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Coordinating Electron Transport Chains to an Electron Donor

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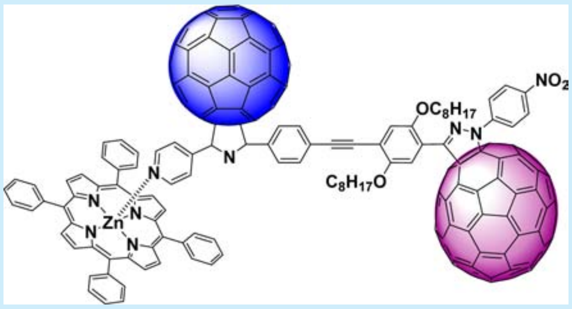
Supporting Information

ABSTRACT: Two electron transport chains (**2** and **3**) featuring two fullerenes with different electron acceptor strengths have been synthesized, characterized, and coordinated to a light harvesting/electron donating zinc porphyrin. Electrochemical assays corroborate the redox gradients along the designed electron transport chains, and complementary absorption and fluorescence titrations prove the assembly of ZnP-**2** and ZnP-**3** hybrids.



Finding new materials for the transformation of sunlight into chemical energy or electricity constitutes a contemporary challenge in science. Nature, for example, uses simple architectures, which inspire scientists for novel designs. Recently, our research groups have described a covalent donor–acceptor$_1$–acceptor$_2$ conjugate (DA$_1$A$_2$), where a C_{60}-based fulleropyrrolidine and a C_{70}-based fulleropyrazoline have been covalently connected to a zinc porphyrin (ZnP), affording a novel ZnP–C_{60}–C_{70} (**1**, Figure 1).[1] Femtosecond pump probe experiments demonstrated the sequence of a unidirectional electron transfer. An initial charge separation yields ZnP$^{\bullet+}$–$C_{60}$$^{\bullet-}$–$C_{70}$ with a lifetime of 100 ps. This event is followed by a subsequent charge shift which leads to ZnP$^{\bullet+}$–C_{60}–$C_{70}$$^{\bullet-}$ with a lifetime of around 100 ns. As such it represents one of the rare cases in which a reductive charge shift from a primary electron acceptor ([60] fulleropyrrolidine) to a secondary electron acceptor ([70]fulleropyrazoline) ensures long-lived charge separation. It illustrates the potential of designing tailored conjugates as artificial mimics of natural photosynthesis. It is important to remark here that ZnP–A$_1$–A$_2$ triads, not containing two electrochemically distinct fullerene units, have been also described in the literature.[2] Encouraged by our own experience in the areas of light harvesting,[3] solar cells,[4] artificial photosynthesis,[5] and supramolecular chemistry,[6] we focused on the preparation of a new family of supramolecular DA$_1$A$_2$ based on ZnP as light harvester/electron donor D and two different C_{60}–C_{70} as electron transport chains A$_1$A$_2$. Importantly, we took advantage of coordination chemistry as a means to control the assembly of ZnP D and C_{60}–C_{70} A$_1$A$_2$.

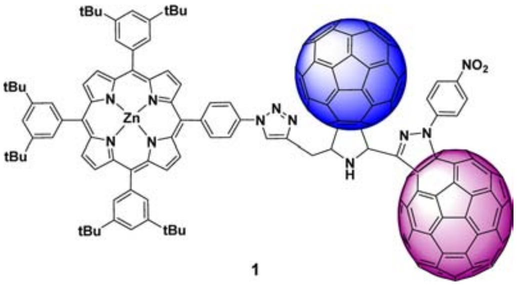


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Figure 1. Covalently linked zinc porphyrin, [60]fulleropyrrolidine, [70]fulleropyrazoline **1**.

To explore the influence of the linker within C_{60}–C_{70} A$_1$A$_2$ we have prepared two new supramolecular DA$_1$A$_2$'s based on metal–ligand interactions. To this end, we have used ZnP as an electron donor and two new electron transport chains based on C_{60}–C_{70} bearing a terminal pyridine. The main structural difference is the distance between [60]fulleropyrrolidine and [70]fulleropyrazoline in each C_{60}–C_{70} A$_1$A$_2$. While in **2** and correspondingly in ZnP·**2** the two fullerenes are directly linked, in **3** and ZnP·**3** the linking bridge is formed by a rigid phenyl–acetylene–phenyl connection (Figure 2).

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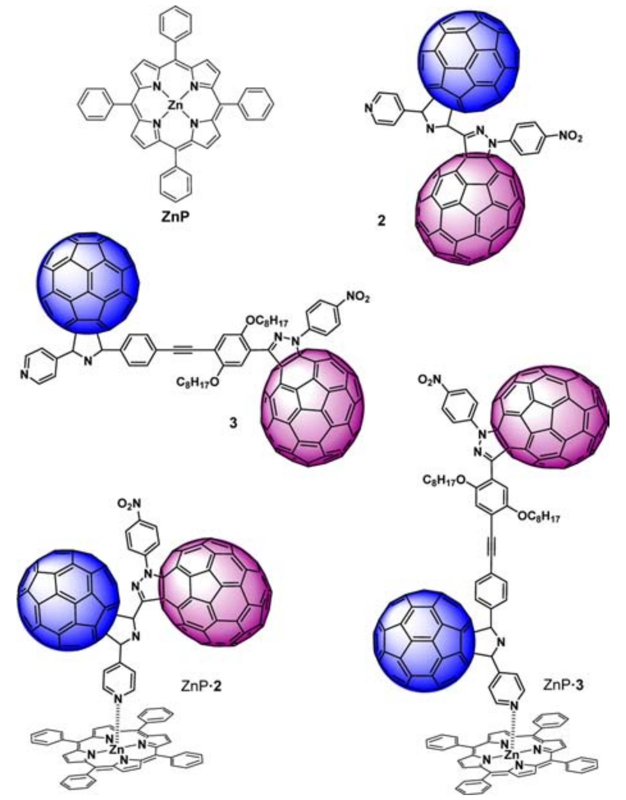
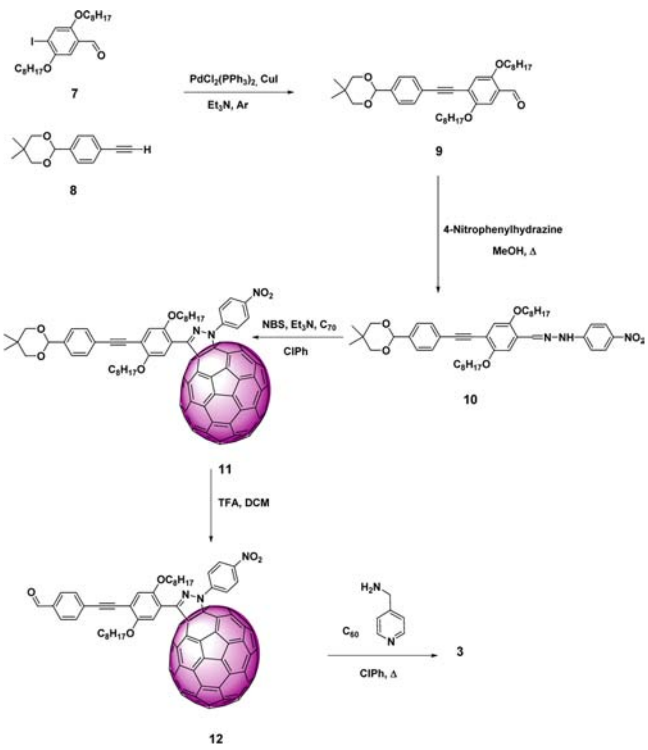


Figure 2. Compounds **2**, **3**, **ZnP** and new non-covalently assembled DA_1A_2 triads ZnP-**2** and ZnP-**3**.

The synthesis of the two new electron transport chains bearing a terminal pyridine unit have been carried out through a demanding multistep synthetic procedure. Scheme 1 shows, for example, the synthetic steps toward **3**. In particular, its synthesis was carried out starting from building block **7**, which is obtained, in turn, in a multistep synthetic procedure as reported by Nierengarten et al.[7] All of the intermediates and final products have been fully characterized using standard ^1H NMR, ^{13}C NMR, HR-MS, and HPLC.[8]

Scheme 1. Multistep Synthetic Procedure Towards Electron Transport Chain 3



ZnP, as it was used to form ZnP-**2** and ZnP-**3**, was obtained as a byproduct of the reactions carried out for the preparation of porphyrin type A_3B.[9]

The electrochemical properties of ZnP and electron transport chains **2** and **3** have been studied by room temperature square wave and cyclic voltammetry in THF.

On one hand, the cyclic voltammogram obtained for ZnP shows two reversible oxidations at +0.66 and +1.02 V. These correspond to the formation of the radical cation and dication of ZnP, respectively (Figure S10). On the other hand, the square wave voltammograms of electron transport chains **2** and **3** show the presence of two sets of reductions owing to the presence of different fullerenes, that is, [70]fulleropyrazoline and [60]fulleropyrrolidine (Figure 3). The first set of reductions at −0.56, −1.12, −1.58, and −1.75 V for **2** and at −0.58, −1.12, −1.54, and −1.88 V for **3** is due to [70]fulleropyrazoline centered processes. The second set of reductions, which is with values of −0.75, −1.31, −1.75, and −2.02 V for **2** and −0.71, 1.25, −1.68, and −2.05 V for **3** cathodically shifted, correlating with the reductions of [60]-fulleropyrrolidine.

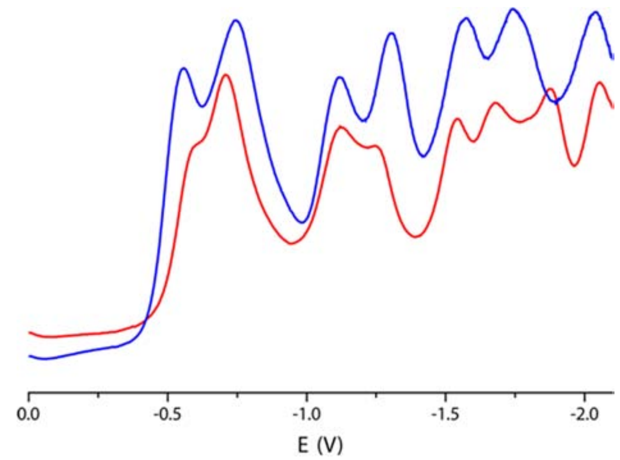


Figure 3. Square wave voltammograms of **2** (blue) and **3** (red) (V vs $Ag/AgNO_3$; GCE as a working electrode; Bu_4NPF_6 0.1 M, THF).

A closer analysis of the voltammograms in Figure 3 suggests that the presence of pyridine does not affect the electrochemical properties of any fragment and, in turn, secures not only the reductive redox gradient in $C_{60}-C_{70}$ A_1A_2 but also the overall redox gradient in $ZnP-C_{60}-C_{70}$ DA_1A_2 in **2**/**3** and ZnP-**2**/ZnP-**3**, respectively.

In verifying the ability of **2** and **3** to form supramolecular complexes through, for example, metal−ligand interactions, we have performed complexation studies with ZnP by NMR, UV−vis absorption, and fluorescence spectroscopy. Metal−ligand interactions between [60]fullerene derivatives, which are structurally similar to **2** and **3**[5] typically give rise to association constants of around 10^3 M^{-1}. Considering, however, the fact that **2** and **3** are a mixture of diastereoisomers renders an NMR experiment as rather difficult. Thus, we turned to 25 °C absorption assays in *o*-DCB and followed changes in terms of

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the diagnostic Soret- and Q-band absorptions upon the addition of increasing amounts of **2** and **3** to a constant concentration of ZnP.

The addition of increasing amounts of **3** (1.2×10^{-4} M) to a solution of ZnP (4×10^{-7} M) caused the appearance of a Soret band shoulder at around 431 nm. As a matter of fact, such a shift of the ZnP Soret absorption band (424 nm → 431 nm) is characteristic of the formation of supramolecular complexes involving fullerenes,[10] yielding, for example, ZnP-**3** (Figure 4a).

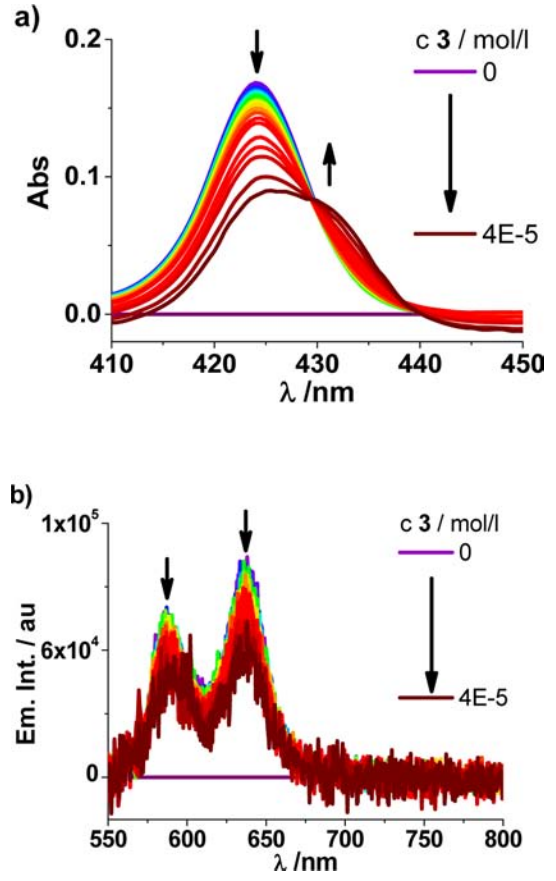

Figure 4. (a) UV−vis titrations with addition of increasing volumes of **3** (1.2×10^{-4} M) to a solution of ZnP (4×10^{-7} M); (b) emission spectra of the same solutions; in *o*-DCB at 25 °C.

As a complement, fluorescence measurements, which were performed with the same solutions of **3** and ZnP, revealed an increasing quenching of the ZnP centered fluorescence features at 595 and 645 nm (Figure 4b). Importantly, the fluorescence spectra were corrected for inner filter effects and for the fluorescence of **3**. As such, the resulting quenching is due to complex formation only (Figure 4b).

Similar experiments have been carried out with **2** and ZnP. As seen for **3**, there is a clear shift in the Soret band from 424 to 431 nm, which nicely confirms the formation of ZnP-**2** (Figure S17). In summary, both the absorption and fluorescence assays provide sound evidence for the formation of ZnP-**2** and ZnP-**3**.

Overall, the fluorescence quenching enabled us to derive the binding constants for ZnP-**2** and ZnP-**3**, which are 8.2×10^4 and 8.6×10^4 M^{-1}, respectively. Our results demonstrate the successful formation of two new DA_1A_2's. Their electrochemical studies suggest that their electroactive units are suitably arranged in order to produce a redox gradient from the ZnP via a transient [60]fulleropyrrolidine to [70]fulleropyrazoline.

In summary, a new family of electron transport chains featuring two fullerenes with different electron acceptor strengths have been synthesized en route toward the realization of photosynthetic mimics ZnP-**2** and ZnP-**3**. Electrochemical assays performed with ZnP, **2**, and **3** confirm, on one hand, the electron donating character of ZnP and, on the other hand, the reductive redox gradient stemming from the two different fullerenes in C_{60}−C_{70} A_1A_2/ZnP−C_{60}−C_{70} DA_1A_2. From the experiments shown in Figure 4, in which variable amounts of **2** and **3** were added to constant concentrations of ZnP and spectroscopically characterized, we concluded the successful complex formation, that is, ZnP-**2** and ZnP-**3**. From future photophysical studies we expect to gather addtional information on the complexation and, more importantly, on the photophysical processes taking place upon photoexcitation. In this regard, a sequential charge shift to afford $ZnP^{\bullet+}\cdot C_{60}-C_{70}^{\bullet-}$ could be expected, as already seen for **1**. The real goal will, however, continue to be focusing on the novel design of artificial photosynthetic systems assembled either covalently or noncovalently.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b02542.

> Synthetic procedures and complete characterizations for all the compounds and its necessary precursors (PDF)

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Notes

The authors declare no competing financial interest.

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