mathew,§*a Negar Ashari Astani,b Basile F. E. Curchod,b§†† Ursula Rothlisberger,b Magdalena Marszalek,††‡ Julien Frey,‖a Mohammad Khaja Nazeeruddin‖a and Michael Grätzel‖b

An ullazine unit was employed as a donor moiety in a donor–π–acceptor (D–π–A) motif, employing the porphyrin macrocycle as a π-system. Synthesis of this ullazine–porphyrin dyad containing sensitizer (SM63) was achieved and an investigation of the electrochemical and spectroscopic properties of this dye was performed. Introduction of the ullazine donor promoted significant enhancements in long and visible wavelength absorption, leading to panchromatic light harvesting. SM63 demonstrated a maximum absorption approaching 750 nm, a significant improvement compared to the model compound LD14-C8, which features a simpler donor component (4-(N,N-dimethylamino)phenyl) and an absorption onset at ~700 nm. The dye SM63 was subjected to a rigorous \textit{ab initio} investigation to gain further insight into its unique absorption and emission properties. Application of the molecular ullazine–porphyrin dyad SM63 into dye-sensitized solar cells afforded a device with significantly improved light harvesting abilities in both the visible region of the spectrum as well as NIR light (~800 nm), demonstrating the value of ullazine unit in developing panchromatic dyes for light harvesting applications.

Introduction

The porphyrin core remains a prominent choice as a π-bridge in the design of D–π–A dyes for application in dye-sensitized solar cells (DSCs), with the porphyrin based dye YD2-o-C8 achieving power conversion efficiencies (PCEs) of 11.9%.

This remarkable result was improved to 12.3% by cosensitization with the dye Y123, possessing complementary absorbance to the green porphyrin sensitizer, thereby increasing the short-circuit current density ($J_{sc}$) of the DSC through enhancing the light harvesting efficiency of the device. In order to improve the overall PCE of the DSC, strategies must be explored to engineer dyes with panchromatic light harvesting abilities. Significant efforts have been undertaken in investigating the use of new, novel electron accepting units that can impart significant perturbations of the porphyrinic electronic structure in order to improve visible light absorption.

In particular, this brand of molecular engineering results in dyes like SM315 that exhibit improved visible and infrared light harvesting resulting in a PCE of 13%, when used in conjunction with cobalt-based redox electrolytes.

In a complementary manner, there has been much work exploring the utility of alternative π-systems as donor groups for porphyrin dyes connected to the central porphyrin core via an acetylene bridge.

All of these dyes exhibited moderate to high performance with iodide/triiodide redox electrolytes. However, a common feature of all such dyes with π-extended donors possess very similar absorbance features, exhibiting a deficit in green light harvesting ability (~550 nm), due to the poor absorption between characteristic porphyrinic B- (Soret) and Q-bands.

The ullazine chromophore is a 16 π-electron heterocycle, isoelectric to pyrene exhibiting simultaneous electron donating and accepting properties. Recently, the utility of this heteroarene was demonstrated by exploiting it as a π-bridge in DSCs.

Of significant value from these investigations was the development of facile synthetic route to meaningful quantities.
of the ullazine core. From this ullazine synthon, the installation of functional groups can facilitate the application of this unique heterocycle in molecular constructs of increasing structural and electronic complexity.

In this work we introduce the ullazine aromatic system as a potential starting point for donors that impart panchromatic absorption to the porphyrin D–π–A framework. We present the first ullazine–porphyrin dyad SM63 (Fig. 1), which is additionally functionalized with an ethynylbenzoic acid as an anchoring group, allowing the corresponding dye to bind to the TiO2 photoanode within the DSC.

Results and discussion

Synthesis
The ullazine–porphyrin dyad SM63 is outlined in Scheme 1. An alkyne-functionalized ullazine 2 was coupled to the meso-dibrominated zinc porphyrin core 3. The alkyln-functionalized ullazine 2 was synthesized from the previously reported formyl-ullazine synthon 1 (ref. 18) via a Corey–Fuchs reaction. Specifically, an initial Wittig reaction of 1 with dibromomethyl-triphenylphosphonium bromide followed by elimination by t-BuOK yielded the alkyne-functionalized ullazine synthon 2 in a 71% yield. Subsequent Sonogashira coupling of this ullazine unit with the previously reported porphyrin component, 5,15-dibromo-10,20-(2,6-dioctyloxyphenyl)porphyrinatozinc(II) 3 (ref. 7) followed by coupling with the 4-ethynylbenzoic acid anchor afforded the complete dye SM63 in Fig. 1. The dye LD14-C8 (ref. 7) was employed as a reference compound to enable comparison to typical porphyrin dyes possessing an acetylene linked 4-dimethylaminophenyl donor and ethynylbenzoic acid acceptor. SM63 was characterized by 1H and 13C NMR spectroscopy and HRMS (ESI†).

UV-Vis spectrophotometric properties
The UV-Vis absorbance spectrum of SM63 was performed in THF solvent (Fig. 2) and compared to LD14-C8, with the relevant data summarized in Table 1. Substitution of the ullazine moiety into the porphyrin core caused a severe deformation of the Soret band in the absorption spectrum of SM63. The introduction of the ullazine donor into the dye structure triggered more excitations leading to a broadening of the Soret band. The experimental spectrum of SM63 affords two discernable Soret absorbances, with the dominant one at 450 nm with a shoulder

Scheme 1  Synthesis of the SM63 sensitizer. Conditions (i) (CHBr2)Ph3PBr, t-BuOK, THF, –78 °C, 1.5 h, 71%. (ii) 3, Pd(PPh3)4, Cul, THF, Et3N, 3 h, 26% (over 2 steps).

Fig. 1  Structure of the SM63 and LD14-C8 sensitizers.
at 474 nm, however the calculated excitations for this dye reveal that the broadening of the Soret band is due a contribution of several new excitations. This is in stark contrast to the absorption spectrum of LD14-C8 possessing a singular Soret absorption peak at 459 nm that exhibits twofold molar absorptivity, originating from the greater degree of electronic symmetry within LD14-C8, evident in both experimental and calculated absorption spectra. Introduction of ullazine as a donor motif in SM63 resulted in a drastic deformation of the B-band of the porphyrin, as a result of the increase in conjugation along the donor–acceptor axis of the dye, which allows differentiation between the two electronic transitions that give rise to the Soret band (in an electronically symmetrical porphyrin)\textsuperscript{4,20,22} Interestingly, the molar absorptivity of the Soret bands experienced a significant decrease in magnitude, implying a decrease in the dipole strength of the transitions leading to these absorptions. However, this splitting of the Soret band in SM63 into two differentiable peaks improved light harvesting ability of the dye when incorporated into a DSC (vide infra). A clear absorption at 530 nm was evident in the UV-Vis spectrum of SM63, affording further improvements in light harvesting in the DSC. The lowest energy Q-band absorbance of SM63 appeared at 693 nm, experiencing a large red-shift compared to LD14-C8 (667 nm), further reinforcing the advantage of the ullazine donor in enhancing light absorption. In a similar fashion to the Soret absorption in SM63, the lowest energy Q-band also experienced a slight decrease in molar absorptivity. The net result of employing the ullazine moiety in the porphyrin dye structure is significant improvement in visible light absorption compared to LD14-C8. Furthermore, the ullazine donor in SM63 extended the π-system of the dye decreasing the optical bandgap to 1.75 eV from 1.84 eV in LD14-C8. Combining the optical bandgap and the oxidation potential (vide infra) demonstrates that the dye SM63 possesses frontier orbitals of energy sufficient for thermodynamically favourable electron injection and dye regeneration in the DSC.

**Steady-state fluorescence properties**

The steady-state emission spectrum (ESI\textsuperscript{†}) of SM63 afforded an emission maximum at 724 nm, red-shifted significantly from the 680 nm emission of LD14-C8 (Table 1). The emission spectrum of SM63 exhibited mirror-image symmetry with the Q-band absorption however the shape of the emission was quite broad compared to LD14-C8, indicative of an enhanced charge transfer character in the excited state upon introduction the ullazine moiety as a donor unit.\textsuperscript{4} The Stokes shift exhibited in solution for SM63 was (618 cm\textsuperscript{-1}, 0.0766 eV) dramatically increased from that of LD14-C8, (287 cm\textsuperscript{-1}, 0.0356 eV) implying that the introduction of the ullazine donor results in a greater degree of geometry distortion upon formation of the excited state after light absorption. These results are also consistent with the improvements in charge transfer character observed in the calculated absorption and emission spectra (vide infra).

**Electrochemical properties**

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were employed to determine the oxidation potential ($E_{ox}$) of the dye SM63 (Fig. 3) with the relevant data presented in Table 1. Measurements were performed in DMF with 0.1 M tetrabutylammonium hexafluorophosphate, using a glassy carbon, Pt plate and Pt wire as the respective working, counter and reference electrodes. The corresponding redox potentials were internally referenced using the ferrocene/ferrocenium (Fe/Fe\textsuperscript{3+}) redox couple and the potentials adjusted to values vs.

**Table 1** Summary of UV-Vis, fluorescence and electrochemical data for SM63 and LD14-C8

<table>
<thead>
<tr>
<th>Dye</th>
<th>$\lambda_{max}^{a}$/nm (e/×10\textsuperscript{3} L cm\textsuperscript{-1} mol\textsuperscript{-1})</th>
<th>$\lambda_{em}^{b}$/nm</th>
<th>$E_{0,a}^{d}$/eV</th>
<th>$E_{ox}^{d}$/V</th>
<th>$E_{red}^{d}$/V</th>
<th>$E_{ox}^{f}$/V</th>
<th>$J_{SC}$ (mA cm\textsuperscript{-2})</th>
<th>$V_{OC}$ (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SM63</td>
<td>450 (113) 474 (67)</td>
<td>724</td>
<td>1.75</td>
<td>0.79</td>
<td>(-0.88)</td>
<td>(-0.96)</td>
<td>14.43 ± 0.27</td>
<td>0.70 ± 0.01</td>
<td>0.73 ± 0.01</td>
<td>7.35 ± 0.13</td>
</tr>
<tr>
<td></td>
<td>530 (17) 693 (49)</td>
<td></td>
<td>.</td>
<td></td>
<td>(-1.16)</td>
<td></td>
<td>15 (15.8)</td>
<td>0.70 (0.70)</td>
<td>(7.70)</td>
<td></td>
</tr>
<tr>
<td>LD14-C8</td>
<td>459 (237)</td>
<td>680</td>
<td>1.84</td>
<td>0.80</td>
<td>(-1.12)</td>
<td>(-1.04)</td>
<td>15.72 ± 0.26</td>
<td>0.73 ± 0.02</td>
<td>0.74 ± 0.01</td>
<td>8.45 ± 0.16</td>
</tr>
<tr>
<td></td>
<td>667 (62)</td>
<td>744</td>
<td></td>
<td></td>
<td>(-1.59)</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

\(a\) Measured in THF. \(b\) Measured in THF using $\lambda_{em} = 660$ nm for LD14-C8 and 475 nm for SM63. \(c\) Determined by the intersection of normalized absorption and emission spectra. \(d\) Measured in DMF with Fe/Fe\textsuperscript{3+} as an internal standard and converted to vs. NHE by addition of +0.691 V (as Fe/Fe\textsuperscript{3+} in DMF/NBu$_4$PF$_6$ = +0.45 V vs. SCE\textsuperscript{†} with SCE = +0.241 V vs. NHE\textsuperscript{9}). \(e\) Irreversible reduction process. \(f\) $E_{ox}^{f}$ is determined from $E_{ox}^{d}$ and $E_{0,a}^{d}$.
NHE by the addition of +0.691 V. The position of $E_{\text{ox}}$ is critical in determining the ability of the dye cation, generated a light absorption of the dye in the cell and subsequent electron injection in TiO$_2$, to successfully undergo regeneration with the I$_2$/C$_6$I$_3$/C$_6$ redox couple. A quasi-reversible $E_{\text{ox}}$ at +0.79 V vs. NHE was observed for SM63. The dye also experiences two reductions at -0.88 and -1.16 V, the first being irreversible in nature. A decrease in the electrochemical bandgap ($1.92 \text{ V and } 1.67 \text{ V for LD14-C8 and SM63 respectively}$ was observed due to the significant increase in π-conjugation within the molecule through incorporation of the ullazine donor. Discrepancy between our data and the previously reported redox data for LD14-C8 can be rationalized by the use of different solvent for electrochemical analyses (i.e. DMF in this work and THF in previous work). The excited state potential ($E^*_{\text{ox}}$) was determined by employing optical and electrochemical data and found to be more negative than the TiO$_2$ conduction band, allowing sufficient overpotential for thermodynamically favourable electron injection from the dye into the semiconductor’s conduction band.

**Computational characterisation**

The optical and electrochemical characterization of SM63 and LD14-C8 were subjected to a complementary investigation by employing DFT/M06/IEFPCM(THF) calculations for geometry optimization and LR-TDDFT/M06/IEFPCM(THF) to determine excitation energies. Complete details of the calculations are given in the ESL.†

The ground state dipole moment of SM63 was calculated to be 8.07 D, lower than that of the 9.85 D calculated for LD14-C8. The frontier Kohn–Sham orbitals of the geometry optimized ground state structures of SM63 and LD14-C8 are presented in Fig. 4. In contrast to the planar LD14-C8, the calculated structure of SM63 revealed a deviation of the alkyne-linked ullazine donor and the porphyrin core from planarity, with a bend angle of 20°.

The origin of this donor bending was surmised to be the result of a non-covalent interaction between the two π-systems of SM63.

In order to gain further insight this donor-bent geometry was rigorously validated by a series of parallel geometry optimizations that employed different functionals that either largely ignore (BLYP) or account (Grimme-D2) for subtle dispersion forces, explained with greater discussion within the ESL.†

This strategy has been used extensively in ascertaining the nature of non-covalent interactions in aromatic systems. These parallel calculations revealed that unlike the overwhelming majority of porphyrin-based dyes, which gain stability from maintaining a well-conjugated planar structure, SM63 sacrifices a small component of electronic conjugation to attain additional stability via van der Waals interactions and dispersion forces. This interaction occurs between the bulky

![Fig. 3 Cyclic voltammograms of LD14-C8 (black) SM63 (red) and in DMF and ferrocene/ferrocenium internal reference.](image)

![Fig. 4 Contour plots of frontier KS orbitals. The orbitals are calculated for geometry-optimized SM63 (top) and LD14-C8 (bottom), using DFT/M06/IEF-PCM(THF) (isovalue = 0.02 a.u.).](image)
aromatic groups of the ullazine and porphyrin (meso-positions) moieties, leading to ground state deformation. The vertical ionization energies (IE) were computed at (U)DFT/M06 level of theory for both dyes calculations showing that the ionization energy of SM63 (4.67 eV) was slightly lower than that of LD14-C8 (4.86 eV). However, this trend correlates well with the electrochemically measured $E_{\text{onset}}$ for the two compounds (Table 1) and imply a weak destabilisation of SM63 HOMO as a result of introducing the ullazine core as a donor. Ullazine, being a stronger electron donor (when connected to the porphyrin through the 5-position of the ullazine core\textsuperscript{46} than dimethylaniline, raises the HOMO energy level and reduces the bandgap which in turn induces a greater red shift to its spectrum compared to LD14-C8. In contrast to the majority of reported porphyrin dyes which are green in colour, SM63 appears brown/black as a solid, and affords a brown solution as a result of broader absorption in the range of 500–620 nm. LR/TDDFT results show two transitions of reasonable oscillator strength in this range for SM63 (512 nm and 566 nm) whereas only one very weak transition at 605 nm is present for LD14-C8. The character of the lower energy (566 nm) excitation of SM63 in this region between the Soret and Q-bands is mostly (78%) composed of HOMO $\rightarrow$ 1 to LUMO transition, where the HOMO $\rightarrow$ 1 is highly delocalized on the ullazine moiety (this is also apparent in Fig. 4). The analogous transition for LD14-C8 (605 nm), is mostly composed of HOMO to LUMO + 1 transition (60%). From this data, we can surmise that the presence of the ullazine leads to a greater delocalization of the highest occupied orbitals in SM63 compared to those of LD14-C8, and increases the charge-transfer character of the corresponding transitions. This is best depicted in the density difference contour plot for the S0 $\rightarrow$ S1 transition (Fig. 5).

In addition to elucidation of the geometric and electronic ground state properties of SM63, we employed a computational method to gain further insight into the structural changes that occur in the excited state, which lead to the significant increase (measured spectroscopically) in Stokes shift for SM63. Briefly, calculated Stokes shifts were obtained by subtracting the energies of the first absorption and emission transitions of the respective ground state and the first excited state optimized (LR-TDDFT) structures, with a detailed discussion in the ESI.\textsuperscript{†} Thus, calculated Stokes shifts of 0.2377 eV and 0.2071 eV were obtained for SM63 and LD14-C8 respectively, consistent with the trend in the spectroscopically derived values. Geometry optimization of the first excited state was performed to computationally assess the degree of conformational distortion that the dye sustains upon excitation from the ground state, with the result given in Fig. 6. Indeed, the excited state geometry of SM63 demonstrated a greater deviation than LD14-C8 from its ground state geometry. Specifically, the SM63 dye distorts at the acetylenic bridge between ullazine and porphyrin systems, with the bend angle of the alkyne changing from 20° to 24° in the excited state, thus underpinning the point of molecular reorganization responsible for the considerable Stokes shift observed spectroscopically. In contrast, the excited state of LD14-C8 experiences a negligible degree of distortion from its ground state geometry, consistent with the small Stokes shift observed both computationally and experimentally.

**Photovoltaic properties**

SM63 was implemented into DSCs employing a photoanode with a double layer structure, consisting of 10 μm transparent (20 nm TiO$_2$) and 3 μm scattering layer (400 nm TiO$_2$) with a total area of 0.25 cm$^2$. The fabrication procedure is similar to that reported previously.\textsuperscript{29} The TiO$_2$ electrode was immersed in a solution of SM63 prior to washing with acetonitrile and sealing (Surlyn, 25 μm) with a platinized FTO counter electrode. An electrolyte consisting of 1.0 M 1,3-dimethylimidazolium iodide (DMIII), 0.03 M I$_2$, 0.05 M LiI, 0.1 M GuNCS, 0.5 M 4-t-butylpyridine in acetonitrile was introduced by vacuum backfilling prior to sealing with...
Surlyn and a glass cover slide. Measurements were performed using a non-reflective metal mask (area 0.16 cm\(^2\)) under standard global AM 1.5G illumination (1000 W m\(^{-2}\)).

Optimization of DSC fabrication conditions was performed by initially employing a THF/EtOH (1 : 4) solution of SM63 (0.2 mM) and 1 mol equivalent of CDCA (0.2 mM). Initial optimizations were performed on the dipping time, with the result given in Fig. S2 and summarized in Table S1.\(^\dagger\) The \(J_{SC}\) (10.9 mA cm\(^{-2}\)) and PCE (5.25%) peaked after a 30 minute sensitization, with the \(J_{SC}\) and FF decreasing with longer dipping times, indicative of excessive aggregation during sensitization. This is not surprising, considering the extensive planar, aromatic surface area and substantial hydrophobicity of the dye SM63.

Increasing the CDCA concentration tenfold (2 mM), afforded a significant improvements \(J_{SC}\) (12.6 mA cm\(^{-2}\)) and \(V_{OC}\) (0.71 V) with a slightly longer (1 hour) sensitization time to achieve a PCE of 5.90% (Fig. S2 and Table S1). To further suppress aggregation of SM63 in the dipping solution, the polarity of the solvent was decreased by employing toluene in place of THF and decreasing the amount of ethanol in the dipping solution (i.e. toluene/EtOH, 1 : 1). This strategy yielded the best result, affording further improvements in \(J_{SC}\) and PCE (vide infra).

Fig. 7a shows the photocurrent–voltage characteristics of DSCs fabricated with SM63 and LD14-C8 as a sensitizer, with the photovoltaic data summarized in Table 1. The current–voltage characteristics of SM63 demonstrated a short-circuit photocurrent \(J_{SC}\) of 14.43 mA cm\(^{-2}\), open-circuit voltage \(V_{OC}\) of 0.70 V, fill factor (FF) of 0.73 and a power conversion efficiency (PCE) of 7.35%. Conversely, LD14-C8 achieved a \(J_{SC}\) of 15.72 mA cm\(^{-2}\), \(V_{OC}\) of 0.73 V, FF of 0.74 and a PCE of 8.45%.

The lower observed \(J_{SC}\) for DSCs fabricated with SM63 can be rationalized by the significant degree of aggregation that the dye experiences upon adsorption to the surface, leading to undesirable quenching of the excited state dye. This is evidenced by improvements in the dye adsorption upon the addition of CDCA and the use of a less polar adsorption solvent (vide supra). Further to this, SM63 features a lower extinction coefficient that may result in a lower degree of light harvesting by the cell.

Rationalization of the reduction of \(V_{OC}\) experienced by DSCs using SM63 required further investigation employing transient photocurrent and photovoltage measurements, where a reduction in \(V_{OC}\) can arise by (a) enhanced recombination of injected electrons from TiO\(_2\) to the dye/electrolyte or (b) a downward shift of the TiO\(_2\) conduction band.\(^{30-32}\)

Measurement of the electron lifetime as a function of chemical capacitance \(C_{\mu}\) (Fig. 7b) afforded insight into the recombination events that occur at the TiO\(_2\)-dye/electrolyte interface in DSCs fabricated with LD14-C8 and SM63 within the TiO\(_2\) film.\(^{33}\) At a given \(C_{\mu}\), the electron lifetimes of SM63 and LD14-C8 are identical and therefore the decrease in \(V_{OC}\) in DSCs featuring SM63 cannot be assigned to an increase in recombination at the TiO\(_2\)-dye/electrolyte interface.

Fig. 7c shows the measurement of the chemical capacitance \(C_{\mu}\) with respect to \(V_{OC}\) gives a direct insight into the conduction band level in devices featuring both SM63 and LD14-C8, as \(C_{\mu}\) and DOS are proportional to each other. The plot demonstrates that sensitization with SM63 results in a displacement of

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**Fig. 7** (a) \(J–V\) curve (\(N = 3\) cells) of LD14-C8 (black) and SM63 (red) under AM 1.5G illumination (1000 W m\(^{-2}\)). (b) Electron lifetime and (c) open-circuit voltage as a function of chemical capacitance obtained through transient photocurrent/photovoltage measurements (d) photocurrent action spectrum of LD14-C8 (black) and SM63 (red).
trap-state distribution to lower energies, ultimately resulting in a reduction of $V_{OC}$ in the DSC. This is further supported by the previous observation that a reduction in dipole moment (8.07 D and 9.85 D for SM63 and LD14-C8 respectively) has been shown to promote a decrease in $V_{OC}$ as a result of a TiO$_2$ conduction band shift with respect to the redox potential of the electrolyte, which is partially followed by the energy level of the dye.$^{34}$

The photocurrent action spectra of LD14-C8 and SM63 are presented in Fig. 7d. LD14-C8 presents a high IPCE across the visible spectrum with the characteristic dip at $\sim 550$ nm (an artefact from the lack of absorbance between Soret and Q-band transitions) and an onset at 750 nm, affording the resulting cell a green colour. In contrast, the IPCE of SM63 presents a gradual decrease in IPCE dip at $\sim 600$ nm in combination with a considerable improvement is red light harvesting ability.

The onset of light harvesting for DSCs employing SM63 appears at 800 nm resulting in a brown coloured cell. This data in particular demonstrates that a significant gain in light harvesting ability can be obtained through using the ullazine as an electron donor. Presumably, part of the large red shift in the photocurrent action spectrum that gives rise to the long wavelength light harvesting ability of DSCs fabricated with LD14-C8 originates from favourable J-aggregation of the dye within the cell.$^{34}$ In spite of this, a better balance must be struck between this favourable, organized interaction and deactivation of the dye through excessive, non-productive aggregation, extraordinarily prominent for SM63, which is potentially caused by the large planar aromatic structure of the dye.

Conclusions

The synthesis of an ullazine–porphyrin dyad was achieved by Sonogashira coupling of an alkyne-functionalized ullazine and zinc porphyrin. The resulting dye, SM63, was additionally functionalized with an ethynylbenzoic acid to enable anchoring to TiO$_2$ and construction of a DSC. SM63 was characterized thoroughly and the UV-Vis absorption spectrum demonstrated a significant perturbation of both Soret and Q-band absorptions, a consequence of the strong electron donating ability of the ullazine unit. The absorption changes of SM63 result in an improved absorption of green ($\sim 550$ nm) and red ($\geq 700$ nm) light compared to the vast majority of D–π–A porphyrin dyes. Measurement of steady-state emission spectra afforded an unusually large Stokes shift for SM63. A thorough computational study of the ground state geometry of SM63 gave a structure with a bent donor group due to a significant dispersion force interaction between pendant phenyl groups on the ullazine and porphyrin groups in SM63. Geometry optimization of the SM63 excited state revealed an enhancement of this donor bending giving an origin to the larger stokes shift for SM63. Computational methods were employed to analyse the distribution of the frontier orbitals and theoretical electronic transitions of SM63. Correlation of the new absorption bands in SM63 to theoretical electronic transitions provided insight into the improved absorption characteristics of the ullazine–porphyrin construct. Finally the dye SM63 was employed in a DSC using an iodide/triiodide electrolyte, affording a slightly lower PCE (7.35%) than a standard dye LD14-C8 (8.45%) under identical conditions, as the dye SM63 experiences significant aggregation in solution as a result of its large hydrophobic aromatic structure. Strikingly, acquisition of the photocurrent absorption spectrum showed a significantly improved green (550 nm) and red (>700 nm) light harvesting ability originating from the improved absorption properties of the SM63 dye. Future work seeks to develop a strategy to suppress the unfavourable aggregation of the ullazine–porphyrin construct to obtain yet higher efficiencies. Concomitantly, there is value in demonstrating the potential of the strongly donating ullazine core to strongly perturb the absorption in other π-systems, leading to the development of a new range of panchromatic dyes for application in photo(electro)chemical devices.

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Notes and references