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Journal:	<i>ChemComm</i>
Manuscript ID	CC-COM-06-2024-003102.R1
Article Type:	Communication

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# Cyclically Conjugated Porphyrin Trimers Linked through Benzo[4,5]imidazo[2,1-a]isoindole Bridges

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Received 00th January 20xx,  
Accepted 00th January 20xx

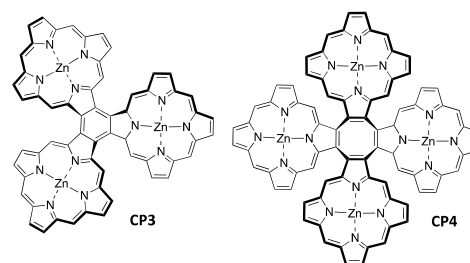
DOI: 10.1039/x0xx00000x

**Cyclically conjugated porphyrin trimers were prepared via a concise synthetic method. Zn-Trimer-1 displayed strong exciton coupling, suggesting the presence of effective electronic interactions. UV-Vis absorption and fluorescence spectra obtained through titration studies on the donor-acceptor adduct (Zn-Trimer-1–C<sub>60</sub>Im) indicate the occurrence of excited state photo-events.**

Inspired by nature's photosynthetic process of plants and bacteria,<sup>1–7</sup> electronically interacting multiporphyrinic systems have long been investigated as synthetic models of natural photosynthetic systems.<sup>8–11</sup> Remarkable successes have been achieved with cyclic porphyrin arrays, where porphyrins are arranged in a wheel-like structure or nanoring as photosynthetic antennae.<sup>12–22</sup> Considerable efforts have also been devoted to construct other porphyrin arrays<sup>23–30</sup> such as molecular wires for potential applications in sensors, solar energy conversion, non-linear optical (NLO) materials, and more. Due to synthetic difficulty, cyclically conjugated porphyrin arrays, where porphyrins are arranged in planar geometry are very rare. Very recently, Anderson and coworkers have reported unprecedented  $\beta,\beta$ -directly linked porphyrin trimer and tetramer with different geometries,<sup>31</sup> propeller and saddle respectively, of which result in distinct photophysical and electrochemical properties (Figure 1a). In this work, we present novel cyclically conjugated porphyrin trimers, which feature planar geometry with porphyrins assembled around aromatic triphenylene at the center (Figure 1b).

The porphyrin trimers were designed and constructed based on a concise reaction between vicinal diamines and benzoporphyrin dicarbaldehyde developed in our laboratory recently.<sup>32, 33</sup> This reaction provides a convenient approach to fuse benzo[4,5]imidazo[2,1-a]isoindole to the porphyrin periphery. Benzoporphyrin dicarbaldehyde **1**, reacted with triphenylene-2,3,6,7,10,11-hexamine **2** in the presence of formic acid and triethylamine to give **FB-Trimer-1** and **FB-Trimer-2** in a total 76% isolated yield (Scheme 1).

(a) Cyclically conjugated porphyrin oligomers reported by Anderson group in 2023



(b) This work

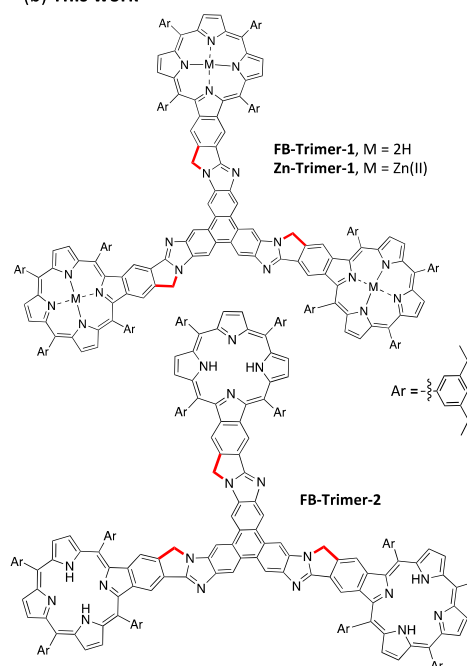


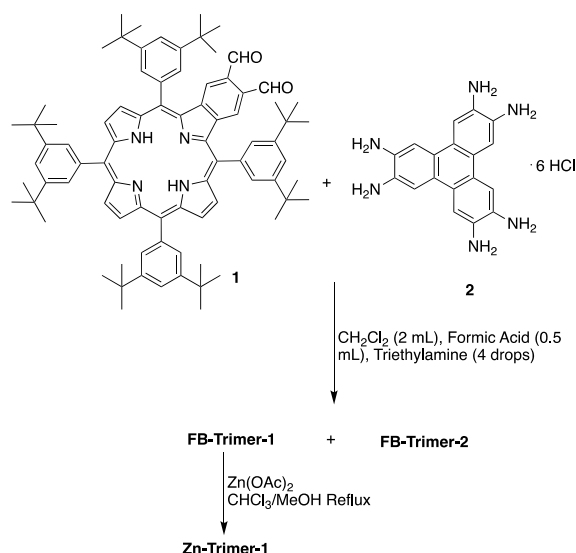
Figure 1 Examples of cyclically conjugated porphyrin oligomers.

Benzoporphyrin dicarbaldehyde **1** was obtained through a Heck-based cascade reaction developed in our laboratory.<sup>32, 33</sup> This reaction is expected to lead to two constitutional isomers **FB-Trimer-1** and **FB-Trimer-2**, which differ only in the way how the porphyrins are arranged around the triphenylene. The identity of the two isomers was assigned based on <sup>1</sup>H NMR

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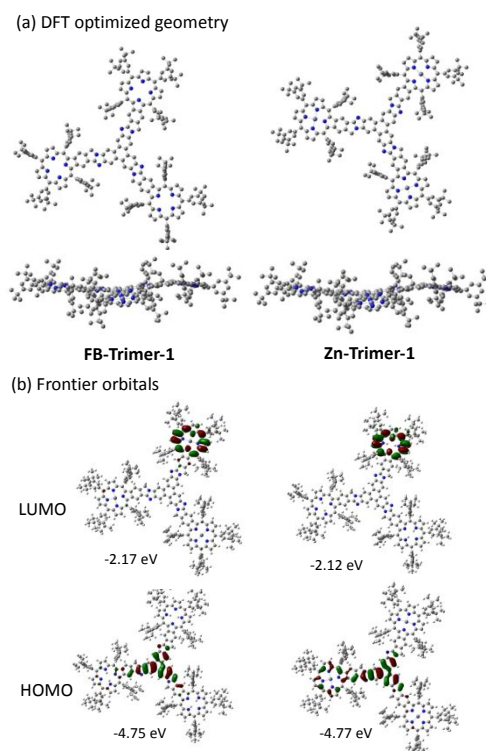
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x



**Scheme 1** Synthesis of porphyrin trimers: **FB-Trimer-1**, **FB-Trimer-2** and **Zn-Trimer-1**.

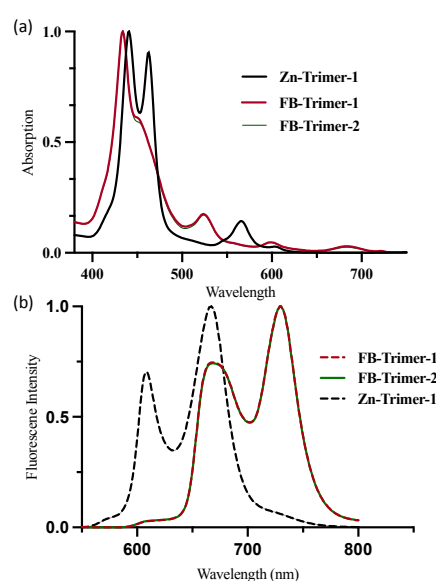
spectroscopy (See ESI). In the 5–5.5 ppm region on the  $^1\text{H}$  NMR spectra, **FB-Trimer-1** showed one singlet peak for the  $\text{CH}_2$  protons of the isoindole ring (highlighted in bold in Figure 1b) and **FB-Trimer-2** displayed two proton shifts, which agree well with the fact that **FB-Trimer-1** has  $\text{C}_3$  symmetry and **FB-Trimer-2** only has  $\text{C}_1$  symmetry. The formation of these trimers was further confirmed with High-Resolution Mass Spectrometry (MALDI). **FB-Trimer-1** and **FB-Trimer-2** were separated through flash column chromatography to give **FB-Trimer-2** as the major product in 44% isolated yield and **FB-Trimer-1** as the minor product with an isolated yield of 28%. Despite numerous attempts, we were not able to grow crystals suitable for single-crystal X-ray crystallography. The structure and geometry of these porphyrin trimers were optimized using DFT calculation (B3LYP/6-31G(d,p)) (Figure 2a). In contrast to the porphyrin trimers and tetramers reported by Anderson and coworkers (Figure 1a), both of which possess non-planar geometry despite their fully cyclically conjugated structures, both **FB-Trimer-1** and **FB-Trimer-2** adopt essentially planar geometry likely attributed to the extended conjugated spacer between the porphyrin and the triphenylene.

The UV-Vis absorption spectra of **FB-Trimer-1**, **FB-Trimer-2** and **Zn-Trimer-1** are compiled in Figure 3a. It is interesting that **FB-Trimer-1** and **FB-Trimer-2** display almost the same absorption spectra, suggesting different arrangement of the porphyrin monomer around the triphenylene does not affect their conjugation pathway significantly. **FB-Trimer-1** and **FB-Trimer-2** has a shouldered Soret band centred at 434 nm, and three weaker Q Bands 524 nm, 599 nm and 684 nm. Except for the small shoulder of the Soret band, the absorption pattern and peaks of **FB-Trimer-1** and **FB-Trimer-2** are reminiscent of the previously reported porphyrin monomer **AMIm-2**,<sup>32</sup> which suggest that only weak electronic interactions exist among these three porphyrins of **FB-Trimer-1** and **FB-Trimer-2**. This result is different from the linearly cyclically conjugated porphyrin dimers,<sup>33</sup> which displayed significant excitonic couplings. On the other hand, the absorption pattern of **FB-**



**Figure 2** B3LYP/6-31G\* optimized structures (a) and frontier orbitals of the indicated molecular systems (b).

**Trimer-1** and **FB-Trimer-2** is similar to that of the tetramer reported by Anderson group (Figure 1a), where the four porphyrin monomers were arranged around an 8-membered ring. In sharp contrast, when **FB-Trimer-1** was inserted with zinc, the Soret band was split into two bands indicating strong excitonic coupling among the porphyrin monomers, which reflect high level of electronic communications among the porphyrin monomers of **FB-Trimer-2**. This phenomenon is well in line with



**Figure 3** UV-Vis absorption spectra (a) and fluorescence spectra of the indicated compounds.

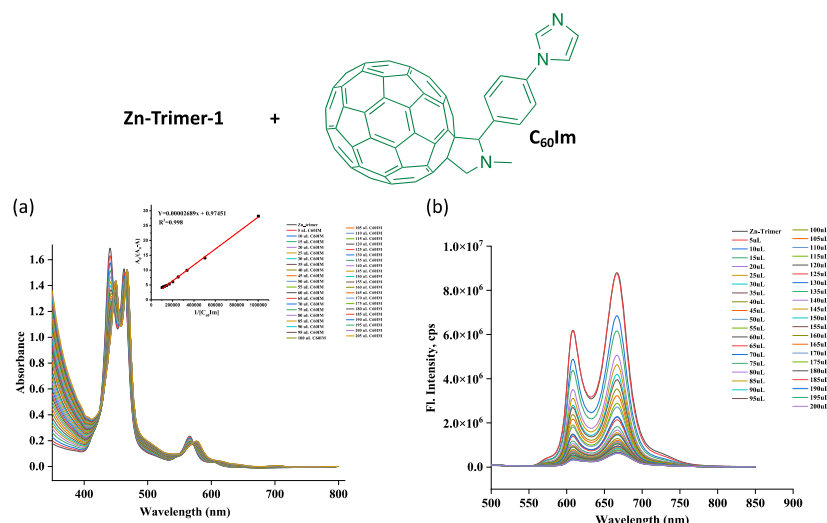


Figure 4 a) Absorption and (b) fluorescence spectral changes of Zn-Trimer-1 on increasing addition of C<sub>60</sub>Im. The Benesi–Hildebrand plot to evaluate the binding constant is shown in the inset of (a). The sample was excited at the Soret band peak maximum (441 nm).

the trend observed for the porphyrin dimers constructed with similar porphyrin monomer,<sup>33</sup> where zinc porphyrin dimer showed stronger excitonic coupling than its corresponding free base porphyrin dimer. However, it should be noted that the excitonic coupling in free base dimers is much stronger than that of the free base trimer (**FB-Trimer-1**). DFT calculations (B3LYP/6-31G(d,p)) of molecular orbitals were conducted to further understand the electronic properties of these porphyrin trimers (Figure 2b). It is interesting that the HOMO and LUMO of **FB-Trimer-1** display orbital segregation with the HOMO residing on the triphenylene component and LUMO on one of the porphyrin components. Such characteristics often suggest intramolecular charge transfer and thus worthy of further investigation. Similar to the LUMO of **FB-Trimer-1**, the LUMO of **Zn-Trimer-1** is mainly located at one of the three porphyrin components. Different from that of **FB-Trimer-1**, the HOMO of **Zn-Trimer-1** is delocalized to involve both the triphenylene component and one of the porphyrin components, which could partially explain the different extent of excitonic coupling observed for **FB-Trimer-1** and **Zn-Trimer-1**. These data suggest that different geometry and arrangement of the porphyrin in oligomers as well as the porphyrin central metals play significant roles in determining the outcomes of electronic interactions of porphyrin monomers in oligomeric assemblies.

Fluorescence (Figure 3b) spectra of **FB-Trimer-1**, **FB-Trimer-2** and **Zn-Trimer-1** were also collected. **FB-Trimer-1** revealed two emission peaks at 667 nm and 730 nm. Like their absorption spectra, **FB-Trimer-2** displayed almost the same emission peaks with the first one slightly red-shifted to 669 nm. **Zn-Trimer-1**

also exhibited two emission peaks at 608 nm and 667 nm, which are blue-shifted relative to those of **FB-Trimer-1** and **FB-Trimer-2**. The fluorescence lifetime of **FB-Trimer-1**, **FB-Trimer-2** and **Zn-Trimer-1** are 11 ns, 10.6 ns and 1.63 ns, respectively, which are typical of porphyrins.

Fullerenes are excellent electron acceptors and have often been used to construct donor-acceptor molecular systems. It is known that the unsaturated zinc of zinc porphyrins can further bind to nitrogenous ligands with moderate stability. As such coordinating a functionalized C<sub>60</sub>, i.e., C<sub>60</sub>Im (Figure 4), to zinc porphyrins provides a convenient approach to assemble donor-acceptor entity.<sup>34, 35</sup> Using this approach, in a previous work we identified an unusually long-lived charge-separation state (CS, 37.4 μs) for molecular donor-acceptor systems constructed with benzo[4,5]imidazo[2,1-a]isindole-fused porphyrin and C<sub>60</sub>Im.<sup>32</sup> A linearly conjugated zinc porphyrin dimer built on a similar monomer also showed interesting competition between energy transfer and electron transfer upon binding with C<sub>60</sub>Im.<sup>33</sup> We decided to investigate how the zinc trimer, **Zn-Trimer-1**, would respond upon binding to C<sub>60</sub>Im through titration of **Zn-Trimer-1** with C<sub>60</sub>Im. Both UV-Vis absorption spectra (Figure 4a) and fluorescence spectra (Figure 4b) were recorded during the process of titration. With increased addition of C<sub>60</sub>Im to a solution of **Zn-Trimer-1** in 1,2-dichlorobenzene (DCB), the UV-Vis absorption spectra revealed diminishing Soret and Q bands and appearance of new absorption peaks of a new species featuring red-shifted absorption bands and split Soret bands. Isosbestic points at 447 nm, 465 nm and 570 nm were observed, suggesting the existence of an equilibrium. The equilibrium

constant,  $K$ , evaluated using the Benesi–Hildebrand method<sup>34</sup> was found to be  $3.62 \times 10^4$  (Figure 4a, inset for the Benesi–Hildebrand plot) suggesting moderate stability of the adducts. The linear plot also suggests a 1: 1 stoichiometry, which indicates independent interaction of each porphyrin component with  $C_{60}$ . On the fluorescence spectrum, both emission bands were quenched over 85% upon addition of  $C_{60}Im$ , reflecting the occurrence of excited state photo-events such as energy transfer and electron transfer.<sup>34</sup> Since no emission band around 715 nm corresponding to  $C_{60}Im$  was observed during the titration process, energy transfer was not likely to be the major quenching mechanism for the donor–acceptor adducts.

In conclusion, we have developed a concise synthetic approach to build novel cyclically conjugated porphyrin trimers. While UV-Vis absorption spectra of free base porphyrin trimers (**FB-Trimer-1** and **FB-Trimer-2**) displayed minimal exciton coupling, that of zinc porphyrin trimer (**Zn-Trimer-1**) showed strong exciton coupling, suggesting effective electronic interaction among the three porphyrin components in **Zn-Trimer-1**. Significant fluorescence quenching was observed upon binding  $C_{60}Im$  to **Zn-Trimer-1**, indicating the occurrence of excited state photo-events. The titration studies further revealed independent electronic interaction of each porphyrin component in **Zn-Trimer-1** with electron acceptor  $C_{60}Im$ . Transient absorption spectroscopy and time-resolved electron paramagnetic resonance (TREPR) spectroscopy will be carried out to further understand the excitation state dynamics and kinetics of **Zn-Trimer-1**– $C_{60}Im$  adducts, their metal-ligand combination scenario as well as porphyrin trimers incorporated with other transition metals such as cobalt and iron.

Author Contributions:

We acknowledge the U.S. Department of Energy, Office of Science, Basic Energy Sciences for financial support under Award DE-SC0016766. We would like to thank Dr. Francis D'Souza, Mr. Ram Kaswan and Mr. Saad Shaikh for helpful discussions.

## Data availability

The data supporting this article have been included as part of the ESI.†

## Conflicts of interest

There are no conflicts to declare.

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The data supporting this article have been included as part of the Supplementary Information.