

## Synthesis and Cation-Mediated Electronic Interactions of Two Novel Classes of Porphyrin–Fullerene Hybrids

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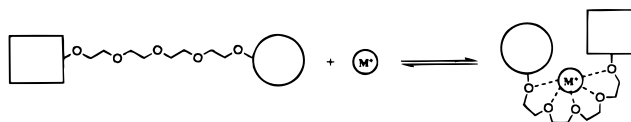
Received February 14, 1997

The unique photophysical properties of C<sub>60</sub> have generated significant research focused on its use as the acceptor in covalently bound donor–acceptor pairs.<sup>1</sup> In particular, photophysical properties of porphyrin-linked C<sub>60</sub> hybrids have received considerable attention.<sup>2</sup> It has been shown that intramolecular electron transfer from the porphyrin to C<sub>60</sub> to generate ion pairs occurs extremely rapidly with zinc porphyrins and with free base dyads in polar solvents; in nonpolar solvents, efficient formation of <sup>3</sup>C<sub>60</sub>\* was seen.<sup>2a,g,3</sup> The extent of such interactions in the ground state has been attributed to the rigid conformation enforced by the linker.<sup>2,3</sup>

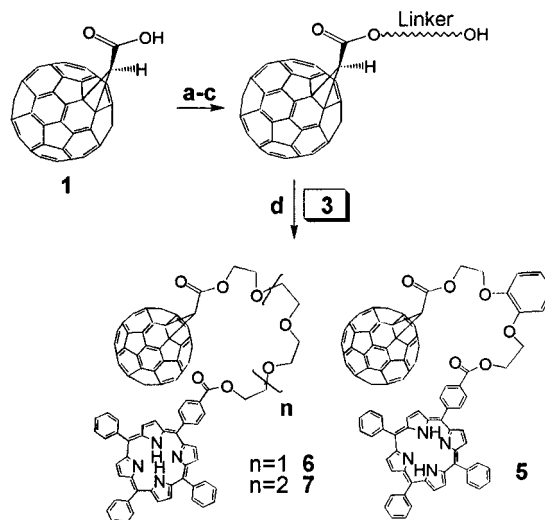
Herein we report the efficient synthesis as well as computational and photophysical studies of two novel classes of porphyrin–C<sub>60</sub> hybrids. These hybrids (i.e., dyads) are unique in that (i) their synthesis utilizes a convergent strategy, providing access to a rich array of new structures, including the first *aza-linked porphyrin–fullerene hybrid*, (ii) despite the fact that the porphyrin moiety is not rigidly connected to C<sub>60</sub>, electronic interactions still occur in the ground state, and (iii) cations induce formation of a complex with open-chain crown-ether mimics **6** and **8** in which there is a dynamic equilibrium between complexed and uncomplexed states (see Scheme 1). In the former state, the two chromophores are brought closer together, significantly increasing intramolecular interactions.

Armed with a facile high-yield route to carboxylic acid **1** via sulfonium ylide addition and subsequent hydrolysis,<sup>4</sup> fullerenes possessing linkers with terminal hydroxyl groups were synthesized through a protection–deprotection sequence by coupling of monoprotected diols with **1**,<sup>5</sup> followed by EDC-mediated coupling<sup>6,7</sup> with 5-(4'-carboxyphenyl)-10,15,20-triphenylporphyrine (**3**, Scheme 2).<sup>7,8</sup> Flexibility in the choice of the

### Scheme 1

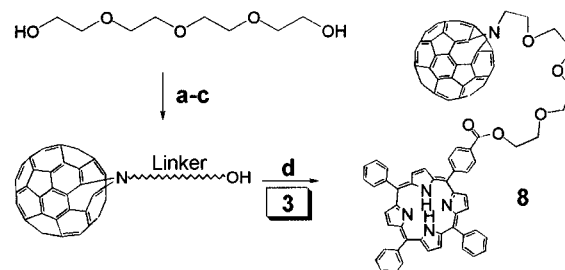


### Scheme 2. Synthesis of Hybrids 5–7<sup>a</sup>



<sup>a</sup> Reagents and conditions: (a) 3 equiv of monosilyl-protected glycol, 3 equiv of DCC, 0.2 equiv of DMAP, 1.1 equiv of BtOH, PhBr:DMSO (5:1), 50°, 12 h 50–70%. (b) 5% oxalic acid:MeOH, 5 min. (c) CH<sub>2</sub>Cl<sub>2</sub>:0.1 N HCl/EtOH:CS<sub>2</sub>:H<sub>2</sub>O (5:1:0.25:10<sup>-4</sup>), 1 h (TBDMS)–8 h (TIPS), 95%. (d) 1 equiv of EDC, 1 equiv of DMAP, CH<sub>2</sub>Cl<sub>2</sub>, 12 h, 48–70%.

### Scheme 3. Second-Generation Hybrid Synthesis<sup>a</sup>



<sup>a</sup> Reagents and conditions: (a) 1 equiv of SOCl<sub>2</sub>, toluene, reflux 2 h. (b) NaN<sub>3</sub>, DMSO, 60 °C, 20 h. (c) C<sub>60</sub>, chlorobenzene, reflux 24 h (53% based on unrecovered C<sub>60</sub>). (d) EDC (1.1 equiv), DMAP (1.1 equiv), 24 h (63%).

diol renders this approach extremely useful in the elaboration of porphyrin–C<sub>60</sub> hybrids in which the topographical relationship of the two chromophores can be varied and controlled.

A second-generation approach (Scheme 3) was undertaken to ascertain the effect of an aza–fullerene linkage ([6,5] open) on photophysics and cation complexation (*vide infra*). Monochlorination of the diol linker followed by NaN<sub>3</sub> displacement furnished the azide which afforded the desired fullerene synthesis.<sup>9</sup> EDC-mediated coupling with **3** afforded hybrid **8**.

UV–vis studies of hybrids **5–7** and their metalated derivatives reveal considerable ground state interactions between the two chromophores. Bathochromic shifts of 6–10 nm are

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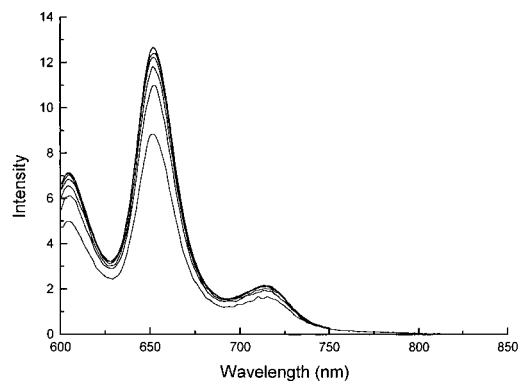
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**Figure 1.** Fluorescence titration of hybrid **6** with  $K^+$  (added as KSCN salt). Excitation of a  $10 \mu\text{M}$  solution at 550 nm.

observed relative to model porphyrin **2** (methyl ester of **3**), while shifts of 2–4 nm are observed for hybrid **8**.<sup>10–12</sup> Fluorescence spectra of the hybrids demonstrate rapid and efficient quenching of the porphyrin  $S_1$  excited state by the  $C_{60}$  moiety.<sup>13</sup> As a control, fluorescence spectra of solutions of an amphiphilic fullerene model and porphyrin **2** at varying concentrations showed little or no effect on  $\Phi_{fl}$ .

The quantitative formation of  $^1O_2$  from  $^3C_{60}^*$  and many of its functionalized derivatives creates the prospect of possible biological applications.<sup>14,20</sup> Using a previously described ultrasensitive Ge-based near-IR detector,<sup>15</sup> quantum efficiencies  $\Phi_{\Delta}$  for hybrid-sensitized formation of  $^1O_2$  based on steady-state emission of  $^1O_2$  at 1270 nm were measured.<sup>16,17</sup> The quantum yields  $\Phi_{\Delta}$  of the hybrids relative to TPP ranged from 0.10 for hybrid **5** to 0.21 for hybrid **6**. Furthermore, **5–7** quench  $^1O_2$  generated by thermolysis of the endoperoxide of 1,4-dimethylnaphthalene,<sup>19</sup> with rate constants  $k_q \sim 10^7\text{--}10^9 \text{ M}^{-1} \text{ s}^{-1}$ , compared to  $\sim 10^5 \text{ M}^{-1} \text{ s}^{-1}$  for  $C_{60}$  itself.<sup>20,21</sup>

In the presence of alkali metal cations, hybrid **6** forms a complex (see Scheme 1) in which intramolecular interactions in both ground and excited states are enhanced. Thus, in the presence of excess KSCN (0.05 M), UV–vis spectra are red-shifted 6–8 nm *vis-à-vis* uncomplexed hybrids; hyperchromic effects and perturbations of the Q-band region are also observed. Similar shifts are observed for the free base and metalated (Co, Zn) hybrids.<sup>22</sup> In the presence of excess NaSCN (0.1 M), only

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(10) Significant splitting patterns observed in the  $^1\text{H}$  NMR spectrum of hybrids **6–8** and the large upfield shift of some pyrrole protons in hybrid **5** also suggest interactions of the linear porphyrin macrocycle with the spherical  $\pi$ -system of  $C_{60}$ .<sup>11</sup> Electrochemical studies of hybrids **6** and **7** also support this conclusion: Baran, P. S.; Boulas, P.; Echegoyen, L.; Schuster, D. I.; Wilson, S. R. Unpublished results.

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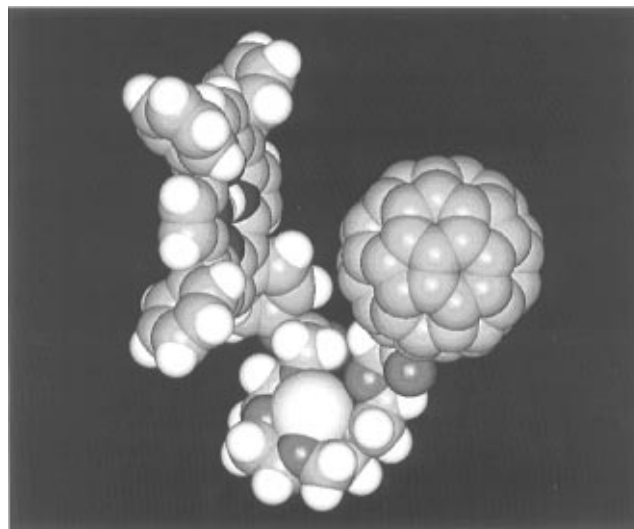
(17)  $\lambda_{ex} = 532 \text{ nm}$ . Values are the average of five determinations in air-saturated  $C_6D_6$  using TPP ( $\Phi_{\Delta} = 0.62$ )<sup>18</sup> as the standard.

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(21) In general, the quantum efficiency decreases in more polar media, presumably due to competing electron transfer.<sup>2a,3</sup> Furthermore, the rate of quenching of  $^1O_2$  increases as solvent polarity is increased. In  $CCl_4$ , the rate of quenching of  $^1O_2$  was on the order of  $10^7 \text{ M}^{-1} \text{ s}^{-1}$ , while in acetone, it was  $10^9 \text{ M}^{-1} \text{ s}^{-1}$ .



**Figure 2.** Minimized structure of complex of hybrid **6** with  $K^+$ .

minor shifts are observed (1–3 nm). Hybrid **8** in the presence of excess KSCN displays 4–6 nm red shifts *vis-à-vis* the uncomplexed hybrid. While addition of the same amount of KSCN or NaSCN to porphyrin **2** does not similarly affect its UV–vis or fluorescence spectrum, addition of KSCN in small portions to a  $10 \mu\text{M}$  solution of **6** in acetone resulted in a substantial decrease in porphyrin fluorescence (Figure 1).<sup>24</sup>

Finally, addition of a small amount of KSCN to a solution of hybrid **6** in methanol- $d_4$ :benzene- $d_6$  (1:2) produces pronounced changes in  $^1\text{H}$  NMR shifts and splitting patterns for protons within the polyether linkage, consistent with that observed for related crown-ether mimics.<sup>25</sup> Smaller shifts were observed for **8** in the presence of  $K^+$ .

Computational studies suggest a change in the conformation of **6** induced by  $M^+$  binding in which the porphyrin system twists so as to face the  $C_{60}$ .<sup>26</sup> In the case of  $Na^+$ , the cation sits above the pseudo crown ether, while a more stable complex is formed with  $K^+$ , in which the cation is nestled within the pseudo crown ether cavity (Figure 2).

In conclusion, we have developed new synthetic methodology which can be efficaciously exploited in the construction of structurally unique conformationally flexible porphyrin–fullerene hybrids in which intramolecular interactions are enhanced as a result of complexation with metal cations.

**Acknowledgment.** We are grateful to the National Science Foundation and the Dean's Undergraduate Research Fund, New York University (to P.S.B.), for support of this work. R.R.M. is an Aaron Diamond Fellow. Mass spectral data were obtained at the Michigan State University Mass Spectrometry Facility.

**Supporting Information Available:** NMR evidence for complexation in **6** and **8** as well as full experimental details for the procedures described herein, characterization of the synthesized compounds, and all photophysical and computational data (18 pages). See any current masthead page for ordering and Internet access instructions.

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