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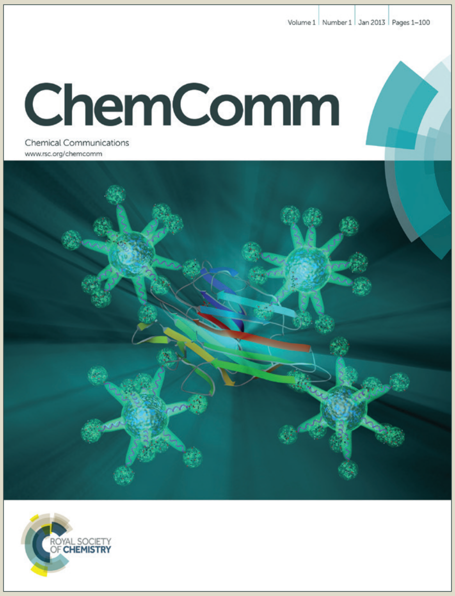

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Host-Guest Interactions Manipulated Self-Assembly of Pyridinium-Tailored Naphthalene

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Host-guest interactions are employed to manipulate the assembled morphology of an amphiphile, 2-NP, which contains an electron-rich naphthalene group and an electron-deficient pyridinium cation linked with a flexible alkyl arm. By encapsulating the pyridinium and the naphthalene group of 2-NP into the cavity of cucurbit[8]uril (CB[8]), a fluorescence-enhanced microsheets formed.

Assembled micro/nanostructures from small molecules driven by non-covalent interactions have been extensively explored for their potential applications in tissue engineering, biosensors, and drug delivery.[1] Considerable efforts have been contributed to control their morphology transformations by manipulating the driving forces, such as hydrogen bonds, electrostatic interactions, π-stacking, charge-transfer (CT), and host-guest interactions.[2] Among of them, host-guest interactions, which can hold two or more molecules or ions together in unique structural relationships through molecular or ionic recognition, have received great attentions in creating new architectures.[3] As a macrocycle, cucurbit[8]uril (**CB[8]**) has eight glycoluril units and a hydrophobic cavity that is accessible through two identical carbonyl laced portals. The polar carbonyl groups at the portals and the hydrophobic cavity allow it to encase small molecules to form host-guest complexes with the high selectivity and the binding affinity.[4] For example, Kim and co-workers reported that the formation of a ternary complex of the electron-deficient 1-dodecyl-1'-methyl-[4,4'-bipyridine]-1,1'-diium and the electron-rich 2, 6-dihydroxy- naphthalene in the hydrophobic cavity of **CB[8]**, and such a complex could assemble into vesicles.[5] Zhang and co-workers have demonstrated that the host-enhanced π-π stacking in the cavity of **CB[8]** could be employed to form water-soluble supramolecular hyperbranched polymers, and the polymerization and depolymerization can be carried out in a controlled manner.[6]

Inspired by those works, herein, we exploit the manipulation of assembled morphology transformations of an amphiphile by the host-guest interactions. As shown in Figure 1a, **2-NP** (1-[11-(naphthalene-2-ylmethoxy)-11-oxoundecyl]pyridinium bromide) was designed and synthesized, in which the electron-rich naphthalene group and the electron-deficient pyridinium cation are linked by a flexible alkyl arm (synthetic details see Supporting Information). Meanwhile, **CB[8]** was introduced into the system to investigate the assembled morphology transformations.

As a general protocol, the assembly behavior of **2-NP** was studied as follows: a methanol solution of **2-NP** (50 μL, 1 M) was added dropwise into the deionized water (2 mL) with the slow stirring speed. After the evaporation of methanol, the aggregates formed, which were characterized by fluorescence microscopy (FM), optical microscopy (OM), scanning electron microscopy (SEM), and atomic force microscopy (AFM). As shown in Figure 1b-e, **2-NP** afforded non-fluorescent microsheets with an average size of 65, 9, and 1 μm in length, width, and thickness, respectively (the statistical analysis see Figure S4a). A broken sheet from SEM image (Figure S5), and the related height profile (Figure 1f) further confirmed that these microsheets had flat surfaces. In order to investigate the molecular packing pattern of microsheets, X-ray powder diffraction (XRPD) experiments were performed, as well as the single crystal which was cultured in the same condition as the microsheets. As shown in Figure 2a, the regularly sharp reflection peaks reveal that the arrangement of **2-NP** is in a highly ordered packing pattern with a calculated *d* value 2.10 nm, which is consistent with the layered distance measured from the single crystal structure (2.09 nm, Figure 2c).

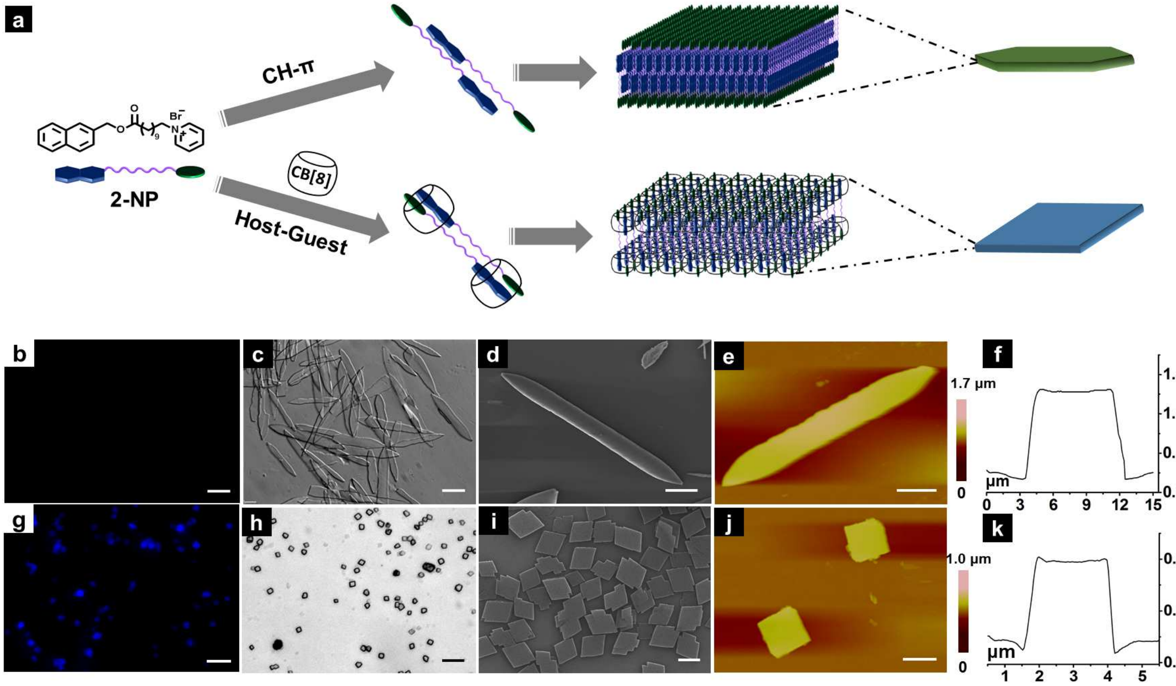

Figure 1. (a) Schematic representation of the assembly process of **2-NP** (top) and **2-NP/CB[8]** (bottom); (b) FM, (c) OM, (d) SEM, (e) AFM, and (f) AFM height profile of **2-NP** in water (conc. $2.5x10^{-2}$ M); (g) FM, (h) OM, (i) SEM, (j) AFM, and (k) AFM height profile of **2-NP/CB[8]** in water (conc. $3.0x10^{-4}$ M, molar ratio, 1:1). Scale bars are 20 μm for (b, c), 10 μm for (d, e, g, h), and 2 μm for (i, j).

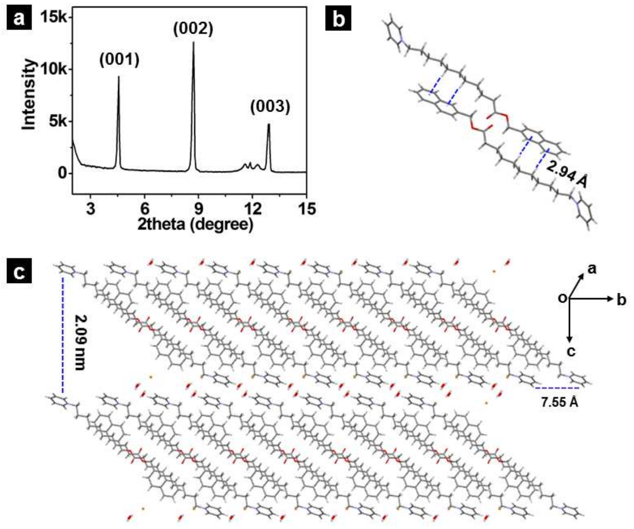

Figure 2. (a) X-ray powder diffraction (XRPD) patterns of non-fluorescent microsheets assembled from **2-NP**; (b) A parallel dimer of **2-NP** driven by the CH-π interactions with a distance of 2.94 Å; (c) Packing view of a single crystal structure of **2-NP**. Oxygen atoms are presented in red, nitrogen atoms in blue, hydrogen atoms in white, and bromide in brown.

It is seen clearly that all the pyridinium cations pack parallelly with a distance of 7.55 Å in each layer, and a tetramer of water and bromide $(H_2O)_2(Br^-)_2$ is located between two layers connected by pyridinium cations (Figure 2c). It should be noted that a paralleled dimer is observed as the basic building block primarily driven by CH-π interactions with a distance of 2.94 Å, not the π-stacking among naphthalene rings, or charge transfer interactions between the naphthalene group and the pyridinium cation. It may be due to the less aromatic area of the naphthalene group, as well as its hydrophobicity. Apparently, the CH-π interactions promote the formation of dimers, which then assemble into the layered structures. Consequently the hydrogen bonds formed by water and bromide combine all these layers together to afford the microsheets (Figure 1a, top).

It is known that the pyridinium cation as an electron-deficient moiety could form CT complex with the electron-rich aromatic groups.[7] Meanwhile, **CB[8]** can be used as a "molecular handcuff" to combine two molecules together to form a stable complex.[8] Therefore, **CB[8]** was added into the **2-NP** aqueous to elucidate its morphology transformation. As a general method, a mixture of **2-NP** and **CB[8]** (0.3 mM, 1.0 mL, molar ratio, 1:1) was sonicated under 60 °C for 10 min. After cooling to room temperature, the micro-scale aggregates formed. Their morphologies were evaluated by FM, OM, SEM, and AFM (Figure 1g-j). Interestingly, **2-NP/CB[8]** afforded the enhanced fluorescent microsheets compared to **2-NP**. The fluorescent microsheets have an average size of 2, 2, and 0.5 μm in length, width, and thickness, respectively (the statistical analysis see Figure S4b). The AFM height profile further confirms that they are flat sheets (Figure 1k).

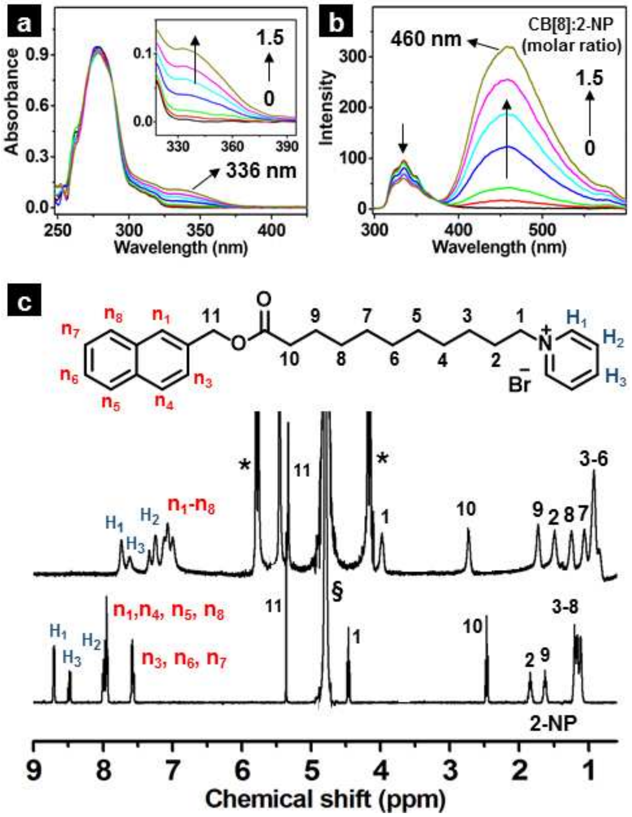

Figure 3. (a) UV-Vis and (b) Fluorescence titration of **CB[8]** with **2-NP** (conc. 0.3 mM); (c) ^{1}H NMR spectra of **2-NP**, and **2-NP/CB[8]** (conc. 0.2 mM, molar ratio, 1:1). § D_2O; *protons of **CB[8]**.

For better understanding the driving forces, UV-Vis and fluorescence titration of **CB[8]** with **2-NP** were performed. Upon the addition of **CB[8]** into **2-NP** aqueous, a new absorbance peak is observed at 336 nm as shown in Figure 3a, which is ascribed to the host-promoted CT interactions between the naphthalene group and the pyridinium ring.[9] Moreover, a 1:1 binding mode of **2-NP** and **CB[8]** is revealed by Job's plots experiment (Figure S6), which can be further confirmed by MALDI-TOF MS spectrum (observed m/z 1733 for **2-NP+CB[8]**-Br, Figure S7). Fluorescence spectrum of **2-NP/CB[8]** displays an efficient quenching in the excited-state fluorescence of monomeric naphthalene, and a new broad emission band is observed from 400 to 600 nm (Figure 3b). That is because the dynamic quenching by intramolecular CT complexation is avoided to a large degree, and the quenching by intermolecular CT formation is also reduced due to the protection of the excited donor molecule in the hydrophobic **CB[8]** cavity.[10] More evidences come from ^{1}H NMR spectra, and the assignment of protons was assisted by 2D-COSY (Figure S8). It can be seen clearly that the protons of pyridinium (H_1-H_3) and naphthalene (n_1-n_8) shift upfield after the formation of the inclusive complex (Figure 3c and Table S1), which is ascribed to electron-transfer between the naphthalene group and pyridinium cation. The fact that the shift of methylene protons (1, 2) adjacent to the pyridinium cation is larger than that of other aliphatic protons indicates that the methylene protons (1, 2) are inside of the cavity, while the others are out of the cavity. Based on the above results, it is apparent that the host-guest interactions promote **2-NP** to form a "head-to-tail" complex in the cavity of **CB[8]** with exposing pyridinium cations at the portals on account of the hydrophilic environment. Then the complex packs into layered structures with the assistance of the hydrophobic effect, which consequently result in the enhanced fluorescent microsheets (Figure 1a, bottom).

Conclusions

We have demonstrated an assembled morphology transformation between **2-NP** and **2-NP/CB[8]** manipulated by the host-guest interactions. In such a complex, a 'head-to-tail' configuration formed in the cavity of **CB[8]** with exposing pyridinium cations at the portals, which consequently led to the formation of the enhanced fluorescent microsheets. We hope our studies in manipulating the morphology by the host-guest interactions could promote the development of material science.

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Notes and references

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Electronic Supplementary Information (ESI) available: [Experimental Section; Synthesis and characterization of **2-NP**; Figure S1-S3 are MS and NMR spectra of **2-NP**; Figure S4-S6; Figure S7-S8 are MS and 2D-COSY spectra of **2-NP/CB[8]**; Table S1; Tables of crystallographic data for **2-NP**]. See DOI: 10.1039/c000000x/

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