Synthesis and photophysical properties of a diporphyrin–fullerene triad

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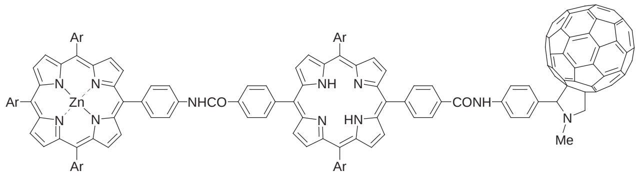
A novel covalently-linked diporphyrin–C_{60} triad has been prepared by 1,3-cycloaddition of C_{60} with a diporphyrin.

Fullerenes have fascinated many researchers during the last decade because of the large size and spherical shape of their delocalized π-electron system with high symmetry.[1] In particular, the unique three-dimensional structures of fullerenes make them a good candidate as an electron acceptor (A). As such, a number of donor (D)–fullerene dyads have been prepared.[2,3] We and other groups have found that C_{60} accelerates photoinduced charge separation (CS) and retards charge recombination (CR) in donor-linked C_{60} dyads. The peculiar effect of C_{60} in electron transfer (ET) is quite similar to the situation in photosynthetic multistep ET, and therefore we were encouraged to design fullerene-containing multicomponent systems as artificial photosynthetic models. There are several reports of triads and a pentad, such as D–S (sensitizer)–C_{60},[4] S–A–C_{60},[5] and S–$(C_{60})_n$ (n = 2,4)[6–11] systems. However, to the best of our knowledge, no reports concerning S–S′–C_{60} systems have appeared so far. Here we report the synthesis and photophysical properties of diporphyrin–C_{60} triad **1**.



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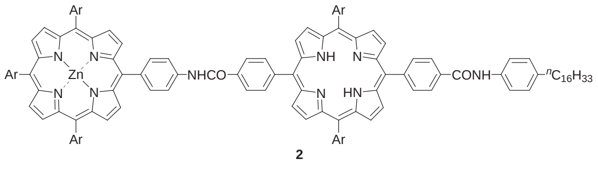

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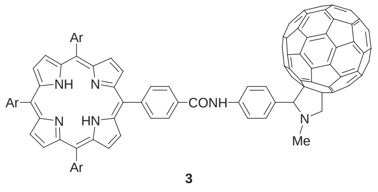

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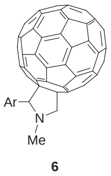

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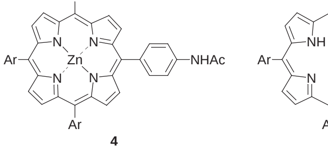

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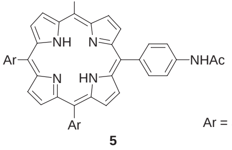

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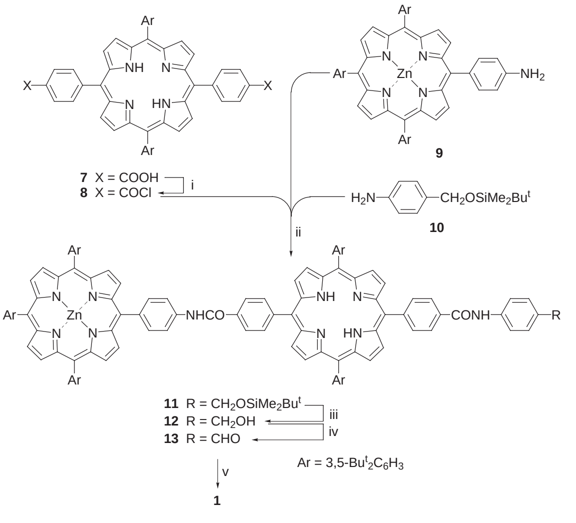
Ar = 3,5-$Bu^t_2C_6H_3$

The synthesis of **1** is shown in Scheme 1. The key features involve selective insertion of a zinc atom into the diporphyrin and its protection from the demetallation. Therefore, after the insertion all the procedures were carried out under neutral or basic conditions. Free base porphyrin carboxylic diacid **7** was converted to the corresponding bis(acid chloride) **8** by treatment with $SOCl_2$. Cross-condensation of **8** with zinc amino porphyrin **9** and 4-*tert*-butyldimethylsiloxymethylaniline **10** in benzene in the presence of pyridine afforded a mixture of porphyrins. The desired diporphyrin **11** was isolated in 34% yield by tedious chromatographic separation. Removal of the TBDMS group in **11** with Bu_4NF gave **12**, which was oxidized using activated MnO_2 to yield **13**. The triad **1** was obtained by 1,3-dipolar cycloaddition using **13**, *N*-methylglycine and C_{60} in toluene in 79% yield.[12] Diporphyrin **2** was synthesized from **8**, **9** and 4-hexadecylaniline by a similar method. The reference compounds **3–6** were also prepared. Their structures were verified by spectroscopic analyses including ^1H NMR and MALDI-TOF mass spectra.†

The absorption spectrum of **1** in THF was almost a linear combination of the spectra of **4**, **5** and **6**, indicating no significant interactions among the three chromophores in the ground state. Absorption due to the two porphyrin chromophores is much stronger than that of C_{60}. The redox potentials of **1–6** were measured by differential pulse voltammetry in CH_2Cl_2 using 0.1 M Bu_4NPF_6 as supporting electrolyte. The potentials of **1** (−1.52, −1.14, +0.29, +0.54 V *vs*. Fc/Fc$^+$) can be roughly explained by the sum of **4**, **5** and **6** (**4**: +0.25 V; **5**: +0.43 V; **6**: −1.54, −1.15 V *vs*. Fc/Fc$^+$), implying weak electronic coupling among the three moieties.

Fig. 1 shows steady-state fluorescence spectra of **1**, **2**, **4** and **5** in THF with excitation at 426 nm. The zinc porphyrin **4** exhibits emission maxima at 604 and 657 nm, while the free base porphyrin **5** displays maxima at 652 and 719 nm. The emission of **2** is almost the same as that of **5**, with no appreciable emission from the zinc porphyrin, which is in good agreement with the results in a similar diporphyrin system.[13] Considering that both the porphyrins in **2** absorb at 426 nm, it is suggested that efficient singlet–singlet energy transfer (EN) occurs from the first excited singlet state of a zinc porphyrin (^{1}ZnP*) to a free



Scheme 1 *Reagents and conditions*: i, $SOCl_2$, pyridine, benzene, reflux; ii, pyridine, benzene, 34% (2 steps); iii, TBAF, THF, 81%; iv, activated MnO_2, $CHCl_3$, 78%; v, C_{60}, $MeNHCH_2CO_2H$, toluene, reflux, 79%.

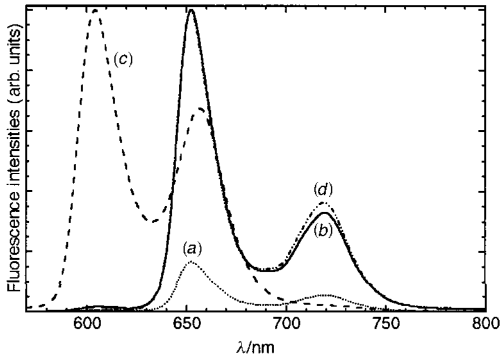


Fig. 1 Fluorescence spectra of (*a*) **1** and (*b*) **2** (2.0×10^{-6} M) in THF with excitation at 426 nm. The normalized spectra of (*c*) **4** and (*d*) **5** are shown as a comparison.

base porphyrin (H_2P). The emission of **1** was quenched strongly as compared with that of **2** when excited at 426 nm under the same concentration (relative intensity: 0.17). No apparent C_{60} emission (λ_{max} = 720 nm) could be detected.‡ Similar quenching behavior was seen for **3** *vs*. **5** (relative intensity: 0.19). These results show the rapid quenching of the excited singlet state of the porphyrin by the C_{60} in **1**.

Preliminary photophysical experiments of **1** and **2** in THF were carried out using a picosecond single photon counting technique with excitation at 422 nm, where both the porphyrins absorb, and monitoring at 655 and 720 nm, where the emission is due to both the porphyrins, and the free base porphyrin and the C_{60}, respectively. Fluorescence decay of **2** at 655 nm was analyzed by two exponential decays with time constants of 44 ps (A = 0.19) and 9.9 ns (A = 0.81). In contrast, the emission at 720 nm was fitted by a rise with a time constant of 44 ps and a decay with a time constant of 9.9 ns (A = 1.00) which agrees well with the fluorescence lifetime (9.8 ns) of **5** in THF. The matching of the time constants between the decay and the rise in **2** strongly supports the efficient EN from $^1ZnP^*$ to H_2P in THF. Based on the results together with the fluorescence lifetime of **4** (2.0 ns) in THF, we can calculate the rate constant of EN to be 2.2×10^{10} s^{-1}. The component with the longer lifetime (9.9 ns) monitored at 655 and 720 nm can be assigned reasonably to the emission from the free base porphyrin. Similar results were obtained in **1**, except that a component corresponding to the longer lifetime showed a decreased time constant of 1.7 ns, which is consistent with the fluorescence lifetime of **3** (1.4 ns) in THF. The shorter time constant (τ = 1.7 ns, A = 1.00) of **1** due to the free base porphyrin, compared with that (9.9 ns) of **2**, indicates the photoinduced ET[4] or partial charge-transfer (CT) from $^1H_2P^*$ to C_{60}[14] as shown in Fig. 2.§ These results suggest that initial photoinduced EN from $^1ZnP^*$ to H_2P and subsequent CS or CT from $^1H_2P^*$ to C_{60} may take place in **1**.¶

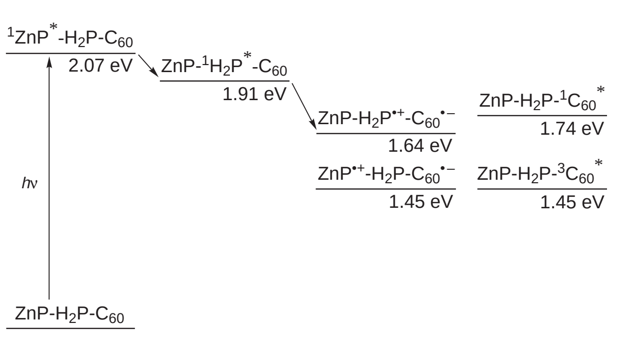


Fig. 2 Plausible reaction scheme and energy diagram for **1** in THF.

In conclusion, a diporphyrin–C_{60} triad has been prepared for the first time. Although our interpretation of the quenching mechanism is consistent with the results obtained by the fluorescence lifetime measurements, further details must wait transient absorption experiments, which are in progress.

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Notes and references

† *Selected data* for **1**: δ_H(270 MHz; $CDCl_3$) −2.84 (s, 2H), 1.53 (s, 90H), 2.67 (br s, 3H), 3.67 (br s, 1H), 4.31 (br s, 1H), 4.50 (br s, 1H), 7.61 (br s, 2H), 7.79 (s, 3H), 7.81 (s, 2H), 7.96 (d, J 8, 2H), 8.04 (s, 4H), 8.09 (s, 6H), 8.20–8.31 (m, 8H), 8.42 (d, J 8, 2H), 8.48 (d, J 8, 2H), 8.70 (br s, 2H), 8.77 (d, J 4, 2H), 8.88–8.90 (m, 6H) and 9.01–9.03 (m, 8H); *m/z* (MALDI-TOF; positive mode) 2794 (M+H$^+$); (MALDI-TOF; negative mode) 721 (C_{60}^-); λ_{max} (THF)/nm 350 (sh), 361 (sh), 404 (sh), 420 (sh), 427, 485, 516, 555, 597, 649 and 704.

‡ In the steady-state fluorescence experiments it was quite difficult to discriminate the emissions from the free base porphyrin and the C_{60} because of overlapping at 700–750 nm as well as the weak fluorescence from the mono-functionalized C_{60}.

§ We cannot rule out the possibility that there are other competitive pathways, where EN from $^1H_2P^*$ takes place to populate $^1C_{60}^*$, followed by ET from the porphyrin to $^1C_{60}^*$ to produce $H_2P^{\cdot+}$–$C_{60}^{\cdot-}$, or equilibration with $^1H_2P^*$ energetically and/or by intersystem crossing from $^1C_{60}^*$ to $^3C_{60}^*$.

¶ Based on the energy level diagram in THF, a charge-shift might occur from ZnP to $H_2P^{\cdot+}$ in the ZnP–$H_2P^{\cdot+}$–$C_{60}^{\cdot-}$ state, leading to the production of $ZnP^{\cdot+}$–H_2P–$C_{60}^{\cdot-}$.

1 M. S. Dresselhaus, G. Dresselhaus and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes*, Academic Press, San Diego, 1996.
2 H. Imahori and Y. Sakata, *Adv. Mater.*, 1997, **9**, 537.
3 N. Martín, L. Sánchez, B. Illescas and I. Pérez, *Chem. Rev.*, 1998, **98**, 2527.
4 P. A. Liddell, D. Kuciauskas, J. P. Sumida, B. Nash, D. Nguyen, A. L. Moore, T. A. Moore and D. Gust, *J. Am. Chem. Soc.*, 1997, **119**, 1400.
5 H. Imahori, K. Yamada, M. Hasegawa, S. Taniguchi, T. Okada and Y. Sakata, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2626.
6 K. Dürr, S. Fiedler, T. Linßen, A. Hirsch and M. Hanack, *Chem. Ber.*, 1997, **130**, 1375.
7 N. Armaroli, F. Diederich, C. O. Dietrich-Buchecker, L. Flamigni, G. Marconi, J.-F. Nierengarten and J.-P. Sauvage, *Chem. Eur. J.*, 1998, **4**, 406.
8 D. Armspach, E. C. Constable, F. Diederich, C. E. Housecroft and J.-F. Nierengarten, *Chem. Eur. J.*, 1998, **4**, 723.
9 S. Higashida, H. Imahori, T. Kaneda and Y. Sakata, *Chem. Lett.*, 1998, 605.
10 J.-F. Nierengarten, L. Oswald and J.-F. Nicoud, *Chem. Commun.*, 1998, 1545.
11 J.-F. Nierengarten, C. Schall and J.-F. Nicoud, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 1934.
12 M. Maggini, G. Scorrano and M. Prato, *J. Am. Chem. Soc.*, 1993, **115**, 9798.
13 D. Gust, T. A. Moore, A. L. Moore, F. Gao, D. Luttrull, J. M. DeGraziano, X. C. Ma, L. R. Makings, S.-J. Lee, T. T. Trier, E. Bittersmann, G. R. Seely, S. Woodward, R. V. Bensasson, M. Rougée, F. C. D. Schryver and M. V. der Auweraer, *J. Am. Chem. Soc.*, 1991, **113**, 3638.
14 H. Imahori, S. Ozawa, K. Ushida, M. Takahashi, T. Azuma, A. Ajavakom, T. Akiyama, M. Hasegawa, S. Taniguchi, T. Okada and Y. Sakata, *Bull. Chem. Soc. Jpn.*, in the press.

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