

# Photocontrolled Coumarin-diphenylalanine/Cyclodextrin Cross-Linking of 1D Nanofibers to 2D Thin Films

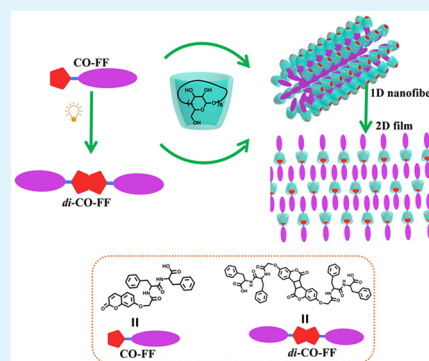
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## Supporting Information

**ABSTRACT:** Using coumarin-modified diphenylalanine (CO-FF) and  $\gamma$ -cyclodextrin ( $\gamma$ -CD) as building blocks, we successfully constructed one-dimensional nanofibers with several nanometers in width and tens of micrometers in length. Through the photodimerization of coumarin units in CO-FF/ $\gamma$ -CD complexes, the resultant nanofibers could be cross-linked to organic 2D thin films with a lateral dimension of tens of micrometers and a thickness of nanometers. The resultant thin films exhibited a significant fluorescence enhancement for twisted intramolecular charge-transfer (TICT) molecules and effective removal of pollutant from water through filtration. This 1D  $\rightarrow$  2D morphological conversion controlled by light may provide a novel strategy to construct the highly ordered nanostructures that can be used as templates for making nanoscaled materials with defined sizes and shapes.



**KEYWORDS:** host–guest complex, supramolecular assembly, photodimerization, diphenylalanine, 2D film

Design of stimuli-responsive supramolecular assemblies and control of the noncovalent interactions to organize small molecules into regular 1D and 2D supramolecular nanostructures have been a formidable challenge of supramolecular chemistry. Among various external stimuli such as temperature, pH, enzyme, and so on, light is especially important because it works reversibly, smartly, remotely, and without generating any invasions to object.<sup>1</sup> Various photochromic groups have been employed as switching units to produce smart molecular assemblies,<sup>2,3</sup> and the majority of previous studies have been focused on the photoisomerization molecules such as azobenzene and diarylethene derivatives.<sup>4</sup> In addition to the photoisomerization, the photodimerization of building blocks, such as coumarin, is another efficient method to construct distinct nanostructures.<sup>5–7</sup> Yuan et al. constructed the polymer nanoparticles labeled with coumarin and realized the formation and breakup of particle clusters through a reversible photodimerization.<sup>8</sup> Priestley et al. demonstrated the size-controlled coumarin-stabilized polymeric nanoparticles by manipulating irradiation.<sup>9</sup> Zhan and co-workers obtained the coumarin-functionalized AuNPs capable of self-assembly and disassembly in response to light irradiation reversibly.<sup>10</sup> Despite these advantages, the application of coumarin derivatives in the regulation of supramolecular nanostructures is still a big challenge.

On the other hand, diphenylalanine (L-Phe-L-Phe, FF) has become a hotspot of self-assembling research because of its biological significance, easy chem-modification,<sup>11</sup> and capability of self-assembling to varieties of nanostructures in solution, such as fibrils, tapes, twisted ribbons, tubes, or barrels.<sup>12</sup>

Although the photodimerization of CO-FF gel<sup>13</sup> and coumarin/ $\gamma$ -CD complex have been reported,<sup>14,15</sup> the morphological conversion from 1D to 2D switched by the dimerization and host–guest complexation has not been reported to the best of our knowledge. In this work, we constructed the supramolecular assembly using CO-FF with  $\gamma$ -CD (Scheme 1). Through host–guest interactions, 1D nanofibers were first formed and then converted to 2D thin films induced by the photodimerization of coumarin group.

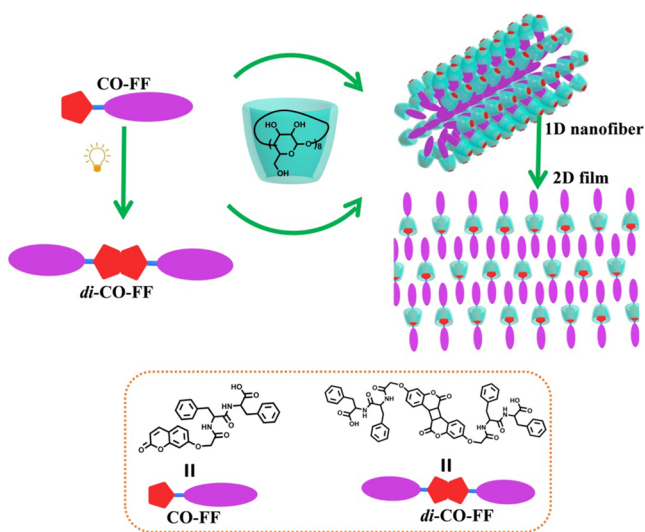
CO-FF was synthesized and purified according to the previous literature.<sup>13</sup> Complexation behavior of CO-FF and  $\gamma$ -CD was investigated by <sup>1</sup>H NMR spectroscopy. As shown in Figure S4, all the proton signals of the coumarin moiety except H<sub>a</sub> exhibited the upfield shifts upon the addition of an equivalent amount of  $\gamma$ -CD, which could be ascribed to the shielding effects of  $\gamma$ -CD cavity. In addition, some phenyl protons (H<sub>f</sub>) in FF also showed the upfield shifts, indicating the partial inclusion of phenyl group in the  $\gamma$ -CD cavity. In the ROESY spectrum (Figure 1), the cross-peak A was assigned to the NOE correlations between the coumarin (H<sub>a–e</sub>)/phenyl (H<sub>f</sub>) protons and the inner protons (H<sub>3</sub> and H<sub>5</sub>) of  $\gamma$ -CD cavity, and the cross-peak B was assigned to the NOE correlations between the coumarin protons (H<sub>b,c</sub>) and the phenyl protons (H<sub>f</sub>). These NOE correlations jointly indicated the coexistence of a phenyl ring and the coumarin moiety in the

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**Scheme 1. Chemical Structure of CO-FF, di-CO-FF, and Schematic Illustration of Their Assemblies with  $\gamma$ -CD**



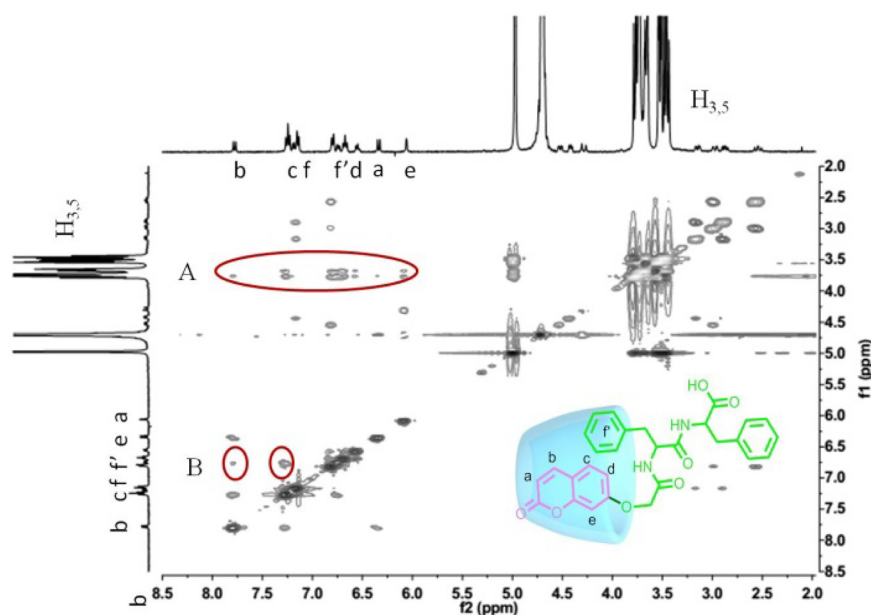
$\gamma$ -CD cavity, like the reported inclusion mode of bipyridinium-modified FF derivative in the CB[8] cavity.<sup>16</sup>

The complexation stoichiometry between CO-FF and  $\gamma$ -CD was determined by the Job analysis via <sup>1</sup>H NMR spectroscopy (Figure S5), and the changes of chemical shifts of coumarin (H<sub>c</sub>) and  $\gamma$ -CD (H<sub>3</sub>) protons versus molar fraction of CO-FF and  $\gamma$ -CD respectively were plotted. As shown in Figure S6, the minimum was achieved at a ratio of 0.5, indicating the 1:1 complex stoichiometry. This inclusion stoichiometry is different from the previously reported one that the  $\gamma$ -CD cavity could accommodate two coumarin units.<sup>14,15</sup> After verifying the 1:1 stoichiometry, the binding constant ( $K_S$ ) for the CO-FF $\gamma$ -CD complex was further calculated to be  $7.01 \times 10^3 \text{ M}^{-1}$  by <sup>1</sup>H NMR titration (Figure S7).

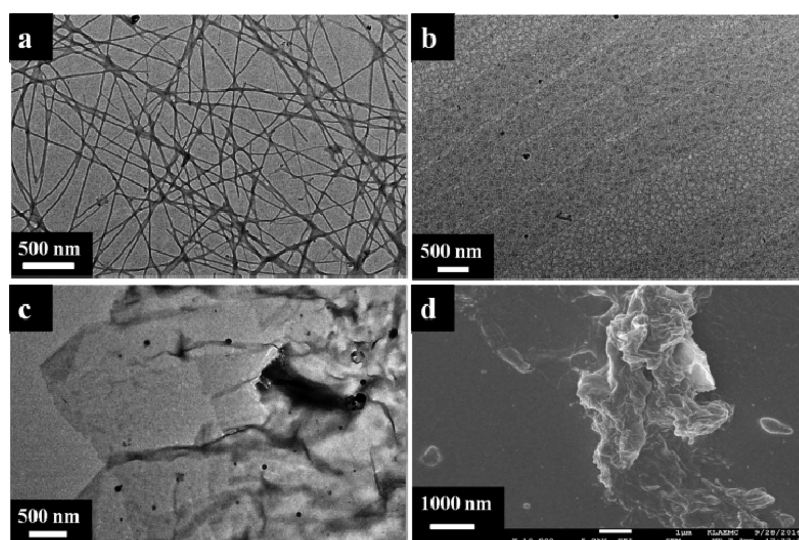
It is well-documented that the irradiation under UV light (365 nm) can result in the photodimerization of two coumarin

moieties to generate a stable cyclobutane-based dimer.<sup>10</sup> The similar phenomenon was also observed in the case of CO-FF $\gamma$ -CD complex. As shown in Figure S8, after irradiation, the original NMR signals of CO-FF $\gamma$ -CD complex became disordered, accompanied by appearance of some new NMR signals, indicating the photodimerization of coumarin moieties.<sup>14</sup> After irradiation for 8 h, the integral area of H<sub>b</sub> proton around 7.9 ppm decreased from 1 to 0.29. Accordingly, the photodimerization ratio of CO-FF was calculated as 71%. In addition, the absorbance of CO-FF $\gamma$ -CD complex at 320 nm decreased ca. 79% (from 0.63 to 0.13), which was basically consistent with NMR results (Figure S9). It is noteworthy that the photodimerization ratio of CO-FF $\gamma$ -CD complex was nearly same as that of free CO-FF under the same condition. Therefore, we deduced a possible photodimerization mode of CO-FF $\gamma$ -CD complex as illustrated in Figure S10. In this mode, a rapid dynamic equilibrium may exist between the free CO-FF and the CO-FF $\gamma$ -CD complex. Therein the free CO-FF underwent a photodimerization process outside the  $\gamma$ -CD cavity, and then the CO-FF dimer subsequently penetrate into the  $\gamma$ -CD cavity to form the di-CO-FF $\gamma$ -CD pseudo[2]-rotaxane, like the previously reported photodimerization pathway by Sivaguru et al.<sup>17</sup> Moreover, the ROESY spectrum (Figure S11) also showed the clear NOE correlations between the dimeric coumarin groups and the inner protons of  $\gamma$ -CD. The mole ratio of  $\gamma$ -CD to CO-FF was calculated to be about 0.5 through element analysis of di-CO-FF $\gamma$ -CD aggregate, (C = 50.75%, N = 2.44%). These results, along with the mass spectrometry data (Figure S12), jointly demonstrated the formation of di-CO-FF $\gamma$ -CD pseudo[2]rotaxane, like the previously reported results by Tian et al.<sup>14,15</sup>

It is also interesting to investigate the different morphology of CO-FF $\gamma$ -CD and di-CO-FF $\gamma$ -CD. As shown in Figure 2, transmission electron microscopy (TEM) images of CO-FF $\gamma$ -CD presented a number of nanofibers with an average width of several nanometers and a length of tens of micrometers, which was very similar to that of free CO-FF under the same condition. After irradiated with UV light (365 nm) for 4 h, the



**Figure 1.** Partial ROESY spectrum of CO-FF $\gamma$ -CD inclusion complex ( $[\text{CO-FF}] = [\gamma\text{-CD}] = 1.0 \text{ mM}$ ) in  $\text{D}_2\text{O}$  at  $25^\circ\text{C}$ . Inset: a possible structure of complex in aqueous solution.



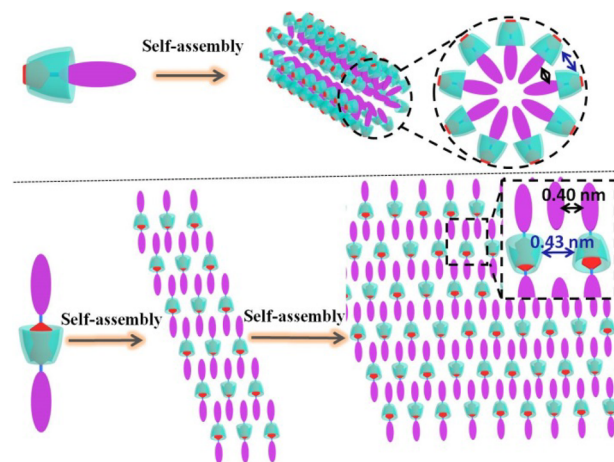
**Figure 2.** TEM images of CO-FFC $\gamma$ -CD irradiated for (a) 0, (b) 4, and (c) 8 h and (d) SEM image for 8 h at 365 nm, respectively.

CO-FFC $\gamma$ -CD nanofibers converted to nanobelts with ca. 300 nm in width and tens of micrometers in length, and the resultant nanobelts could further transformed to puckered ultrathin two-dimensional films with a lateral dimension of tens of micrometers after irradiation under UV light (365 nm) for 8 h. Generally, the organic materials with a thickness smaller than other dimensions by a few orders of magnitude was called the organic 2D (O2D) materials, which is promising owing to the soft characteristics and suitability in various biomedical applications.<sup>18–22</sup> The similar photoinduced 1D  $\rightarrow$  2D (nanofibers  $\rightarrow$  O2D film) morphological conversion of CO-FFC $\gamma$ -CD was also observed in the scanning electron microscope (SEM) images (Figure S13). In addition, atomic force microscope (AFM) images revealed the thickness of O2D film as 4.5 nm (Figure S14). In the control experiments, the pure di-CO-FF kept the fibrous morphology but converted to the 2D morphology after the addition of  $\gamma$ -CD (Figure S15). This observation demonstrated that the phototransformation of CO-FFC $\gamma$ -CD to di-CO-FFC $\gamma$ -CD plays an important factor in the formation of O2D films.

The assembly mode of CO-FFC $\gamma$ -CD and di-CO-FFC $\gamma$ -CD were further confirmed by circular dichroism (CD) spectroscopy, and small-angle X-ray scattering (SAXS). The CD spectra of CO-FF, CO-FFC $\gamma$ -CD and di-CO-FFC $\gamma$ -CD (Figure S16) all showed the strong positive peaks at 214 nm assigned to the  $n$ - $\pi^*$  transition of FF moiety.<sup>23</sup> However, the moderate positive peaks in the CD spectra of CO-FF and CO-FFC $\gamma$ -CD at 330 nm assigned to  $\pi$ - $\pi^*$  transition of coumarin moiety disappeared in the spectra of di-CO-FFC $\gamma$ -CD, indicating the assembly mode of di-CO-FFC $\gamma$ -CD may be different from those of CO-FF and CO-FFC $\gamma$ -CD. The SAXS spectra of CO-FF, CO-FFC $\gamma$ -CD and di-CO-FFC $\gamma$ -CD (Figure S17) presented the same diffraction peaks at  $q = 16.7, 15.8, 14.6,$  and  $12.1 \text{ nm}^{-1}$ , corresponding to the  $d$  values of 0.37, 0.40, 0.43, and 0.52 nm, respectively. Therein, the  $d$  values of 0.37, 0.40 nm were assigned to the  $\pi$ - $\pi$  stacking distance, and 0.43, 0.52 nm was assigned to the distance among peptides. The value at 0.72 nm might be ascribed to the channel diameters in the nanofiber structure.<sup>24</sup>

Therefore, we can deduce a possible supramolecular assembly and the morphological interconversion mechanism as illustrated in Scheme 2, where O2D films actually developed

### Scheme 2. Possible Self-Assembly Mode of the 1D and 2D Nanostructures



from many fibers along with transformation of CO-FFC $\gamma$ -CD complex to pseudo[2]rotaxane di-CO-FFC $\gamma$ -CD. In CO-FF and CO-FFC $\gamma$ -CD assemblies, the aromatic groups generate  $\pi$ - $\pi$  stacking arrangements, which serve as glues between the cylinders of peptide main chains based on hydrogen bonds and promote the fiber formation.<sup>25</sup> This is in accordance with the previous reports that the short peptides had a pronounced tendency to form long fibers in aqueous solutions.<sup>23</sup> However, the di-CO-FFC $\gamma$ -CD would grow along two perpendicular directions. That is, di-CO-FFC $\gamma$ -CD adopted a side by side array along the horizontal direction but a head to tail array along the vertical direction, and the resultant two-dimensional structure was stabilized by the hydrogen bonds and  $\pi$ - $\pi$  interactions among adjacent di-CO-FFC $\gamma$ -CD units.

Spatially separating the organic dyes by incorporating them into supramolecular self-assembly is an effective strategy to enhance the fluorescence of twisted intramolecular charge-transfer (TICT) molecules.<sup>26,27</sup> Among the confinement systems, biomaterials have attracted many attentions recently due to their potential applications in cell biology such as biological imaging, sensing, and medical delivery.<sup>28,29</sup> However, until now, biomaterial media have been very restricted. Trans-4-

[4-(Dimethylamino)styryl]-1-methylpyridinium iodide (DASPI), as a typical TICT dye, was selected as the model dye to investigate the fluorescence enhancement effect of 1D nanofibers and O2D films. As shown in Figure S18, the emission intensity of DASPI experienced a significant enhancement upon addition of aggregates. A possible reason may be that the aggregates can provide spatial confinement for DASPI through noncovalent interactions, such as H-bonds,  $\pi$ - $\pi$  stacking, electrostatic forces, and hydrophobic effects.<sup>30</sup> The spatial confinement effect can reduce the nonradiative decay of TICT state and minimize the aggregation-caused quenching. The fluorescence intensity of DASPI loaded with O2D films is stronger than with 1D nanofibers. This might be ascribed to the more absorption and/or more confinement of the dye as a result of their larger surface area.<sup>31</sup> To the best of our knowledge, this is the first utilization of FF-based supramolecular aggregate to confine and then enhance emission intensity of the TICT dye.

The high surface area of the O2D film enables the effective removal of organic contaminants from water. Herein, rhodamine B was chosen as a model filtered pollutant to demonstrate this capacity. Through a simple filtration of the di-CO-FF  $\gamma$ -CD solutions (10 mL, 0.5 mM), the O2D films was trapped as a thin layer on a 0.2  $\mu$ m syringe filter. Then rhodamine B aqueous (20 mL, 0.01 mM) was passed rapidly through the filter. UV-vis spectra (Figure S19) indicate the O2D films display a high efficiency and removed 90% of the rhodamine B from the solution.

In summary, we controlled the topological interconversion between 1D nanofibers and 2D thin films through the application of host-guest complexation and photodimerization of coumarin diphenylalanine derivative, where the 1D CO-FF $\gamma$ -CD nanofibers could photo-cross-link to 2D di-CO-FF $\gamma$ -CD thin film under 365 nm light irradiation. The 2D assemblies exhibited the greater fluorescence enhancement of TICT dye and effective removal of organic contaminants from water. These supramolecular assemblies with controlled topological features may provide unique opportunity for the applications in many adjustable material and devices.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b18755.

Compound characterization and additional figures in the optical experiments (PDF)

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### Notes

The authors declare no competing financial interest.

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