



Azulene – Thiophene – Cyanoacrylic acid dyes with donor- π -acceptor structures. Synthesis, characterisation and evaluation in dye-sensitized solar cells

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ABSTRACT

We report the synthesis of five new azulene containing dyes, having D- π -A type structures. These dyes are synthesised using a sulfonium salt cross-coupling reaction. The dyes have been evaluated spectroscopically, electrochemically, crystallographically, and as sensitizers in dye-sensitized solar cells. We propose a rationale for the dyes' spectroscopic properties and performance in cells, based on conformational data derived from their crystal structures.

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1. Introduction

Since the earliest reports on dye-sensitized solar cells (DSSCs) over 25 years ago,^{1,2} much effort has been expended in the optimisation of these devices, in pursuit of higher photoelectric conversion efficiencies (PCEs, η). Central to this effort has been the design, synthesis and evaluation of dyes with enhanced properties in terms of photon capture, electron injection, dye adhesion and device lifetimes, etc.^{3,4} Dyes consisting of ruthenium polypyridyl complexes such as N719⁵ achieved notably high PCEs, but the high cost of ruthenium is an impediment to the commercialisation of cells based on such dyes. In contrast, DSSCs that use wholly organic dye molecules can avoid the use of expensive metals. Design principles for high efficiency organic dyes have been established, with the donor- π linker-acceptor-anchor (D- π -A) assembly proving to be highly successful.^{6,7} Of the various known electron

donor motifs, arylamines have proven especially effective.^{8–10} Regarding the π linker motif, a wide variety have been explored, mostly heterocycles, amongst which thiophenes, oligothiophenes and annulated thiophenes have all proven often to influence positively the overall cell efficiency.^{11–16} An anchoring group is required to immobilise the dye molecule on the metal oxide surface; a variety of different anchor groups have been investigated, including phosphonic acids and carboxylic acids and their derivatives (esters, acid chlorides, carboxylate salts or amides).^{17,18} Carboxylic acid and cyanoacrylic acid groups are most frequently used for DSSC dyes. More specifically, because of its excellent electron withdrawing characteristics, cyanoacrylic acid is used in most D- π -A organic dyes, where it fulfils the dual role of acceptor and anchor. In contrast, simple carboxylic acid anchors are usually used for transition metal complexes where metal-to-ligand-charge-transfer (MLCT) predominates.

The aims of the present study were to synthesise organic dyes for DSSCs that comprise an azulene ring as the donor motif, to characterise these dyes using a variety of techniques, and to evaluate their performance in solar cells. Azulene (**1**) is a bicyclic, nonbenzenoid aromatic hydrocarbon and is an isomer of

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naphthalene (**2**). Azulenes have long been of interest to chemists due to their striking colours, interesting chemistry and unusual electronic properties. Azulene derivatives may be used as advanced materials for optoelectronic^{19–25} and electrochromic²⁶ devices, charge-transport,^{27–29} nonlinear optics³⁰ and chemical sensing³¹; some recent reviews serve to summarise these areas.^{32,33} Some azulene derivatives have also been shown to have anti-inflammatory,^{34,35} antiulcer,^{36–38} anticancer^{39–42} and anti-HIV⁴³ properties. Azulene is a non-alternant hydrocarbon, unlike naphthalene, which leads to HOMO nodes at C2 and C6 and LUMO (S_1) nodes at C1 and C3 (Fig. 1), causing relatively small repulsion between the electrons occupying these orbitals, meaning a low $S_0 - S_1$ transition energy, in the visible region.⁴⁴ With naphthalene **2**, the coefficient magnitude at different carbons is the same for the HOMO and LUMO, giving a higher degree of overlap, and the electrons occupy the same space with consequent higher repulsion and higher transition energy in the UV. Therefore naphthalene is colourless but azulene **1**, because the $S_0 - S_1$ transition corresponds to the green and red regions of the spectrum, is a deep blue colour. The absorption spectra for substituted azulenes are very sensitive to the electronic nature of the ring substituents.⁴⁵ Hence, by careful design of the substituents, the entire visible (and IR) spectrum is accessible. This ability to tune the chromophore's absorption spectrum makes azulene an attractive motif for exploitation in DSSCs.

In the context of solar cells, sporadic reports of azulene derivatives have appeared in various contexts. Emrick and co-workers employed copolymers of 2-substituted azulene with zwitterionic methacrylates in bulk-heterojunction (BHJ) solar cells.⁴⁶ Imahori and co-workers evaluated copolymers of 1,3-disubstituted azulene and diketopyrrolopyrroles or benzothiadiazoles⁴⁷ in BHJ solar cells, shortly after which and Liu, Zhang and co-workers reported two similar azulene copolymers, as well as a further example possessing distinct connectivity (a 4,7-disubstituted azulene).⁴⁸ Most recently, Gao and co-workers reported a copolymer incorporating a 6,6'-disubstituted 2,2'-biazulenyli.⁴⁹ Aside from polymer BHJ solar cells, Huang and co-workers recently reported the use of an azulene-squaraine small molecule in an organic photovoltaic (OPV) device.⁵⁰ Torres, Guldi and co-workers reported an OPV device comprising azulenocyanines immobilised on carbon nanotubes.⁵¹ In the area of perovskite solar cells, an azulene-containing hole-transport material has been shown by Wakamiya, Saeki, Scott, Murata and co-workers to exhibit performance superior to that of Spiro-OMeTAD, the most commonly used hole-transport

material.⁵² There have been reports of electron injection from an azulene into the conduction band of titania, from Piotrowiak, Galoppini and co-workers^{53,54} (either employing azulene itself, sequestered in a hemicarceplex, or using azulenes bearing methyl ester anchoring groups), but in no instance was construction of a DSSC attempted.

To our knowledge, the peer-reviewed literature contains only two reports of azulene containing dyes being used in DSSCs. In 2007, Cheng, Wang, Zhang and co-workers reported the synthesis of dyes **3–6** (Fig. 2), comprising either an azulene attached directly to a cyanoacrylic acid (**3**, **5**), or with a vinylene linker between the azulene and the anchor motif (**4**, **6**).⁵⁵ They found the presence of the vinylene linker led to a bathochromic shift of λ_{max} and an increase in η with respect to the dyes lacking this motif, due to increases in both J_{SC} and V_{OC} . Additionally, they observed an increase in η for alkylated azulenes **5** and **6** compared to their respective non-alkylated counterparts **3** and **4**. The authors ascribe this latter effect to the alkyl groups disfavouring dye aggregation on the titania surface. In 2014, Hanaya and co-workers reported the evaluation of phenylazulene **7** (Fig. 2) as a dye in a DSSC.⁵⁶ The focus of this study was the evaluation of an alternative redox mediator, $\text{Br}^-/\text{Br}_3^-$, in place of the more commonly used I^-/I_3^- system, with the authors finding that the $\text{Br}^-/\text{Br}_3^-$ system afforded a greater V_{OC} and hence η . The patent literature also contains azulene dyes for DSSCs. Two patents filed by TDK^{57,58} describe azulenes **8–17** (Fig. 2). The emphasis of the patent is on the fact that these dyes are all more resistant to photobleaching than a comparator ruthenium-based dye; no further data are given. A patent from Solvay⁵⁹ reports azulenocyanines of type **18** (Fig. 2), which differ from those reported previously by Torres, Guldi and co-workers⁵¹ in that the azulenocyanines bear anchoring groups for the specific purpose of attachment to titania and use in a DSSC. (Azulenes are also described elsewhere in the patent literature in the broader context of photovoltaics.^{60,61}) Finally it should be noted that prospective azulene-based dyes for DSSCs have been considered theoretically.⁶²

2. Results and discussion

In the present study, we undertook two rounds of dye design, synthesis and characterisation. In the first instance we targeted dyes of the D- π -A design, with a 1-substituted azulene as the donor motif (as per the majority of examples in Fig. 2), and a cyanoacrylic acid as the acceptor and anchor motif. For the π -linker, we opted to employ a thiophene ring, whose ability to induce bathochromic shifts of absorption maxima and to afford increased extinction coefficients has been documented.^{11–16} Specifically we targeted azulene-thiophene-cyanoacrylic acid (“Az-tcaa”) **19** and 4,6,8-trimethylazulene-thiophene-cyanoacrylic acid (“TMAz-tcaa”) **20** (Fig. 3). The rationale for targeting **20** was that the methyl substituents may disfavour dye aggregation on the titania surface, analogous with the reason proposed previously⁵⁵ for the increased performance of **6** with respect to **4**. Retrosynthetically, it was envisaged that the targets could be accessed by a Knoevenagel condensation of aldehyde **22** and cyanoacetic acid. Aldehyde **22** would be accessed in turn using cross-coupling methodology, from an appropriately functionalised azulene **23** and a thiophene-2-carbaldehyde metallated at the 5-position, **24**. The C1 and C3 positions of azulene are the most nucleophilic, so a haloazulene of type **23** would be expected to be accessible from the parent azulene (**1** or **25**) through an $\text{S}_{\text{E}}\text{Ar}$ halogenation.

Of the various cross-coupling methodologies that could be used to synthesise **22**, we opted to employ a Suzuki–Miyaura reaction, since there is precedent for such couplings using 1-haloazulenes as the substrate,⁶³ in conjunction with bulky monodentate phosphine

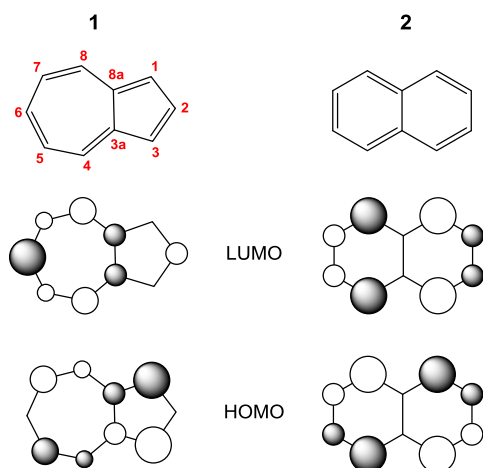


Fig. 1. Structures of azulene and naphthalene; their HOMOs and LUMOs.

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