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SYNTHESIS AND PHOTOPHYSICS OF A NOVEL PORPHYRIN-C_{60} HYBRID

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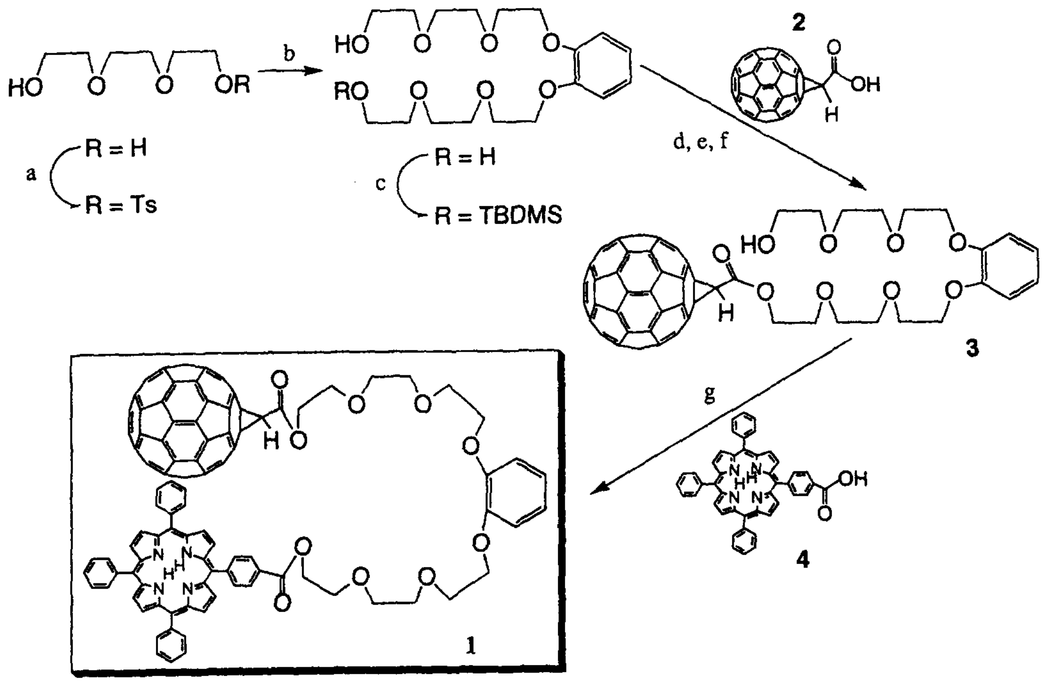
Abstract: In the pursuit of a porphyrin-fullerene linked hybrid with increased solubility and superior cation complexation abilities, hybrid **1** was synthesized. The amphiphilic hybrid **1** was found to be slightly soluble in DMSO, displayed a lower affinity for metal cations than expected, and had a surprisingly high quantum yield (Φ_Δ) for formation of singlet oxygen ($^1O_2$). © 1997 Elsevier Science Ltd.

The first reported synthesis and characterization of a porphyrin-C_{60} hybrid[1] followed the elucidation of the remarkable photophysical properties of C_{60}.[2] Especially significant are long lived fullerene triplet states which undergo energy transfer to ground state oxygen to generate singlet oxygen quantitatively. For biological purposes, such as photodynamic therapy, it is critical that the molar absorptivity of the sensitizer be high in the region of 500-700 nm, and that the solubility be such that introduction into polar media such as DMSO is feasible.[3] C_{60} itself absorbs very weakly in the visible region and is completely insoluble in polar media. Thus, attachment of a porphyrin unit serves two purposes: it serves as an antenna to harvest light at longer wavelengths, while the linker used to connect the two species doubles as a solubilizer of the entire system. Several reports have appeared on the construction and unique characteristics of several types of these hybrid molecules.[4] We have recently reported a series of novel porphyrin-C_{60} hybrids, which form complexes with metal ions *via* allosteric interactions with polyether linkers which function as crown ether mimics. These hybrids are readily accessible synthetically from C_{60}-methanocarboxylic acid **2**.[5,6]

In the present letter, we report the synthesis, characterization, absorption and fluorescence spectra of a new C_{60}-porphyrin hybrid **1**, which is a very effective singlet oxygen sensitizer. Also included are the effect of metal cations on the UV-VIS absorption spectrum of **1**.

The synthesis commences as outlined in Scheme 1. The cornerstone of the synthesis relies on a route to isomerically pure [6,6] closed C_{60}-methanocarboxylic acid **2** in gram quantities[6] and efficient EDC-mediated[7] coupling of fullerene synthon **3** to porphyrin carboxylic acid **4**.[8] The ^1H NMR spectrum of hybrid **1**[9] is essentially a superposition of **3** with **4**, suggesting that the porphyrin and fullerene moieties are completely separated in space. UV-VIS absorption spectra[10] bolster this hypothesis as hybrid **1** displays only a slight bathochromic shift relative to a model porphyrin (methyl ester of **4**). Fluorescence of the porphyrin S_1 state of **1** is indeed quenched (Φ_{fl} = 0.20 relative to the model porphyrin)[11] but not as effectively as with the first generation of analogous hybrids.[5]

SCHEME 1



(See footnote 16 for reagents and conditions)

In contrast to the previously reported hybrids,[5] **1** did not undergo conformational reorganization in the presence of metal cations. Addition of potassium, sodium, lithium, or *tert*-butylammonium thiocyanate to an acetone solution of hybrid **1** produced little or no effect on its UV-VIS absorption spectra. The lack of significant intramolecular interactions in **1** suggests that in this case the linker functions only to physically separate the porphyrin and fullerene chromophores. The greater conformational flexibility of the linker in **1** compared with the polyether linkers in analogous hybrids[5] appears to inhibit crown ether-like complexation with metal cations. Alternatively cation complexation may take place with only one arm of the linker, which would not necessarily enhance porphyrin-fullerene electronic interactions. These results coupled with those of previous studies[5] should aid in the design of new porphyrin-fullerene hybrids which will show very strong binding to metal cations.[12]

Using a previously described ultrasensitive near-IR Ge detector,[13] we measured the steady state quantum yield for triplet-sensitized formation of $^1O_2$, Φ_Δ, on irradiation of hybrid **1** in air-saturated benzene-d_6 at 532 nm[14] relative to that of tetraphenylporphine ($\Phi_\Delta = 0.62$).[15] The value of Φ_Δ for hybrid **1** was 0.40 ± 0.04 (average of 6 scans), the highest value yet observed for a porphyrin-C_{60} hybrid (see Figure 1). Previous values of Φ_Δ for C_{60}-porphyrin hybrids have ranged from 0.10 to 0.21.[1,5] The origin of the unusually high value of Φ_Δ for **1** is currently under study.

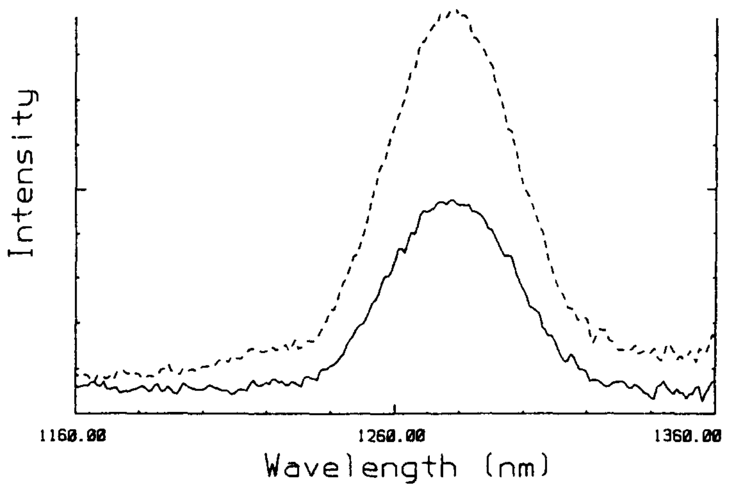


FIGURE 1. Emission of $^1O_2$ at 1270 nm[17] on excitation of hybrid **1** (—) and TPP (- - - -).

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References and Notes:

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9. Selected data for **1**: MALDI-MS (*matrix*: sinapinic acid; *calibrant*: neurotensin) M + 1 = 1777; ^1H NMR (200 MHz, $CDCl_3$) δ 8.8 (m, 8H, pyrrole-H), 8.48 (d, 2H, *m*-H of substituted phenyl), 8.28 (d, 2H, *o*-H of subst. phenyl), 8.2 (m, 6H, *o*-H of phenyl), 7.75-7.80 (m, 9H, *p,m*-H of phenyl), 6.9 (m, 4H, catechol), 4.8 (s, 1H, methanofullerene-H), 4.7 (t, 2H, por-$\mathbf{CH_2}CH_2$), 4.6 (t, 2H, C_{60}-$\mathbf{CH_2}CH_2$), 4.52 (t, 2H, por-$CH_2\mathbf{CH_2}$), 3.50-4.28 (m, 18H, polyether-CH_2).

10. UV-VIS spectra were measured on a Perkin-Elmer Lambda LS-2 spectrophotometer. Data for hybrid **1**: (acetone), 332 (36700), 428 (146800), 522 (12800), 552 (9000), 598 (5400), 656 (4100).

11. λ_{ex} = 550 nm; c = 10 mmol; solvent = acetone; emission from 600-850 nm.

12. For a review on the design of similar systems see Cram, D.J.; Cram, J.M. *Acc. Chem. Res.* **1978**, *11*, 8; for similar systems, see Marquis, D.; Greiving, H.; Desvergne, J.-P.; Lahrahar, N.; Marsau, P.; Hopf, H.; Bouas-Laurent, H. *Liebigs Ann.* **1997**, 97; Gokel, G.W. *Crown Ethers and Cryptands* (Ed.: J.F. Stoddart), The Royal Society of Chemistry, Cambridge, **1991**; Tummler, B.; Maass, G.; Weber, E.; Wehner, W.; Vögtle, F. *J. Am. Chem. Soc.* **1977**, *99*, 4683.

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16. (a) CH_2Cl_2, 1 eq. TsCl, 1 eq. pyridine, 3 h, 54%; (b) dry acetone, K_2CO_3, 15h, 55%; (c) CH_2Cl_2, 1 eq. TBDMSCl, 0.2 eq. DMAP, 1.1 eq. Et_3N, 33%; (d) **2**, 3 eq. DCC, 0.2 eq. DMAP, 1.1 eq. BtOH, PhBr:DMSO (5:1), 50°, 12h, 80%; (e) 5% oxalic acid:MeOH, 5 min., 100% (f) **3**, CH_2Cl_2:0.01N HCl/EtOH (100:1) 8h, 95%; (g) **4**, 1 eq. EDC, 1 eq. DMAP, CH_2Cl_2, 12h, 70%.

17. This emission completely disappeared upon addition of β-carotene.

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