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Novel fullerene–porphyrin–fullerene triad linked by metal axial coordination: Synthesis, X-ray crystal structure, and spectroscopic characterizations of *trans*-bis([60]fullerenoacetato)tin(IV) porphyrin†

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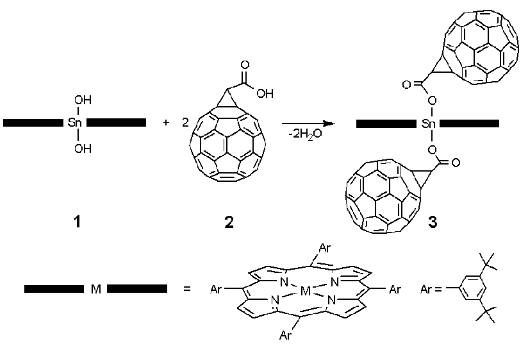
A novel fullerene–porphyrin–fullerene triad linked by the axial coordination of tin(IV) porphyrin is reported, exhibiting strong π–π interactions between the tin porphyrin and fullerene moieties owing to their close proximity.

Porphyrins[1] and fullerenes[2] are attractive molecular components for the design of novel artificial photosynthesis and applications in molecular electronic devices because of their unique structures and rich photoelectronic properties. Accordingly, a great variety of porphyrin–fullerene architectures involving covalent or noncovalent linkages have been studied.[3] However, coordinatively linked porphyrin–fullerene architectures have been only focused on dyads assembled by the axial coordination of functionalized fullerene bearing a nitrogen donor ligand to Zn(II)[4] or Ru(II) porphyrins.[5] Furthermore, the fullerene–porphyrin–fullerene triads linked by axial coordination have not been explored yet.[6] To explore this new type triad, we have been interested in supramolecular architectures based on the Sn(IV) porphyrins since the Sn(IV) porphyrins usually adopt stable six-coordinate structures with two *trans* axial ligands.[7] The strong preference of Sn(IV) porphyrins for coordination to oxyanionic ligands such as carboxylates and alkoxides has been recently used to construct elaborate multiporphyrin arrays.[8] Here we report a novel fullerene–porphyrin–fullerene triad, in which the two fullerene units are coordinatively linked to the central metal ion of Sn(IV) porphyrin. To the best of our knowledge, this is the first example of a fullerene–porphyrin–fullerene triad linked by axial coordination of two fullerene units to a metalloporphyrin.

Bis([60]fullerene)–tin(IV) porphyrin triad **3** was synthesized by the reaction of *trans*-dihydroxo[*meso*-tetrakis(3,5-di-*tert*-butylphenyl)-porphyrinato]tin(IV) complex **1**[9] with 2 equiv. of [60]fullerenoacetic acid **2**[10] (Scheme 1). The triad **3** was characterized by various spectroscopic methods and elemental analysis.† In the ^{1}H NMR spectrum of **3**, a singlet resonance attributed to the proton of the bridge head in [60]fullerenoacetate moiety is significantly shifted to higher field ($\Delta\delta = -2.82$ ppm) compared to that of free [60]fullerenoacetic acid **2**. The upfield shift of this resonance implies that the [60]fullerenoacetate moiety is linked to the Sn(IV) porphyrin moiety *via* Sn-carboxylate coordination. IR spectroscopy also supports the Sn-carboxylate coordination, since the absorption of the C=O shifted from 1700 cm^{-1} of **2** to 1667 cm^{-1} for **3**. The MALDI-TOF mass spectrum of **3** exhibits a parent ion peak at $m/z = 1956.8$ resulting from the loss of one [60]fullerenoacetate ligand, although the molecular ion peak was not observed.



Scheme 1

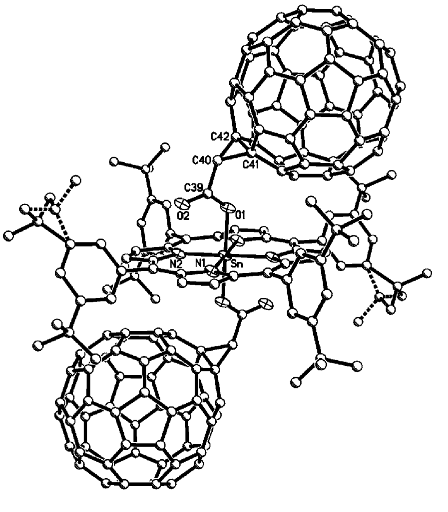


Fig. 1 X-ray crystal structure of **3**. The co-crystallized solvent molecules and hydrogen atoms are omitted for clarity.

The structure of **3** has been confirmed by X-ray crystallography.‡ The X-ray structural analysis of **3** revealed the expected axially coordinated structure with 1 : 2 stoichiometry of the Sn(IV) porphyrin and fullerene moieties, as depicted in Fig. 1. The Sn center is octahedrally coordinated by the porphyrin occupying the square base and axial coordination of two [60]fullerenoacetate groups. The Sn atom lies on an inversion center, so that the two [60]fullerenoacetate groups also lie in an *anti* orientation with respect to each other. The Sn–N distances are found to be 2.098(5) and 2.081(6) Å which are similar to those of reported Sn(IV) porphyrins.[7] But the Sn–O distance of 2.116(4) Å is somewhat longer than those of other carboxylato Sn(IV)

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† Electronic supplementary information (ESI) available: details of synthetic, X-ray crystallographic and spectroscopic experiments. See http://www.rsc.org/suppdata/cc/b4/b411482e/

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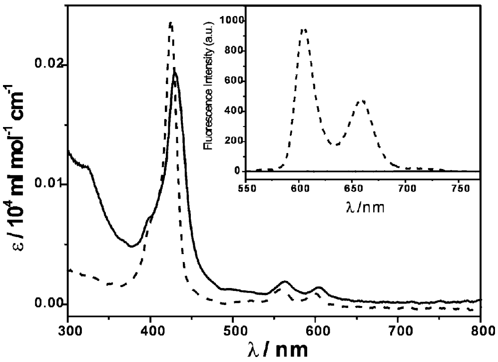

Fig. 2 Absorption and fluorescence (inset, $\lambda_{exc} = 430$ nm) spectra obtained in toluene of **3** (solid line) and **4** (dashed line).

porphyrins.[7] This may be attributed to the large steric demand of the porphyrin moiety and [60]fullerenoacetate ligands. The center-to-center distance, that is, the distance between the Sn(IV) ion and the inner center of fullerene spheroid, is estimated to be ~7.9 Å. The distances from the Sn center to C41 and C42, the [6,6] ring carbon atoms of the fullerene to which the acetate group is attached, amount to 5.016(6) and 5.146(7) Å, respectively. Most importantly, the two chromophores are so closely located to electronically interact despite the unfavorable steric interactions. The closest distance between the porphyrin π-ring carbon (α-pyrrole) and the one of the [5,6] ring carbon atoms of the fullerene, edge-to-edge distance, is found to be 3.371(9) Å. The distances between the porphyrin mean plane and the carbon atoms of the closest 5-membered ring in the fullerene moiety also range from 3.212(8) to 3.845(8) Å, in which the 5-membered ring of fullerene moiety is slightly tilted with respect to the porphyrin ring by about 15.8° (Fig. S1†). The structural analysis indicates that the porphyrin and fullerene π-electrons in **3** would strongly interact owing to their close proximity.

Furthermore, we found that the close proximity between the two π-systems in **3** considerably affects the spectroscopic properties of the triad **3**. As shown in Fig. 2, the UV/vis/near-IR absorption of **3**, compared to those of dibenzoate Sn(IV) porphyrin **4**,[9] exhibits red-shifts in both the Soret (422 → 430 nm) and Q bands (556 → 564, 596 → 604 nm) with noticeable broadening and near-IR absorption tail reaching up to about 2000 nm. Considering that the absorption spectrum of the 1 : 2 mixture of **1** and *tert*-butyl [60]fullerenoacetate **5**[11] is superimposable on the sum of the absorbances of the two individual molecules, the spectral features of **3** due to either the coordination of acetate ligands or intermolecular interactions between Sn(IV) porphyrin and fullerene species can be excluded.

We also carried out fluorescence experiments to confirm the existence of strong π–π interactions between the Sn(IV) porphyrin and the fullerene moieties in **3**. The steady-state fluorescence for **3** revealed the efficient fluorescence quenching of the Sn(IV) porphyrin in toluene, as shown in Fig. 2. The fluorescence intensity of **3** is *ca.* 140 times weaker than that of **4**. The fluorescence decay profiles ($\lambda_{exc} = 430$ nm, $\lambda_{em} = 607$ nm; Fig. S2†) of **3** and **4** in toluene measured by time-correlated single photon counting (TCSPC) technique also revealed that the fluorescence lifetime for **3** (16 ps) is much shorter than that for **4** (1.0 ns), which evidently supports that the Sn(IV) porphyrin and fullerene π-systems strongly interact with each other owing to their close proximity as confirmed by X-ray crystallography. More specifically, the transient absorption spectra ($\lambda_{pump} = 400$ nm, $\lambda_{probe} = 560$ and 620 nm for Q-band bleaching and S_1 state induced absorption of Sn(IV) porphyrin, respectively; Fig. S3†) of **3** in toluene by pump-probe femtosecond transient absorption spectroscopy reveal ultrafast energy transfer with a time constant of 2.7 ± 0.2 ps along with broad absorption in entire visible region. On the other hand, in benzonitrile, the ultrafast bleaching recovery at 560 nm (*ca.* 450 fs) as well as the fast rise of transient absorption at 670 nm corresponding to the Sn(IV) porphyrin cation radical at the same rate is likely to represent the fast electron transfer process from the Sn(IV) porphyrin to the fullerene moieties, which also competes with the energy transfer process (3 ± 0.2 ps) as revealed in toluene (Fig. S4†).[12]

In summary, we synthesized and fully characterized the first fullerene–porphyrin–fullerene triad linked by the axial coordination of Sn(IV) porphyrin. The X-ray crystallographic and spectroscopic characterizations reveal that the Sn(IV) porphyrin and fullerene π-systems strongly interact with each other owing to their close proximity. This triad may provide new insights into the design of artificial photosynthetic systems and molecular electronic devices.

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Notes and references

‡ Crystal data for **3**: $C_{200}H_{94}N_4O_4Sn{\cdot}5CHCl_3{\cdot}2CH_2Cl_2{\cdot}3H_2O$, $M = 3556.22$, monoclinic, $a = 40.6082(17)$, $b = 13.5086(6)$, $c = 29.0086(12)$ Å, $\beta = 106.771(1)°$, $U = 15236.1(11)$ Å^3, $T = 100(2)$ K, space group $C2/c$ (no. 15), $Z = 4$, $\mu = 0.571$ mm^{-1}, 46436 reflections measured, 18033 unique ($R_{int} = 0.0809$). Final full matrix least-squares refinement on F^2 converged to $R_1 = 0.1052$ ($I > 2\sigma(I)$) and $wR_2 = 0.3423$ (all data) with GOF = 1.052. CCDC 245797. See http://www.rsc.org/suppdata/cc/b4/b411482e/ for crystallographic data in .cif or other electronic format.

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12 The transient absorption spectra exhibit a very weak signal of Sn(IV)porphyrin cation radical around 670 nm with ultrafast rise (within 500 fs) and long decay (> 1 ns). The signal-to-noise ratio in the transient absorption spectral of **3** in benzonitrile is not so good as that in toluene mainly due to its poor solubility.