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EDGE ARTICLE

Powering reductive charge shift reactions—linking fullerenes of different electron acceptor strength to secure an energy gradient†

Carmen Villegas,^a Juan Luis Delgado,^{ab} Pierre-Antoine Bouit,^b Bruno Grimm,^c Wolfgang Seitz,^c Nazario Martín^{*ab} and Dirk M. Guldi^{*c}

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We report here on one of the rare cases that realizes a reductive charge shift from a primary electron acceptor (C_{60}) to a secondary electron acceptor (C_{70}) in a $ZnP-C_{60}-C_{70}$ conjugate. Initially, charge separation evolves from an excited state electron donor (ZnP). By far the most far reaching benefit from such a reductive pathway is a marked slow down of the energy wasting charge recombination when compared to the $ZnP-C_{60}$ conjugate (*i.e.*, picoseconds *versus* nanoseconds).

Introduction

Nature employs a myriad of interlocking principles to create sophisticated and amazing architectures, in which a formidable level of control over organizing individual building blocks and replacing them has been realized. To this end, the structure of the bacterial photosynthetic reaction centers provides important incentives for arranging electron donors and electron acceptors. Sunlight is harvested by antenna chlorophylls before it is unidirectionally funneled to the special “bacteriochlorophyll dimer” pair. Here, excited state interactions in the form of an electron transfer yield an oxidized special “bacteriochlorophyll dimer”, while the electrons are inserted into a redox chain. Importantly, a directed cascade of electron transfer reactions mediates the electrons through the well-balanced redox gradients in the redox chain and retards the charge separation.¹

Fullerenes are readily available and exhibit exciting characteristics.² For example, the delocalization of charges within the giant, spherical carbon framework together with the rigid, confined structure of the π -sphere offers unique opportunities for stabilizing charged entities.³ Above all, the small reorganization energies of fullerenes in charge-transfer reactions have led to a notable breakthrough in multicomponent electron donor–acceptor systems by providing accelerated charge separation and

decelerated charge recombination.⁴ In most of such multicomponent systems, photoexcitation is the inception to reduce the electron accepting fullerenes and to generate a hole at the electron donor. A redox gradient governs a hole transfer from the primary electron donor to the secondary electron donor, *etc.*⁵

In general, there have been only a small number of multicomponent electron donor–acceptor systems, in which a unidirectional flow of electrons evolves and, in turn, mediates electrons between different electron acceptors rather than holes between different electron donors.⁶ This is what the current work addresses. In particular, we present a paradigm shift by using two fullerenes that are covalently linked to each other and an excited state electron donating ZnP —see Chart 1. To ensure an unambiguous characterization of the electron transfer pathways, two different fullerenes, that is, C_{60} and C_{70} , were chosen. Implementation of a redox gradient was realized by using different fullerene functionalization. In particular, a fulleropyrrolidine of C_{60} and a fulleropyrazoline of C_{70} —to improve the electron

Chart 1 Structure of $ZnP-C_{60}-C_{70}$ (**1**), $C_{60}-C_{70}$ (**2**), ZnP azide (**3**), formyl containing 2-pyrazolino[70]fullerene (**4**) and $ZnP-C_{60}$ (**5**). Compounds **1**, **2**, **4** and **5** were obtained as isomeric mixtures.

^aDepartamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Ciudad Universitaria s/n, 28040 Madrid, Spain. E-mail: nazmar@quim.ucm.es; Fax: (+34) 91-394-4103; Tel: (+34) 91-394-4227

^bIMDEA-Nanociencia, Facultad de Ciencias, Módulo C-IX, 3^a planta, Ciudad Universitaria de Cantoblanco, 28049 Madrid, Spain

^cDepartment of Chemistry and Pharmacy & Interdisciplinary Center of Molecular Materials (ICMM) Friedrich-Alexander-University Erlangen-Nuremberg Egerlandstr. 3, 91058 Erlangen, Germany. E-mail: dirk.guldi@chemie.uni-erlangen.de; Fax: (+49) 9131-85-28307

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acceptor character—served as primary and secondary electron acceptor, respectively.

Results and discussion

The synthesis of **1** has been carried out by means of copper catalyzed “click-chemistry” of fullerene dimer (**2**) with zinc porphyrine azide (**3**)⁷ in moderate yields (40%).⁸ **2**, on the other hand, was formed by reacting formyl containing 2-pyrazolino[70] fullerene (**4**)⁹ with 2-propargyl-glycine and C₆₀ (57% yield).¹⁰ Finally, as a reference system, we have synthesized **5** bearing only one fragment of **1**, following a similar methodology.^{8,11} It is worth mentioning that compounds **1**, **2**, and **4** were obtained as a mixture of isomers stemming from the difference site and regioselectivity in the cycloaddition reaction on the C₇₀ fullerene.¹²

1 displays in THF (Figure S1†) the absorption characteristics of C₆₀ and C₇₀ at 253/315 and 360/465 nm, respectively. The presence of the Soret- and Q-bands of ZnP at 426 and 557/597 nm complete the characterization of **1**. A closer inspection reveals, however, that the absorption spectrum of **1** fails to resemble the sum of the individual spectra, that is, **2** and **3**.

Electrochemistry

The electrochemical properties of **1–3** have been investigated by means of room temperature cyclic voltammetry/osteryoung square wave voltammetry experiments (Figure S3, Table S1†). For **3**, the first oxidation process occurs at 0.52 to yield the ZnP radical cation. The ZnP dication, on the other hand is formed at 0.90 V. Reduction processes at –1.84 and –2.00 V relate to the reduction of ZnP to the corresponding radical anion and dianion, respectively. At –1.62 V, the reduction of the azide fragment set in. In principle, C₆₀ and C₇₀ exhibit nearly identical reduction processes.¹³ In **2**, however, the electron withdrawing effects of the pyrazoline ring¹⁴ shifts the C₇₀ reduction processes of the fulleropyrazoline to –0.72, –1.13, –1.50, and –1.87 V. The C₆₀ reduction processes of the fulleropyrrolidine are cathodically shifted that are detectable at –0.85, –1.26, –1.64, and –2.02 V. **1** shows two oxidation processes at 0.52 and 0.89 V to lead to the ZnP radical cation and ZnP dication. On the reductive side, several redox processes are noted. Whereas the reduction of the fulleropyrazoline of C₇₀ involves processes at –0.72, –1.13, –1.52, and –1.86 V, reduction of the fulleropyrrolidine of C₆₀ is seen at –0.85, –1.25, –1.62, and –2.01 V generating the C₇₀/C₆₀ radical anion, the C₇₀/C₆₀ dianion, the C₇₀/C₆₀ trianion, and the C₇₀/C₆₀ tetraanion, respectively. The reduction of ZnP to the corresponding radical anion and dianion at –1.86 and –2.01 V, respectively, and the reduction of the triazole at –1.62 V are superimposed to the reduction processes of C₆₀ and C₇₀ and intensity the reductive currents in the corresponding regions.

Photophysical studies

Transient absorption measurements in THF with the references were performed in the following order—ZnP (**3**), pyrrolidino[60] fullerene, and pyrazolino[70] fullerene (**4**)—before turning to the

C₆₀–C₇₀ (**2**) and ZnP–C₆₀ conjugates (**5**) and, finally, to the ZnP–C₆₀–C₇₀ conjugate (**1**).

When photoexciting the ZnP reference (**3**) at 420 or 550 nm, within 2.0 ps the higher singlet excited state features of ZnP transform into those of the lowest singlet excited state. Specifically, characteristic maxima at 455, 580, and 630 nm as well as minima at 565 and 605 nm are clear attributes of the singlet–singlet absorptions of ZnP.¹⁵ On a time-scale of up to 3.0 ns, the fate of the ZnP singlet excited state is dominated by intersystem crossing—driven by a strong spin–orbit coupling—to afford the corresponding triplet excited state (2.1 ns–4.8 × 10⁸ s^{–1}). The latter was identified by a long-lived (100 μs–1.0 × 10⁴ s^{–1}) and strongly absorbing triplet–triplet transition that maximizes at 840 nm.¹⁶

Excitation of the pyrrolidino[60] fullerene and pyrazolino[70] fullerene references at 387 nm or 550 nm (not shown) populates their singlet excited states with characteristic absorption maxima at 610/920 and 610/1290 nm, respectively. Both singlet excited states undergo intersystem crossing to the corresponding triplet manifolds with characteristic lifetimes of 1.4 ns (7.0 × 10⁸ s^{–1}) for C₆₀ and 0.97 ns (1.03 × 10⁹ s^{–1}) for C₇₀ as well as characteristic maxima at 700 and 970 nm.¹⁷

When conjugating C₆₀ with C₇₀, the transient absorption features that were recorded immediately upon photoexcitation of (**2**) are best described as the superimposition of the C₆₀ and the C₇₀ singlet excited states featuring maxima at 610/920 and 610/1290 nm, respectively. Particularly interesting is the fact that the C₆₀ singlet excited state decays in the presence of C₇₀ with dynamics (15 ps–6.0 × 10¹⁰ s^{–1}) that are appreciably faster than those seen in the C₆₀ reference. Owing to the sheer impossibility of oxidizing C₆₀ or C₇₀ in the photochemical processes, the aforementioned seems to prompt an intramolecular transduction of singlet excited state energy from C₆₀ to C₇₀. In fact, the sole photoproduct decays with dynamics that resembles those seen for the intersystem crossing in the C₇₀ reference (0.97 ns–1.03 × 10⁹ s^{–1}). Crucial support for the energy transfer notion comes from the observation that the only triplet excited state seen at time delays of 3.0 ns and beyond was that of C₇₀ with its fingerprint absorption at 970 nm.¹⁸ Our transient absorption measurements failed, on the other hand, to provide for **2** any appreciable evidence for the 700 nm maximum of the C₆₀ triplet excited state.¹⁹

Next, the transient absorption changes of the ZnP–C₆₀ conjugate (**5**) were recorded with several time delays after the 550 nm laser pulse and compared with those seen for the ZnP reference—see Fig. 1. At early times, these are practically identical to those of the ZnP reference, disclosing a strong maximum at 455 nm and a strong bleaching at 565 nm. However, at delay times of around 10 ps, the 455 nm absorption starts to decay and simultaneously a new transition grows in the visible, that is, a maximum around 630 nm (50 ps–2.0 × 10¹⁰ s^{–1}), which is accompanied by a near-infrared feature, namely a 1005 nm maximum. Based on a spectral comparison with former spectroelectrochemical and pulse radiolitical investigations,²⁰ we ascribe the earlier band to the ZnP π-radical cation (ZnP^{•+}), while the latter band corresponds to the C₆₀ π-radical anion (C₆₀^{•–}). In accordance with these results, we propose that charge separation evolves from the ZnP singlet excited state to the electron accepting fullerene to yield ZnP^{•+}–C₆₀^{•–}. The absorption of the

Fig. 1 Upper part—differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (550 nm) of ZnP-C₆₀ in THF with several time delays between 0 and 3000 ps at room temperature—see figure legend for time delays. Lower part—time-absorption profiles of the spectra shown in the upper and central parts at 455, 630, and 1005 nm monitoring the charge separation and charge recombination.

ZnP⁺-C₆₀⁻ state decays in the nanosecond regime (1.3 ns – $7.6 \times 10^8 \text{ s}^{-1}$). Notable is that the semiflexible spacer connecting ZnP with C₆₀ provides ample room for configurational changes in the ZnP-C₆₀ conjugate. Based on previous studies, such changes in configuration are likely to be the inception for through space rather than through bond electron transfer interactions.²¹

Finally, we turned to the ZnP-C₆₀-C₇₀ conjugate (**1**)—see Fig. 2. Immediately upon 550 nm photoexcitation we noticed the characteristics of the ZnP singlet excited state in the visible and those of the C₇₀ singlet excited state in the near-infrared with maxima at 455 and 1290 nm, respectively. Both are, however, metastable and transform rapidly (10 ps – $1.0 \times 10^{11} \text{ s}^{-1}$) into a new transient product. To this end, evidence for the ZnP π -radical cation (ZnP⁺) evolves in the visible region—550 to 800 nm. Changes in the near-infrared region, namely at 1005 and 1315, on the other hand, relate to the involvement of the C₆₀ π -radical anion (C₆₀⁻) and the C₇₀ π -radical anion (C₇₀⁻).^{22,23} Important is that at time delays of around 1.0 ns, only the features of the C₇₀ π -radical anion (C₇₀⁻) are discernable at 1315 nm, while those of the C₆₀ π -radical anion (C₆₀⁻) at 1005 nm have completely disappeared. From analyzing the C₆₀

Fig. 2 Upper part—differential absorption spectra (visible) obtained upon femtosecond flash photolysis (550 nm) of ZnP-C₆₀-C₇₀ in THF with several time delays between 0 and 3000 ps at room temperature—see figure legend for time delays. Central part—differential absorption spectra (extended near-infrared) obtained upon femtosecond flash photolysis (550 nm) of ZnP-C₆₀-C₇₀ in THF with several time delays between 0 and 3000 ps at room temperature—see figure legend for time delays. Lower part—time-absorption profiles of the spectra shown in the upper and central parts at 455, 1005, and 1300 nm monitoring the charge separation and charge shift.

π -radical anion (C₆₀⁻) decay at, for example, 1005 nm, we have determined a lifetime of 135 ps ($7.1 \times 10^9 \text{ s}^{-1}$). A comparison with the intrinsic lifetime of ZnP⁺-C₆₀⁻ (1.3 ns – $7.6 \times 10^8 \text{ s}^{-1}$) leads us to conclude that the nature of the ZnP⁺-C₆₀⁻-C₇₀ decay

is an exothermic and unidirectional charge shift, which involves an electron shift between the two electron accepting fullerenes. The correspondingly formed $\text{ZnP}^+-\text{C}_{60}-\text{C}_{70}^-$ shows no appreciable decay in the 1100 to 1500 nm range on the 3.0 ns time scale. Such an impressive gain in stability is also substantiated when inspecting the visible region. Here, the $\text{ZnP} \pi$ -radical cation (ZnP^+), which absorbs between 550 and 800 nm, is stable without showing any noticeable decay. From complementary nanosecond experiments a lifetime of 100 ± 30 ns—Figure S18—has been derived. As far as the $\text{ZnP}^+-\text{C}_{60}-\text{C}_{70}^-$ quantum yield is concerned, a multiwavelength analysis reveals 30%. One factor that may prevent higher quantum yields is the semiflexible spacer.

Conclusions

In short, a fulleropyrrolidine of C_{60} and a fulleropyrazoline of C_{70} have been integrated together with ZnP into a novel $\text{ZnP}-\text{C}_{60}-\text{C}_{70}$ conjugate towards creating a gradient of redox centers. In femtosecond flash photolysis studies we confirm fluorescence experiments that are not discussed and the occurrence of an electron transfer sequence.²⁴ In particular, an initial charge separation yields $\text{ZnP}^+-\text{C}_{60}^--\text{C}_{70}$ —with a lifetime of one hundred picoseconds—and is followed by a subsequent charge shift to afford $\text{ZnP}^+-\text{C}_{60}-\text{C}_{70}^-$ —with a lifetime of around one hundred nanoseconds. Overall, our finding constitutes one of the rare cases, in which reductive charge shift from a primary electron acceptor (C_{60}) to a secondary electron acceptor (C_{70}) retards charge recombination as opposed to the more common oxidative charge shift from primary to secondary donors.

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