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A Bisfullerene–Bis(dipyrrinato)zinc Complex: Electronic Coupling and Charge Separation in an Easy-to-Assemble Synthetic System

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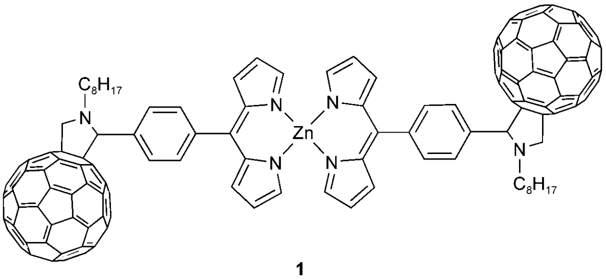
The use of a bis(dipyrrinato)zinc ((dpy)–Zn–(dpy)) linker allows for the facile construction of a bis-C_{60} system that undergoes effective charge separation upon laser photoexcitation at $\lambda = 480$ nm.

Fullerenes, such as C_{60}, have been extensively exploited as electron-poor acceptors in the construction of model photosynthetic systems and in the development of rudimentary photovoltaic devices. In the context of this general framework, considerable effort has been devoted to the construction and study of dimeric systems in which two C_{60} subunits are linked by various spacer units.[1] Such systems are of fundamental interest in terms of understanding the interaction between ostensibly equivalent redox partners and the effect that varying the coupling can have on these interactions. However, a drawback of most such dimers is that they rely on covalent synthesis to establish the requisite linkage. Thus, there is an incentive to prepare systems that take advantage of easy-to-manipulate noncovalent interactions to create the desired C_{60}–C_{60} arrangements. Diederich et al.[2] and Nierengarten et al.[3] have employed such a strategy to connect fullerenes through platinum and copper complexes, respectively. Moreover, our group and, separately, the team of Martin, Rebek, and Guldi have taken advantage of Watson–Crick base-pairing interactions to link C_{60} acceptors to various donors through hydrogen bonds.[4] In a different vein, Diederich et al. and, more recently, Khlobystov and Schröder et al. have used pyridine–metal coordination to link two C_{60} derivatives.[2,5] Unfortunately, the first of these approaches necessarily produces systems that are not symmetrical, whereas the latter gives rise to complexes without apparent electronic interaction between the fullerene subunits. Thus, we sought a new approach that would allow the creation of a linked C_{60}–C_{60} pseudodimer while providing for effective coupling between the fullerene subunits. Herein, we report the synthesis and preliminary photophysical characterization of system **1** (C_{60}–(dpy)–Zn–(dpy)–C_{60}), which achieves these paired objectives; this new system is based on the use of a bis(dipyrrin)zinc ((dpy)–Zn–(dpy)) linkage.



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Dipyrrin systems and their applications in the construction of model electron- and energy-transfer systems have been extensively studied. For instance, dipyrrins[6] have been used as auxiliary dyes and linkers in multiporphyrin arrays and in a wide variety of solar harvesting models.[7] Almost without exception, these systems have been predicated on the use of functionalized boron complexes of dipyrrins (e.g., borondifluorides). As such, they do not rely on dipyrrin as a linking moiety. On the other hand, bis(dipyrrinato)metal

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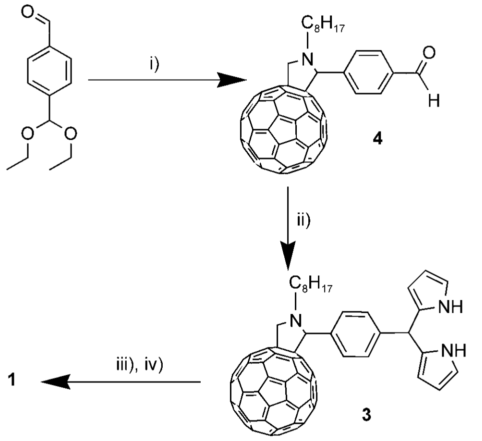
complexes of divalent metal ions, such as zinc, have been known since the days of Fischer,[8] and have been exploited as a linking subunit by various researchers since the late 1960s.[6,9] Moreover, Bocian, Holten, Lindsey et al. have exploited the (dpy)–Zn–(dpy) linkage to create bisporphyrin-based energy-transfer systems.[10] However, to the best of our knowledge bridging bis(dipyrrinato)zinc motifs have not been used as linking moieties to produce charge-separating devices. Complex **1** was designed to test this potential utility.

The synthesis of complex **1** is summarized in Scheme 1. It involves several key precursors. The first of these, fulleropyrrolidine **4** (Scheme 1), was obtained in 37 % yield from a 1,3-dipolar cycloaddition of an azomethine ylid, which was generated in situ from 4-(diethoxymethyl)benzaldehyde and *N*-octylglycine,[11] to C_{60} followed by acidic cleavage of the resulting acetal.[12] The resulting aldehyde was then used to prepare the corresponding 5-aryl-substituted dipyrromethane **3** by treatment with an excess of pyrrole in the presence of acid and in the absence of air (Scheme 1).[13] Oxidation with *p*-chloranil (to produce a putative dipyrromethene **2**; structure not shown) followed by treatment with zinc acetate gave complex **1** (for experimental details see the Supporting Information).



Scheme 1. Synthesis of complex **1**. i) C_{60}/*N*-octylglycine, toluene, reflux then HCl, 37 %; ii) pyrrole, trifluoroacetic acid, 62 %; iii) *p*-chloranil; iv) $[Zn(OAc)_2]\cdot H_2O$, $CHCl_3$/MeOH, 74 %.

Complex **1** gave NMR spectroscopic and mass spectrometric data consistent with its proposed structure (see the Supporting Information). The spectra also confirmed that the ground state UV/Vis absorption spectrum of **1** is more than just the linear sum of the component spectra. Whereas the long wavelength absorption (i.e., λ_{max} for the 0–*0 transition) for (dpy)–Zn–(dpy) appears at $\lambda = 485$ nm and C_{60} shows a characteristic 0–*0 transition at $\lambda = 690$ nm (and also maxima at $\lambda = 435$ and 330 nm), complex **1** gives rise to a spectrum that is best described as a broad absorption with scarcely visible peaks at $\lambda = 485$ and 435 nm (see the Supporting Information). Such differences are consistent with the presence of strong electronic interactions between the individual constituents (i.e., C_{60} and (dpy)–Zn–(dpy)) in complex **1** and leads us to conclude that the bis(dipyrrinato)zinc linker provides effective electronic coupling between the two fullerene subunits.

Deeper insight into the extent of electronic communication between the constituents in **1** came from fluorescence measurements. In line with their different 0–*0 transitions ($\lambda = 485$ nm for (dpy)–Zn–(dpy) and $\lambda = 690$ nm for C_{60}), (dpy)–Zn–(dpy) and C_{60} exhibit *0–0 fluorescence maxima around $\lambda = 520$ (quantum yield 6.0×10^{-3}) and 715 nm (quantum yield 6.0×10^{-4}), respectively.[14] It is fairly well established that substituents, if they are redox- and photoinactive, play an insignificant role in modulating the basic properties of fulleropyrrolidines.[15] This appreciation led us to chose *N*-methyl fulleropyrrolidine as a reference. In the case of **1**, excitation was effected at a number of different wavelengths, namely $\lambda = 330$, 400, 435, and 485 nm, which correspond to a C_{60} maximum, a (dpy)–Zn–(dpy) absorption maximum, nearly equal C_{60}/(dpy)–Zn–(dpy) absorption intensities, and a maximal absorption for the (dpy)–Zn–(dpy) fragment, respectively. Taken in concert, these studies thus served to confirm the observation of little appreciable emission from the (dpy)–Zn–(dpy) fragment (>99 % quenching in the case of excitation at $\lambda = 485$ nm) and the presence of appreciable C_{60}-centered fluorescence at $\lambda = 715$ nm (see Figure 1). Although the quantum yield of the latter emission was found to vary somewhat based on the specific choice of excitation wavelength and solvent, such findings are fully consistent with effective energy transfer from the (dpy)–Zn–(dpy) linker to the flanking C_{60} acceptor subunits. Notably, they provide support for a facile but not necessarily quantitative transduction of singlet excited states with efficiencies of up to 50 % (50 % in toluene, 41 % in THF, 33 % in benzonitrile). When excitation wavelengths of $\lambda_{ex} = 330$ and 400 nm are used, the quantum yields are close to 6.0×10^{-4} (i.e., identical to that of the C_{60} reference) in toluene and THF. With $\lambda_{ex} = 435$ nm the quantum yield is somewhat lower (i.e., 3.6×10^{-4}), and with an excitation wavelength of $\lambda_{ex} = 485$ nm, these quantum yields are around 3.0×10^{-4}, 2.5×10^{-4}, and 2.0×10^{-4} in toluene, THF, and benzonitrile, respectively.

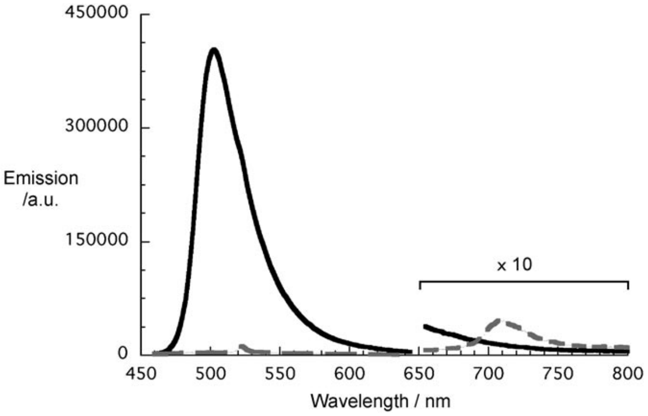
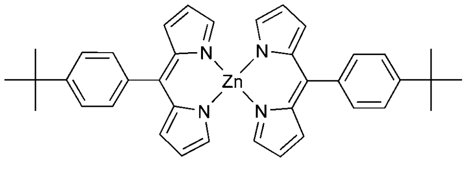


Figure 1. Fluorescence spectra of (dpy)–Zn–(dpy) (black) and **1** (grey) in THF at RT, with an identical optical absorbance intensity of 0.2 at an excitation of $\lambda = 480$ nm; please note that the $\lambda = 650$–800 nm region has been amplified by a factor of 10 to facilitate interpretation.

Further support for the proposed energy transfer mechanism came from an analysis of the excitation spectrum; here, the C_{60} fluorescence at $\lambda = 715$ nm was used. A spectrum was observed under these conditions that is in reasonable agreement with the ground-state absorption, including the $\lambda = 435$, 485, and 690 nm features that are ascribed to both constituents.

Additional support for the (dpy)–Zn–(dpy)-to-C_{60} energy transduction hypothesis came from monitoring the fluorescence lifetime of **1** at $\lambda = 715$ nm following excitation at $\lambda = 480$ nm. This linked complex failed to give any detectable fluorescence signal at $\lambda = 520$ nm (corresponding to (dpy)–Zn–(dpy) emission; vide supra) within our instrumental time resolution of 0.1 ns, a lifetime of 1.6 ns was observed for the emission at $\lambda = 715$ nm in all solvents. This lifetime matches that seen for the C_{60} reference and is thus fully consistent with the proposed energy-transfer process. Considering that the C_{60} fluorescence lifetime is not affected by the presence of (dpy)–Zn–(dpy), we postulate that yet another deactivation mechanism is operative in photoexcited form of **1**. It is also worth noting that quantum yield for the C_{60} emission following irradiation of the (dpy)–Zn–(dpy) linker is reduced compared with that obtained upon exclusive C_{60} excitation. On this basis, we conclude that an electron-transfer process could be competing with the proposed energy-transfer deactivation.

Conclusive information about the photoproducts, that is, electron versus energy transfer, came from transient absorption spectroscopy. As a predicate for studying linked system **1**, a differential spectrum was recorded immediately after subjecting C_{60} to excitation with a $\lambda = 387$ nm laser pulse; this produced a spectrum characterized by a broad absorption maximum at $\lambda = 880$ nm, which is attributed to the C_{60} singlet excited state ($E_{\text{singlet}} = 1.76$ eV), a species formed with a rate constant of $1 \times 10^{12}\,\text{s}^{-1}$. The features of the singlet excited state decay slowly ($8.0 \times 10^{8}\,\text{s}^{-1}$) through intersystem crossing to the energetically lower-lying triplet excited state ($E_{\text{triplet}} = 1.50$ eV), with a triplet quantum yield close to unity. In contrast, femtosecond transient absorption measurements of the control linker (dpy)–Zn–(dpy) (model compound **5**; see the Supporting Information) with excitation at $\lambda = 480$ nm revealed strong singlet–singlet features ($E_{\text{singlet}} = 2.47$ eV) that start to grow in immediately following photoexcitation.



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This fast process, with a half-life that varies from 9 to 22 ps depending on the solvent polarity, is followed by a much slower process. This latter slower-decaying component exhibits a lifetime that is typically in the order of thousands of picoseconds; however, its kinetics of decay vary strongly with solvent polarity. For example, in toluene the lifetime is as short as 80 ps, whereas in anisole, THF, and *ortho*-dichlorobenzene the lifetimes are 2300, 900 and 1700 ps, respectively. Mechanistically, we assign this process to an intersystem crossing.

In contrast with the above, photoexcitation of **1** at $\lambda = 480$ nm reveals a new transient spectrum that is distinctly different from the singlet or triplet features of the C_{60} and (dpy)–Zn–(dpy) constituents (see Figure 2), in addition to the typical transient bleaching of the excited (dpy)–Zn–(dpy) state seen upon irradiation of the linker alone. For instance, transient maxima at $\lambda = 510$ and 1005 nm are seen roughly 50 ps after the laser pulse. The $\lambda = 1005$ nm feature is a fingerprint absorption characteristic of the one-electron-reduced radical anion of C_{60}.[14] On the basis of comparison with the spectrum of the radiolytically generated one-electron-oxidized radical cation of (dpy)–Zn–(dpy), the $\lambda = 510$ nm feature is assigned to an oxidized bis(dipyrrinato)zinc linker. Thus, the observation of maxima at $\lambda = 510$ and 1005 nm is taken as unambiguous evidence for a fast intramolecular charge-separation process involving formation of a radical-ion-pair state.

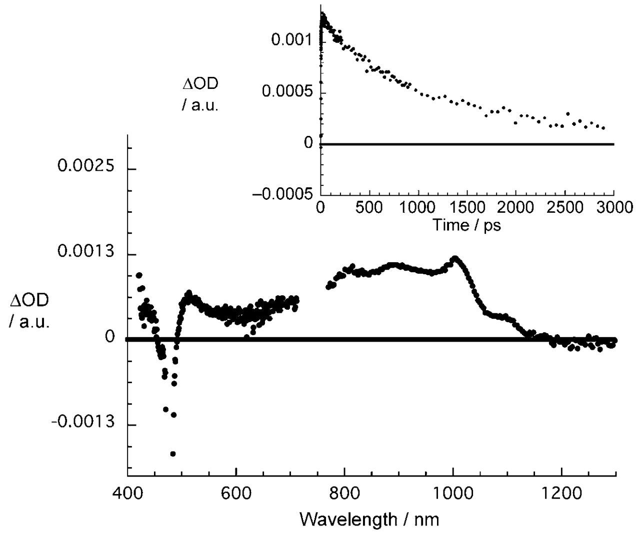

Figure 2. Differential absorption spectra (visible and near infrared) obtained upon femtosecond flash photolysis ($\lambda = 480$ nm) of **1** (ca. 1.0×10^{-6} M) in THF, 20 ps after the laser excitation, at RT. Inset: Time-absorption profile of the spectra shown above at $\lambda = 1005$ nm, reflecting the formation and decay of a radical ion pair state.

The radical-ion-pair state produced following $\lambda = 480$ nm photoexcitation is metastable and recombines on the time scale of several hundred picoseconds. Applying unimolecular fitting functions to the transitions in the near-infrared (i.e., one-electron-reduced radical anion of C_{60}) allowed the following radical-ion-pair-state lifetimes to be determined: 1130 ps in toluene (with $\lambda = 387$ nm photoexcitation), 1516 ps in anisole (with $\lambda = 387$ nm photoexcitation), 990 ps in THF (with $\lambda = 480$ nm photoexcitation), and 1290 ps in *ortho*-dichlorobenzene (with $\lambda = 480$ nm photoexcitation). Similar lifetimes were also derived from the analogous multiwavelength analysis of the $\lambda = 510$ nm transition (i.e., one-electron-oxidized radial cation spectrum of (dpy)–Zn–(dpy)); in this latter case, competing processes, such as energy transfer and intersystem crossing, hampered an accurate kinetic analysis.[16]

Analyzing the transient changes that are still present at the end of the charge-recombination process, namely, at around 3000 ps following excitation, reveals a reasonable agreement with the features that corresponds to the C_{60} triplet excited state, a species characterized by a maximum at $\lambda = 690$ nm. The same $\lambda = 690$ nm feature is also observed in complementary nanosecond experiments performed in toluene and THF. Thus, it appears that the immediate fate of the charge-separated species is not regeneration of the ground state of **1**, but rather a longer-lived triplet. Such a finding is, of course, fully consistent with the proposed initial charge-separation process.

Electrochemical experiments with **1** in dichloromethane provided thermodynamic insights into the competition between electron and energy transfer. By simply adding the first oxidation potential of (dpy)–Zn–(dpy) and the first reduction potential of C_{60}, the radical-ion-pair-state energy was determined to be 1.9 eV in dichloromethane. The C_{60} singlet excited state, as the other deactivation product of **1**, is around 1.76 eV. It is implicit that changing the solvent polarity from, for example, toluene to benzonitrile impacts the radical-ion-pair-state energy, whereas the singlet excited state energies of (dpy)–Zn–(dpy) and C_{60} remain invariant. In other words, electron transfer becomes increasingly favorable, in a thermodynamic sense, over energy transfer.

In summary, the use of a (dpy)–Zn–(dpy) linker allows the facile tethering of two C_{60} subunits and gives rise to an electronically coupled system that allows for effective charge separation following photoexcitation. This linker acts as a versatile redox relay and ensures the efficient mediation of charges across this unit. The ease of this approach leads us to propose that it can be used to produce a range of charge-separating and photovoltaic devices. In an effort to build on the present approach and create systems that might be capable of stabilizing the formation of longer-lived charged separated states, current work is focused on the synthesis of multicomponent donor-acceptor systems linked through (dpy)–Zn–(dpy) motifs.

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Keywords: electron transfer · fullerenes · supramolecular chemistry

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