Supplementary Material (ESI) for Chemical Communications

Supporting Information

Construction of Trimeric Porphyrin-Fullerene-Porphyrin Stacks within Surface-Derived Pores of Nano-scale Dimensions

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1) Silica Particle preparation:

a) Preparation of Amino Modified Silica Colloids.[S1] Colloidal silica nanoparticles with a mean diameter of 100 nm were prepared according to standard method. All glass reaction vessels were cleaned extensively to ensure that no nucleation sites were present (washing procedure: filling with 3% hydrofluoric acid for an hour, rinsing with Milli-Q water and finally rinsing with distilled ethanol). In a reaction vessel, which had been dried for 3 h at 120 ^{o}C, TEOS (1.5 mL) and ammonia (3 mL, 28%) were dissolved in 50 mL of anhydrous ethanol, and the reaction mixture was slowly stirred at room temperature for 24 h in the dark. Milli-Q water (400 µl) was added and stirred for a further 2 h. Following this, (3-Aminopropyl)triethoxy silicate (APTS) (400 μl) was added, and the mixture was stirred overnight. The resulting silica sol was warmed to 80 $^{\circ}$C and refluxed at this temperature for 10 h under an argon atmosphere. The amino-modified silica colloids with a diameter of 100 nm were considered suitable for use after cooling to room temperature (Figure S1).

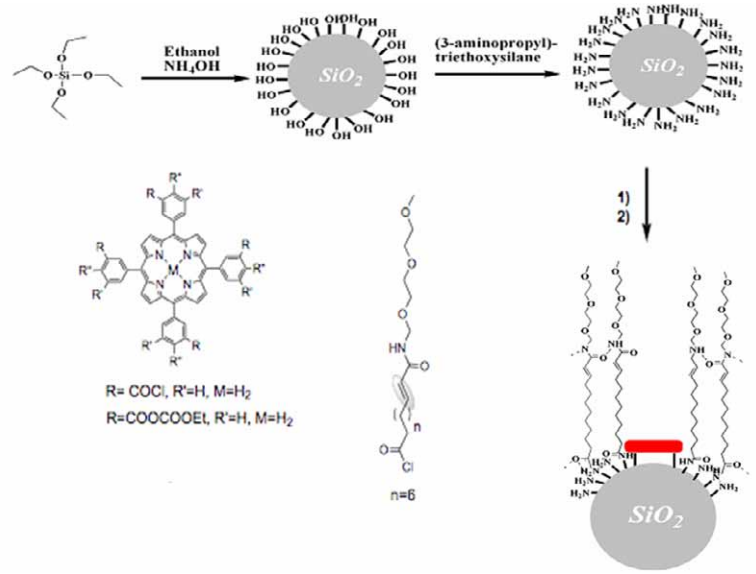

Figure S1. Preparation of aminated silica particles and self-assembly to form 2 nm gaps (yoctowell).

b) Construction of 1.[S1] Silica particles coated with voids and closed membranes were prepared as follows: The above-mentioned silica colloid (0.5 g) was washed 4 times with anhydrous ethanol and anhydrous CH_2Cl_2 by repeated centrifugation, dispersion, and ultrasonocation. The resultant silica particles were dissolved in 50 mL of CH_2Cl_2 containing 1 mL of dry triethylamine. Whilst applying vigorous stirring, 4 mL of CH_2Cl_2 solution of porphyrin **1** (1 mg)[S1] was added dropwise. After stirring the mixture for 2 h, 5 mL of a CH_2Cl_2 solution of bola **3** (2 mg)[S1] were added and the resulting suspension was stirred in the dark overnight. The membrane coated nanoparticles (Figure S1) were isolated by repeated centrifugation, dispersion, and ultra-sonication using CH_2Cl_2 and were used for further measurements, as described.

Preparation of zinc metalated porphyrin yoctowells (1b)
100 mg of the membrane coated nanoparticles were dispersed in 10 mL of methanol : chloroform (1:1). Once dispersed, 10 mg of zinc acetate was added and the particles were refluxed for 4 hrs with gentle stirring. After completion conversion to the zinc porphyrin yoctowell (**1b**) (as confirm by UV/Visible and fluorescence spectroscopy, shown in Figure S2) the modified silica particles were isolated by repeated centrifugation, dispersion, and ultrasonication using methanol and chloroform to remove excess zinc acetate.

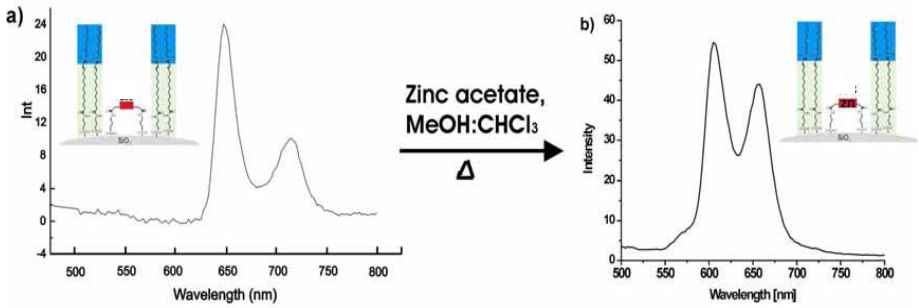

Figure S2. Fluorescence spectra of (a) free base porphyrin yoctowell **1a** converted to (b) zinc porphyrin yocotwell **1b.**

Fluorescence Quenching Experiments.[S1] Fluorescence measurements and quenching experiments were performed on a Perkin-Elmer spectrometer (LS50B). The silica colloid coated with perforated membranes (3 mg) was dispersed in 3 mL of water and placed in a quartz cuvette. A 30 µl aliquot of the aqueous solutions of the quenchers, such as Mn(III)TPPS **2** (10^{-4} M), was added. The fluorescence of base bound zinc porphyrin on the particle surface was continuously checked.

UV/Visible Spectroscopy of Silica Colloids. UV/Visible absorption spectra of membrane coated silica colloids were acquired using a Perkin-Elmer Lambda 16 spectrometer.

Functionalization of walls of 1.[S1] Amino functionalization of the surface tethered bola **3** was achieved by taking 20 mg of the zinc porphyrin yoctowell (**1b**) dispersed in 10 mL of an aqueous solution of methylamine (10 mM) and stirring for 2h. After this time the silica particles were collected by centrifugation and washed several times using Milli-Q water.

Titration experiments. Silica colloids **1b** (3 mg, zincporphyrin = ~1×10^{-6} M) was dispersed in 3 mL of chloroform and placed in a quartz cuvette. Aliquot of 1 µL of the guest fullerene solution, such as a C_{60} (0-14 equivalent of 10^{-5} M) from toluene, was added to the cuvette until the titration was complete. The change in absorption and fluorescence of base zinc porphyrin on the particle surface were the monitored over the course of these experiments. The resultant inclusion complexes were isolated by centrifugation (2000 rpm, 5 min) and dried in air.

Capping Experiments. The C_{60} included **1b** coated silica particles with amino functionalized gaps (0.5 g) were dispersed in 5 mL of Milli-Q water. The anionic porphyrin (Mn(III) TPPS) **2** (0.1 mg) was added and the reaction mixture was stirred for 30 min then left overnight in darkness. The capped silica particles were isolated by washing several times with Milli-Q water, and were characterized by UV/Visible and fluorescence spectroscopy.

Once the integrity of the yoctowells on silica particles by the size-exclusion assay was realized, fresh samples of the yoctowells were suspended in milli-Q water and then titrated with guest fullerenes solutions (Figure S3) and the fluorescence output of bottom porphyrin monitored. Once complex formed then the particles were then isolated by centrifugation, redispersed in water and finally tetrasulphanato porphyrin (Mn(III)TPPS **2**) was added for overnight, excess porphyrin **2** was removed with centrifugation, redispersed in water (3 times). The obtained UV-Visible absorption results shows zincporphyrin-fullerene-manganeseporhyrin are in the 1:1:1 ratio.

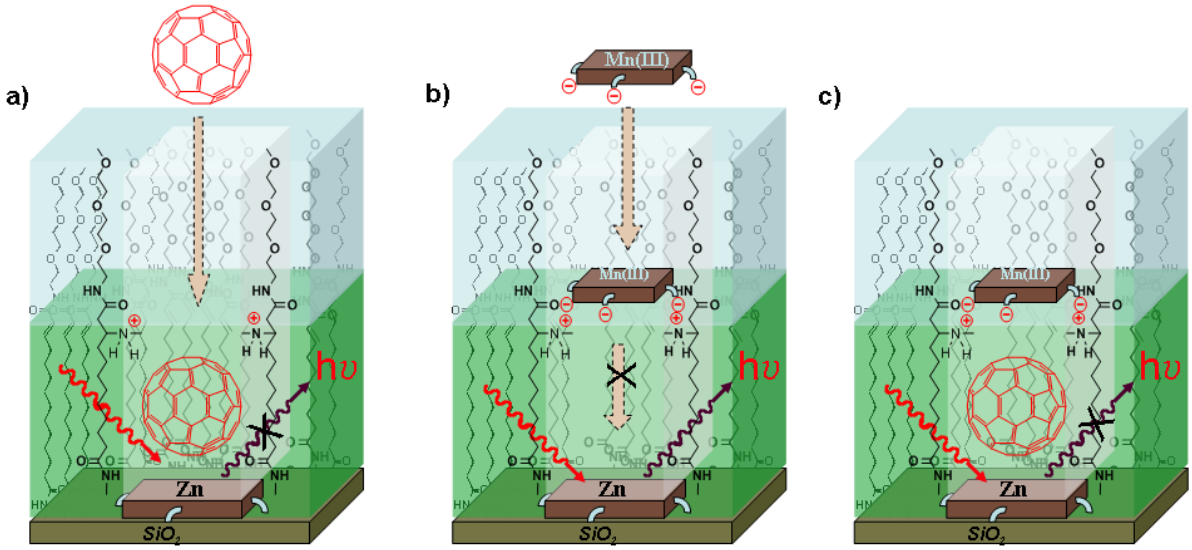

Figure S3. Excitation of bottom zinc porphyrin yoctowell **1b** ($\lambda_{max} = 433$ nm) (a) Insertion of a fullerene into the pore of the yoctowell causes fluorescence quenching. (b) Tetraanionic porphyrin (Mn(III)TPPS **2**) bind to positively rim of the walls and cannot enter into the gaps, hence a substrate that doesn't interfere strongly with the porphyrin's fluorescence. (c) Inclusion complex of C_{60} leads to fluorescence quenching of the zinc porphyrin and anionic porphyrin act as cap of the yoctowell.

Calculation of K_{assoc}. Benesi-Hildebrand equation (Equation 1) was applied to determine the binding constant K_1 of each of the fullerene guests.[S2]

$$\frac{b}{\Delta A} = \frac{1}{S_t K \Delta\varepsilon[L]} + \frac{1}{S_t \Delta\varepsilon} \qquad (1)$$

where b is the optical path length (1 cm), ΔA is the change in absorbance at 433 nm, at which the largest change was observed, S_t is the total concentration of substrate, [L] is the concentration of ligand. $\Delta\varepsilon = \varepsilon_{11} - \varepsilon_S - \varepsilon_L$, where ε_{11}, ε_S, and ε_L are the molar absorptivities of the 1:1 complex, S, and L at 433 nm, respectively.

An association constant (K_{assoc}) for the binding of C_{60} in toluene was calculated based on the decrease in absorption intensity at 433 nm in the collected UV-Visible absorption data, by applying the Benesi-Hildebrand equation.

Transmission Electron Microscopy (TEM): TEM samples were prepared by dropping 10 μl aliquots of colloidal solution (ethanol/H_2O 1:1) onto a carbon-coated grid (yoctowell with and without fullerenes). After about 1 min, the remaining solution was blotted off with a filter paper. A Philips M12 transmission electron microscope operated at 100 kV was used to obtain the images of Figure 2b (manuscript) and Figure S4 shows C70 into the hydrophobic yoctowells. Which shows the addition of C_{60} acts to phase contrast the boundary of the particles without C_{60} or in the presence of C_{70} we didnot observed such phase contrast.

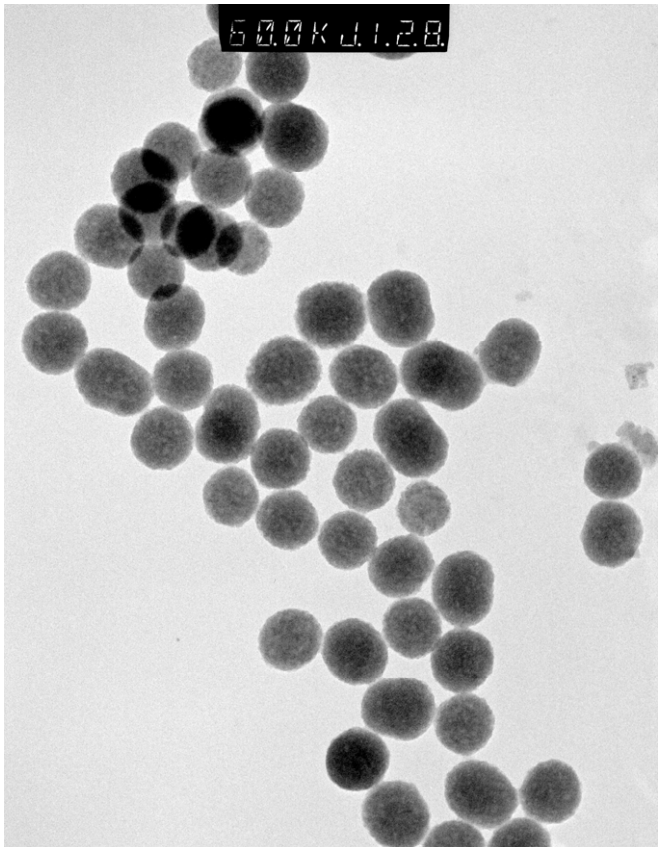

Figure S4. TEM images of 1⊃C_{70}

Supporting References:

[S1]. G. Li, S. V. Bhosale, T. Wang, S. Hackbarth, B. Roeder, U. Siggel and J.-H. Fuhrhop, *J. Am. Chem. Soc.*, 2003, **125**, 10693.
[S2]. K. A. Connors, *Binding Constants*, Wiley, New York, 1987, pp. 141.