

# Light harvesting tetrafullerene nanoarray for organic solar cells†‡

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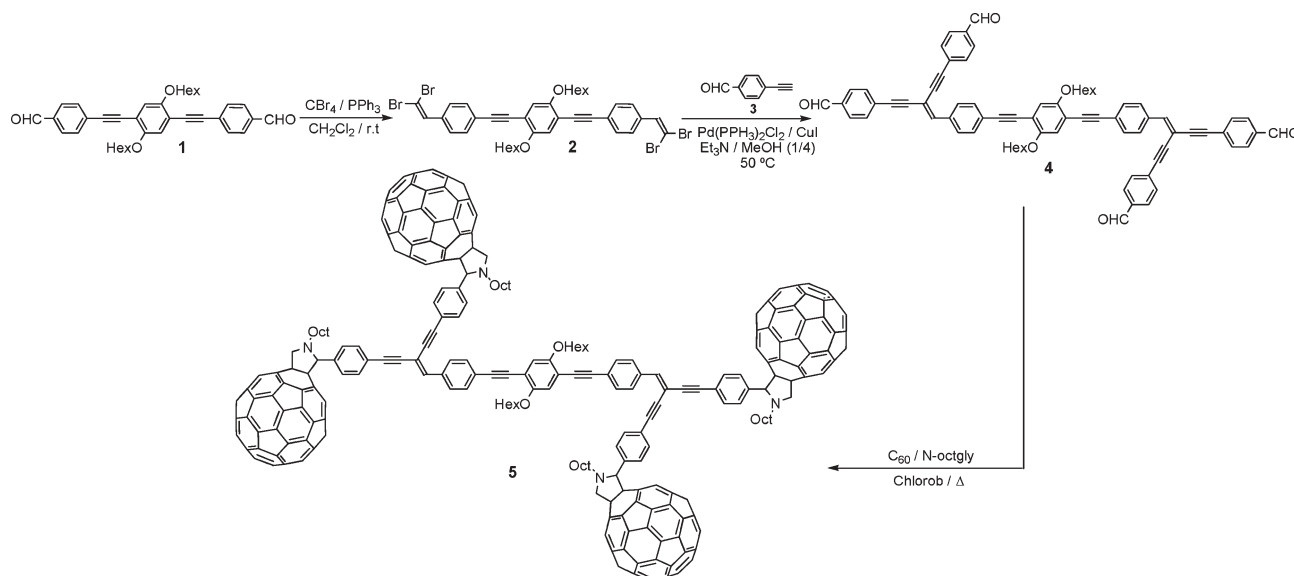
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A light absorbing  $\pi$ -conjugated oligomer–tetrafullerene nanoarray has been synthesized and its photophysical study reveals the presence of an intramolecular energy transfer. A photovoltaic device fabricated from this nanoarray and poly(3-hexylthiophene) shows an external quantum efficiency of 15% at 500 nm.

A challenging task in organic electronics is the integration of single organic structures and materials into devices that exhibit a wide range of functions (*i.e.*, signal processing, data storage, *etc.*).<sup>1</sup> To function independently such integrated devices may use molecular photovoltaics (PV) as a source of energy. A particularly interesting strategy towards molecular PV is covalently attaching electron donor moieties to C<sub>60</sub> and incorporating these molecular systems into a PV device.<sup>2</sup> Because of the covalent bond and

close proximity of the electroactive units, these molecular donor–acceptor systems generally provide a high efficiency for photoinduced charge generation and can be tailored to exhibit long radical ion state pair lifetimes. Molecular PV devices bear close resemblance to bulk-heterojunction polymer solar cells, in which a mixture of a  $\pi$ -conjugated polymer, acting as p-type material, and a soluble C<sub>60</sub> derivative as n-type material, constitutes the photoactive layer. These bulk-heterojunction solar cells give power conversion efficiencies of up to 4.4%.<sup>3,4</sup> To ensure efficient charge transport, the fullerene content in most bulk heterojunctions is high, often 4 : 1 by weight with respect to the polymer. In this respect, one drawback of the molecular PV systems employed so far is the relatively low fullerene content,<sup>2</sup> usually one donor moiety per fullerene, leading to poor charge transport. To resolve this issue, we set out to prepare conjugated oligomers with four fullerene units linked by a single  $\pi$ -conjugated core. In this communication we report the synthesis and photophysical properties of a new tetrafullerene nanoarray, in which four C<sub>60</sub>'s are covalently attached to a  $\pi$ -conjugated light-absorbing oligomeric central core. We address the use of this nanoarray in photovoltaic devices.

The multistep synthetic procedure that gives nanoarray **5** starts from the previously reported diformyl functionalized oligomer **1** (Scheme 1).<sup>5</sup> 1,1-Dibromo-1-alkene **2** was readily prepared by reacting **1** with CBr<sub>4</sub> and PPh<sub>3</sub> according to Corey's procedure.<sup>6</sup> A Sonogashira cross-coupling reaction<sup>7</sup> between **2** and **3**<sup>8</sup> leads to the



Scheme 1 Synthesis of light harvesting multifullerene nanocomposition **5**.

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‡ We wish to dedicate this work to Professor Siegfried Schneider on the occasion of his 65th birthday.

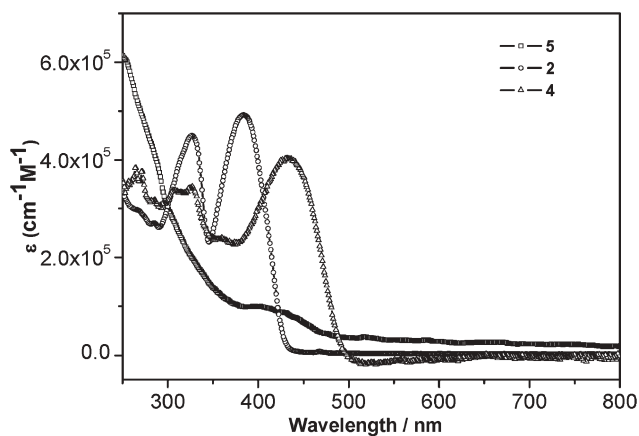


Fig. 1 UV-Vis spectra of compounds **2**, **4** and **5** in  $\text{CH}_2\text{Cl}_2$ .

highly light-absorbing tetraaldehyde **4** in 72% yield. This synthetic strategy has been proven by Kim *et al.* as a very useful method to tune the absorption and emission properties of  $\pi$ -conjugated oligomers.<sup>9</sup> Finally, Prato's 1,3-dipolar cycloaddition reaction between the azomethine ylide, generated *in situ* by reacting *N*-octylglycine and **4**, and one of the double bonds of  $\text{C}_{60}$ , yielded **5** as a diastereomeric mixture.<sup>10</sup> All mentioned compounds have been fully characterized through a variety of spectroscopic techniques (See Electronic Supplementary Information (ESI<sup>†</sup>)).

When comparing the electronic spectra of **2** and **4**, a bathochromic shift of the  $\pi$ - $\pi^*$  absorption band into the visible region of the solar spectrum (Fig. 1) is observed as a consequence of the increased length of the  $\pi$ -system. By attaching four  $\text{C}_{60}$  units to the central oligomeric moiety in **5** the conjugation length is only slightly reduced as evidenced from a small hypsochromic shift (Fig. 1). However, **5** still shows an appreciable absorption over the entire visible region up to  $\sim 700$  nm.

The redox properties of **4**, **5** and  $\text{C}_{60}$ , were determined by cyclic and differential pulse voltammetry (Table S-1, Fig. S-1, ESI<sup>†</sup>). In nanoarray **5**, as many as eight redox processes—three of them corresponding to the oxidation of the central oligomeric core and the remaining ones due to the reduction of the  $\text{C}_{60}$  units and the central  $\pi$ -conjugated moiety—are seen. The presence of both electron donor ( $\pi$ -conjugated oligomer) and  $\text{C}_{60}$  moieties in ensemble **5** account for the amphoteric redox behavior observed. As expected, four quasi-reversible waves appear corresponding to the fullerene cages ( $-0.88$ ,  $-1.27$ ,  $-1.81$  and  $-2.26$  V vs  $\text{Ag}/\text{Ag}^+$  in ODCB/MeCN) similarly to other related multifullerene conjugates.<sup>11</sup> A diagnostic wave at  $-1.50$  V can also be seen for the reduction of the oligomer fragment.

The PV properties of **5** were evaluated by spin casting a thin layer of the pure material and of a 1 : 1 blend with poly(3-hexylthiophene) (P3HT) onto a PEDOT : PSS covered ITO layer on a glass substrate and completing the device with an LiF/Al back contact. Pure **5** gave no significant PV effect, but in combination with P3HT the devices showed a short-circuit current of  $1.2 \text{ mA cm}^{-2}$ , an open circuit voltage of 0.65 V, and a fill factor of 0.17 under illumination with a white-light wolfram-halogen lamp ( $75 \text{ mW cm}^{-2}$ ) (Fig. S-2, see ESI<sup>†</sup>). The external quantum efficiency of the devices reached 0.15 electrons per photon at 500 nm (Fig. 2). This demonstrates that **5** acts as an

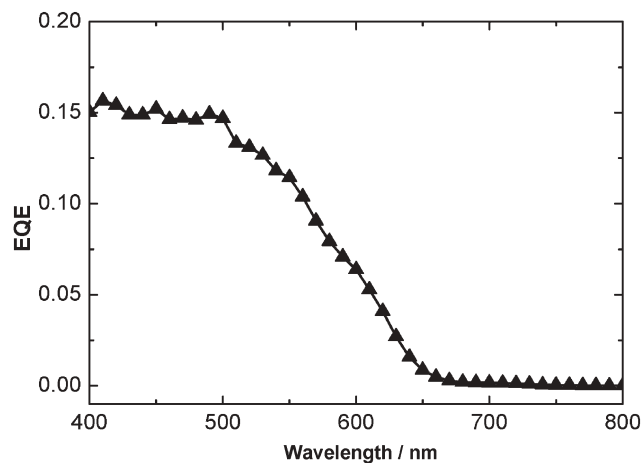


Fig. 2 Spectral response of a glass/ITO/PEDOT : PSS/P3HT : **5**/LiF/Al photovoltaic device.

efficient electron acceptor in combination with P3HT as an electron donor.

To explain the absence of PV activity in pure **5** and to elucidate the role of the various electroactive components in its photophysical behavior, a series of experiments—steady-state/time-resolved fluorescence and transient absorption spectroscopy—were performed. Considering the strongly fluorescing features of  $\pi$ -conjugated oligomers, we tested the fluorescence of compound **4** as a reference system and compared that with our newly synthesized nanoarray **5**. Regardless of solvent polarity we find fluorescence quantum yields of  $0.55 \pm 0.02$  for **4** and a fluorescence lifetime of 1.14 ns (in  $\text{CHCl}_3$ ). Upon investigating compound **5**—see Fig. 3—several important aspects should be emphasized. First, we see strongly reduced fluorescence quantum yields (*i.e.*, toluene:  $4.3 \times 10^{-4}$ ; THF:  $3.8 \times 10^{-4}$ ; *o*-dichlorobenzene:  $2.9 \times 10^{-4}$ ). Second, the fluorescence is dual, that is, besides the oligomer relevant features in the 400–700 nm domain, we see in the 650–850 nm region additional features. Third, the 650–850 nm characteristics bear close resemblance with that seen for the fullerene fluorescence in *N*-methylfulleropyrrolidines.<sup>5</sup>

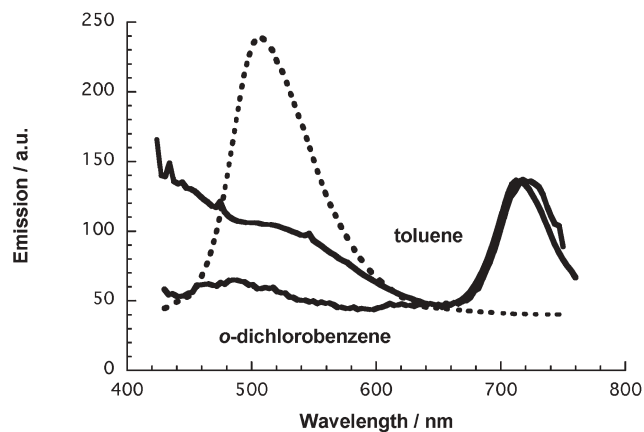


Fig. 3 Room temperature fluorescence spectra of **4** (dot) and **5** in various solvents (solid)—see labels—recorded with solutions that exhibit optical absorptions at the 415 nm excitation wavelength of 0.5. The fluorescence spectrum of **4** is reduced by a factor of 500.

Fourth, determining the quantum yield of the fullerene fluorescence (*i.e.*,  $6.0 \times 10^{-4}$  in toluene and *o*-dichlorobenzene) shows that its formation is quantitative in **5**, despite the exclusive excitation of the oligomer fragment.

To gather mechanistic evidence for the fullerene fluorescence we inspected the excitation spectrum of the 650–850 nm features. Since, the resulting spectrum matches the ground state spectrum of the oligomer (Fig. S-3, see ESI†), we postulate a quantitative transfer of singlet excited state energy from the high lying oligomer singlet state (2.45 eV) to the lower lying fullerene singlet (1.76 eV).

Undisputable evidence for the reaction sequence considered above came from time-resolved transient absorption measurements. Singlet and triplet features of **4** and *N*-methylfulleropyrrolidines were described recently.<sup>5</sup> Important for the current work are only the singlet–singlet characteristics that include maxima at around 600 and 880 nm, for compound **4** and *N*-methylfulleropyrrolidines, respectively. Upon 387 nm femtosecond excitation of the oligomer–fullerene conjugate, where the oligomer absorption is dominant, led initially to the singlet excited absorption of the oligomer fragment with a strong maximum at 875 nm. In contrast to the reference, which shows a fairly stable singlet–singlet signature, **5** reveals an ultrafast singlet deactivation (Fig. S-4 and S-5, see ESI†). Hereafter, only the fullerene singlet–singlet transitions are observed at 5 ps (Fig. S-4, see ESI†) with a maximum around 890 nm. Again, a singlet energy transfer is responsible for this observation. The kinetics of the energy transfer can be (i) estimated from the  $\sim 1000$ -fold fluorescence quenching in **5** and the 1.14 ns fluorescence lifetime of **4** to be extremely fast, *i.e.* on the order of  $10^{12} \text{ s}^{-1}$  (1 ps) and (ii) determined from the femtosecond experiments (Fig. S-5, see ESI†) as  $8.3 \pm 0.5 \times 10^{11} \text{ s}^{-1}$ . Singlet excited *N*-methylfulleropyrrolidines are known to form the corresponding triplet state with near unit quantum yield *via* the intersystem crossing dynamics (*i.e.*,  $6.6 \times 10^8 \text{ s}^{-1}$ ). The same process occurs in the nanoarray **5**—Fig. S-6† shows, for example, the triplet–triplet transition in the 550–950 region, as detected at the conclusion of the femtosecond experiments (*i.e.*, 1.5 ns). When extending the time-resolved measurements into the nanosecond and microsecond time windows the same triplet features were found—see Fig. S-6†—with an overall quantum yield of 0.98. Under our experimental conditions the oxygen-sensitive fullerene triplet decays with a lifetime of about 20  $\mu\text{s}$  and reinstates hereby—in the absence of molecular oxygen—the singlet ground state of **5**.

This photophysical relaxation and the PV effects of pure **5** and its blend with P3HT are confirmed by photoinduced absorption experiments on thin solid-state films recorded at 80 K (Fig. S-7, see ESI†). Under these conditions, pure **5** shows the broad featureless spectrum of the fullerene triplet state and a vibronically resolved photoluminescence at 1.68 and 1.52 eV. No photoinduced charges are observed, consistent with the absence of a PV effect. In contrast, a mixture of P3HT and **5**, measured under identical conditions shows the clear features of P3HT radical cations at  $\sim 0.5$  and 1.3 eV. Importantly, the spectrum of the P3HT : **5** blend differs considerably from that of neat P3HT, which is dominated by a triplet band at 1.06 eV and that of **5**.

In summary, a visible light-absorbing nanoarray—integrating four  $\text{C}_{60}$  moieties and a single  $\pi$ -conjugated oligomer—has been synthesized from bisaldehyde **1**. The redox studies reveal an amphoteric redox behavior stemming from the presence of both

electron donor OPE unit and electron acceptor fullerene moieties. Although energy transfer processes between  $\text{C}_{60}$  and the central  $\pi$ -conjugated oligomer<sup>12</sup> prevents an efficient photoconversion performance, the combination of **5** and P3HT led to external quantum efficiencies of 15%. Work is currently in progress towards the preparation of new nanoarrays and nanoensembles with better donor abilities and light-absorbing properties. This is expected to improve their applicability as active components in solar cells.

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