Synthetic Approaches to a Variety of Covalently Linked Porphyrin−Fullerene Hybrids

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There is substantial interest in dyads in which C_{60} is covalently linked to electron donors, such as porphyrins, which absorb light strongly in the visible region. We present here the details of the syntheses of such compounds, which can be broadly organized into categories depending upon the nature of the linker joining the two chromophores. The structural aspects of intramolecular electronic interaction that we have sought to explore have dictated the synthetic strategies employed to generate these classes of molecules. Flexible glycol linkers were used to allow close approach between the fullerene and porphyrin, facilitating through-space interactions. These linkers also allowed studies of the effects of metal cation complexation. Naphthalene and alkyne linkers were used to examine the possible effects a conjugated or aromatic linker might have on photophysical properties. Finally, steroids were used as linkers in dyads expected to possess a large distance between the two chromophores, in which only through-bond interactions between the fullerene and porphyrin should be possible.

Introduction

The photophysical properties of covalently linked porphyrin−fullerene hybrids have been a focus of recent intense investigation. C_{60} has received a great deal of interest as an electron acceptor due to its high electron affinity and extremely low reorganization energy in electron-transfer processes, which promotes forward-electron transfer from photoexcited electron donors while simultaneously retarding back-electron transfer.[1] Potential applications of these dyads include use as photosensitizers in photodynamic therapy through generation of singlet molecular oxygen,[2] as well as applications in energy storage devices.[1a] A large variety of such donor−acceptor systems have been synthesized by a number of groups, including our own, and have proven useful in the elucidation of energy transfer and charge separation processes.[1,3] We have previously reported the photophysical characterization of a variety of such hybrids.[4]

Results and Discussion

All dyads, as well as most synthetic intermediates, were characterized by their ^{1}H NMR and UV−vis spectra and either FAB-MS or MALDI-MS. The ^{1}H NMR spectra were all consistent with the proposed structures. The ^{13}C NMR spectra for all Hirsch−Bingel (methanofullerene) and Prato (fulleropyrrolidine) addition products were consistent with [6,6]-closed linkages on the fullerene cage. The spectral evidence for the addition pattern of azafullerenes **12** and **13** is described below. Mass spectrometry showed molecular ion peaks for all compounds examined.

In our first efforts to gain insight into excited-state interactions between porphyrin and fullerene moieties in covalently linked hybrid systems, flexible poly(ethylene glycol) linkers were employed.[4a] These linkers allow extremely close approach of the two chromophores, as theoretical calculations suggested that conformations in which the porphyrin and fullerene moieties are in close proximity are preferred, attributed to van der Waals interactions. This unique type of interaction has been confirmed by Reed and co-workers, who showed that porphyrins readily form ordered cocrystals with fullerenes.[5] The efficient syntheses of these flexibly linked hybrids were accomplished by the convergent strategy outlined in Scheme 1.[4a] Sulfonium ylide addition to C_{60} and subsequent hydrolysis afforded methanofullerene carboxylic acid **1**[6] in high yield. DCC/DMAP coupling of **1** to mono-silyl-protected diols **3** and **4** in 5:1 bromobenzene/DMSO, followed by acidic deprotection, yielded synthons **7** and **8** in 40−76% yield. EDCI-mediated coupling of

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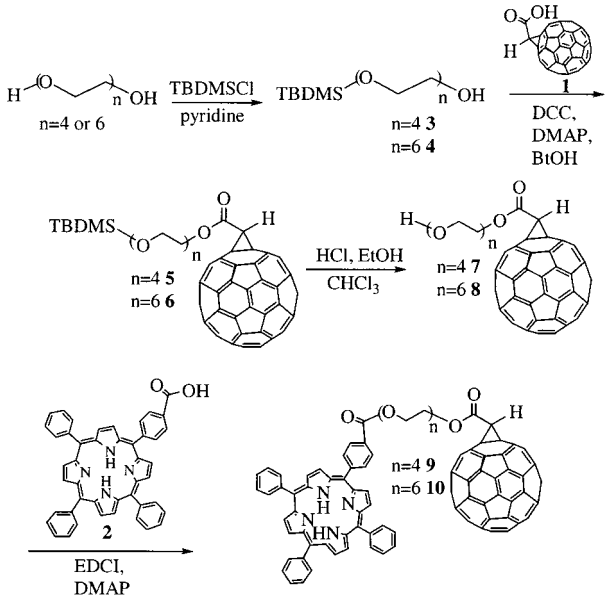
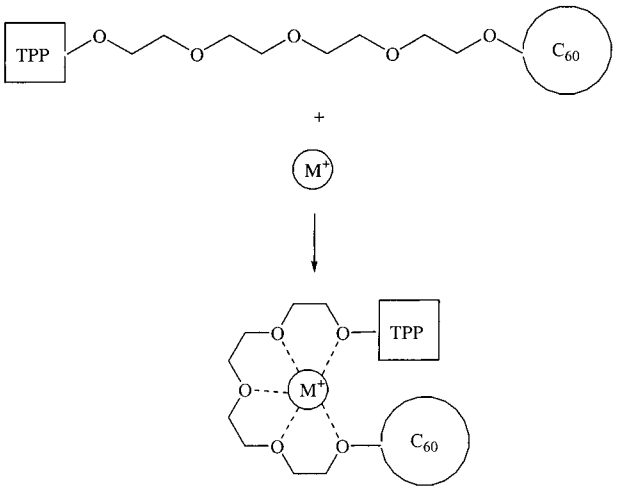
Scheme 1. Synthesis of Glycol-linked C_{60} Porphyrin Dyads



Scheme 2. Metal Ion Complexation

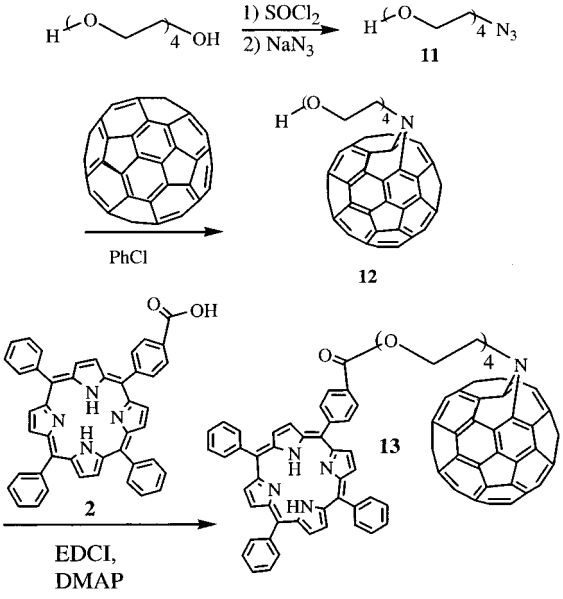


these synthons with 5-(4′-carboxyphenyl)-10,15,20-triphenylporphyrin **2**[7] in 1:1 dry CH_2Cl_2/CS_2 yielded hybrids **9** and **10** in 48−70% yield. The dyads were characterized using ^{1}H NMR, MS, UV−vis and fluorescence spectroscopy.

Complexation of hybrids **9** and **13** with metal cations resulted in open-chain crown-ether host−guest mimics.[4a] This approach, illustrated in Scheme 2, was exploited to bring the two chromophores into even closer proximity, as verified by computational studies.[4a] Complexation with Na^+ and K^+ was accomplished with NaSCN and KSCN in acetone. Indeed, stronger intramolecular electronic interactions were observed for the complexed hybrids, as evidenced by fluorescence quenching studies.

Compound **13**, representing the first aza-linked fullerene−porphyrin hybrid, was prepared to explore the effects of changing the nature of the linkage to the fullerene sphere on photophysics and complexation.[4a] Scheme 3 outlines the strategy employed in its synthesis. Monochlorination of tetraethylene glycol with thionyl

Scheme 3. Synthesis of Aza-Linked C_{60}−Glycol−Porphyrin Dyad



chloride and subsequent nucleophilic substitution with NaN_3 in DMSO generated mono-azide **11**, which was heated at reflux with C_{60} in chlorobenzene[8] to give the aza-linked synthon **12** in 55% yield. The ^{13}C NMR spectrum of **12** is consistent with a [5,6]-open aza-linked fulleroid structure as there are no peaks for fullerene sp^3 carbon atoms. This is in agreement with results of previous studies of azide additions to fullerenes.[9] Subsequent EDCI mediated coupling of **12** to **2** proceeded in 63% yield to yield hybrid **13**, which was characterized spectroscopically by ^{1}H NMR, MALDI-MS, and UV−vis. In particular, the ^{1}H NMR spectrum showed peaks attributable to the glycol linker between 3.5 and 4 ppm, as well as characteristic peaks for **2** between 7.5 and 9 ppm.

In pursuit of a porphyrin−fullerene hybrid with increased solubility and superior cation complexation abilities, hybrid **19** was prepared.[4b] The synthesis is outlined in Scheme 4. Catechol was first reacted with excess tetraethylene glycol mono-tosylate in the presence of potassium carbonate to generate **15**, which was subsequently monoprotected with trimethylsilyl chloride and coupled to **1** using the DCC/DMAP protocol, generating **17**. Hybrid **19** was generated after deprotection of **17** and EDCI-mediated coupling of **18** to **2**. While the dyad did not show any conformational reorganization in the presence of metal cations, as indicated by fluorescence quenching studies, it showed a surprisingly high quantum yield (0.40) for photosensitized formation of singlet oxygen.

Subsequent work sought to explore the effects of conjugated and aromatic linkers on the photophysics of fullerene−porphyrin hybrids. To this end, hybrids **23** and **27** were prepared using the strategy outlined in Schemes 5 and 6 in 16% and 20% yield, respectively.[4c] Mono-silyl protection of 2-butyn-1,4-diol was accomplished as in Scheme 1, while dihydropyran was employed for protection of 2,7-naphthalenediol as its mono-THP derivative. The attachment of porphyrin and fullerene moieties was

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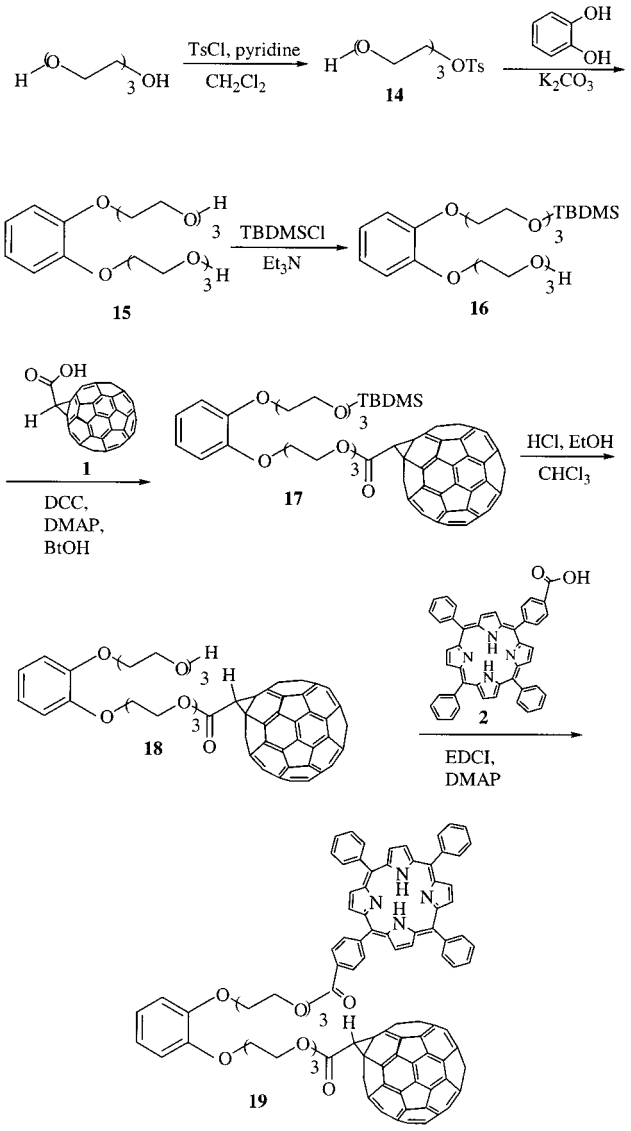
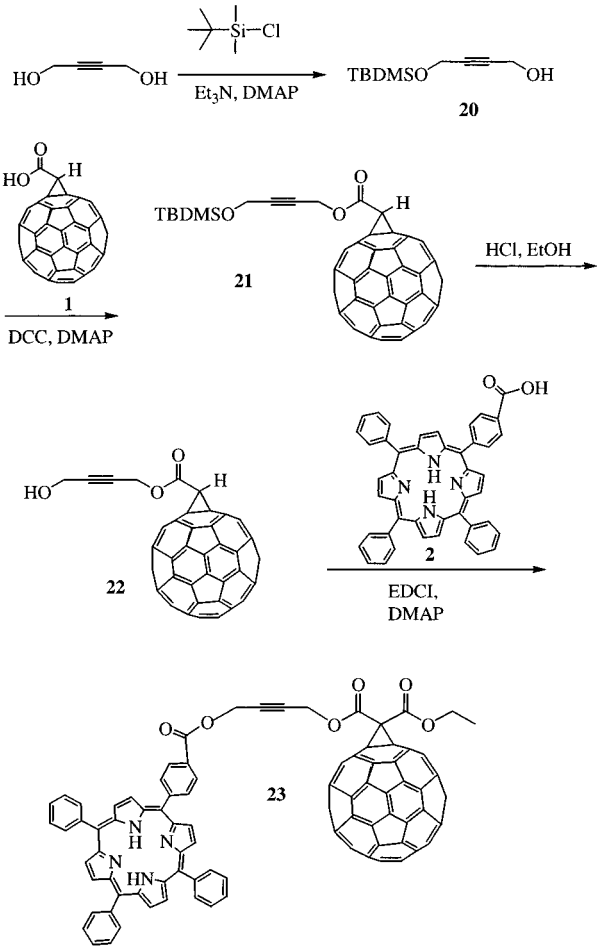
Scheme 4. Synthesis of Catechol-Linked C_{60}−Porphyrin Dyad



Scheme 5. Synthesis of Alkyne-Linked C_{60}−Porphyrin Dyad



accomplished using the methodology employed in the syntheses of **9** and **10**. Dyads **23** and **27** were characterized by ^{1}H NMR, ^{13}C NMR, MALDI-MS, UV−vis, and fluorescence spectroscopy. Surprisingly, significant quenching of porphyrin fluorescence was observed in **23** and **27**, indicating substantial interaction between the chromophores in the excited state.[4d] Computational studies indicated that these linkers were sufficiently flexible to permit close approach between the porphyrin and fullerene moieties.

Seeking to explore the contribution of through-bond interactions to the excited-state conversion between the porphyrin and fullerene moieties, a series of rigidly linked hybrids with a large distance of separation between fullerene and porphyrin moieties were needed to control for through space effects. To this end, hybrids **34**−**36** were prepared[4d] using a synthetic approach inspired by Maggini's work on steroid-linked ruthenium *tris*-bipyridyl fulleropyrrolidines.[10] The steroid-derived linkers used in that study, namely 3-keto-17-ols, were thought to be ideal candidates for our purposes, providing a rigid polycyclic spacer capable of separating covalently linked donor (porphyrin) and acceptor (fullerene) well beyond the range of van der Waals contact. This approach was modeled on the classic work of Closs and co-workers, who showed that long-range electron transfer occurred in systems where the donor and acceptor were separated by a steroid linker.[11] However, because of the possibilities of *syn* and *anti* conformations at the porphyrin ester linkage, the porphyrin and fullerene chromophores in these dyads may actually be in fairly close proximity or very far apart. Insight II calculations place the center to center distance between the porphyrin and the fullerene moieties in the two conformations, at 6.55 and 21.94 Å, respectively.[12] In fact, the computations predict that the *syn* conformation, which is energetically unfavorable in most esters, is actually significantly more stable, due to van der Waals attraction between the fullerene and the porphyrin[5] (the distance from the center of the porphyrin to the nearest point on the surface of the fullerene in the *syn* conformer is just over 3 Å). While the actual conformational population in these steroid-linked dyads in solution is not known, the fact that the porphyrin fluorescence is quenched by only 52−74%,[4d] much less than in the flexibly linked dyads, suggests that these systems do not exist solely in the *syn* conformation.

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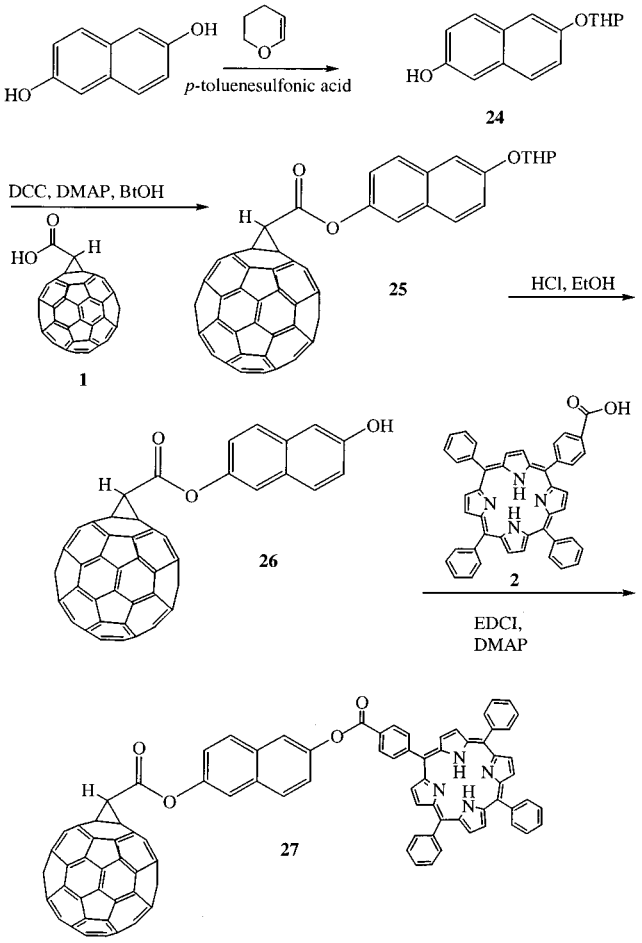
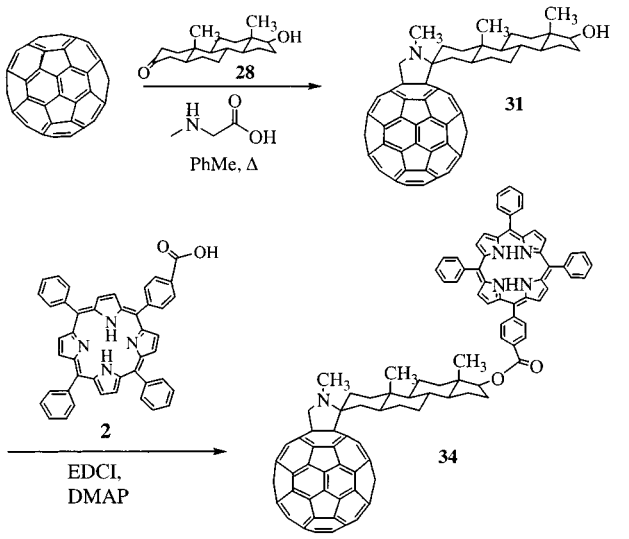
Scheme 6. Synthesis of Naphthalene-Linked C_{60}–Porphyrin Dyad

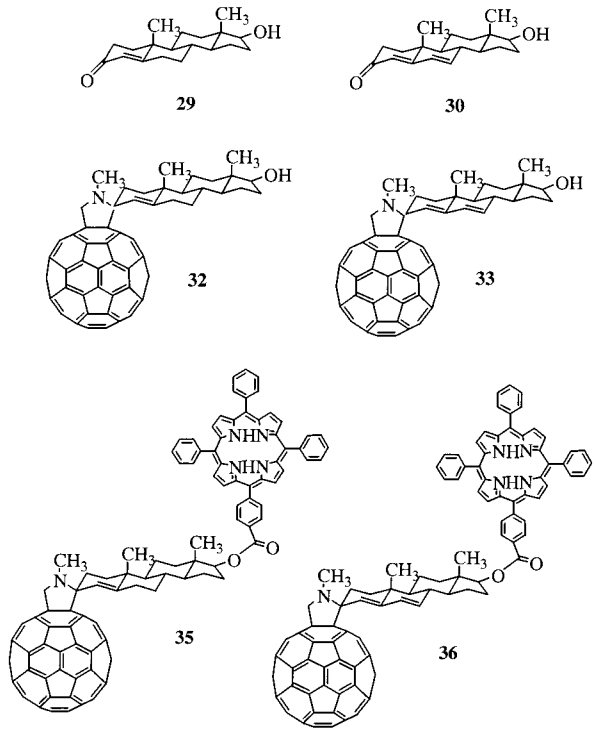


Scheme 7. Synthesis of Steroid-Linked C_{60}–Porphyrin Dyads



As outlined in Scheme 7, the synthetic route to steroid-linked dyad **34** involved the addition of an azomethine ylide derived from steroid precursor **28** to C_{60} in refluxing toluene, yielding fulleropyrrolidine synthon **31** in 31% yield (see Scheme 7). Similar Prato additions were carried out using unsaturated steroids **29** and **30** to give analogous fulleropyrrolidines **32** and **33** (see Scheme 8). Consistent with the mechanism of addition, increased conjugation in the steroid ketone decreased the yield and

Scheme 8. Steroid-Linked C_{60}–Porphyrin Dyad Structural Intermediates



facility of the Prato reaction. Reaction products in all cases were generated as a 3:1 mix of diastereomers, corresponding to the two possible orientations at the spiro ring junction, as determined by ^{1}H NMR and HPLC analysis. Subsequent EDCI-mediated union of these synthons with **2** as in Scheme 1 yielded hybrids **34**–**36** as a mix of diastereomers in 12–25% yield. These isomeric mixtures were characterized by ^{1}H NMR, MALDI-MS, UV–vis, and fluorescence spectroscopy. The dyads displayed ^{1}H NMR spectra with characteristic peaks for their respective steroid linkers between 1 and 2 ppm, peaks between 3 and 4.5 ppm attributable to the protons from the fulleropyrrolidine, as well as peaks between 7.5 and 9 ppm derived from porphyrin **2**. An attempt was made to chromatographically separate the diastereomers of **34**, the most abundant of these steroidal dyads, but this was only partially successful, as both ^{1}H NMR and HPLC analysis of fractions indicated only moderate enrichment of one or the other of the diastereomers. No difference in the fluorescence spectra or intensities of these enriched fractions was seen, suggesting no significant difference in photophysical properties of the two diastereomers.

Ongoing interest in soluble fullerenes, as well as the difficulty of working with the relatively insoluble hybrids that have thus far been made, prompted the use of carboxylic acid **37** in place of **1**. The synthesis of **37** has been reported by Diederich and co-workers.[13] Triethylene and tetraethylene glycol linked hybrids **40** and **41** were prepared by the procedure outlined in Scheme 9.[4e] Increased solubility of **37** led to higher coupling yields and enabled more facile collection of spectroscopic data. Also, use of an excess of the diol precursor in the DCC coupling step avoided the need for protecting groups, in

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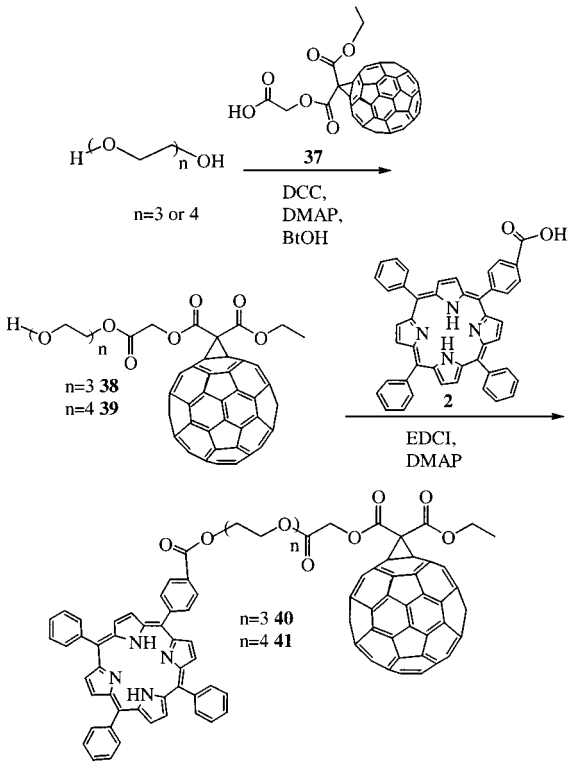
Scheme 9. Synthesis of Glycol-Linked C_{60}−Porphyrin Dyads



contrast to the protection-deprotection technique applied in the synthesis of analogous hybrids **9** and **10**. Dyads **40** and **41** were characterized by ^{1}H NMR, FAB-MS, UV−vis, and fluorescence spectroscopy (Scheme 9). Not surprisingly, dyads **40** and **41** have been shown to exhibit photophysical properties similar to those of related hybrids **9** and **10**,[4a] in particular almost complete quenching of porphyrin fluorescence and very rapid generation of charge-separated states. Details will be reported elsewhere.

Conclusions

Over the course of research into the dynamics of excited-state interactions in porphyrin−fullerene hybrids, a variety of synthetic approaches have been developed to generate classes of compounds suited to the exploration of theoretical questions that have arisen as our knowledge of these interactions has grown.[14] The various schema presented here provide access to a large array of flexibly and rigidly linked hybrid systems. Along with the host of other synthetic approaches that have recently been developed, including the synthesis by our group of a semirigid "parachute-shaped" hybrid via Bingel chemistry,[4f] the possibilities are indeed great for the generation of a myriad of novel hybrid systems for the further elucidation of energy transfer and charge separation processes occurring in these unique donor acceptor hybrids, and larger supramolecular complexes derived from them.

Experimental Section

General Methods. All reactions were performed under dry nitrogen. All glassware was dried in an oven at 200 °C prior to use. C_{60} was obtained from MER corporation; all other chemicals were purchased from Aldrich. Reaction solvents were distilled over calcium hydride prior to use. Flash chromatography was performed using 200−300 mesh silica gel purchased from Natland. Concentration of reaction mixtures was performed on a Büchi rotary evaporator. ^{1}H NMR spectra were obtained on Varian 200-MHz and 300-MHz spectrometers, with ^{13}C NMR at 75 MHz and 125 MHz. Peaks are reported relative to TMS. UV−vis spectra were recorded on a Perkin-Elmer Lambda 2 spectrophotometer. Fluorescence spectra were recorded on a Perkin-Elmer LS-50 fluorimeter. MALDI mass spectra were recorded on a Kratos Kompact MALDI I V4.0.0 spectrometer. FAB-MS were obtained at the Michigan State University Mass Spectrometry Facility, which is supported, in part, by a grant (DRR-00480) from the Biotechnology Research Technology Program, National Center for Research Resources, National Institutes of Health.

Mono-silyl Protection of Diols: General Procedure for Preparation of 3, 4, 16, and 20. *tert*-Butyldimethylsilyl chloride (1 equiv) was added in a dropwise manner to a solution of the appropriate diol (5 equiv), 4-(dimethylamino)-pyridine (0.2 equiv), and triethylamine (1 equiv) in dry CH_2Cl_2. After completion of the reaction, the mixture was washed with water and saturated aqueous ammonium chloride and then dried over sodium sulfate. The solvent was removed in vacuo, and the products were purified by column chromatography on silica. **Compound 3**: yield 72%; eluant ethyl acetate; TLC R_f = 0.5 (ethyl acetate); ^{1}H NMR ($CDCl_3$, 200 MHz) 1.0−1.1 (21H, m), 2.8 (1H, bs), 3.5−4.0 (16H, m); ^{13}C NMR ($CDCl_3$, 50 MHz) 12.6, 18.3, 62.1, 64.0, 71.3, 71.4, 73.6. **4**: yield 46%; eluant ethyl acetate; TLC R_f = 0.3 (ethyl acetate), ^{1}H NMR ($CDCl_3$, 200 MHz) 0.0 (6H, s), 0.8 (9H, s), 3.5−3.9 (24H, m); ^{13}C NMR ($CDCl_3$, 50 MHz) 26.5, 62.2, 63.2, 70.9, 71.1, 73.1. **16**: yield 33%; eluant ethyl acetate; TLC R_f = 0.8 (2:8 methanol/ethyl acetate); ^{1}H NMR ($CDCl_3$, 200 MHz) 0.0 (6H, s), 0.8 (9H, s), 3.0 (1H, s), 3.4−4.2 (24H, m), 6.8 (4H, s); ^{13}C NMR ($CDCl_3$, 50 MHz) 4.6, 26.5, 62.1, 63.2, 69.4, 70.3, 70.9, 71.3, 73.1, 115.6, 122.1. **20**: yield 72%; eluant 3:2 ethyl acetate/petroleum ether; TLC R_f = 0.7 (3:2 ethyl acetate/petroleum ether); ^{1}H NMR ($CDCl_3$, 200 MHz) 0.1 (6H, s), 0.9 (9H, s), 3.3 (1H, s), 4.2 (2H, s), 4.3 (2H, s).

DCC/DMAP Coupling of Methanofullerenecarboxylic Acid 1 to Protected Alcohols: General Procedure for Preparation of 5, 6, 17, 21, and 25. A 5:1 mixture of bromobenzene/DMSO was added to an Ar-purged flask containing **1** (1 equiv), 4-(dimethylamino)pyridine (0.2 equiv), 1-hydroxybenzotriazole hydrate (1.1 equiv), and 1,3-dicyclohexylcarbodiimide (3 equiv). The solution was sonicated for 30 min. The appropriate monoprotected alcohol (3 equiv) was added, and the reaction was held at 50 °C with constant stirring for 16 h. Bromobenzene was removed in vacuo, and the mixture was diluted with $CHCl_3$. Oxalic acid (10%) in methanol was added, and the mixture was sonicated for 1 min. The resulting solution was washed with water, 10% $CaSO_4$, and brine and dried over sodium sulfate. The solvent was removed in vacuo, and the residue was dissolved in CS_2, filtered, and evaporated in vacuo to obtain the corresponding ester in the form of shiny brown plates. **Compound 5**: yield 47%; ^{1}H NMR. **6**: yield 41%. **17**: yield 50%; ^{1}H NMR ($CDCl_3$, 200 MHz) 0.0 (6H, s) 0.8 (9H, s) 3.4−4.3 (22H, m) 4.6 (2H, t) 4.8 (1H, s) 6.8 (4H, s); MALDI-MS (M^+ = 1255.6, calcd = 1249.6) **21**: yield 53%; ^{1}H NMR ($CDCl_3$, 200 MHz) 0.1 (6H, s) 0.8 (9H, s) 4.3 (2H, s), 4.8 (1H, s) 5.1 (2H, s). **25**: yield 49%.

Removal of the Protecting Group: General Procedure for Preparation of 7, 8, 18, 22, and 26. The appropriate protected alcohol was stirred in a 5:1:0.25 CH_2Cl_2−0.05 N HCl/EtOH−CS_2 solution at room temperature for 8 h. The resulting solution was diluted with CH_2Cl_2 and extracted with water and brine, and the solvent was removed in vacuo. The residue was subjected to flash chromatography on silica to yield the corresponding alcohol. **7**: Yield 95+%; eluant 5% acetic acid/chloroform; TLC R_f = 0.3 (5% acetic acid/chloroform); ^{1}H NMR ($CDCl_3$, 200 MHz) 3.4−4.2 (16H, m), 4.6 (1H, t), 4.9 (1H, s). **8**: yield 95+%; eluant 5% acetic acid/chloroform; TLC R_f = 0.2 (5% acetic acid/chloroform). **18**: yield 52%; eluant chloroform; TLC R_f = 0.4 (20% acetic acid/toluene. **22**: yield 95+%; eluant

(14) Schuster, D. I. *Carbon* **2000**, *38*, 1607.

chloroform; TLC $R_f = 0.2$ (chloroform), characterization by ^{1}H NMR ($CDCl_3$, 200 MHz) 4.4 (2H, s), 4.8 (1H, s), 5.1 (2H, s). **26**: yield 95+%; eluant chloroform; TLC $R_f = 0.2$ (chloroform); ^{1}H NMR ($CDCl_3$, 200 MHz) 5.0 (1H, s), 7.1 (1H, d), 7.3 (1H, d), 7.6−7.7 (3H, m), 7.9 (1H, s), 9.3 (1H, s).

EDC-Mediated Coupling of Fullerene Synthons to Porphyrincarboxylic Acid 2: General Procedure for Preparation of 9, 10, 13, 19, 23, 27, 34−36, 40, and 41. A solution of fullerene synthon (1 equiv) in CS_2 was added to a solution of porphyrin **2** (1.01 equiv), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (1.01 equiv), and 4-(dimethylamino)-pyridine (1.01 equiv) in absolute CH_2Cl_2 at room temperature. The mixture was stirred for 12 h, diluted with CH_2Cl_2, washed with saturated aqueous ammonium chloride, and brine, dried over sodium sulfate, and evaporated to give the crude product, which was purified by flash chromatography on silica to give the pure dyad. **Compound 9**: yield 53%; eluant chloroform; TLC $R_f = 0.2$ (chloroform); ^{1}H NMR ($CDCl_3$, 200 MHz) 3.5−4.0 (16H, m), 4.7 (1H, s), 7.5−9 (27H, m); FAB-MS (M^+ = 1594.4, calcd = 1594.3). **10**: yield 60%; eluant chloroform; TLC $R_f = 0.1$ (chloroform); ^{1}H NMR ($CDCl_3$, 200 MHz) 3.4−4.0 (24H, m), 4.7 (1H, s), 7.7−9.0 (27H, m); MALDI-MS (M^+ = 1683.8, calcd = 1682.4). **13**: yield 53%; eluant 10% acetic acid/chloroform; TLC $R_f = 0.65$ (chloroform); ^{1}H NMR ($CDCl_3$, 200 MHz) 3.4−4.2 (16H, m), 4.6 (1H, s), 7.5−9 (27H, m); FAB-MS (M^+= 1683.8). **19**: yield 51%; eluant 20% acetic acid/toluene; TLC $R_f = 0.56$ (20% acetic acid/toluene); ^{1}H NMR ($CDCl_3$, 200 MHz) 3.5−4.3 (18H, m), 4.5−4.7 (6H, m), 4.8 (1H, s), 6.9 (4H, m), 7.7−8.9 (27H, m); MALDI-MS (M^+ = 1777.7, calcd = 1776.3). **23**: yield 26%; eluant chloroform; TLC R_f = 0.4 (chloroform); ^{1}H NMR ($CDCl_3$, 200 MHz) 4.6 (1H, s), 5.2−5.2 (2H, d), 5.3 (2H, d), 7.7−8.9 (27H, m); ^{13}C NMR 14.1, 22.7, 29.4, 38.2, 53.8, 61.6, 70.0, 70.5, 72.9, 120.4, 126.7, 127.8, 128.2, 134.5, 142.0, 143.4, 144.3, 144.9; MALDI-MS (M^+ = 1488.1, calcd = 1487.5). **27**: yield 20%; eluant chloroform; TLC R_f = 0.45 (chloroform); ^{1}H NMR ($CDCl_3$, 200 MHz) 4.9 (1H, s), 7.5−7.6 (2H, m), 7.7 (10H, m), 8.0 (2H, m), 8.2 (9H, m), 8.4 (1H, d), 8.6 (1H, d), 8.9 (8H, m); ^{13}C NMR ($CDCl_3$, 125 MHz) 28.7, 38.8, 69.7, 70.3, 120.5, 126.8, 127.8, 128.4, 128.6, 130.9, 131.1, 134.6, 134.9, 136.3, 140.77, 140.9, 141.8, 141.9, 142.1, 142.6, 143.0, 143.4, 143.7, 144.4, 144.8, 144.9, 145.0, 145.4, 148.6, 148.2, 165.3, 166.1; MALDI-MS (M^+ = 1556.9, calcd = 1561.6) **34**: yield 14%; eluant 1:10 ethyl acetate/toluene; TLC $R_f = 0.4$ (1:10 ethyl acetate/toluene); ^{1}H NMR ($CDCl_3$, 200 MHz) 0.8−2.2 (28H, m), 2.9 (3H, s), 4.6 (2H, s), 7.7−9.0 (27H, m). **35**: yield 12%; eluant 1:10 ethyl acetate/toluene; TLC $R_f = 0.4$ (1:10 ethyl acetate/toluene); ^{1}H NMR ($CDCl_3$, 200 MHz) 0.8−2.1 (25H, m) 2.8 (2H, s) 4.5 (2H, s) 5.7 (1H, s) 7.7−9.0 (27H, m). **36**: yield 10%; eluant 1:10 ethyl acetate/toluene; TLC R_f = 0.4 (1:10 ethyl acetate/toluene); ^{1}H NMR ($CDCl_3$, 200 MHz) 0.8−2.2 (21H, m), 2.8 (3H, s), 4.5 (2H, s), 5.6−5.9 (2H, m), 6.1 (1H, m), 7.7−9.0 (27H, m). **40**: yield 41%; eluant 1:9 ethyl acetate/toluene; TLC $R_f = 0.4$ (1:9 ethyl acetate/toluene); ^{1}H NMR ($CDCl_3$, 200 MHz) 1.5 (3H, t), 3.6−4.0 (8H, m), 4.3−4.7 (6H, m), 4.9 (2H, s), 7.6−8.9 (27H, m); FAB-MS (M^+ = 1745.1, calcd = 1745.8). **41**: yield 47%; eluant 1:10 ethyl acetate/toluene; TLC $R_f = 0.4$ (1:10 ethyl acetate/toluene); ^{1}H NMR ($CDCl_3$, 200 MHz) 1.5 (3H, t), 3.6−4.0 (12H, m), 4.3−4.7 (6H, m), 4.9 (2H, s), 7.7−9.0 (27H, m); FAB-MS (M^+= 1788.3, calcd = 1789.8).

Preparation of Tetraethylene Glycol Mono-azide 11. Thionyl chloride (9 g) was added to a solution of tetraethylene glycol (15 g) dissolved in dry toluene (70 mL) over 1 h. The reaction mixture was then heated at reflux under argon for 2 h. After evaporation of the solvent in vacuo, 20 mL of dry toluene was added, and again the solution was evaporated to dryness. Purification by flash chromatography (SiO_2, CH_2Cl_2, followed by 5% CH_3OH/ethyl acetate) provided 8.3 g of an oil (51%). To a solution of the presumed monochloro derivative in DMSO (10 mL) was added NaN_3 (800 mg), and the mixture was heated at 60 °C for 20 h. After cooling, the mixture was poured into 100 mL of water and extracted with CH_2Cl_2 (5 × 20 mL); the combined extracts were dried over sodium sulfate and evaporated to furnish 700 mg of a tan oil (68%). Purification of the product was accomplished by passing through a plug of silica to yield **11**, which was characterized as follows: ^{1}H NMR ($CDCl_3$, 200 MHz) 2.9 (1H, s), 3.3−3.7 (16H, m); ^{13}C NMR ($CDCl_3$, 50 MHz) 41.5, 51.2, 62.1, 70.5, 70.8, 71.1, 73.0.

Synthesis of Azafullerene 12. Mono-azide **11** dissolved in 20 mL of chlorobenzene was added over 1 h to a solution of C_{60} (500 mg) in refluxing chlorobenzene (300 mL). Heating was continued for 24 h, after which time the solution was evaporated in vacuo. The product was purified (SiO_2, benzene, then CH_2Cl_2) to afford 70 mg of **12** (55% based on recovered C_{60}), which was characterized as follows: ^{1}H NMR ($CDCl_3$, 200 MHz) 3.6−4.4 (16H, m); ^{13}C NMR ($CDCl_3$, 125 MHz) 52.5, 71−72 (5 peaks), 131.3, 138−149 (29 peaks), 167.1; MALDI-MS (M^+= 913.7, calcd = 911.9).

Preparation of Triethylene Glycol Monotosylate 14. *P*-Toluenesulfonyl chloride (1 equiv) dissolved in dry CH_2Cl_2 was added in a dropwise manner to a solution of triethylene glycol (1 equiv) and pyridine (1 equiv) in dry CH_2Cl_2 at 0 °C. After complete addition of tosyl chloride, the reaction mixture was stirred for 3 h at room temperature, subsequently extracted with 5% aqueous HCl, saturated aqueous sodium bicarbonate, and water, and dried over sodium sulfate, and the solvent was removed under reduced pressure. The crude product was purified (SiO_2, ethyl acetate, TLC $R_f = 0.4$) to afford the desired product **14** (54%), which was characterized as follows: ^{1}H NMR ($CDCl_3$, 200 MHz) 2.4 (3H, s), 3.5−4.2 (12H, m), 7.3 (2H, d), 7.8 (2H, d); ^{13}C NMR ($CDCl_3$, 50 MHz) 22.1, 62.1, 69.1, 69.7, 70.7, 71.2, 72.9 128.4, 130.3.

Preparation of Glycol-Derived Catechol 15. Catechol (1 equiv) in dry acetone containing K_2CO_3 was heated at reflux for 15 h with triethylene glycol monotosylate **14** (2 equiv). The mixture was filtered, the solvent was removed under reduced pressure, and the crude product was redissolved in ether, washed with 5% aqueous NaOH and water, dried over sodium sulfate, and chromatographed (SiO_2, 2:8 methanol: ethyl acetate, TLC $R_f = 0.5$) to afford the desired product **15** (55%), which was characterized as follows: ^{1}H NMR ($CDCl_3$, 200 MHz) 3.1 (2H, s), 3.5−4.3 (24H, m), 6.9 (4H, s); ^{13}C NMR ($CDCl_3$, 50 MHz) 62.2, 69.5, 70.3, 71.0, 71.4, 73.1, 115.6, 122.2.

THP Protection: Synthesis of 24. Dihydropyran (1.1 equiv) was added in a dropwise manner to *p*-toluenesulfonic acid (0.2 equiv) and 2,7-dihydroxynaphthalene (1 equiv) in dry CH_2Cl_2. After completion, the reaction mixture was washed with water and saturated aqueous ammonium chloride and then dried over sodium sulfate. The solvent was removed in vacuo, and the product was purified by flash chromatography (SiO_2; 3:2 ethyl acetate/petroleum ether). **24**: yield 76%; R_f = 0.7 (3:2 ethyl acetate/petroleum ether); ^{1}H NMR ($CDCl_3$, 200 MHz) 1.2−1.9 (6H, m), 3.5 (2H, t), 7.1 (3H, d), 7.6 (2H, t), 8.1 (1H, s), 9.6 (1H, s).

Prato Addition of Steroidal Azomethine Ylides to C_{60}: General Procedure for Preparation of 31−33. A solution of C_{60} (1 equiv), sarcosine (2 equiv), and the appropriate steroid ketone (**28**−**30**) (5 equiv) was heated at reflux in toluene for 12 h. The solvent was removed in vacuo, and the product was purified by flash chromatography (SiO_2, 1:4 ethyl acetate/toluene). **Compound 31:** yield 31%; TLC $R_f = 0.3$ (1:4 ethyl acetate/toluene); ^{1}H NMR ($CDCl_3$, 200 MHz) 0.8−2.2 (28H, m), 3.0 (3H, s), 4.6 (2H, s). **32**: yield 22%; TLC $R_f = 0.3$ (1:4 ethyl acetate/toluene); ^{1}H NMR ($CDCl_3$, 200 MHz) 0.8−2.1 (25H, m), 2.8 (2H, s), 4.6 (2H, s), 5.7 (1H, s). **33**: yield 20%; TLC $R_f = 0.3$ (1:4 ethyl acetate/toluene); ^{1}H NMR ($CDCl_3$, 200 MHz) 0.8−2.2 (21H, m), 2.9 (3H, s), 4.6 (2H, s), 5.6−5.9 (2H, m), 6.2 (1H, m).

DCC/DMAP Coupling to Diols: Preparation of 38 and 39. A 5:1 mixture of bromobenzene/DMSO was added to an Ar-purged flask containing **37** (1 equiv), 4-(dimethylamino)-pyridine (0.2 equiv), 1-hydroxybenzotriazole hydrate (1.1 equiv), and 1,3-dicyclohexylcarbodiimide (5 equiv). The diol (10 equiv) was added, and the reaction was held at 50 °C with constant stirring for 16 h. Bromobenzene was removed in vacuo, and the mixture was diluted with $CHCl_3$. After addition of 10% oxalic acid in methanol, the mixture was sonicated for 1 min. The resulting solution was washed with water, 10% $CaSO_4$, and brine. After being dried over sodium sulfate, the solvent was removed in vacuo. The residue was purified by

flash chromatography (SiO_2, 1:9 ethyl acetate/toluene). **38**: yield 61%; TLC $R_f = 0.3$ (1:9 ethyl acetate/toluene); ^{1}H NMR ($CDCl_3$, 200 MHz) 1.5 (3H, t), 3.5−4.1 (10H, m), 4.4 (2H, t), 4.6 (2H, q), 5.0 (2H, s). **39**: yield 64%; TLC $R_f = 0.3$ (1:9 ethyl acetate/toluene); ^{1}H NMR ($CDCl_3$, 200 MHz) 1.5 (3H, t), 3.5−3.9 (14H, m), 4.4 (2H, t), 4.6 (2H, q), 5.0 (2H, s).

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Supporting Information Available: Copies of ^{1}H NMR for all new compounds, as well as ^{13}C NMR and mass spectral data where appropriate. This material is available free of charge via the Internet at http://pubs.acs.org.

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