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Here, aromatic core expansion of 21,23-dithiaporphyrins is undertaken through ring fusion of acenaphthyl groups, resulting in a curved structure. The curved pi-system exhibited low energy absorption bands (>1000 nm) and demonstrated an interaction with [60]fullerene.

Supramolecular interactions between porphyrins and fullerenes have been of great interest to the chemistry community because of the potential to participate in photoinduced electron transfer reactions.<sup>1-3</sup> Despite much effort, there are few reports of porphyrins exhibiting  $\pi$ - $\pi$  interactions in solution, most likely due to the planar porphyrin shape mismatch with the curvature of fullerene. Thus, most porphyrin:[60]fullerene literature describes multi-porphyrin arrays linked to a scaffold that creates a binding pocket for efficient fullerene binding.<sup>4–15</sup> This strategy, although very successful at achieving high binding affinities, adds considerable synthetic steps and additional components to the complex system. Alternatively, metallo-porphyrins have been used to coordinate fullerene analogs, such as pyridyl derivatives,<sup>16-19</sup> as model systems to study electron transfer. Subporphyrins derivatives, which have curved  $\pi$ -conjugated surface, show strong binding to fullerenes in solution, as demonstrated by Yoshida and Osuka.<sup>20</sup> Through ring fusion, a curved porphyrin structure is possible, as shown by Saeugusa and co-workers,<sup>21</sup> and enables binding fullerene through  $\pi$ - $\pi$ interactions.

A secondary objective is to design curved porphyrin structures that possess broad, bathochromic absorption profiles, which is a topic of interest for the organic electronics community. In recent literature,<sup>22–26</sup> porphyrins have been largely successful in their applications to organic photovoltaic cells, becoming some of the leading materials for small molecule, highly efficient solar

devices. Typically, these devices contain metalated porphyrins, functionalized non-symmetrically at the *meso*-positions to obtain red-shifted absorbance profiles. Literature<sup>27–30</sup> has shown that the incorporation of thiophene in place of pyrrole into the porphyrin ring system results in bathochromic absorbance profiles and metal-free chromophores. In addition, we and others<sup>31–35</sup> have shown that expansion of the aromatic system by ring fusion to both the backbone of the pyrrolic or thiophene units of the porphyrin, as well as  $\pi$ -conjugated extension of the *meso*-positions have pushed the absorption envelope into the near IR range.

Herein, we report a core-expanded (acenaphtho[1,2-*c*]thiophene) and its subsequent formation of 21,23-dithiaporphyrins with the objectives of achieving low-energy light absorptions and fullerene binding. There are reports of porphyrin:fullerene networks, which demonstrate strong binding affinities  $(10^3 \text{ M}^{-1} \text{ to } 10^8 \text{ M}^{-1})$ ,<sup>13-15</sup> but these systems generally require fullerene to be either encapsulated by porphyrins or metal-coordinated. Here we report an example of a curved-shape dithiaporphyrin interacting with [60]fullerene in solution and in the solid state.

Aromatic, core expanded, dithiadiacenaphthyl fused dithiaporphyrins **1a–c**, shown in Scheme **1**, were synthesized according to procedures described in the ESI.†

Upon the fusion of acenaphthene to the backbone of the two thiophene rings in dithiaporphyrin, the typically planar macrocyclic core becomes distorted, resulting in saddle-shaped molecules. This distortion from planarity is supported by DFT calculations performed at the B3LYP/6-31G+(d) level using Gaussian  $09^{36}$ (ESI<sup>†</sup>). The energy minimized structure of a truncated **1b** (Me groups replaced dodecyl chains), shown in Fig. 1, adopts a pseudo boat conformation with both acenaphthyl groups *syn* and a close S–S distance (3.18 Å), which is more apparent in the side view of Fig. 1b, highlighting the intersecting angle between ancenaphthyl planes at  $117^{\circ}$ . Dithiaporphyrin **1a** adopts a similar saddle-shape with less curvature at  $125^{\circ}$  for the same plane intersection angle.

The UV-Vis absorption spectra for dithiaporphyrins **1a** and **1b** are shown in Fig. 2 and **1c** was precluded from optical assessment due to poor solubility. The ring fusion of the acenaphthyl groups

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Information regarding the synthesis and DFT characterization for porphyrins **1a–c**; variable temperature <sup>1</sup>H NMR spectra showing aggregation behavior of porphyrin **1a**; <sup>13</sup>C{<sup>1</sup>H}NMR spectra, and solid state thin film pictures of the porphyrin **1b** with C<sub>60</sub>. UV-Vis absorption spectrum for porphyrin **1c**. See DOI: 10.1039/c6nj03353a



Scheme 1 Structures of 21,23-dithiadiacenaphtho[1,2-c]porphyrins 1a-c.



Fig. 1 Optimized geometries of truncated **1b** using DFT (B3LYP/6-31G+(d)). (a) Top view, (b) side view. (c) Skew angle to highlight the saddle shape.



Fig. 2 UV-Vis absorbance spectrum of 1a (dotted line) 1b (solid line) in chloroform at  $10^{-6}$  M.

to thiophene has altered the optical properties significantly, which was observed for tetra-pyrrolic analogues previously.<sup>31,37</sup> Both **1a** and **1b** show bathochromic shifts of the Soret-like bands at 575 nm and 530 nm, respectively, compared to the Soret bands at 498 nm and 453 nm for the analogous dithiaporphyrins without ancenaphthyl fusion. Also, tetrayne **1a** shows a splitting of the Soret peak and a lowering of the optical transition strength. Dithiaporphyrins **1a** and **1b** have onsets of absorptions at 1000 nm and 1100 nm, respectively, which was unexpected since the related *meso*-position functionalised alkynes typically experience bathochromic absorption onsets compared the *meso*-phenyl analogs. We attribute the difference in absorption onsets to aggregation of **1a** (ESI<sup>†</sup>) because a splitting of the Soret-like absorption band can also be generated by **1b** using a less favourable solvent, such as toluene, to induce aggregation.

Variable temperature UV-vis spectra (ESI<sup>†</sup>) also show a shift in the Soret-like band as solution temperature increases, indicating aggregation. Further support of aggregation can be seen in the UV-vis spectra of the diprotonated species,  $H_2 1a^{2+}$  and  $H_2 1b^{2+}$ , in the ESI,<sup>†</sup> whereby the diprotonated spectra are consistent with monomer absorption. Absorption onsets provide an estimated optical HOMO–LUMO energy difference of 1.2 eV and 1.1 eV, which are lower than the comparable systems without the acenaphthyl groups fused.

Due to the curvature of **1a** and **1b** and the low oxidation potentials (ESI<sup>†</sup>) of -0.18 V and 0.06 V vs. Fc/Fc<sup>+</sup>, respectively, we assessed the affinity for [60]fullerene. Briefly, a toluene solution of [60]fullerene was prepared and allowed to dissolve overnight, then small aliquots were added to a cuvette containing porphyrins **1a** or **1b** in CH<sub>2</sub>Cl<sub>2</sub>. The changes in the UV-visible absorption spectra are shown in Fig. 3a as [60]fullerene was added to **1b**. Surprisingly, **1a** did not shown an interaction with [60]fullerene (ESI<sup>†</sup>). The titration experiment involving **1a** and C<sub>60</sub> resulted in a simple dilution with no perturbation in the optical bands.

Fig. 3a clearly shows a change in spectral features with added fullerene, suggesting an electronic interaction between **1b** and [60]fullerene is present. Please note, the titration experiment shown in Fig. 3a is unconventional because two solvents were used, such that the monomeric form of **1b** was available to bind, and details of the solvent composition and species concentrations can be found in the ESL<sup>†</sup> Following best practices for determining supramolecular associations outlined in the tutorial review article by Thordarson<sup>38</sup> resulted in no association, as demonstrated in



Fig. 3 (a) UV-visible spectra of the titration of [60]fullerene in toluene into 1b (3 × 10<sup>-6</sup> M) in methylene chloride. (b) UV-visible spectra of the titration of a fixed concentration of 1b (4 × 10<sup>-6</sup> M) with variable [60]fullerene concentrations ranging from 8 × 10<sup>-7</sup> M to 1 × 10<sup>-4</sup> M in a mixed solvent of 80 : 20 CH<sub>2</sub>Cl<sub>2</sub> : toluene.

Fig. 3b. For example, when constant solvent compositions were examined, both <sup>1</sup>H-NMR and UV-vis titration experiments did not show an association. Tetrachloroethane was employed for both <sup>1</sup>H-NMR and UV-vis experiments; in addition, the UV-vis titration experiments also explored either pure toluene or  $CH_2Cl_2$  and an 80:20 ( $CH_2Cl_2:Tol$ ) solvent mixture. We suggest the observed association effects in Fig. 3a are a consequence of solvent effects. The UV-vis spectral titration experiments, shown in Fig. 3b only exhibit an increase in the absorption bands for fullerene at 400 nm and 600 nm as their concentrations were increased. The difference between the two titration experiments is intriguing and points to an interaction that is dominated by solvent effects. The use of a variable solvent composition during titration precludes a complete association constant determination.

In addition to optical absorbance experiments, <sup>13</sup>C-NMR experiments (ESI<sup>+</sup>) of a 1:1 solution of [60]fullerene to porphyrin **1b** (at a total concentration of  $2 \times 10^{-4}$  M in  $d_8$ -toluene) showed the carbon peak assigned to [60]fullerene shifts from 143.57 ppm to 143.54 ppm upon interaction with porphyrin 1b. While this shift of 0.03 ppm is small, it is consistent with another report of porphyrin interactions<sup>39</sup> with fullerene. Furthermore, the toluene solvent peaks are not affected, indicating that the small shift in the [60]fullerene signal cannot be attributed to bulk solvent effects.<sup>39</sup> The same <sup>13</sup>C-NMR experiments involving 1a and [60]fullerene did not result in a fullerene signal shift (ESI<sup>†</sup>). At the NMR concentrations examined, it is possible that aggregation of 1b is occurring, which may account for the small chemical shift changes in [60]-fullerene. In addition, at 0.2 mM concentration the <sup>13</sup>C-signals of **1b** in toluene, were not observed after 70 000 scans. The combined optical and NMR experiments could suggest the degree of curvature in the host porphyrin binding to [60]fullerene plays a role; however, aggregation may preclude [60]fullerene interactions with 1a.

Fig. 4 shows the solid state UV-Vis spectra collected on thin films prepared by drop casting solutions from toluene on glass slides of both dithiaporphyrin **1b**, as well as a 1:1 mixture of dithiaporphyrin **1b** and [60]fullerene. Dithiaporphyrin **1b** dries as a pink film, whereas the 1:1 mixture of **1b** with [60]fullerene



**Fig. 4** Normalized UV-Vis absorbance spectrum of **1b** in solution (dotted line, methylene chloride at  $10^{-6}$  M), a drop cast film (solid black line), and a 1:1 1b :  $C_{60}$  drop cast film (red line). Inset: Soret peak position of solution (dotted line) and thin film (solid line).

dries as a blue film. In the solid state, porphyrin **1b** displays a slight hypsochromic shift of the Soret band from 532 nm to 526 nm, perhaps indicative of an H-aggregate, which has been observed in thin films of porphyrins.<sup>40</sup> The 1:1 mixture of dithiaporphyrin **1b** and [60]fullerene results in a dramatically bathochromically shifted Soret band from 532 nm to 603 nm indicating a clear electronic interaction between the two compounds in the solid state, suggesting the solution binding interaction is persistent in the solid-state.

In conclusion, metal-free dithiaporphyrin **1b** shows shape complementarity with [60]fullerene resulting in an association under specific solvent conditions, which are prominent in the solid state. In addition, these acenaphthyl-fused dithiaporphyrins exhibit broad visible light spectrum absorptions extending into the near-IR range and undergo multielectron electrochemical oxidations. Moving forward, other fused ring systems on dithiaporphyrins will be explored to tune the curvature and induce fit of other fullerenes and study the excited state dynamics of photoinduced electron transfer as model photosynthetic reaction centers.

## **Experimental section**

5,10,15,20-Tetra(4-dodecyloxyphenyl)-21,23-dithiadiacenaphtho[1,2*c*]porphyrin (1b): the dialcohol acenaphtho[1,2-c]thiophene-7,9bis[(4-dodecyloxyphenyl)-hydroxymethyl] (76 mg, 0.1 mmol) and freshly distilled pyrrole (7 µL, 0.1 mmol) were added under nitrogen to methylene chloride (40 mL to achieve a concentration of 2.5 mM). The flask was wrapped in tin foil, then BF<sub>3</sub>·OEt<sub>2</sub> (5 µL, 0.04 mmol) was added and let stir no longer than 5 min. DDQ (65 mg, 0.3 mmol) was then added and let stir in ambient atmosphere for no longer than 5 min. The resulting mixture was then filtered through an alumina slug using methylene chloride as eluent. The methylene chloride was removed under reduced pressure and the resulting crude pink/black waxy solid was subjected to column chromatography using methylene chloride and methanol (4.5:0.5) to afford 5,10,15,20-tetra(4-dodecyloxyphenyl)-21,23dithiadiacenaphtho[1,2-c]porphyrin as a pink powder (31 mg, 19%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.37 (d, J = 8.5 Hz, 8H), 8.28 (s, 4H), 7.67 (d, J = 8.0 Hz, 4H), 7.34 (d, J = 8.6 Hz, 8H), 7.21 (t, *J* = 7.7 Hz, 4H), 6.20 (d, *J* = 7.3 Hz, 4H), 4.23 (t, *J* = 6.5 Hz, 8H), 2.03-1.92 (m, 8H), 1.66-1.55 (m, 8H), 1.46-1.29 (m, 64H), 0.96–0.85 (m, 12H). <sup>13</sup>C NMR (101 MHz,  $CDCl_3$ )  $\delta$  160.4, 159.1, 148.6, 138.7, 137.3, 136.5, 135.4, 134.1, 133.9, 132.4, 129.7, 127.6, 127.4, 126.1, 115.0, 68.5, 31.9, 29.7, 29.7, 29.7, 29.7, 29.5, 29.4, 29.3, 26.2, 22.7, 14.1. HR-MS (MALDI-TOF): calcd for  $C_{112}H_{132}O_4N_2S_2 [M + H]^+$  1633.9701, found 1633.9637.

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