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ARTICLE TYPE

A fulleropyrrolidine-squaraine blue dyad: synthesis and application as organic light detector

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A properly designed fulleropyrrolidine-squaraine dyad enables the preparation of efficient single component organic
10 **photodiodes.**

The condensation of two equivalents of anhydrobases in the positions 1 and 3 of squaric acid affords a peculiar type of charge-compensated cyanines known as 1,3-squaraines.[1] They share the well known optical properties of cyanines (intense and narrow
15 absorption in the Vis-NIR region) and gained an increasing attention in all those fields which require strong electrical and optical responses,[2] including photovoltaics,[3] photosensing,[4] photodetection,[5-10] and light emitting OFETs.[11] These applications are often subordinate to the combined use of a good electron
20 acceptor with high electron mobilities which can promote exciton dissociation via photoinduced charge transfer (CT), such as fullerene derivatives. In this term, [60]fullerene and its derivatives possess three high lying LUMO levels (-4.3 eV vs. vacuum), able to accept up to 6 electrons. In addition, the deep HOMO level (-6.1
25 eV) of [60]fullerene derivatives is responsible for an efficient photoinduced hole transfer to the donor.[12] These favourable conditions have directed many efforts towards the optimization of the interaction between the molecular components in photoelectroactive materials, where the donor is an electron-rich
30 dye and the acceptor is a fullerene derivative.[13-15]
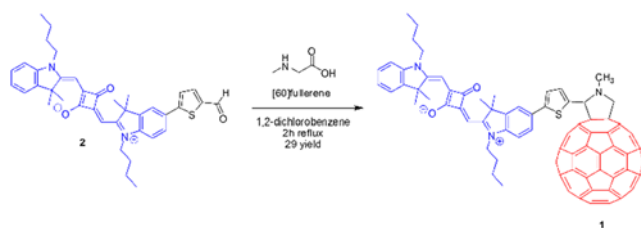
Scheme 1. Synthesis of dyad **1** by the 1,3-dipolar cycloaddition to [60]fullerene of the azomethine ylide that forms when aldehyde **2** reacts with sarcosine in refluxing 1,2-dichlorobenzene.[16]

35 Given the recent availability of a squarylium dye bearing an aldehyde group,[17] we implemented the synthesis of a novel fulleropyrrolidine-squaraine dyad by treatment of the aldehyde **2** with sarcosine and [60]fullerene in refluxing 1,2-dichlorobenzene for 2 h under nitrogen atmosphere.
40 The product was obtained in 29% yield after purification by column chromatography and characterized by ^{1}H-NMR, [13]C-

NMR, FT-IR and mass spectroscopy (see ESI). The condensation of **1** with sarcosine results in the disappearance of the aldehydic signatures from NMR (^{1}H-NMR peak at 9.9 ppm and ^{13}C-NMR
45 peak at 184 ppm in CD_2Cl_2) and IR spectra (sharp peak at 1660 cm^{-1}) contextually to the appearance of the NMR signals of the pyrrolidine ring (Figure S7).
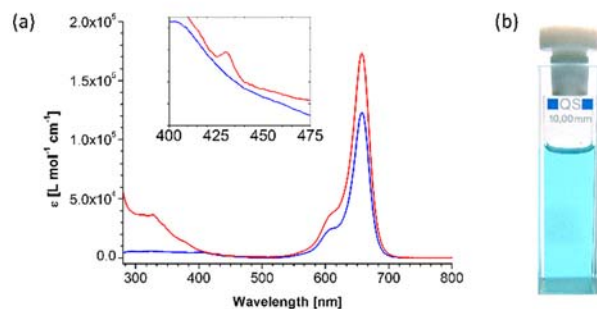

Figure 1. (a) Absorption spectra of the aldehyde **2** (*blue*) and dyad **1** in
50 chloroform (*red*). The inset highlights the peak at 430 nm characteristic of 1,2-monoadduct of [C_{60}]fullerene. (b) Photograph of a solution of **1** in chloroform in a quartz cuvette.

The product dissolves in common organic solvents and the solutions obtained are bluish. The absorption spectrum of **1** (red
55 trace of Figure 1) shows two distinct absorption bands. Its low energy branch is essentially superimposable to that of the corresponding squaraine not bearing the fullerene end (blue trace of Figure 1). The high energy portion shows the weaker UV signature of the fulleropyrrolidine. The inset in Figure 1 highlights
60 indeed the presence of the peak at 430 nm which is diagnostic of the formation of 1,2-monoadducts of [C_{60}]fullerene. The loss of the aldehydic residue upon reaction with [C_{60}]fullerene is responsible for the hyperchromic shift from 123000 ± 7000 to 173000 ± 5000 L mol^{-1} cm^{-1} of the n$\rightarrow\pi$* transition of the squaraine core.
65 The influence of the conjugation on the excited states is far more dramatic. While the precursor **2** has a fluorescence quantum yield of 85% in chloroform, the fluorescence of the dyad is quenched down to <1% (see ESI). The photoluminescence decay of a solution of dyad **1** in toluene results in a bi-exponential curve
70 including a predominant fast decay with a lifetime of 20 ps and a slower component with a lifetime of about 0.8 ns, as reported in Figure 2. A similar behaviour was found for other

fulleropyrrolidine dyads in which the first excited state of the donor group relaxes through a non-radiative decay (charge transfer) due to the interaction with the fullerene acceptor.[18]
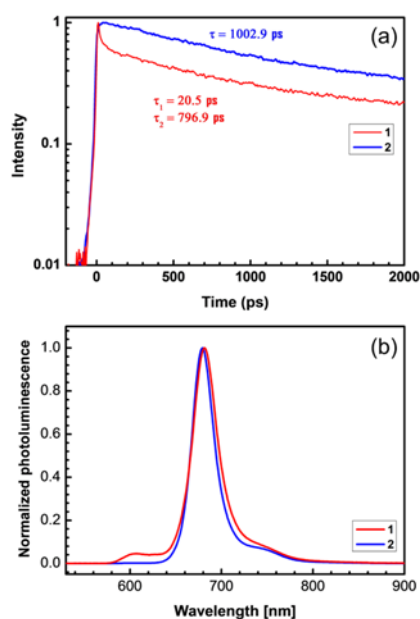
5 **Figure 2**. Time-domain intensity decay of the emission at 678 nm (a) and steady-state luminescence (b) of precursor squaraine **2** (*blue*) and dyad **1** (*red*) in air-equilibrated toluene excited at 380 nm.

On the other hand, the electrochemical behaviour of the fulleropyrrolidine-squaraine dyad is consistent with the reported 10 electronic decoupling between the donor and the acceptor fullerene cage.[19] Indeed the two peaks at half-wave potentials $E_{1/2}$ of +0.44 and +0.93 V vs. SCE correspond to the oxidation of the electron-rich enaminic moieties of the squaraine (peaks A and B, Figure S17).[20] The three reduction peaks at -0.74, -1.13, and -1.64 V (II, 15 III and V) were instead attributed to three subsequent reductions of the fullerene moiety.[21] Notice that the peak at -0.67 V observed in the CV curve in DCM (peak I in Figure S17) was attributed to adsorption of the pristine molecule. Such a behaviour was much less evident in THF (Figure S18). The high reversibility of all 20 peaks proves the chemical stability of the electrogenerated species on the voltammetric timescale. In view of its final use in a solid-state photoactive device (v. infra), the redox properties of a film of dyad **1** drop-cast onto an ITO electrode were also investigated. The CV curve shown in Figure S22 was obtained at 0.1 V/s in an 25 aqueous solution and displays one reduction and one oxidation peak that are significantly shifted to higher overpotentials with respect to the redox properties in the homogeneous phase. This is consistent with the additional kinetic limitations associated to hindered transport of charge-compensating ions within the film. 30 On the basis of the onset potentials of the two peaks (0.94 V and -0.25 V, respectively), an estimate of the charge-separated state energy (oxidised squarine/reduced fulleropyrrolidine) in the solid-state is 1.2 eV.

The use of donor-fullerene dyads as the single active component in 35 photovoltaic devices has recently been reviewed.[22] Whilst such strategy provides excellent exciton dissociation yields, as it reduces down to the molecular scale the interface between donating and accepting domains, its overall effectiveness is

questionable. In particular, charge transport could become a 40 limiting factor to the device efficiency as bi-continuous interpenetrated networks encompassing the electron-conducting fragments and the hole-conducting fragments, required to efficiently collect charges at the electrodes, are hardly achievable with a single molecule active material. While this aspect can be 45 very critical for a solar cell, in the case of photodetectors an external voltage bias can be applied in order to help charge transport and collection. Hence, in this case, the excellent exciton dissociation properties of dyad **1** could be more effectively reflected in a high quantum efficiency device. As such, dyad **1** 50 could be an appropriate active component for photodetector.[23, 24] Therefore, we prepared a simple device with a vertical architecture by spin coating a solution of the dyad in chloroform on top of a PEDOT:PSS film deposited on ITO.
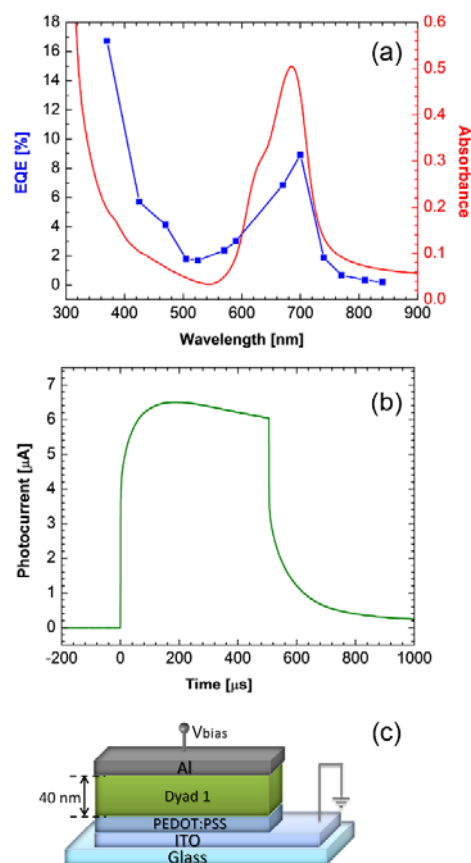
55 **Figure 3.** (a) In blue the EQE of the photodetector (PD) operating under a reverse bias voltage (1 V) when illuminated with 500 μs light pulses with intensity of about 10 mW/cm². In red the absorbance of the solid state film. (b) Photocurrent as a function of time upon illumination with a 500 μs light pulse at 670 nm. (c) Schematic diagram of the PD device.

60 After that an aluminium cathode was deposited by thermal evaporation defining an operating area of 1 mm². A comparison between the thermogravimetric analyses of the squaraine **2** and of the dyad **1** in Figure S11 shows that the latter preserves the excellent thermal stability of the precursor squaraine up to 130 °C, 65 unlike other cyanine-fullerene dyads which degrade during the thermal evaporation of the cathode.[25] The absorption spectrum of the resulting active thin film in Figure 1 resembles the absorbance profile of the dyad **1** in chloroform solution and thus confirms the

proficiency of squaraine dyes to maintain their optical characteristics when cast from solution to a substrate. We then measured the transient currents generated by irradiating the photodiode under vacuum with pulsed LED light at different wavelengths to match the entire absorption profile of the active layer under a reverse voltage bias of 1 V. As shown in Figure 3a, the device responded to illumination and gave rise to photocurrents, that were used to calculate the external quantum efficiency (EQE) of the device as a function of wavelength. The profile of the EQE matches the spectral absorbance of the dyad in the active layer confirming that the photocurrent is generated via an exciton-mediated process.[23] In particular, the EQE approaches 10% in the NIR due to the efficient photoinduced electron transfer from the excited state of the squaraine to the LUMO of the fulleropyrrolidine. Below 400 nm instead, where the donor does not appreciably absorb light, the EQE benefits from the photoinduced hole transfer from the fullerene acceptor to the HOMO of the squaraine. A close-up look at the typical time-response of the photodiode is reported in Figure 3b: the transient response to a 500 μs-long pulse at 670 nm showed a 90-10% decay time of about 200 μs. The measured responsivity of about 65 mA/W and the on/off ratio (I_{light}/I_{dark}) of about 5×10^2 at 1V bias and with impinging light intensity of ~ 5 mW/cm^2 are both coherent with the values previously recorded for other squaraine/PCBM mixtures.[8] The fast time response exhibited by the dyad is a further indication of an efficient exciton generation and dissociation promoted by the CT interaction between the donor squaraine and the covalently linked fullerene acceptor, combined with satisfactory charge collection efficiency. In conclusion we have synthesized and characterized a fulleropyrrolidine dyad that shows advantageous properties as an active material for light detection. In particular, dyad **1** would enable the preparation of efficient single component devices, with obvious advantages over two-component mixtures, such as skipping the need for long and tedious optimization of the donor/acceptor ratio. Moreover, thanks to the versatility of fulleropyrrolidine synthesis, further modifications of the dyad can be easily envisioned, such as derivatives bearing proper groups for the grafting to solid substrates, thus widening the range of possible applications.

Notes and references

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