

## Supporting information

### Fine-tuning charge transfer interactions toward the efficient separation of endohedral metallofullerenes.

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### Experimental Methods

The synthesis and characterization of the trimetallic endohedral fullerenes (**4** and **5**) – as supramolecular guests – have been described in earlier work. Calixarene bisporphyrin hosts (**1** and **2**) were synthesized as described by Hosseini *et al.*<sup>1</sup> Toluene, acetonitrile and ortho-dichlorobenzene (oDCB) were used as HPLC grade solvents, the endohedral fullerenes were purchased from Luna Innovations, whereas [60]fullerene (**3**) was acquired from Sigma Aldrich.

*Photophysics:* Steady-state absorption spectroscopy was performed using a Shimadzu 1601 UV/Vis spectrophotometer. Steady state fluorescence studies were carried out with a Fluoromax 3 (Horiba). All solvents were spectroscopic grade and were further purified by passing twice through alumina (GlassContour) immediately prior to use.

Femtosecond TA measurements were made using a Ti:sapphire laser system detailed previously.<sup>2,3</sup> The instrument response function (IRF) for the pump-probe experiments was 180 fs. Typically 5 s of averaging was used to obtain the transient spectrum at a given delay time. Samples were photoexcited with 532 nm and 650 nm, 130 fs, 1.00 μJ laser pulses focused to a 200 μm spot in a 2 mm

pathlength quartz cuvette. The optical density at the pump wavelength was kept between 0.5-0.7. Analysis of the kinetic data was performed at multiple wavelengths using a Levenberg-Marquardt nonlinear least-squares fit to a general sum-of-exponentials function convoluted with a Gaussian instrument response function.

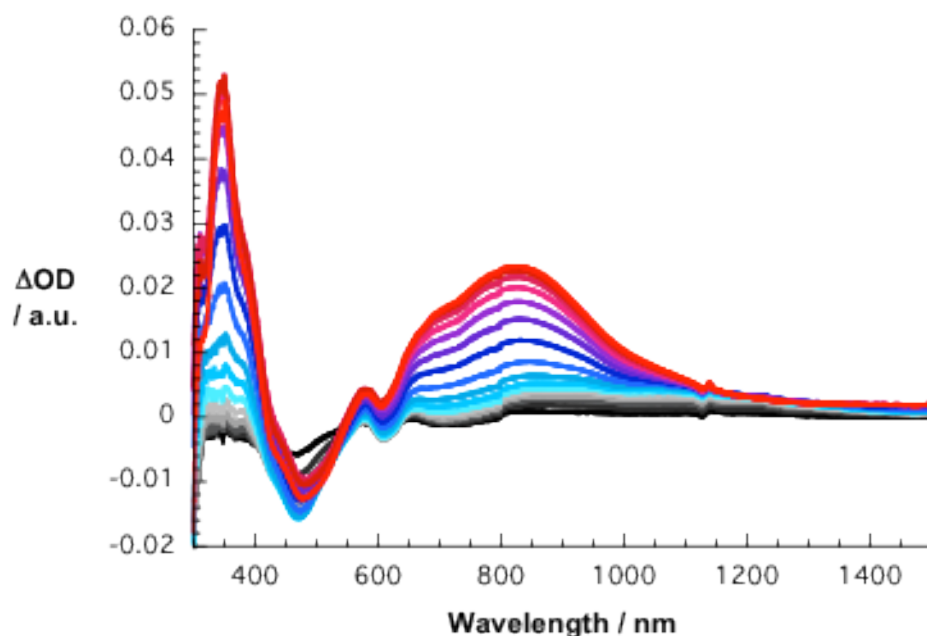
Samples for nanosecond transient absorption spectroscopy were placed in a 10 mm path length quartz cuvette equipped with a vacuum adapter and subjected to four freeze-pump-thaw degassing cycles. The samples were excited with 6 ns laser pulses generated using the frequency-tripled output of a Continuum 8000 Nd:YAG laser to pump a Continuum Panther OPO. The laser pump power was 1.2 mJ at 640 nm and 1.7 mJ at 532 nm. The excitation pulse was focused to a 5 mm diameter spot and matched to the diameter of the probe pulse generated using a xenon flashlamp (EG&G Electro-Optics FX-200). The signal was detected using a photomultiplier tube with high voltage applied only to four dynodes (Hamamatsu R926). The total instrument response time is 7 ns and is determined primarily by the laser pulse duration.

*Electrochemistry:* Differential Pulse Voltammetry (DVP) measurements were performed in ortho dichlorobenzene containing 0.1 M (Bu)<sub>4</sub>NClO<sub>4</sub> as supporting electrolyte and Ferrocene as internal standard. A glassy carbon electrode (3 mm diameter) was used as the working electrode, a platinum wire as the counter, and an Ag wire as the reference electrode. All electrochemical measurements were performed with an E.G.C. Princeton Applied Research model 263A potential/galvanostat.

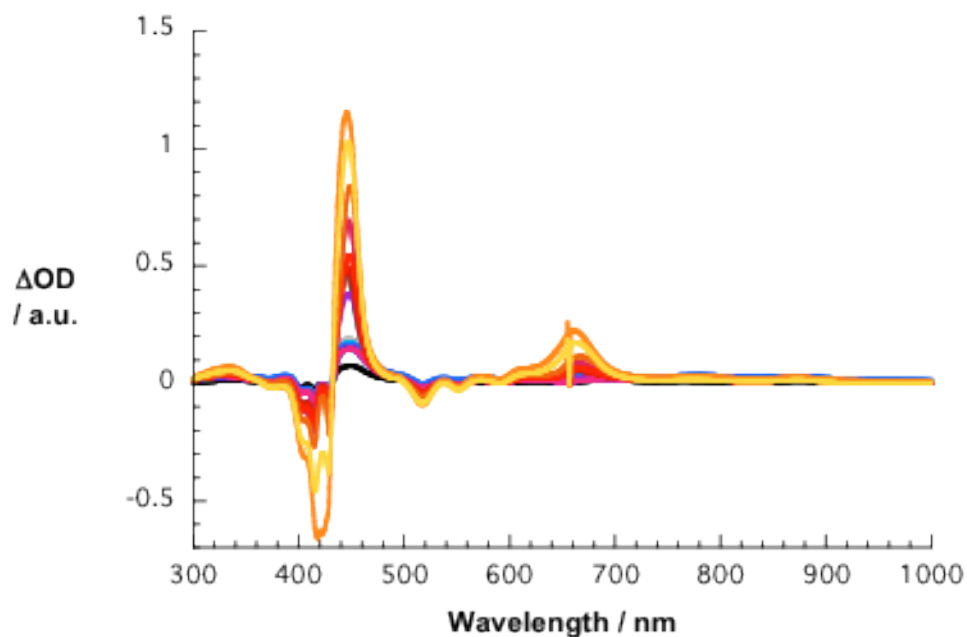
*Computational Studies:* Molecular models of the calixarene-bis-porphyrin complex with C<sub>60</sub> were constructed using the program Gaussview. In the case of Sc<sub>3</sub>N@C<sub>80</sub> the I<sub>h</sub> structural isomer observed in the x-ray structure of the Co(II)octaethylporphyrin cocrystallate was used. The bis porphyrin host was the nickel porphyrin derivative. Full geometry optimization was carried out using a QM/MM model based on the ONIOM method of Morokuma.<sup>4, 5</sup> All calculations were performed with the Gaussian 09 program.<sup>6</sup> The high level part in the ONIOM calculation was a density functional model B3LYP/6-31G(d) for the calixarene amido moiety whilst the low level part included the porphyrin and fullerene components with the universal force field model.<sup>7</sup> This was necessary as common density functionals are not able to account for the dispersive interactions between

porphyrins and fullerenes. The UFF contains the appropriate van der Waals terms and has been found to well reproduce the fullerene porphyrin approaches in cocrystallate and host guest structures.<sup>8, 9</sup>The nickel porphyrin derivative has been found to maintain planar porphyrin moieties within the UFF model, as is observed in x-ray structures.

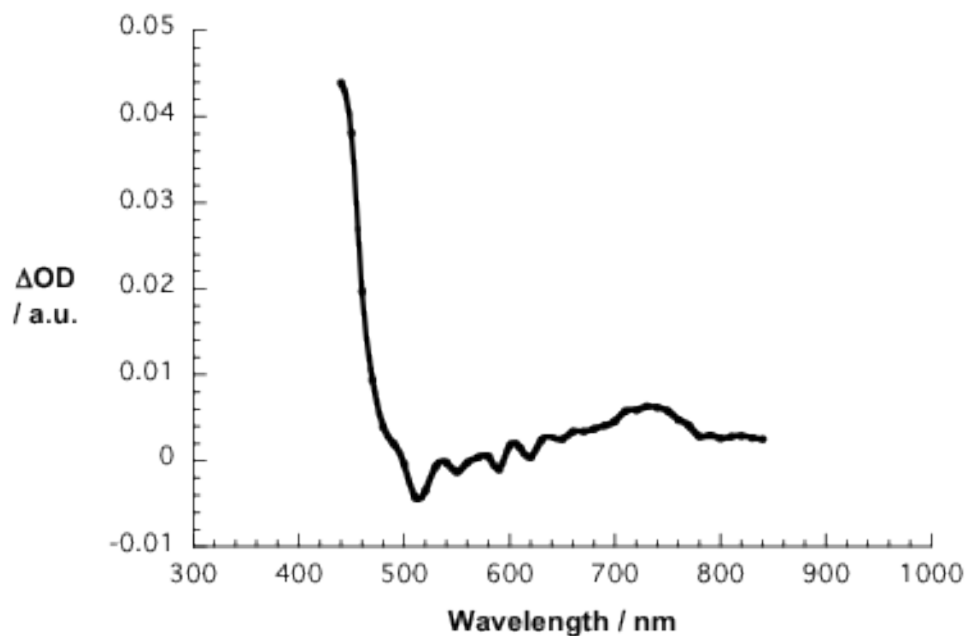
The interaction energies of the porphine molecule with  $C_{60}$  and  $Sc_3N@C_{80}$  were calculated using a dispersion corrected density functional method (DFT-D). Full geometry optimizations were carried out on each of  $C_{60}$ ,  $Sc_3N@C_{80}$ ,  $C_{60}$ ..porphine and  $Sc_3N@C_{80}$ ..porphine. The B97D functional of Grimme<sup>10</sup> was used with the TZVP basis of Ahlrichs<sup>11</sup> for carbon, nitrogen and hydrogen atoms and a pseudopotential and corresponding basis from the Stuttgart group<sup>12, 13</sup> for scandium. The full porphine fullerene models for  $C_{60}$  and  $Sc_3N@C_{80}$  had 1680 and 2208 basis functions respectively. The density fitting approximation was used with fitting basis sets generated using the Auto keyword in the Gaussian09 program.



**Fig. S1** Differential absorption changes following electrochemical oxidation of **4** in ortho-dichlorobenzene at a potential of +0.61 V versus  $Fc/Fc^+$ .



**Fig. S2** Differential absorption changes following electrochemical reduction of **1** in ortho-dichlorobenzene at a potential of -2.02 V versus Fc/Fc<sup>+</sup>.



**Fig. S3** Differential absorption changes following pulse radiolytic reduction of H<sub>2</sub>P in a deoxygenated solvent mixture containing toluene, 2-propanol and acetone with (CH<sub>3</sub>)<sub>2</sub>C<sup>•</sup>OH and (CH<sub>3</sub>)<sub>2</sub>C<sup>•</sup>O<sup>-</sup> radicals.

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