Supramolecular Assembly with Multiple Preorganised π -Electronic Cages

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The construction of highly ordered assemblies with welldefined topology is an important topic in the fields of chemistry, materials, and life sciences, as they always uncover fascinating and unexpected functionality that cannot be obtained with simple building blocks.^[1] A variety of noncovalent interactions have been employed as driving forces for the formation of highly ordered assemblies including hydrogen-bonding,^[2] metal-ligand coordination,^[3] $\pi \cdots \pi$ stacking^[4] and host-guest couples.^[5] To build truly operational supramolecular materials, extremely strong interactions between subunits is a prerequisite to achieve positive cooperative effects. As a consequence, multivalent binding has emerged as an effective strategy that introduces multiple simple binding modes into one rationally designed monomer.^[6] This straightforward strategy has been ubiquitously practiced in diverse biorecognition processes,^[7] such as RNA metabolism, peptide folding, cellular signaling and carbohydrateprotein interactions. Inspired by nature, artificial assemblies^[8] have gained considerable attention in recent years, in whichmultivalent binding plays a key role in building highly ordered nanoarchitectures with well-defined topology, optimising and amplifying their desired physicochemical properties.

In this paper, we utilise two attractive classes of functional dyes, porphyrin and phthalocyanine, and a multivalent binding strategy to construct a supramolecular linear assembly with the following features: 1) taking advantage of the high affinity between permethyl- β -cyclodextrin (PMCD) and sulfonated porphyrin,^[9] the linear assembly was formed with high stability arising from quadruple binding; 2) phthalocyanine and porphyrin are significant chromophores with broad spectral ranges in the near infrared region which are widely used in light-harvesting and light conversion;^[10] 3)[60]fullerene (C₆₀) can be effectively captured in the assembled lattice and represents an elegant carrier of C₆₀ are integratively gathered by hierarchical assembly, and the desired excited energy/electron transfers occur within the ternary complex,

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making this artificial nanoassembly an appealing candidate for applications in photodynamic therapy^[11] and molecular photovoltaics.^[12]

The bulky PMCDs modified with zinc phthalocyanine (1) were synthesised from 8-fold-alkynylated phthalocyanine $(3)^{[13]}$ and excess mono-(6-deoxy-6-azido)-PMCD (4) in THF/H₂O through "click chemistry" in 43.8 % yield (Scheme 1), and comprehensively characterised by ¹H and ¹³C NMR spectroscopy, MALDI-TOF and elemental analysis (Figures S1–S3 in the Supporting Information). 1 showed a satisfactory solubility of up to 2.0 mM in water (25.3 mgmL^{-1}) which was attributed to the solubility of the PMCD units. Due to the strong noncovalent interactions between PMCD and 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (2),^[9] the linear supramolecular polymer could be conveniently constructed through complexation of 1 and 2 in water. The complex was identified using dynamic light scattering (DLS), viscosity measurements and electron microscopy as described below.

The photophysical behaviour accompanying the assembly process of **1** and **2** were investigated by UV/Vis and fluorescence spectroscopy. As shown in Figure 1, the Soret band absorption of **2** gradually changed with stepwise addition of **1**, ultimately resulting in a complexation-induced bathochromic shift from 413 to 417 nm, indicative of a transition from free **2** to the **1**-associated species.^[14] Moreover, the absorbance changes of **2** levelled off in the presence of 0.25 equivalents of **1**, implying the formation of a stable 1:4 complex between **1** and **2** (Figure 1, inset). The host–guest stoichiometry was also examined by a Job's plot, in which an inflection point of complex-induced changes of absorbance (ΔA) appeared at a molar fraction of 0.2 further supporting the 1:4 host–guest stoichiometry.(Figure S4 in the Supporting Information).

As shown in Figure S5 (see the Supporting Information), the fluorescence emission spectrum of **2** completely overlapped with the Q-band absorption spectrum of **1** in the range of 575–800 nm, implying that an efficient excited-energy-transfer (EET) process could occur from porphyrin to phthalocyanine in the complex of **1** and **2**. When excited at 514 nm, the emission peak of **2** at 643 nm was quenched upon gradual addition of **1**, accompanied by the formation of two new peaks at 692 and 760 nm, corresponding to the characteristic emission peaks of phthalocyanine (Figure 2). In control experiments, no appreciable emission of phthalocyanine could be observed when free **1**, **2**/**3**, and **3**/**4** systems were excited at 514 nm (Figure S6 in the Supporting Information).

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Scheme 1. Synthetic route to compound 1 and molecular structure of porphyrin derivative 2.



Figure 1. Soret band spectral changes of $2 (1.0 \times 10^{-6} \text{ M})$ upon addition of 0–0.30 equivalents of 1 (from a to 0) in pH 7.2 phosphate buffer solution at 25 °C. Inset: the absorption change versus 1/2 molar ratio recorded at $\lambda = 416$ nm.

mation). These phenomena jointly demonstrate that complexation of PMCD and porphyrin draws the donor and acceptor chromophores into close proximity and is of utmost importance in the EET process. In addition, the excitation spectrum of assembly 1.2 was recorded by holding the emission wavelength at 693 nm, which was similar to the combined absorption spectra of porphyrin and phthalocyanine entities in the range of 200–700 nm, providing an alternative evidence for the EET process (Figures S7 and S8 in the Supporting Information).

Subsequently, the EET efficiency (E) in the 1:1 complex of 1.2 was calculated to be 89.8% according to Forster's



Figure 2. Fluorescence spectral changes of $2 (1 \times 10^{-6} \text{ M})$ upon addition of 1 (0-1.02 equiv) in the direction of the arrows in increments of 0.06 equivalents in pH 7.2 phosphate buffer solution at 25 °C ($\lambda_{ex} = 514 \text{ nm}$).

rules.^[15] It is worth noting that this E value is higher than those reported in which covalently linked and cooperatively-coordinated phthalocyanine–porphyrin dyads were used as light-harvesting antennas. Furthermore, the centre-tocentre distance between the donor and acceptor moieties was also calculated as 29.68 Å, which is consistent with the optimised molecular modulation result (27.30 Å) by the minimised energy method in Figure S9 (see the Supporting Information).

The highly efficient EET process between **1** and **2** may be explained as follows. The cyclodextrin moieties in **1** act as sterically demanding substituents at the periphery of the phthalocyanine core and prohibit intrachromophoric interactions of self-associated dimers or oligomers which would lead to unfavourable factors for EET.^[17] In addition, the hydrophobic nature of the cyclodextrin cavity could offer a microenvironment which may hinder random collisional

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quenching of free porphyrins and prevent interactions with solvent molecules.

Moreover, DLS measurements showed free 1 or 2 did not form large assemblies, whereas the main hydrodynamic diameter of aggregates was increased to 130.4 nm in the case of assembly 1.2, providing evidence for the existence of large-scale aggregation in aqueous solution (Figure S10 in the Supporting Information). Additionally, viscosity serves as further evidence for the formation of assembly species, in which a critical aggregation concentration value could be observed as a transition from the formation of monomers or oligomers to highly ordered supramolecular polymers.^[18] As shown in the logarithmic plot of specific viscosity versus concentration of assembly 1.2 (Figure S11 in the Supporting Information), the predominance of the resulting assembly was gradually increased with its concentrations, accompanied with the appearance of a clear inflection point at 3.98 $\times 10^{-6}$ M. Taking the aforementioned discussions into account, we undoubtedly infer the supramolecular polymerisation process of 1 with 2 in water.

The intuitive morphology of the assembly 1.2 was characterised by atomic force microscopy (AFM) and transmission electron microscopy (TEM) experiments. A number of micron-long wires, approximately 4.2 nm in height were found in AFM images, corresponding to the height of a single molecule of 1 (Figure 3a and Figure S12a in the Supporting Information) TEM images also displayed several linear structures with lengths greaterthan 1 μ m (Figure 3c and Figure S12c in the Supporting Information).

Furthermore, molecular modelling studies were performed to give the computational minimum-energy structures of free **1** and assembly **1**·**2** (Figure S9 in the Supporting



Figure 3. Typical AFM (a, b) and TEM (c, d) images of the linear assembly 1.2 (a, c) and the complex of $1.2 \cdot C_{60}$ (b, d), respectively.

Information). Free **1** gave relatively disordered steric configurations, whereas the orientation of cyclodextrins in assembly **1**·**2** was highly ordered, indicating that the robust hostguest interaction between PMCD and the water-soluble porphyrin is the key factor in the formation of the linear assembly **1**·**2**. More interestingly, π -electronic cages were formed in assembly **1**·**2**, composed of one phthalocyanine, eight cyclodextrins and four porphyrins. The volume of the π -electronic cage is very suitable for two fullerenes (Figure S13 in the Supporting Information). It is wellestablished that planar π -conjugated systems, such as porphyrin and phthalocyanine, can favourably attract C₆₀ through π ··· π interactions.^[19] We therefore explored the capturing capability of **1·2** for C₆₀ using its π -electronic cage as the binding unit.

Capture of C_{60} with 1·2 was achieved using a grinding method in water, providing the water-soluble complex of 1·2· C_{60} . In comparison to complex 1·2, three new bands appeared at 216, 261 and 345 nm in the UV/Vis spectrum of 1·2· C_{60} (Figure 4). These bands were assigned to the charac-



Figure 4. UV/Vis spectra of 1.2, 2.4 C_{60} , and 1.2 C_{60} ([1.2 C_{60}]=[1.2]= [2.4 C_{60}]=7.5×10⁻⁷ M) at 25 °C. Inset: the magnified area of 660–780 nm.

teristic absorption of C60.[20] Moreover, the Q-band absorption of the phthalocyanine moiety in 1 underwent an appreciable bathochromic shift from 684 to 692 nm upon complexation with C_{60} , indicating the existence of $\pi \cdots \pi$ interactions between C_{60} and phthalocyanine.^[21] In contrast, no bathochromic shift was observed in the UV/Vis spectrum for 1 with 2 using the same grinding procedure. This phenomenon also confirms that the C₆₀ molecule was spatially constrained by the phthalocyanine moiety rather than encapsulated in the PMCD cavity. Moreover, no wavelength shift was observed in the Soret band absorbance of 2, indicating that the introduction of C60 has minimal effect on the binding geometry between PMCD in 1 and porphyrin 2.^[22] In addition, the fluorescence of both porphyrin and phthalocyanine in $1.2 \cdot C_{60}$ was approximately 28% weaker than that of 1.2, mainly due to the intermolecular photoinduced electron transfer from porphyrin/phthalocyanine to C₆₀ (Figure S14 in the Supporting Information).

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The complex $1.2 \cdot C_{60}$ was further characterised by FTIR (Figure S15 in the Supporting Information), Fourier transform high-resolution mass spectrometry (FT-MS) and thermogravimetric analyses (TGA). The FTIR spectrum of $1.2 \cdot C_{60}$ showed two characteristic vibrations at 527 and 576 cm⁻¹, corresponding to pristine and truncated icosahedral C₆₀ with high symmetry,^[23] which provided qualitative evidence that C₆₀ was included and stabilised by the assembly 1.2. Furthermore, a peak at m/z 1519 was observed in the positive ion mode of the FT-MS spectrum, assigned to $[1{\cdot}2{\cdot}C_{60}$ + 2Na^+ + 10H^+]/12, which provides further evidence for the formation of the $1{\cdot}2{\cdot}C_{\rm 60}$ complex (Figure S16 in the Supporting Information). TGA curves also showed that the assembly 1.2 lost 88.4% of its original weight when heated from room temperature to 800°C, whereas the weight loss of ternary complex 1.2.C₆₀ was only 80.2% in the same temperature region (Figure S17 in the Supporting Information). Considering that C_{60} is very thermally stable and its decomposition temperature is above 850°C,^[24] the additional 9.3% residue of combustion should be assigned to the content of C_{60} in $1.2 \cdot C_{60}$, which is in good accordance to the theoretical value (7.9% calculated as two C_{60} molecules in each of π -electronic cage) and elemental analysis. Furthermore, as discerned from Figure 3b and 3d, and Figure S12b and S12d in the Supporting Information, the introduction of C₆₀ did not profoundly affect the intuitive morphology of the obtained supramolecular assembly of 1.2. Combining all the characteristic data described above, we can deduce a possible complexation process involving extensive intermolecular interactions of 1 and 2 with C_{60} , as illustrated in Scheme 2.



Scheme 2. Schematic illustration of the inclusion–complexation process of C_{60} into assembly 1.2.

To confirm the assumption that C_{60} was encapsulated in the π -electronic cage, but not in the cavity of cyclodextrin, capturing C_{60} by complex 2·4 were carried out as control experiments. No absorption band of C_{60} was observed under the same experimental conditions (Figure 4), demonstrating that C_{60} could not displace 2 from the cyclodextrin cavity. This suggests that PMCD possesses a much higher binding affinity for 2 (>10⁷ m⁻¹) than C_{60} .^[9] The capturing ability of 1·2 for C_{60} was further evaluated by a solvent-extraction experiment, in which the pristine C_{60} was extracted from toluene phase to 1·2 aqueous solution. The assembly 1·2 gave the extractability of 9.1%, which is pronouncedly higher than the extractabilities of building unit 1 (3.2%) and the

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control complex 2·4 (0.8%). These results reveal that the preorganised cage structure in 1·2 plays a crucial role in capturing C₆₀. Additionally, complex 1·2·C₆₀ is kinetically stable and no colour change or flocculation was observed in the stock solution even after standing for a period of one month (Figures S18 and S19 in the Supporting Information). TGA experiments show good thermal stability of 1·2·C₆₀ (above 300 °C).^[25]

Considering that the linear nanoarchitecture of 1.2 and its resulting ternary assembly $1.2 \cdot C_{60}$ contains multivalent lightactivated moieties, DNA cleavage experiments were carried out to investigate their potential application in photodynamic therapy. The agarose gel electrophoresis assay of plasmid DNA is illustrated in Figure 5. In the absence of light, nei-



Figure 5. Photocleavage of PET-21b plasmid DNA ($6 \text{ ng}\mu L^{-1}$) by 1·2 (Lane 2, $1 \times 10^{-5} \text{ M}$), 1 (Lane 3, $1 \times 10^{-5} \text{ M}$), 1·2·C₆₀ (Lane 4, $1 \times 10^{-5} \text{ M}$) and 2/PMCD systems (Lane 5, $4 \times 10^{-5} \text{ M}$) in the presence (+) and absence (-) of visible light, respectively. Lane 1 is the blank control.

ther 1·2 nor 1·2·C₆₀ displayed DNA cleavage ability. Remarkably, the supramolecular 1·2·C₆₀ system showed extremely high DNA photocleavage activity with an efficiency of 82 % under visible-light irradiation, in which the closed supercoiled DNA was mostly cleaved to nicked circular DNA (lane 4) due to the generation of singlet oxygen (¹O₂) species and subsequent DNA damaging processes.^[26] As control measurements, 1, 2/PMCD, and 1·2 systems showed merely weak or moderate cleavage activity (lanes 2, 3, and 5).

In conclusion, through adopting a multivalent-binding strategy and exploiting the robust host-guest couples of PMCDs and sulfonated porphyrins, we successfully constructed a novel linear-supramolecular assembly 1.2 with highly ordered structure, good stability, and low critical aggregation concentration. Noticeably, π -electronic cages were formed in assembly 1.2, composed of one phthalocyanine, eight PMCDs and four porphyrin units, which were efficient at capturing C₆₀ in water. Moreover, as an initial exploration, 1.2.C60 displayed promising photoinduced DNA cleavage capability. Considering that phthalocyanine, porphyrin and C60 are well known light-harvesting molecules, the linear nanoarchitecture of 1.2 and its resulting ternary assembly, $1.2 \cdot C_{60}$ are likely to find applications in the areas of light-heat conversion, optically healable materials and photodynamic therapy.

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Materials, methods and characterisation techniques are described in the Supporting Information.

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