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## COMMUNICATION

Facile synthesis of a flexible tethered porphyrin dimer that preferentially complexes fullerene C<sub>70</sub><sup>†‡</sup>Matthew Jurow,<sup>a</sup> Christopher Farley,<sup>a</sup> Cesar Pabon,<sup>a</sup> Brian Hageman,<sup>a</sup> Aaron Dolor<sup>a</sup> and Charles Michael Drain<sup>\*ab</sup>

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**A simple, high yield, two-step synthesis yields a porphyrin dimer linked by a flexible dithiol tether that preferentially binds fullerene C<sub>70</sub> over C<sub>60</sub> in toluene solution. The complex forms stable aggregates when cast on glass.**

Porphyrins are known to closely associate with the curved surface of fullerenes both in solution and as co-crystals.<sup>1</sup> These systems are used extensively in the creation of donor–acceptor materials to study charge separated states as part of artificial photosynthetic materials. The chemical stability and tuneable photonic properties of the p-type porphyrins couple well with the electronic properties of the n-type fullerenes to form nearly ideal donor–acceptor systems.

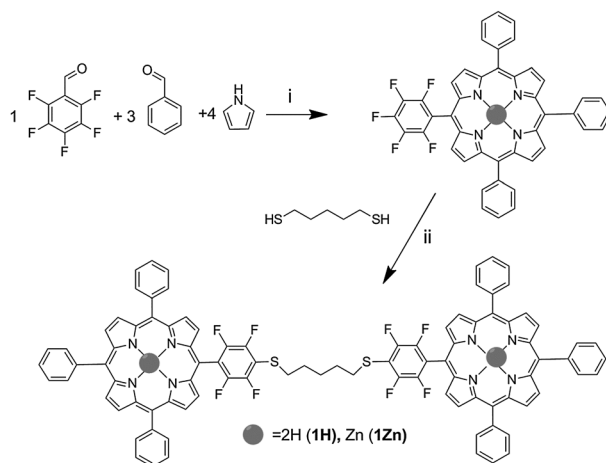
Covalently linked porphyrin/fullerene donor–acceptor systems have also served as model systems for the study of electron transfer for over 20 years.<sup>2</sup> Many groups have synthesized covalently linked porphyrin/fullerene systems with diverse architectures that demonstrated functionalities that can be potentially used in the development of optoelectronic devices.<sup>3–10</sup> In general, as the architectural complexity and added functional entities of the donor–acceptor target increases, the synthetic yield decreases. Rigorously synthesized and carefully designed systems with rigid tethers are examples.<sup>11,12</sup> High yield coupling and click-type reactions provide access to some porphyrin/fullerene systems with better yields.<sup>13</sup> Supramolecular approaches can mitigate synthetic complications, but one drawback of molecular designs with covalent, coordination,<sup>14</sup> hydrogen bonding,<sup>15</sup> and electrostatic<sup>16</sup> tethers is that derivatives of fullerenes are usually not as good acceptor motifs as the parent fullerene.<sup>17</sup>

Supramolecular approaches to porphyrin systems that bind the underivatized fullerene can result in materials with similar or better photonic functionalities.<sup>18–23</sup> Synthesis of the fullerene hosts range from simple to complex, but the former have greater

commercial potential. The porphyrin dimer described in this investigation is synthesized by a simple two-step procedure in high yield (Scheme 1).

The free base (1H) and zinc(II) (1Zn) dimers are designed with a flexible  $\alpha,\omega$ -dithiol alkane linker to allow for an induced-fit, sandwich type binding of fullerenes such as C<sub>60</sub>, C<sub>70</sub> (Fig. 1), and single wall carbon nanotubes. The inclusion of the perfluorophenyl linker allows for easy dimerization by simple click-type substitution reactions with thioalkanes and may help promote interaction with the conjugated pi system of the chosen fullerene molecule.<sup>24</sup> The modular design allows the length of the linker to be easily varied by substituting the pentane dithiol with any of the numerous commercially available dithioalkanes.

In toluene, the 1H and 1Zn dimers complex fullerene C<sub>70</sub> greater than 10-fold better than C<sub>60</sub> (Table 1).§ UV-visible and fluorescence titrations of the fullerenes into solutions of the dimers reveal systematic red shifts in the former and quenching in the latter. Values for *K* in Table 1 were calculated from the slope of Stern–Volmer plots (e.g. fluorescence data in Fig. 2), and competition experiments, wherein the dimers were titrated with a ~ 1 : 1 mixture of C<sub>60</sub>:C<sub>70</sub>, indicate that the dimer preferentially binds C<sub>70</sub> more than 10-fold better than C<sub>60</sub>. 1Zn demonstrated a binding constant of  $1.1 \times 10^4 \text{ M}^{-1}$ , which is competitive with much more synthetically demanding molecules.



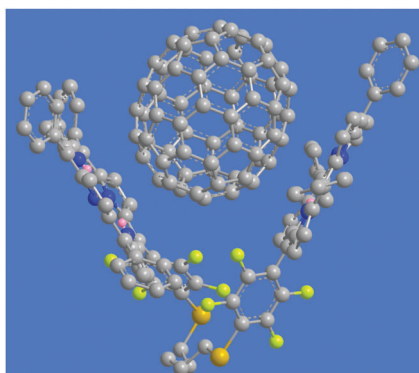
**Scheme 1** Reagents and conditions: i: reflux in propionic acid, separate isomers; ii: metalation with Zn(OAc)<sub>2</sub> in CHCl<sub>3</sub>/CH<sub>3</sub>OH followed by addition of pentane-1,5-dithiol in DMF<sup>†</sup>

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<sup>‡</sup> Electronic supplementary information (ESI) available: experimental details, UV-visible, fluorescence, AFM, TEM, EDAX. See DOI: 10.1039/c2cc31340e



**Fig. 1** MM2 calculated structure of **1H** and  $C_{70}$  where grey = C, blue = N, yellow = F, and orange = S, and H are left out for clarity.

The UV-visible absorption spectra (Fig. S1–S6†) of both **1H** and **1Zn** show a small but real ground state interaction with  $C_{70}$  indicated by a decrease and slight redshift of the Soret peak. This is illustrated in the insets to Fig. S1–S6†, which plot the difference between the predicted and observed absorbance of the combined solutions as a function of fullerene concentration. For the monomeric compounds and the titration of  $C_{60}$  for the dimer, no such effect is observed.

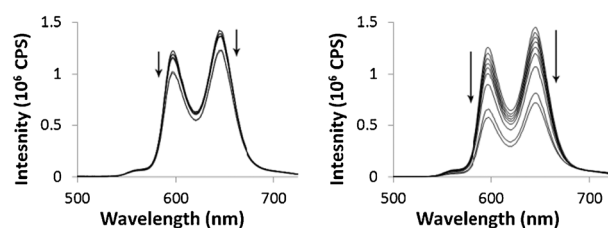
Steady state fluorescence measurements demonstrate fullerene quenching of the porphyrin excited state (Fig. 1, S7, S8†). Stern–Volmer plots (Fig. S9†) show greater quenching by  $C_{70}$  than by  $C_{60}$  for all species studied. The porphyrin fluorescence lifetimes measured by time correlated single photon counting experiments show virtually no change (9 ns for **1H** and 2 ns for **1Zn** in toluene excited at 425 nm), and a static quenching mechanism is indicated. Assuming there is no significant difference in the nature of energy transfer from the various fluorophore species, and expecting that complexation behaviour is driven by van der Waals forces with small contributions from electrostatics and coordinate bonding, we conclude that the greater quenching observed in the case of the  $C_{70}$  can be attributed to a stronger interaction due to the larger, flatter surface in the equatorial region of the fullerene molecule.<sup>25</sup> We have done these studies in toluene to compare to published data, but solvation of both the dimer and the fullerenes diminish the intermolecular interactions, and more polar solvents may enhance complexation.<sup>26</sup>

To study the system in the solid state, films were prepared on ozone cleaned glass by drop casting from toluene solutions of fullerene, fullerene and **1H**, fullerene plus **1Zn**, or pure **1**. The resulting films were examined by atomic force microscopy (AFM),

**Table 1** Binding constants for **1H**, **1Zn** and for several reported fullerene binding porphyrinic compounds in toluene

Host	$K_{C_{60}}/M^{-1}$	$K_{C_{70}}/M^{-1}$	$K_{C_{70}}/K_{C_{60}}$	Ref.
MPF	$5.0 \times 10^2$	$3.7 \times 10^3$	7.4	this work
<b>1H</b>	$7.1 \times 10^2$	$8.9 \times 10^3$	12.5	this work
<b>1Zn</b>	$8.0 \times 10^2$	$1.1 \times 10^4$	13.8	this work
cyclic $H_2$ Por	$7.94 \times 10^5$	$1.58 \times 10^7$	19.9	1 <sup>a</sup>
cyclic ZnPor	$6.31 \times 10^5$	$2.00 \times 10^7$	31.7	1 <sup>a</sup>
jaws $H_2$ Por	$5.20 \times 10^3$	—	—	1 <sup>a</sup>
jaws ZnPor	$1.95 \times 10^3$	—	—	1 <sup>a</sup>
calix. $H_2$ Por	$4.92 \times 10^3$	$2.11 \times 10^4$	4.29	11
calix. ZnPor	$8.6 \times 10^3$	$2.80 \times 10^4$	3.26	11

<sup>a</sup> Also references therein, see ESI for structures.

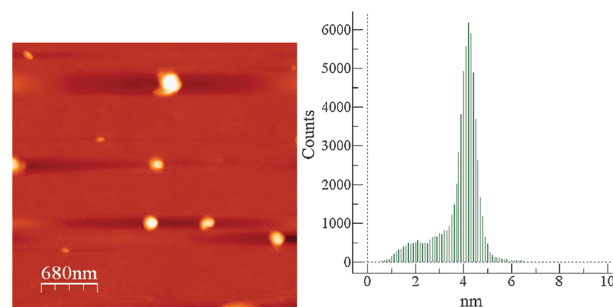


**Fig. 2** Fluorescence emission spectra of a titration of (left)  $C_{60}$  and (right)  $C_{70}$  into 10  $\mu M$  **1Zn** solution in toluene. Both graphs show quenching of the porphyrin excited state, but the effect due to  $C_{70}$  is much more significant. The solutions were excited at 417 nm

and transmission electron microscopy (TEM). Solutions of **1** and  $C_{70}$  form 3–5 nm films of the supramolecular material when cast on clean glass surfaces (Fig. 3). A few islands of larger aggregates of the materials are also observed. Monomeric porphyrins form simple aggregates on the glass surface. Pure 0.5 mM  $C_{70}$  solutions cast on the glass form large nanoaggregates, while solutions of pure  $C_{60}$  form long narrow rods. Lower concentrations form sparse films. When combined with **1**, the dimensions of the  $C_{60}$  aggregates remain constant but are more uniformly dispersed aggregates. The self-organized films demonstrate the increased affinity of **1** to  $C_{70}$  but the architecture of the molecules in the films may be different than in solution. TEM studies of the films show similar morphologies and the energy dispersive X-ray microanalysis clearly shows the Zn in films of **1Zn**: $C_{70}$ . There are three possible supramolecular structures consistent with the AFM heights: the sandwich-type complex shown in Fig. 1, the  $C_{70}$  sitting on top of a closed dimer where the porphyrins are cofacially pi-stacked, and two open dimers sandwiching two  $C_{70}$  (see supporting information†).

Carbon nanotubes share many of the interesting properties of fullerenes and have also been extensively used in porphyrin based D/A systems.<sup>27–29</sup> When THF solutions of **1** were incubated with large excess of single walled carbon nanotubes (SWCNT), sonicated for 10 min and centrifuged at 8000 RPM for 10 min. UV-visible spectra show small red shifts in the dimer. The supernatant demonstrated similar fluorescence quenching and UV spectral changes to the experiments with the fullerene  $C_{70}$ , indicating that the dimer interacts favourably with the larger SWCNT.

In summary, simple porphyrin dimers with flexible linkers can bind fullerenes, and this molecular design allows rapid synthesis of molecules with different tethers to evaluate other supramolecular design principles. Future studies will include



**Fig. 3** Left: AFM of a 1 : 1 **1Zn**:  $C_{70}$  (10  $\mu M$  each in toluene) cast onto ozone cleaned glass shows a  $\sim 4$  nm thick film with larger 10–25 nm high islands of the fullerene complexed by the dimer. Right: histogram of particle sizes.

synthesis of differently tethered dimers, and characterization of the dimer interaction with SWCNT. These synthetically scalable dimers may be used as a means for purifying crude fullerene mixtures. The photophysical data indicates electron transfer from the porphyrin donor to the C<sub>70</sub> acceptor. Nanoscale films of the supramolecular complex are similarly quenched. If porphyrin-fullerene films are to reach potential applications,<sup>30–38</sup> scalability is a central issue.

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## Notes and references

§ For each of the porphyrins investigated: the free base dimer (1H), the metalloporphyrin dimer (1Zn), and the monomeric control: tri-5-10-15-phenyl-20-perfluorophenylporphyrin (MPF); solutions of the desired concentration were prepared first and titrated with solutions containing C<sub>60</sub> or C<sub>70</sub>. Care was taken to ensure a constant porphyrin concentration throughout the titration. AFM samples were prepared by dropcasting from toluene solutions on to ozone cleaned glass slides. Nanotubes were an average of 1 µm in length and 0.7–1 nm in diameter and were of 99% purity. In the experiments with SWCNT, the precipitate, which is likely a complex of the SWCNT and the dimer species, has not yet been characterized.

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