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A highly efficient supramolecular photoswitch for singlet oxygen generation in water[†]

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A series of water-soluble supramolecular assemblies were constructed from dithienylethene-modified permethyl- β -cyclodextrins and porphyrin derivatives, accompanied by a high FRET efficiency, and could be applied in the control of singlet oxygen generation in a 1% ethanol aqueous solution upon irradiation of different wavelength light. These findings will provide a feasible and convenient way to construct a potential photodynamic therapy material.

Energy transfer and singlet oxygen generation is greatly significant in the materials science and medicine fields,¹ particularly for photodynamic therapy (PDT),² and the ability of these processes to be selectively regulated is becoming increasingly important.³ Recently, a number of porphyrin/dithienylethene-based photocontrolled reversible energy transfer systems⁴ and their singlet oxygen generation functions have been reported.⁵ For example, Feringa et al. reported a noncovalent strategy to regulate singlet oxygen generation using a diarylethene/zinc-tetraphenylporphyrin system through photochemical control.^{5a} Zhou et al. synthesized a class of photochromic metal-organic frameworks, which also realized the reversible photo-control of singlet oxygen generation.^{5b} However, most of these systems were operated in the organic phase due to their poor water solubility, which greatly limited their applications in the physiological environment. Therefore, the design of smart singlet oxygen generation systems with good water solubility and biocompatibility is still a challenge.

Herein, we wish to report a series of photo-controlled reversible and repeatable supramolecular assemblies possessing the ability to generate singlet oxygen from dithienylethene-modified permethyl- β -cyclodextrins (DTE-PMCD) and tetrakis(4-sulfonatophenyl)porphyrins (Scheme 1). As compared with the reported porphyrin/ dithienylethene systems, the present supramolecular assemblies possessed inherent advantages as (1) the introduction of the permethyl- β -cyclodextrin unit greatly improved the water solubility and biocompatibility, which enabled the photo-controlled singlet oxygen generation to fully operate in the aqueous phase; (2) the strong association of permethyl- β -cyclodextrin with tetrakis(4sulfonatophenyl)porphyrin⁶ enabled a close proximity of porphyrin (donor) to dithienylethene (acceptor), which consequently led to a high FRET efficiency (up to 93.4%) and a fairly fast switch on/off rate for singlet oxygen generation (switch on \rightarrow off: 50 s; switch off \rightarrow on: 120 s).

Dithienylethene derivatives **1** and **2** modified with permethyl- β -cyclodextrin units (Scheme S1, ESI[†]) were successfully synthesized in satisfactory yields. Therein, the methylation of 4,4'-(4,4'-(perfluorocyclopent-1-ene-1,2-diyl)bis(5-methylthiophene-4,2-diyl))diphenol **6**⁷ afforded the DTE derivative **7** in a 45% yield. Subsequently, the treatment of **7** with 3-bromoprop-1-yne in acetone in the presence of K₂CO₃ produced **8** in an 85% yield. Then, the click reaction of **8** with 6-deoxy-6-azide-permethyl- β -cyclodextrin **5**⁸ in DMF by using CuI as a catalyst gave the asymmetric host **1**. Similarly, the symmetrical host **2** could be obtained by the click reaction of **5** with **9**. The chemical compositions of all new compounds were characterized by ¹H NMR, ¹³C NMR, ¹⁹F NMR and HR-MS (see Fig. S1–S17, ESI[†]).

Benefiting from the dithienylethene unit, the host 1 exhibited reversible photoisomerization and photochromism behaviors



Scheme 1 Chemical structures of DTE-PMCD 1–2, porphyrins 3–4 and the intermediate 5.

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Fig. 1 (a) Absorption spectra variation of 1 upon irradiation by 254 nm light. (b) Absorption spectra variation of 2 upon irradiation by 254 nm light. Inset: Changes in the chemical structures and the photographic images of 1 and 2 upon alternating UV and visible-light irradiation in a 5% EtOH phosphate buffer solution (PBS, pH 7.2) ($[1] = [2] = 20 \ \mu$ M).

in an aqueous solution, and a trace amount of ethanol was added to increase the hydrophobic microenvironment.⁹ Irie's group also developed some excellent water-soluble photochromic systems.¹⁰ As shown in Fig. 1a, 1 underwent photoisomerization from an open-form (OF) to a closed-form (CF) under irradiation with UV light ($\lambda = 254$ nm) for 50 s (Fig. S18a, ESI[†]), accompanied by the obvious color change from colorless to blue. In the UV-vis spectrum, a new absorption maximum appeared at 594 nm (ϵ , 1.25 × 10⁴ L mol⁻¹ cm⁻¹) due to the formation of the closed conformer. In addition, a well-defined isosbestic point at 326.8 nm indicated that the open-form of 1 (OF-1) was converted into the photocyclized product, *i.e.* the closed-form of 1 (CF-1). The photocyclization quantum yield (Φ_{o-c}) corrected for the active conformer was determined to be 0.50 for 1 and the ring-closing conversion rate was detected to be ca. 95% by liquid chromatography. The relevant optical properties are shown in Table S1 (ESI[†]). Upon irradiation under visible-light (>420 nm) for 80 s, the blue solution of CF-1 returned to colorless, indicating a cycloreversion from CF-1 to OF-1. Interestingly, this photochromic switch showed good reversibility, and no apparent deterioration could be observed after repeating the above cycles at least seven times (Fig. S21a, ESI⁺). Moreover, host 2 gave similar photochromic switch recycling to 1, but its switch rate was a little slower than that of 1. That is, host 2 changed from the openform to the closed-form under irradiation of UV light for 80 s (Fig. S18b, ESI^{\dagger}), with a Φ_{o-c} of 0.42, and returned to the initial open-form upon irradiation by >420 nm light for 120 s (Fig. 1b and Fig. S21b, ESI[†]).

Owing to the introduction of the permethyl- β -cyclodextrin unit, **1** and **2** showed a good water solubility. Moreover, it was well documented that permethyl- β -cyclodextrin could strongly bind to 5,10,15,20-tetrakis(4-sulfonatophenyl) porphyrin **3** (TSPP) and 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin zinc(π) (Zn-TSPP) **4**.⁶ These advantages enabled the easy construction of the supramolecular assemblies $3 \subset 1$ (or $4 \subset 1$) and $3 \subset 2$ (or $4 \subset 2$) by simply mixing **3** (or **4**) and **1** (or 2) in an aqueous solution. The binding stoichiometry of **3** (or **4**) with **1** was verified by a Job's plot, where a maximum peak at a molar ratio of 0.33 (Fig. S22, ESI[†]) was observed, indicating a 2:1 hostguest binding stoichiometry. On the other hand, the Job's plot of **3** (or **4**) with **2** gave a 1:1 host-guest binding stoichiometry. The UV-vis titration spectra of **3** (or **4**) with permethyl- β cyclodextrin (Fig. S23, ESI[†]) gave the binding constants (K_s) between PMCD and 3 (or 4) in 5% EtOH PBS (pH = 7.2) aqueous solution as $K_1 = 4.24 \times 10^9 \text{ M}^{-1}$, $K_2 = 6.17 \times 10^7 \text{ M}^{-1}$ for permethyl- β -cyclodextrin/3 binding and $K_1 = 4.87 \times 10^9 \text{ M}^{-1}$, $K_2 = 1.39 \times 10^7 \text{ M}^{-1}$ for permethyl- β -cyclodextrin/4 binding, which were basically consistent with the previous reports.⁶ In addition, the UV-vis absorption maxima of 3 and 4⊂PMCD (3 or 4⊂1 or 2) all exhibited an apparent red shift as compared with that of 3 (or 4) (Fig. S24, ESI†). The emission spectra also showed that the emission peaks of 3 (or 4) gave certain shifts, accompanied by the obvious intensity changes, with the addition of PMCD, 1 or 2 (Fig. S24, ESI†).

The additional evidence comes from the circular dichroism spectroscopy. As shown in Fig. S25 and S26 (ESI^{\dagger}), both $3 \subset 1$ (or $4 \subset 1$) and $3 \subset 2$ (or $4 \subset 2$) assemblies gave similar, but stronger, circular dichroism signals compared to that of the $3 \subset PMCD$ (or $4 \subset PMCD$) system around 416 nm (or 424 nm). In the control experiment (Fig. S25 and S26, red line, ESI⁺), 3 and 4 presented no appreciable circular dichroism signals at the same wavelength. These phenomena jointly indicated that the porphyrin backbone in 3 (or 4) was associated with the permethylβ-cyclodextrin cavities of 1 (or 2). Furthermore, the $3 \subset 2$ (or $4 \subset 2$) assembly exhibited relatively high circular dichroism signals with excitation coupling peaks between 375 and 435 nm (or 390-438 nm) resulting from the adjacent two porphyrin units with respect to $3 \subset 1$ (or $4 \subset 1$), which implied that a linear assembly was formed. Additionally, the stronger circular dichroism signals of $3 \subset 2$ were detected in the concentrated solution (Fig. S25b, pink line, ESI⁺) relative to the dilute solution (Fig. S25a, pink line, ESI[†]), indicating that a larger assembly was generated. Moreover, similar phenomena could also be observed for $4 \subset 2$ (Fig. S26, ESI \dagger). Therefore, a possible assembly mode of 3 (or 4) with 1(or 2) is shown in Scheme S2 (ESI⁺).

Further structural information comes from TEM, AFM and DLS (Fig. S27, ESI⁺). The TEM image gave a rough insight into the size and shape of the 3 ⊂ 2 assembly. From the TEM image (Fig. S27a, ESI⁺) recorded at a relatively high concentration (20 µM), we could find a number of rod-like nanostructures with an average width of 19 nm, indicating a possible secondary aggregation of the linear $3 \subset 2$ assemblies into rods. Moreover, the length of the rod-like arrays could reach approximately 153 nm, being formed by the joining together of approximately 450 units of $3 \subset 2$. Furthermore, a highly dilute solution of the $3 \subset 2$ assembly (2 µM) was used for the preparation of the samples for AFM experiments so as to avoid the secondary aggregation of individual assemblies. As can be seen in Fig. S27b (ESI^{\dagger}), diluting the solution of the $3 \subset 2$ assembly to a lower concentration resulted in the original rods shown in the AFM images changing to linear structures,^{6d} and the average height of the linear structures (ca. 1.2 nm) was basically consistent with the outer diameter of a PMCD cavity. In addition, the hydrodynamic radius of $3 \subset 2$ (ca. 128.9 nm) observed by DLS was also consistent with the assembly length observed in TEM (Fig. S27c, ESI[†]). In the control experiment, the TEM images of the $3 \subset 1$ assembly showed many near-spherical nanoparticles (Fig. S28, ESI[†]) with a homogenous diameter of *ca.* 30 nm, which is distinctly different from the structural features of the $3 \subset 2$ assembly.

Possessing both photo-switched units (dithienylethene) and donor-acceptor pairs (porphyrin-dithienylethene) in a single supramolecular structure, the resultant assemblies exhibited significant photo-controlled Förster resonance energy transfer (FRET) behaviors. The UV-vis spectrum (Fig. S29a, ESI⁺) of OF-1 showed only one absorption maximum at 295 nm, but that of CF-1 gave two different absorption maxima at 346 nm and 594 nm. Judging from the emission bands of 3 (600-800 nm, excited at 413 nm) and 4 (550-750 nm, excited at 422 nm), we could deduce that the FRET process could only occur between the closed-ring form of 1 (CF-1) and 3 (or 4) due to the obvious spectral overlap of the absorption band of CF-1 with the emission band of 3 (or 4) over 550 nm, which was consistent with the previously reported results.^{5,6i} Similar phenomena were also observed in the case of the $3 \subset 2$ (or $4 \subset 2$) assembly (Fig. S29b, ESI⁺). Interestingly, the FRET process of the assemblies could be easily controlled by light irradiation. As shown in Fig. 2a, the $3 \subset OF-2$ assembly gave two emission peaks at 644 nm and 715 nm when excited at 413 nm. However, by irradiating the $3 \subset OF-2$ assembly with 254 nm light for 50 s, its emission intensity was greatly quenched. In the control experiment (Fig. S24c, ESI[†]), the change of the fluorescence intensity of 3 was negligible after adding the dithienylethene derivatives OF-1 or OF-2, indicating that the quenched fluorescence was not due to light absorption by the non-emissive dithienylethene unit. Therefore, we deduced a possible reason to be that: the UV light (254 nm) irradiation resulted in the conversion of the open-ring isomer of 2 (OF-2) to a closed-ring one (CF-2), and the FRET process from porphyrin 3 (donor) to CF-2 (acceptor) led to the quenched fluorescence. However, the quenched fluorescence of the 3 COF-2 assembly was recovered to its original level upon subsequent irradiation by visible light (>420 nm) for 50 s because of the reverse photoisomerization from CF-2 to OF-2. Significantly, this cycle could be repeated without fatigue over at least seven cycles (Fig. S30a, ESI[†]). Besides the fluorescence spectroscopy, the photo-controlled FRET process could also be readily monitored by the naked eye. Generally, the solution of the $3 \subset OF-2$ assembly was red due to the fluorescence of 3, but the color turned fairly weak after irradiation by UV light (254 nm).



Fig. 2 (a) Fluorescence spectral change of the assembly $3 \subset OF-2$ upon irradiation with 254 nm UV light. (b) Fluorescence spectral change of the assembly $4 \subset OF-2$ upon irradiation with 254 nm UV light. (c) Schematic representation for photo-controlling the FRET process of the assembly 3 (or 4) \subset 2. ([OF-2] = [3] = [4] = 2 μ M; in 5% EtOH pH 7.2 PBS.)

Subsequently, when the solution was further irradiated by visible light (>420 nm), the color of the solution returned to red (Fig. 2a). The schematic representation for the photo-controlled FRET process is preferably illustrated in Fig. 2c. Similar phenomena were also observed in the cases of the $4 \simeq 2$ (Fig. 2b), $3 \simeq 1$ and $4 \simeq 1$ (Fig. S31, ESI†) assemblies. On the other hand, the assembly geometry was optimized by DFT calculations (Fig. S32, ESI†), and the center-to-center distance between 3 and CF-2 (or CF-1) was estimated as 28.9 Å (or 15.6 Å). This value was obviously lower than the Förster radius ($R_0 = 30.7$ Å),¹¹ so the FRET process should be facilitated. Accordingly, the order of the photocontrolled energy transfer efficiency (*E*) was calculated to be $4 \simeq 2$ (93.4%) > $3 \simeq 2$ (81.7%) > $4 \simeq 1$ (71.2%) > $3 \simeq 1$ (63.7%), as listed in Table S2 (ESI†), which was basically consistent with the results when preparing 3 (or 4) \subset CF-1(or CF-2) (Fig. S33, ESI†).

It is also important to investigate the photo-controlled ¹O₂ generation capacity of the $3(\text{or } 4) \subset 1(\text{or } 2)$ assembly because the porphyrin photosensitizers in the assembly were reported to be able to transfer the triplet excited energy to triplet oxygen $({}^{3}O_{2})$ and generate singlet oxygen (¹O₂) under light irradiation.¹² Then, the fraction of singlet oxygen produced by water-soluble porphyrins 3 and 4 was monitored directly by the near-infrared emission spectroscopy through the phosphorescence of ¹O₂ at 1283 nm¹³ (Fig. S34, ESI[†]). As shown in Fig. 3a, the brief irradiation of the solution of 3 COF-2 at 254 nm for 50 s led to the emission at 1283 nm prominently decreasing (ca. 75.9%) intensity was quenched). Interestingly, when the 3 CF-2 system was further irradiated by visible light (>420 nm) for 120 s, its emission intensity almost completely recovered to the original level of the system. Significantly, this cycle can be repeated for at least four times with no apparent deterioration (Fig. 3c). Similar phenomena are observed in the systems of $4 \subset 2$ (Fig. 3b and d), $3 \subset 1$ and $4 \subset 1$ (Fig. S35, ESI⁺). Therefore, these assemblies could be used as a photo-controlled efficient and reversible ${}^{1}O_{2}$



Fig. 3 (a) NIR emission spectra changes of ${}^{1}O_{2}$ generated by 3 in the presence of 2. (b) NIR emission spectra changes of ${}^{1}O_{2}$ generated by 4 in the presence of 2. (c) The reversibility of ${}^{1}O_{2}$ generation by 3 = 2 was monitored by the change of emission intensity at 1283 nm over four cycles. (d) The reversibility of ${}^{1}O_{2}$ generation by 4 = 2 was monitored by the change of emission intensity at 1283 nm over four cycles. (d) The reversibility of ${}^{1}O_{2}$ generation by 4 = 2 was monitored by the change of emission intensity at 1283 nm over four cycles. (The experiments were performed in O_{2} equilibrated EtOH/ $D_{2}O$ (v/v, 1:100) alternatively irradiated with 254 nm and >420 nm light; 3, excitation at 413 nm; 4, excitation at 422 nm. [2] = 5[3] = 5[4] = 10 \,\muM.)

generator in water. Their order of efficiency of generating ${}^{1}O_{2}$ by photo-control was measured to be $4 \subset 2$ (>78.6%) > $3 \subset 2$ (>75.9%) > $4 \subset 1$ (>39%) > $3 \subset 1$ (>34%).

To further verify the photo-controlled ¹O₂ generation mechanism, DFT calculations on the lowest singlet and triplet state energies of 1-2 were performed (Table S3, ESI⁺). The results showed that the large energy difference between the open form and closed form of 1 (or 2) at the singlet and triplet states supported the possibility of switching on/off the energy transfer from the photosensitizer 4, which had the singlet and triplet energies located in the gap. The proposed mechanism of photo-controlled singlet oxygen generation in these assemblies is clearly displayed in Fig. S36 (ESI⁺). The lowest triplet excited state energy of 4 (1.53 eV) was higher than that of CF-1 (1.20 eV) or CF-2 (1.20 eV), but lower than that of OF-1 (3.04 eV) or OF-2 (2.95 eV), indicating that the energy could only transfer from 4 to the closed form, but not to the open form. Additionally, the lowest excited state energy of ${}^{3}O_{2}$ (0.97 eV)¹⁴ was lower than that of CF-1 or CF-2. That means that CF-1 or CF-2 could intercept the energy transfer from the triplet excited state of 4 to ${}^{3}O_{2}$. In the process, the triplet-triplet energy transfer should be the major contributor, because the inter-conversion rate from the singlet state to the triplet state was much faster than the rate for FRET.¹⁵ Therefore, when 4 was excited by 422 nm light in the presence of CF-1 or CF-2, the system could be inhibited to generate ¹O₂. Furthermore, the lowest singlet excited state of 4 (2.05 eV) was approximately equal to CF-1 or CF-2 (2.05 eV), indicating that the FRET process would occur between 4 and CF-1 (or CF-2) if they were located at an appropriate distance. In addition, there may also be some possibility of filter-effects of the closed-form because of the overlap between the emission spectrum of porphyrin 3 (or 4) and the absorption spectrum of the closed-form of 1 (or 2).¹⁶

In summary, taking advantage of the strong binding affinity between permethyl- β -cyclodextrin and tetrasulfonatophenyl porphyrins, a series of dithienylethene/permethyl- β -cyclodextrin/ porphyrin supramolecular assemblies were successfully constructed from dithienylethene-modified permethylated β -cyclodextrins and porphyrin derivatives in water. Crucially, the good photoisomerization property of the dithienylethene units enables the resultant assemblies to act as a fluorescent molecular switch, which can be efficiently applied in switching on/off singlet oxygen generation under alternative irradiation of UV or visible light. The photo-switchable singlet oxygen generation property in water, along with the facile preparation, good water solubility and biocompatibility, may make this supramolecular assembly approach highly suitable for developing a water-soluble and biocompatible photo-responsive switchable system in photodynamic therapy and other potential applications in the fields of biotechnology and biomaterials.

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