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Synthesis and Photophysical Properties of Steroid-Linked Porphyrin–Fullerene Hybrids

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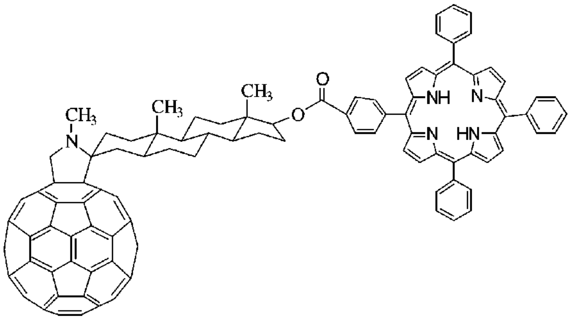
ABSTRACT



The photophysical properties of porphyrin-linked fullerene hybrids have generated significant interest, and a number of these hybrids synthesized by this group and others have been extensively characterized with respect to energy and charge-transfer processes that take place upon photoexcitation. Present studies of steroid-linked dyads demonstrate the extent to which through-bond effects operate in these systems.

The unique photophysical properties of C_{60} have been discussed extensively in the recent literature.[1] C_{60} has been shown to be an effective electron and energy acceptor toward a variety of photoactivated donors.[2] In particular, considerable attention has been devoted to the study of covalently linked porphyrin−fullerene hybrids.[3] Since these compounds are useful in the elucidation of energy transfer and charge separation processes and have potential application in photodynamic therapy,[4] a large variety of porphyrin−fullerene hybrids have been produced and studied by a number of groups including our own.[3,6−9]

Photoexcitation of porphyrin in these dyads leads to two competing processes. The first is energy transfer (ET), in

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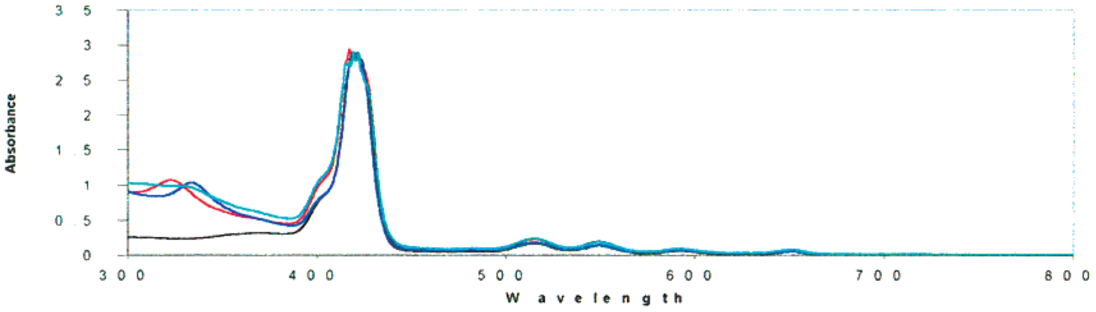


Figure 1. UV−vis spectrum of 20 μM **1**, **2**, **3**, and **4** in benzene.

which porphyrin transfers its excitation to C_{60}, generating a short-lived singlet excited state of C_{60} ($\tau = 1.3$ ns). Rapid intersystem crossing produces the long-lived triplet excited state of C_{60} ($\tau = 133\ \mu$s),[5] which transfers energy efficiently to $^3O_2$, generating $^1O_2$ ($^1\Delta_g$) with unity quantum yield.[1] The other competing process is charge separation (CS), in which electron transfer gives a porphyrin radical cation/fullerene radical anion pair that usually returns to the ground state through charge recombination (CR), but occasionally leads to the formation of fullerene triplets. To determine the circumstances under which one or the other or these competing processes is dominant, early work in the area made use of hybrids prepared by Diels−Alder cycloaddition[3a,b,d,e,g] or azomethine ylide addition of porphyrin derivatives to C_{60}.[3c,f]

From these studies, it was concluded that ground-state interactions between the porphyrin and fullerene moieties were governed by their distance of separation, which was fixed by the linker.[3a,g,6] For free base dyads, it was shown that energy transfer is favored in nonpolar solvents, while polar solvents or zinc-porphyrins favor the formation by electron transfer of an extremely long-lived ion pair state.[3a,g,4]

A variety of dyads, triads, and even very recently hexads[7] have been prepared to probe the details of these excited state processes. In particular, our group has studied a series of dyads with poly(ethylene glycol) and catechol-derived linkers.[8] These flexible linkers allow extremely close approach between the porphyrin and fullerene moieties. Evidence for intramolecular interactions was provided by strong fluorescence quenching and singlet oxygen sensitization. In some cases, metal ion complexation with the poly(ethylene glycol) crown ether mimic brought the two chromophores into even closer contact, thus facilitating electronic interaction according to fluorescence titration experiments. Very recently doubly linked, strapped "parachute" hybrids, in which the two chromophores are rigidly forced into very close proximity have been reported.[9] In these systems, the porphyrin fluorescence is almost totally quenched.

The extensive interactions between the two chromophores that have been observed to date have been attributed primarily to through-space interactions. The question naturally arises as to what extent through-bond effects can contribute to the conversation between the two chromophores in the excited state. The role of this mode of interaction in complex hexads has been discussed recently.[6] A dyad system in which the porphyrin and fullerene are rigidly separated by a large distance would therefore serve as a nice control in this area of research, allowing the contribution of through-bond effects to be elucidated.

Pursuant to this idea, a series of hybrids with steroid linkers (**1**, **2**, and **3**) was prepared. The synthetic approach was suggested by the work of Maggini and colleagues,[10] in which electronic interactions in steroid-linked ruthenium bipyridyl hybrids were examined. As large, rigid polycyclic frameworks, steroids are ideal linkers for constructing hybrids in

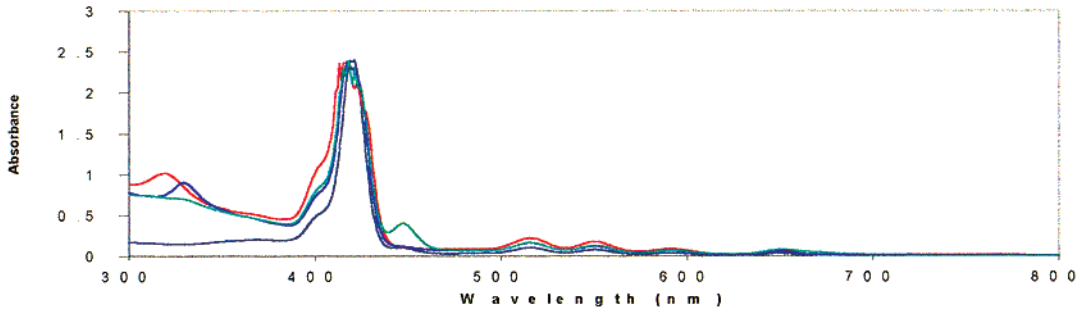
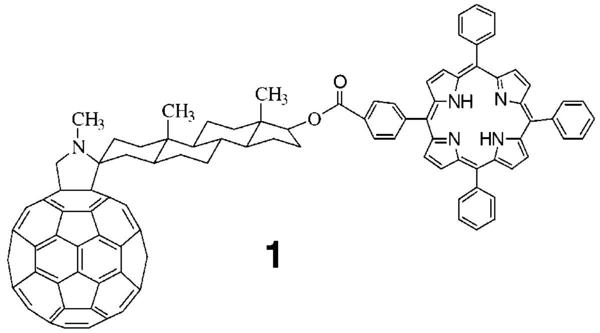


Figure 2. UV−vis spectrum of 20 μM **1**, **2**, **3**, and **4** in chloroform.



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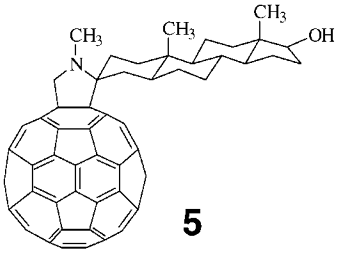

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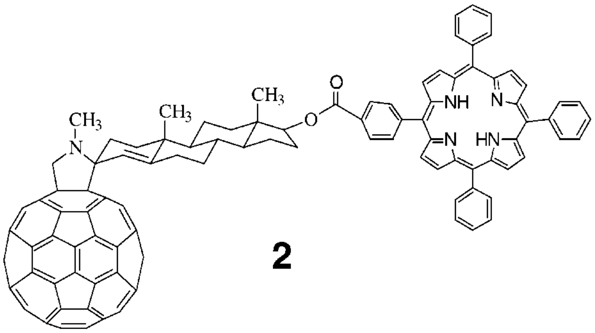

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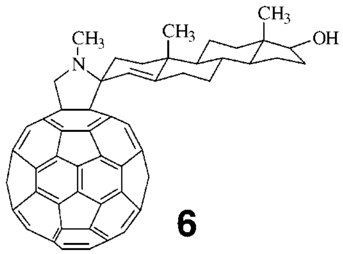

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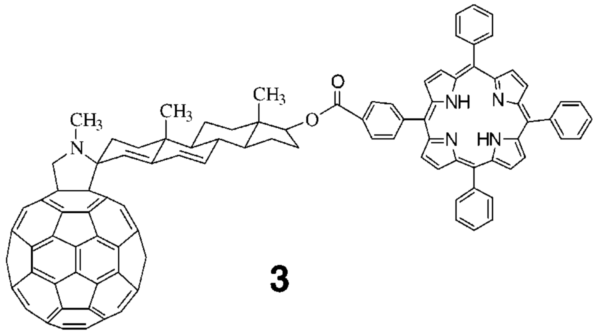

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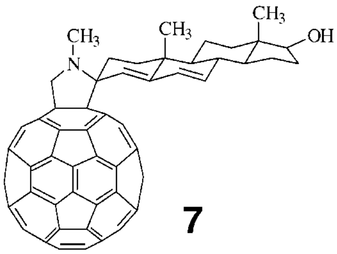

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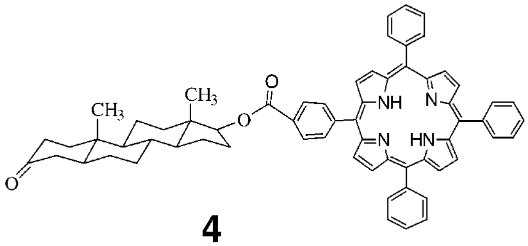

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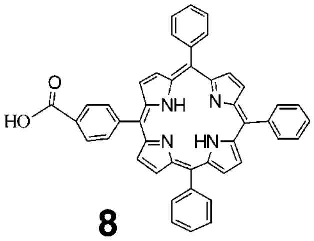

8

which the porphyrin and fullerene moieties are forced to be far apart in space (≈12 Å).

Synthesis of these hybrids began with the Prato reaction, which provides a facile route to the steroidal fulleropyrrolidine precursors **5**, **6**, and **7** via azomethine ylide addition to C_{60}.[11] These precursors are then linked to tetraphenylporphyrin carboxylic acid **8** through standard EDCI coupling.

It's noteworthy to point out that each of the hybrids obtained form this method was prepared as a mixture of diastereomers corresponding to the two possibilities of attachment at the spiro junction. Spectroscopic data were obtained on the nonseparated mixtures of **1**, **2**, and **3**, but the conclusions of this paper do not depend on having the pure isomers. Furthermore, given the spherical nature of C_{60}, its orientation with respect to the porphyrin moiety should not affect the excited state interactions of the dyads given the fixed separation of the two chromophores.

Results. The steady-state absorption spectra of **1**, **2**, and **3** in benzene (Figure 1) and chloroform (Figure 2) indicate insignificant electronic interactions between the chromophores in the ground state.

The fluorescence emission spectra of **1**−**3** were measured in benzene (Figure 3) and chloroform (Figure 4) at fixed optical density at the excitation wavelength, which was 550 nm. In benzene, the fluorescence of dyads **1**, **2**, and **3**, were quenched by 52%, 58%, and 71% respectively, relative to model compound **4**, indicating significant interaction between porphyrin singlet excited state and fullerene ground state. In the more polar solvent chloroform, the fluorescence quenching for the dyads relative to that of model compound

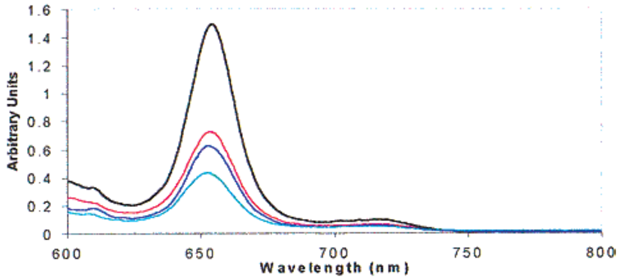

Figure 3. Fluorescence emission spectrum of 20 μM **1**, **2**, **3**, and **4** in benzene.

4 is slightly larger, 66%, 69%, and 74%, respectively, suggesting that electron transfer may be playing a key role in these interactions. This awaits verification by time-resolved fluorescence and transient absorption spectroscopy. Identical fluorescence quenching was observed with both diastereomers of dyad **5**.

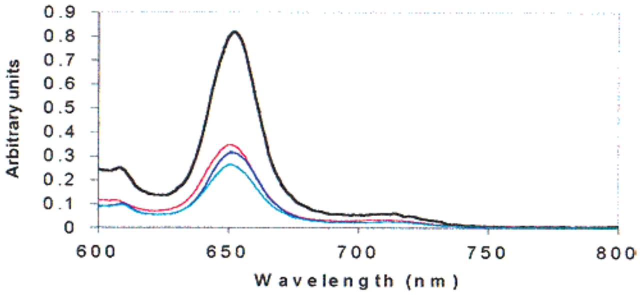

Figure 4. Fluorescence emission spectrum of 20 μM **1**, **2**, **3**, and **4** in chloroform.

To be certain that the observed interactions are intramolecular as opposed to intermolecular, the fluorescence emission spectrum of an equimolar mixture of **4** and **5** (20μM) was taken and was found to be indistinguishable from that of model compound **4**, also 20 μM, in both benzene (Figure 5) and chloroform (Figure 6).

Conclusion. This study shows that through-bond effects play a significant role in the interactions between the two chromophores in porphyrin−fullerene hybrids.[12] Through-space effects have been excluded in this study by employing steroidal linkers that rigidly maintain a large distance of separation between the porphyrin and fullerene moieties. The quenching of porphyrin fluorescence in these steroid-linked hybrids indicates that the two chromophores do indeed talk to each other in the excited state. Although the precise characterization of this dialogue awaits the results of transient and time-resolved studies, this result is surprising and significant. Ongoing research in the area of covalently linked porphyrin−fullerene hybrids has application to the design of agents for photodynamic therapy[13] and photosynthetic reaction center mimics, as well as further elucidation of the photophysics of C_{60} and its derivatives.

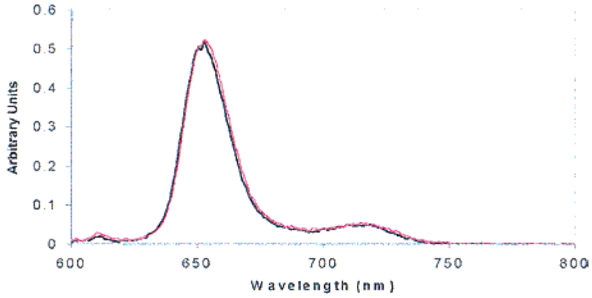

Figure 5. Fluorescence emission spectrum of **4** and an equimolar mixture of **4** and **5** in benzene (all 20 μM).

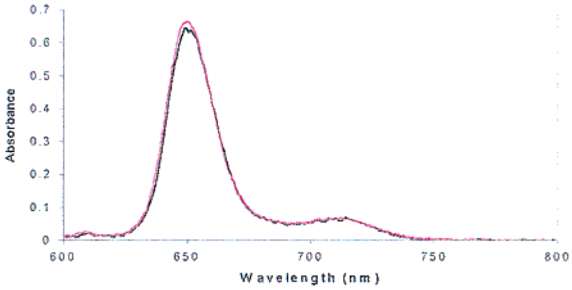

Figure 6. Fluorescence emission spectrum of **4** and an equimolar mixture of **4** and **5** in chloroform (all 20 μM).

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Supporting Information Available: ^{1}H NMR spectra of **1**−**8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[12] For related effects in a quite different system, see: Williams, R. M.; Koeberg, M.; Lawson, J. M.; An, Y.-Z.; Rubin, Y.; Paddon-Row, M. N.; Verhoeven, J. W. *J. Org. Chem.* **1996**, *61*, 5055−5062. See also: Maggini, M.; Guldi, D. M.; Mondini, S.; Scorrano, G.; Paolucci, F.; Ceroni, P.; Roffia, S. *Chem. Eur. J.* **1998**, 1992−2000.

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