Photoreaction-driven two-dimensional periodic polyrotaxane-type supramolecular nanoarchitecture†

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A 2D polypseudorotaxane-type assembly was constructed using cucurbit[8]uril and styrylpyridinium-bearing triphenylamine. In addition, tunable non-covalent to covalent transition was achieved by [2+2] photodimerization of styrylpyridinium units. Thus, a more stable 2D polyrotaxane-type nanoarchitecture was obtained, which could capture [60]fullerene and further exhibit an excellent photodynamic therapy effect.

Two-dimensional (2D) nanostructures have been utilized as a significant class of materials with diverse promising applications.1 Currently, some successful bottom-up strategies for the construction of 2D nanosheets are mainly dependent on the self-assembly of organic small molecules via multiple interactions, such as metal–ligand coordination, hydrogen-bonding interconnection, and dynamic chemical bonds.2 In this regard, macrocycle-based supramolecular methods provide more opportunities to fabricate various 2D nanostructures with structural and functional diversity.3 For example, Li and co-workers presented a 2D supramolecular organic framework, in which cucurbituril was used as rigidified macrocycle to stabilize the dimers of aromatic components through host–guest interactions.4 Our group also reported a supramolecular 2D nanoassembly system via the supramolecular assembly of adamantyl diphenylalanine with azobenzene-bridged bis(β-cyclodextrin), thus displaying photo-controlled morphological interconversion from 1D nanotubes to 2D nanosheets.5

Despite the recent remarkable progress in developing macrocycle-based 2D supramolecular assemblies, the commonly used strategies are achieved based on complex- or pseudorotaxane-type structures, which may result in the undesirable structural instability and eventually impede their practical applications. With this in mind, we herein report a convenient approach to construct a porous and stable 2D supramolecular assembly through photoreaction-driven transformation from pseudorotaxane to rotaxane, which can synergistically combine the immense advantages of desirable controllability from noncovalent complexation and high stability from a covalently bonded molecular skeleton (Scheme 1).

In our case, a paddle-shape triphenylamine bearing styrylpyridinium unit (TPA-SP) was synthetized, which could form layered supramolecularrotaxane-type nanostructure upon inclusion complexation with cucurbit[8]uril (TPA-SP< CB[8]). More interestingly, the obtained TPA-SP< CB[8] assembly could be readily transformed to a more stable 2D periodic polyrotaxane-type nanostructure.

Scheme 1 Schematic illustration of the formation of a 2D periodic polyrotaxane-type nanostructure in water.
(TPA-SPPD⊂CB[8]), ‘PD’ denotes photodimerization) via the macrocycle-assisted [2+2] photodimerization of styrylpyridinium units under visible light irradiation. Furthermore, the well-defined TPA-SPPD⊂CB[8] nanosheets could efficiently capture [60]fullerene in water, thus presenting an excellent DNA cleavage ability and photodynamic therapy effect arising from the photoinduced generation of reactive oxygen species. To the best of our knowledge, the TPA-SPPD⊂CB[8] assembly is one of the rarely reported photoreaction-driven 2D free-standing nanoarchitectures consisting of periodic polyrotaxanes in water.

There are two structural features of our designed TPA-SP as the guest molecule: (1) the TPA core presented a three-bladed propeller structure, which can effectively prevent the unsuitable intermolecular aggregation and (2) the peripheral styrylpyridinium (SP) units not only play the role of anchoring points to bind with CB[8] at a molar ratio of 2:1 in a head-to-tail stacking pattern, but also act as the active sites for the intermolecular cross-linking in photochemical reactions.

First, the molecular binding behaviors between CB[8] and TPA-SP were investigated. The proton signals of TPA-SP in D2O alone were indistinguishable due to its long-range and rotatable molecular skeleton (Fig. S12b, ESI†). Unexpectedly, the proton signals became identifiable and clear upon gradual addition of CB[8]. All the proton signals of TPA-SP reached the equilibrium state with 1.5 equiv. CB[8] and no obvious chemical change was observed in the presence of excess CB[8] (Fig. S12c–e, ESI†). The Job’s plot further confirmed that the binding stoichiometry was 2:3 in the TPA-SP⊂CB[8] complexation (Fig. S13, ESI†). Moreover, UV/vis spectroscopic titration quantitatively revealed the high association constants between TPA-SP and CB[8] (Fig. S14, ESI†). Accordingly, the dynamic light scattering (DLS) data also showed that the average hydrodynamic diameter of the TPA-SP⊂CB[8] assembly was 269 nm, indicative of the existence of a large-sized supramolecular assembly in water (Fig. S15, ESI†).

To shed more light on the binding mechanism between TPA-SP units and CB[8], a model compound M-SP with a single arm was synthesized as described in Scheme S2 (ESI†). 1H NMR titrations were further conducted to investigate the host-guest complexation of M-SP with CB[8]. As discerned from Fig. S17d (ESI†), all the proton signals of M-SP displayed upfield shifts upon addition of 0.5 equiv. CB[8]. Moreover, the 2D NOESY spectrum revealed that the two M-SP units were simultaneously immersed in the cavity of CB[8] in a head-to-tail stacking pattern, which was propitious for the photodimerization of two adjacent SP units (Fig. S19, ESI†).

With these results in mind, we next investigated the formation of polyplexedrotaxane mediated by two SP units in the CB[8] cavity. Transmission electron microscopy (TEM), scanning electron microscopy (SEM), and atomic force microscopy (AFM) were employed to characterize the morphology of the TPA-SP⊂CB[8] assembly. As shown in Fig. 1, layered graphene-like structures were observed in the TEM image, and the thickness of the obtained nanosheets was investigated via the tapping-mode AFM experiments, presenting a uniform height of approximately 1.91 nm, corresponding to the outer diameter of CB[8]. Moreover, similar 2D nanosheets were also observed in the SEM images (Fig. S21, ESI†). These experimental results indicated that a single-layer 2D supramolecular assembly was constructed by TPA-SP⊂CB[8] complexation. To further explore the structural information, a grazing incidence small angle X-ray scattering (GI-SAXS) experiment was performed for the solid sample of the TPA-SP⊂CB[8] assembly. A sharp peak at a spacing of 3.8 nm, which was consistent with the simulated pore diameter of 3.9 nm, appeared in the small angle region (Fig. S14, ESI†). Moreover, UV/vis spectroscopic titration and photodimerization behaviors, the conversion of photoreaction of M-SP alone with both photoisomerization and photodimerization reaction. Thus, the photoreaction properties of M-SP were explored (Fig. S25–S27, ESI†). Compared to the photoreaction of M-SP alone with both photoisomerization and photodimerization behaviors, the conversion of photodimerization was obviously improved upon addition of CB[8]. Therefore, it seems that CB[8] could not only act as the host molecule for the formation of a 1:2 complex but also offer a catalytic environment for the photodimerization of SP units at the same time. In addition, the pKα value of the TPA-SP⊂CB[8] system was also determined before light irradiation (Fig. S28, ESI†). After analysis of the absorbance versus pH value, no obvious change was observed in the titration curve before and after addition of CB[8] to the TPA-SP solution, suggesting that the protonation site was virtually unaffected by CB[8]. Moreover, to investigate the stability of the supramolecular assembly, the Job’s plot and association constant were explored in 50 mM glycine–hydrochloric acid buffer (pH = 2.2). No change in either binding stoichiometry or stability constant was observed under the acidic conditions, implying the high stability of the TPA-SP⊂CB[8] assembly (Fig. S29 and S30, ESI†).

The photoreaction of TPA-SP⊂CB[8] was further examined in both the neutral state and acidic state (pH = 2.2).
No dramatic change was observed in the UV/vis spectra after irradiating the sample in the neutral state at 420 nm for 60 min, demonstrating that the SP units were almost not photodimerized because the triphenylamine unit in TPA-SP acted as an electron donating group which could form an intramolecular charge transfer state by photoexcitation and thus inhibit the photoreaction process (Fig. S31, ESI†). In contrast, the absorbance at 462 nm decreased obviously in the acidic media corresponding to the photodimerized SP units, which was contributed to the protonation of the triphenylamine unit. As shown in Fig. 2, the photodimerization reaction was accelerated in the first 20 min and then virtually completed in 60 min. After photodimerization was accomplished, the product was dialyzed for 24 hours to eliminate the unreacted substrates and excess hydrochloric acid. The Fourier transform infrared (FTIR) spectra of the freeze-drying sample of the TPA-SPPD/CB[8] assembly presented a declining peak of the C≡C stretching band at 1590 cm⁻¹ and C–C–H out-of-plane bending bands at 992 and 828 cm⁻¹, which could be assigned to the vinylene group (Fig. S33, ESI†).12

More satisfactorily, the photodimerization product TPA-SPPD/CB[8] was soluble and quite stable in water, benefiting from the protective effect of CB[8]. In addition, the size and morphology of the TPA-SPPD/CB[8] assembly before and after light irradiation manifest that the graphene-like 2D structure was well conserved in DLS and SEM experiments (Fig. S34 and S35, ESI†). As shown in Fig. 3, the TEM and AFM experiments demonstrated a single-layer structure in the 2D periodic polyrotaxane-type TPA-SPPD/CB[8] assembly. This well-defined nanostructure was further confirmed by GI-SAXS with sharp scattering peaks at 2θ = 2.47° and 4.17° (Fig. S36, ESI†). The corresponding pore diameter value of the TPA-SPPD/CB[8] assembly (3.4 nm) was relatively smaller than that of TPA-SP/CB[8] (3.9 nm), because of the more rigidified structure after photodimerization. Furthermore, a competitive compound Ad-com with higher binding constant with CB[8] was synthesized (Scheme S3, ESI†) and utilized to confirm the stability of TPA-SPPD/CB[8] (Fig. S37, ESI†).13

After understanding the porous structure of the obtained TPA-SPPD/CB[8] assembly, we next investigated its encapsulation properties toward guest molecules with an appropriate molecular size. As one kind of allotrope of carbon, [60]fullerene (C₆₀) is widely attractive for materials science and medicine application.14 Therefore, the capture ability of TPA-SPPD/CB[8] for C₆₀ was studied in aqueous solution. In our case, the pristine C₆₀ was added into the solution of TPA-SPPD/CB[8] under ultrasonic conditions, and then the excess undissolved C₆₀ was removed by centrifugation. The absorbance at 266 and 358 nm in the UV/vis spectra as well as the vibration bands at 524 and 573 cm⁻¹ in the FTIR spectrum of C₆₀@TPA-SPPD/CB[8] collectively suggested the formation of an advanced supramolecular assembly (Fig. S39 and S40, ESI†).15 In contrast, TPA-SP/CB[8] exhibited a weaker ability to capture C₆₀ through the same operation, due to the lack of compactness and stability (Fig. S41, ESI†). In addition, the BET value decreased from 35 m² g⁻¹ for TPA-SPPD/CB[8] to only 7 m² g⁻¹, and the pore size distribution (Fig. S42 and S43, ESI†), as well as the TGA curve (Fig. S44, ESI†) changed before and after treatment of TPA-SPPD/CB[8] with C₆₀.16

Based on these experimental results, we speculated that the possible mode is that C₆₀ molecules were encapsulated in the nanopores of TPA-SPPD/CB[8].17

It is well-documented that C₆₀ possesses an excellent DNA photocleavage ability due to the production of reactive oxygen species (ROS) under visible light irradiation.18 Since C₆₀@TPA-SPPD/CB[8] is highly water-soluble, agarose gel electrophoresis assay was performed to explore its potential application in photodynamic therapy.19 Thus, pBR322 plasmid DNA was chosen to investigate the C₆₀@TPA-SPPD/CB[8] cleavage ability. As shown in Fig. 4a, C₆₀@TPA-SPPD/CB[8] displayed a concentration-dependent cleavage ability, and close superfoced DNA (form I) was cleaved into nicked DNA (form II) by C₆₀@TPA-SPPD/CB[8] at a concentration of 12 μM under white light irradiation for 30 min. Comparatively, the control experiments showed that C₆₀@TPA-SPPD/CB[8] could not exhibit any DNA cleavage ability in the dark, suggesting that no ROS product was generated without light irradiation (lanes 7–13).

Furthermore, A549 cells (the human lung tumor cell lines, obtained from the cell Center of Peking Union Medical College)
had good biocompatibility and low toxicity. As expected, in the dark, these three supramolecular systems exhibited transformation in TPA-SP

nanostructure through controlled non-covalent and covalent strategy to design a photoreaction-driven 2D polyrotaxane-type assembly could be utilized as an efficient C60 capture agent and then exhibit an excellent photodynamic therapy effect owing to the ROS production by the trapped C60. It is envisaged that our strategy for developing 2D polyrotaxane-type nanoarchitectures can provide us with a convenient avenue for the creation of novel functional nanomaterials with good stability and biocompatibility.

We thank NNSFC (21432004, 21871154, 21772099, and 21861132001) for financial support.

**Conflicts of interest**

There are no conflicts to declare.

**Notes and references**


