Supporting Information

Microbelts and Flower-like Particles of Hexakis-(4-(5-styryl-1,3,4-oxazodiazol-2-yl)-phenoxy)-cyclotriphosphazene: Self-assembly and Photoreaction

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1. Synthesis

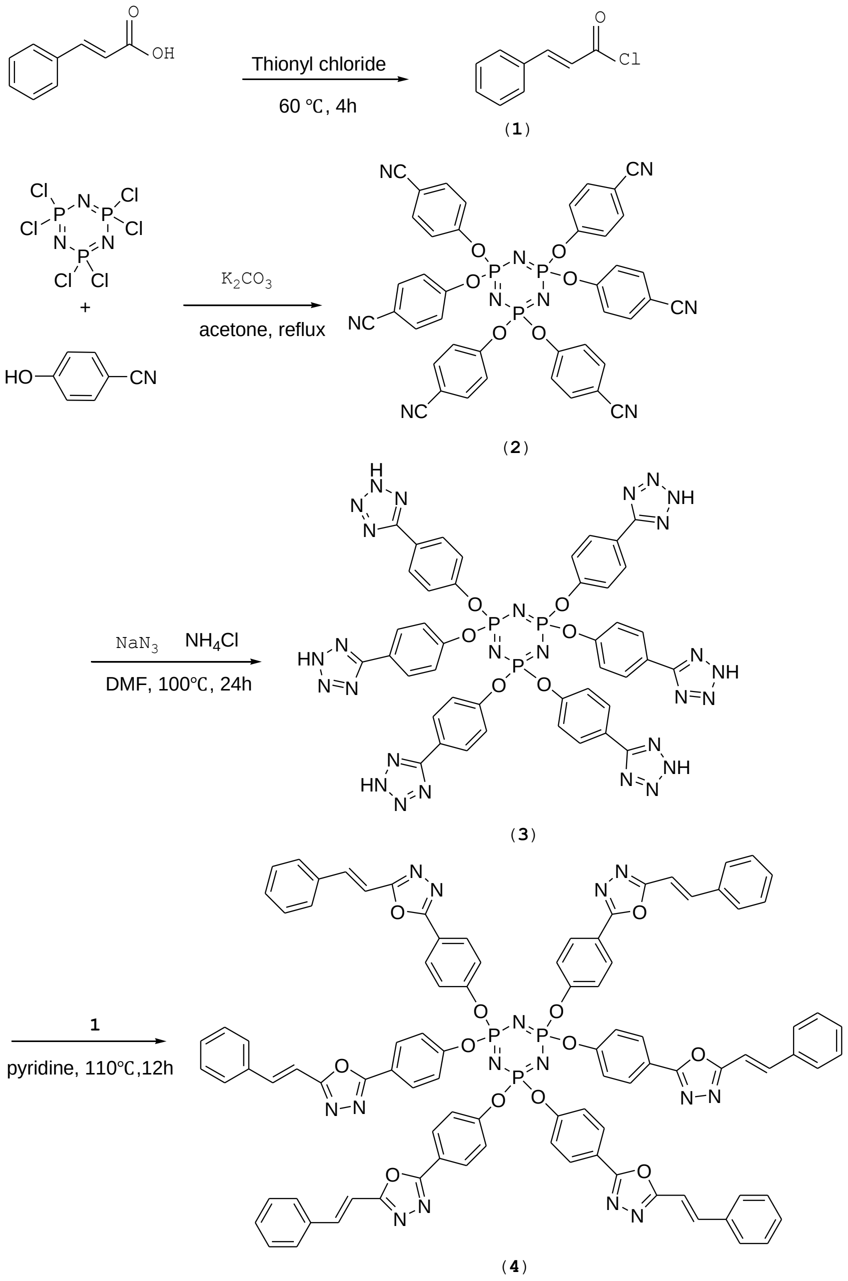
The Cyclotriphosphazene appended with six 1,3,4-oxadiazole-containing derivative, 4 (HSCP), investigated in the present study was synthesized by a multistep process (Scheme S1), in which the final step involved the conversion of tetrazole to 1,3,4-oxadiazole by the Huisgen mechanism.[1] The cinnamic acid chloride was freshly prepared, and the cinnamic acid amount was near 3 equiv to the tetrazole group to ensure complete reaction of the multitetrazole. All intermediates and final product were characterized by FTIR, NMR, and elemental analysis was also conducted for the final product. In the ^{31}P NMR spectrum, HSCP showed only one signal at 7.96 ppm, which indicates that HSCP is symmetrical in the sense that all three phosphorus atoms displayed the same chemical shift; this result supports hexa-substitution on the cyclotriphosphazene ring. Synthetic procedures and characterization details are provided as following.

Materials. Hexachlorocyclotriphosphazene (HCCP) (synthesized as described in the literature[2]) was recrystallized from dry hexane followed by sublimation (60 °C, 0.05 mmHg) twice before use (mp 112.5–113 °C). 4-Cyanophenol, and sodium azide were used as received from Aldrich. The K_2CO_3 was dried at 140 °C for 2 h, and NH_4Cl was dried at 100 °C for 4 h prior to use. The acetone used as the solvent was predistilled from $KMnO_4$, and further distilled from anhydrous $CaSO_4$. The *N,N*-dimethylformamide (DMF) was dried with anhydrous magnesium sulfate, and distilled under vacuum. The pyridine was refluxed with CaH_2 for 6 h and distilled before use. The other solvents were used without further purification.

Characterization. The Fourier transform infrared (FTIR) spectra were recorded in the range of 4000–400 cm^{-1} with a Bruker FT Equionx 55 spectrometer, and the UV–vis–NIR spectra were recorded in the range of 200–500 nm with a Vmini UV–vis 2550 spectrometer. NMR spectra were recorded on Bruker AV–400 M instruments. ^{1}H and ^{13}C {^{1}H}-NMR are given in δ relative to TMS. The sizes and shapes of the nanostructures were observed with a Sirion 200 field-emission scanning electron microscope (FESEM). The samples for SEM observations were prepared by casting several drops of the suspension onto a clean glass cover slip, followed by drying in air and then annealing overnight in an oven at 40 ^{o}C. To minimize sample charging, the dried samples were coated with gold prior to the SEM imaging. The transmission electron microscopy (TEM) was performed with a FEI Tecnai G20 microscope operating at an accelerating voltage of 200 kV. The samples for TEM studies were prepared by dropping the ethanol suspension containing the uniformly dispersed products onto a copper grid and then dried in air for a few hours.

Synthesis of Cinnamic Acid Chloride (1). Cinnamic acid 7.4 g (50mmol) was stirred with 10 mL thionyl chloride at room temperature, then reacted at 60℃ for 4h. After evaporation under vacuum, the crude product was used for the next step without further purification.

Synthesis of Hexakis-(4-(5-styryl-1,3,4-oxazodiazol-2-yl)-phenyloxy)-cyclotriphosphazene (HSCP) 4. Synthesis of Hexakis-(4-(5-styryl-1,3,4-oxazodiazol-2-yl)phenyloxy)-cyclotriphosphazene **(4)** is described as the general procedure (Scheme S1). The synthesis of Hexakis-(4-tetrazolylphenyloxy)-cyclotriphosphazene (**2**) was described in our early report.[3] Hexakis-(4-tetrazolylphenyloxy)-cyclotriphosphazene (3.3 g 3 mmol) was suspension in 100 mL Pyridine (partly dissolved), then added cinnamic acid chloride (**1**) by dropping, and the resulting mixture was stirred for 12 h at 110 ℃ under nitrogen. The suspension was dissolved in the heated process. After reaction, the solution was concentrated and the residue was dropped into methanol. The primrose yellow powder was collected by vacuum filtration. The solid was then washed twice with 10% KOH (100 × 2 mL) and brine (100 × 2 mL), respectively, and then dried in vacuum at 40 ℃. After recrystallization twice from chloroform and ethyl acetate (1:3), yellow powder was obtained. Yield: 17.41 g, 88.90%. ^{1}H NMR ($CDCl_3$): δ [ppm] 8.00–8.02 (d, 2H), 7.58–7.62 (d, 1H, -CH=C$\underline{\text{H}}$-), 7.53–7.54 (m, 2H), 7.4–7.42 (m, 3H), 7.22–7.24 (d, 2H), 6.99–7.30 (d, 1H, -C$\underline{\text{H}}$=CH-). ^{13}C NMR ($CDCl_3$): 164.52, 162.99, 152.67, 139.28, 134.72, 130.02, 128.99, 128.56, 127.66, 121.54, 121.34, 109.64. ^{31}P NMR ($CDCl_3$): 7.96. Anal. found (calcd) for $C_{96}H_{66}N_{15}O_{12}P_3 \cdot H_2O$: C, 66.50 (66.55); H, 3.93 (3.96); N, 12.47 (12.13).



Scheme S1. Synthesis of HSCP (4)

2. Characteristic of hexakis-(4-(5-styryl-1, 3, 4-oxazodiazol-2-yl)-phenoxy)-cyclotriphosphazene (HSCP).

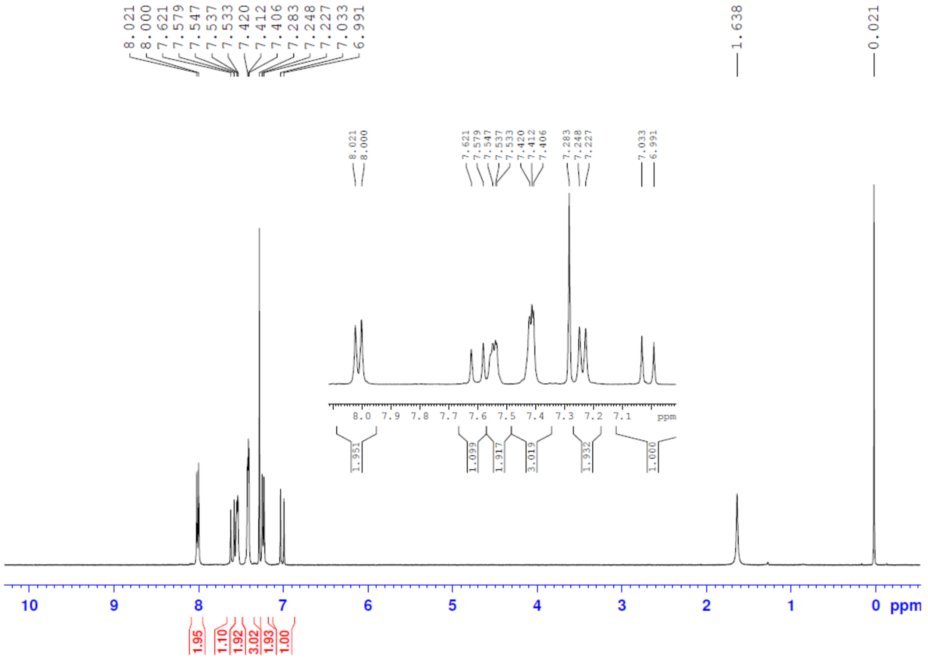


Fig. S1 ^{1}H NMR spectrum of **HSCP** (**4**).

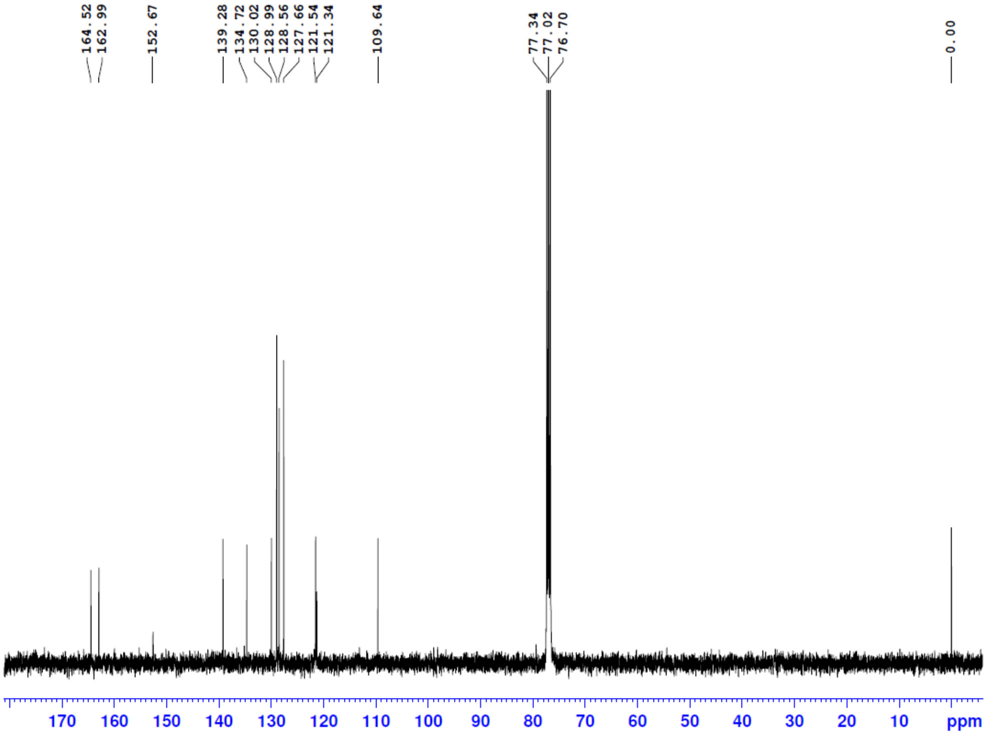


Fig. S2 ^{13}C NMR spectrum of **HSCP** (**4**).

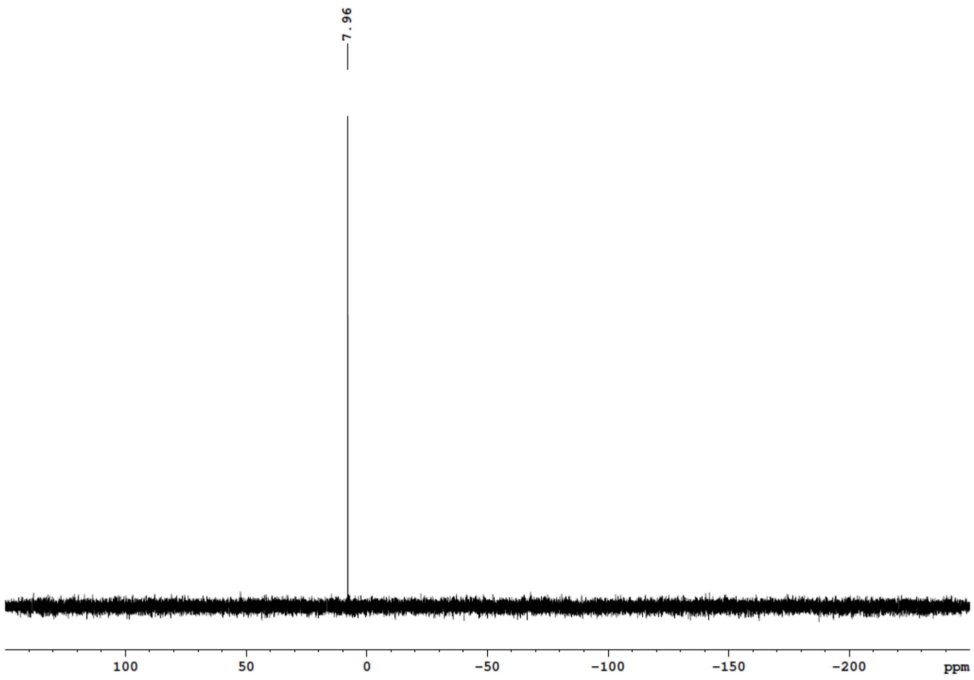


Fig. S3 ^{31}P NMR spectrum of **HSCP (4)**.

3. Self-assembly Process. The self-assembly of the microbelts and flower-like micro particles of HSCP was performed through a solvent exchange processing, in which the molecules were transferred from a “good” solvent ($CHCl_3$) into a “poor” solvent (ethanol) where the molecules have limited solubility and thus self-assembled into 1D microbelts or flower like micro particles via molecular stacking. Such a self-assembly approach takes the advantage of the strong intermolecular π–π interaction, which is enhanced in a solvent where the solvophobic interaction is maximized. Similar methods have previously been used for self-assembling of one-dimensional nanostructure of symmetric PTCDIs and other planar aromatic macromolecules.[4] The solutions of HSCP were made in chloroform/ethanol at 0.6 and 0.3mmol/L with the volume ratio of chloroform to ethanol of 1:1, 1:2, 1:3, 1:4, and 1:5 for the experiments on the concentration and solvent ratio dependence.

4. Additional Microscopy characterization of the microstructures.

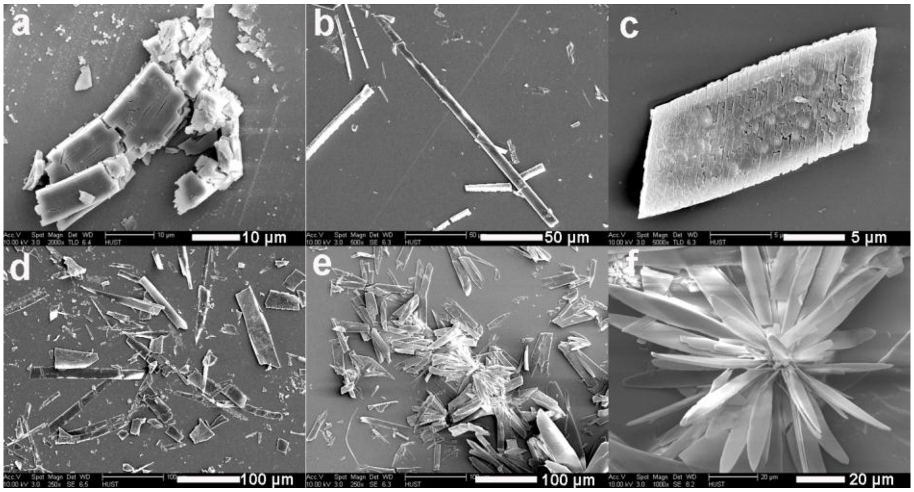


Fig. S4 SEM images of HSCP morphologies obtained by solvent exchange processing (chloroform to ethanol) at the concentration of 0.6 mmol/L, with the volume ratio of chloroform to ethanol (a) 1:1; (b,c)1:2; (d,e) 1:3; and (f) 1:4, respectively.

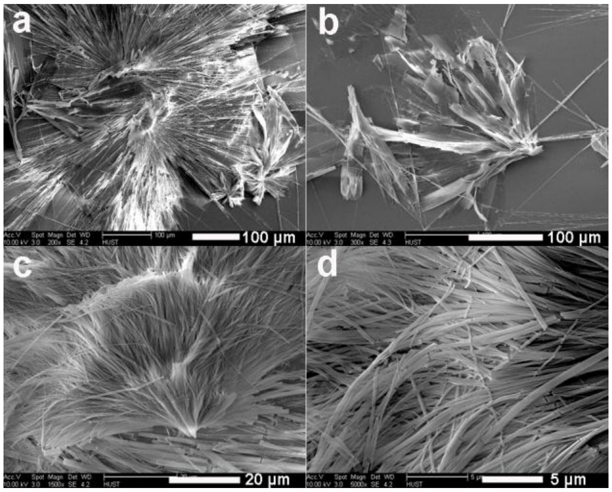


Fig. S5 SEM images of **HSCP** morphologies obtained by solvent exchange processing, with the volume ratio of chloroform to ethanol of 1:5 at 0.6 mmol/L. (a) A large-area SEM image; (b) Some flake like structures; (c) Enlarge SEM image showing the growth of belts from the central seeding particulate of selected regions; (d) Enlarge image showing the belt morphology and broken of the belt.

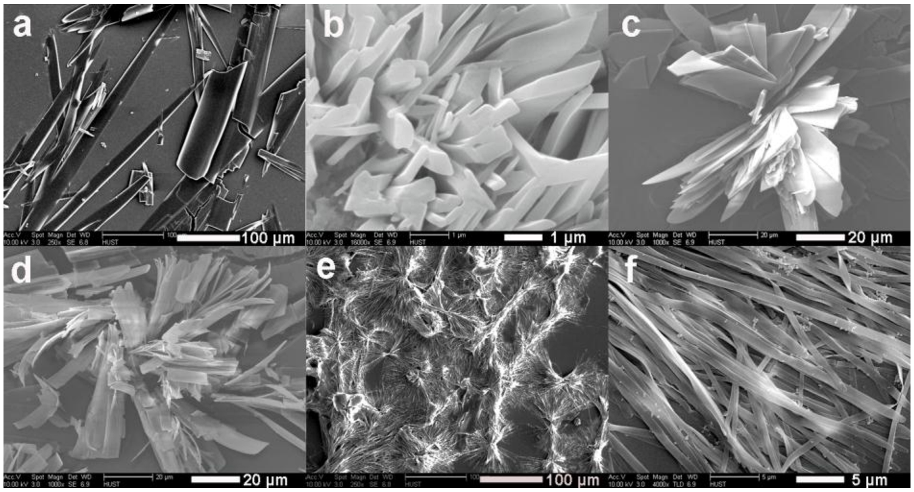


Fig. S6 SEM images of **HSCP** morphologies obtained by solvent exchange processing (chloroform to ethanol) at the concentration of 0.3 mmol/L, with the volume ratio of chloroform to ethanol (a) 1:1; (b)1:2; (c) 1:3; (d) 1:4; and (e,f) 1:5, respectively.

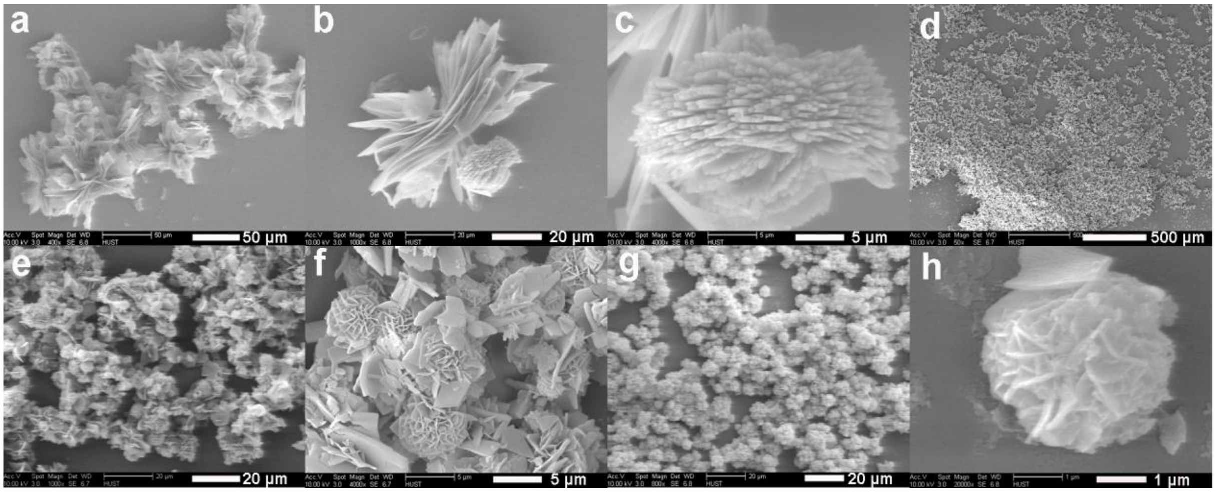


Fig. S7 Additional SEM images of **HSCP** morphologies obtained by solvent exchange processing (chloroform to ethanol), with the volume ratio of 1:8 at different concentration: (a,b) Flower-like structures formed at 15 mmol/L; (c) Enlarge image showing the cockscomb like structures composed of micro-ribbons; (d,e,f) The resulting structures obtained at 1.5 mmol/L; (g,h) A large-area and an enlarge SEM image of the micro particles obtained at 0.15 mmol/L.

5. Photophysical Studies.

Figure S8 shows the variation in the ^{1}H NMR spectrum of a solution of HSCP in chloroform with various irradiation times. In this experiment, the photoirradiation was taken out in an NMR tube directly. Actually, 10 mg HSCP was dissolved in 0.5 ml d-chloroform, the solution in NMR tube was exposed to UV light with a Luzchem photoreactor (8 W dark blue phosphor lamps, measured intensity ca. 1.75 mW/cm2) at 365 nm and measured at0, 0.5, 1 and 2 h.

In a typical experiment, the nanobelts of HSCP were cast on clean glass which was subjected to photo-irradiation with a 400 W high-pressure mercury lamp (350-400 nm) at 25 °C from a distance of 20 cm. The sample was exposed to UV light for 20 min, by doing this, the result products still can dissolved in chloroform.

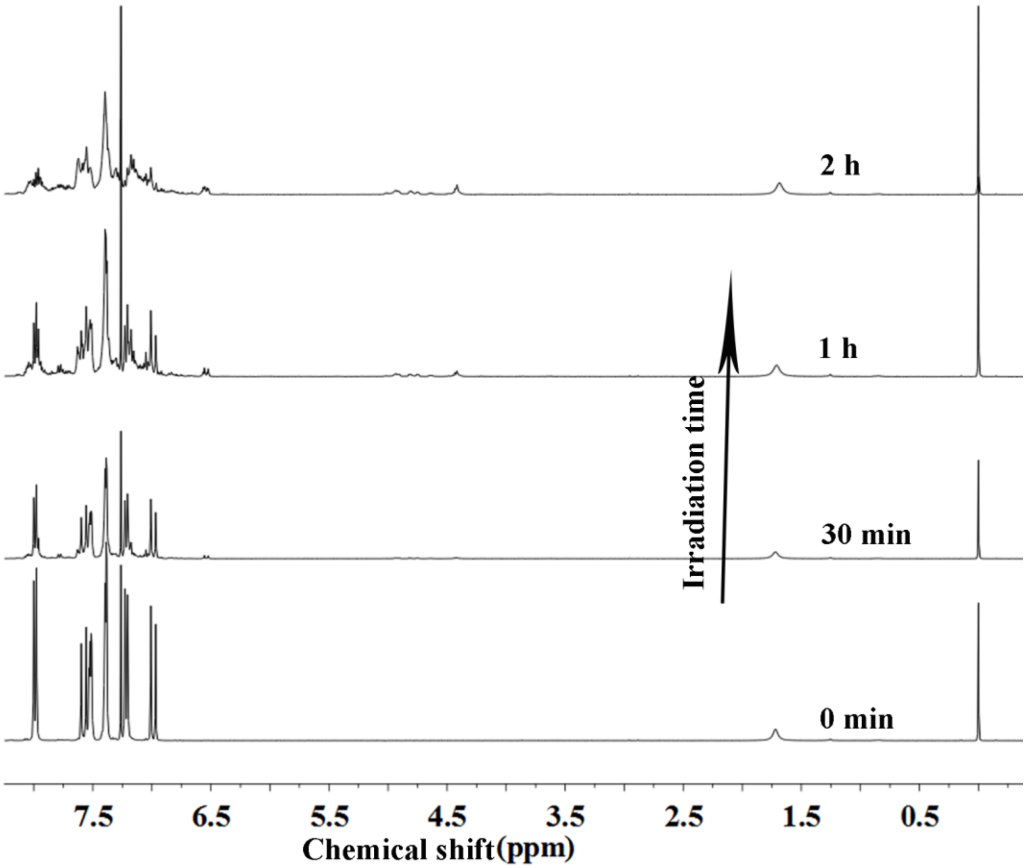


Fig. S8 The ^{1}H NMR spectra ranging from the corresponding [2 + 2] photodimerization products after various irradiation times of HSCP in chloroform solution.

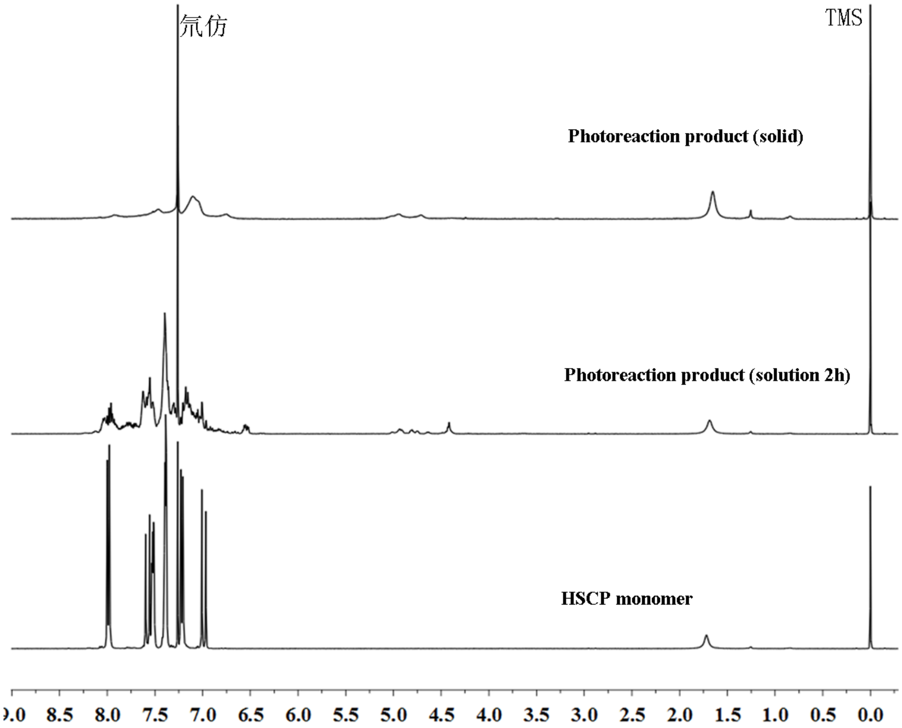


Fig. S9 ^{1}H NMR spectra of HSCP and its solution and solid state photoreaction products.

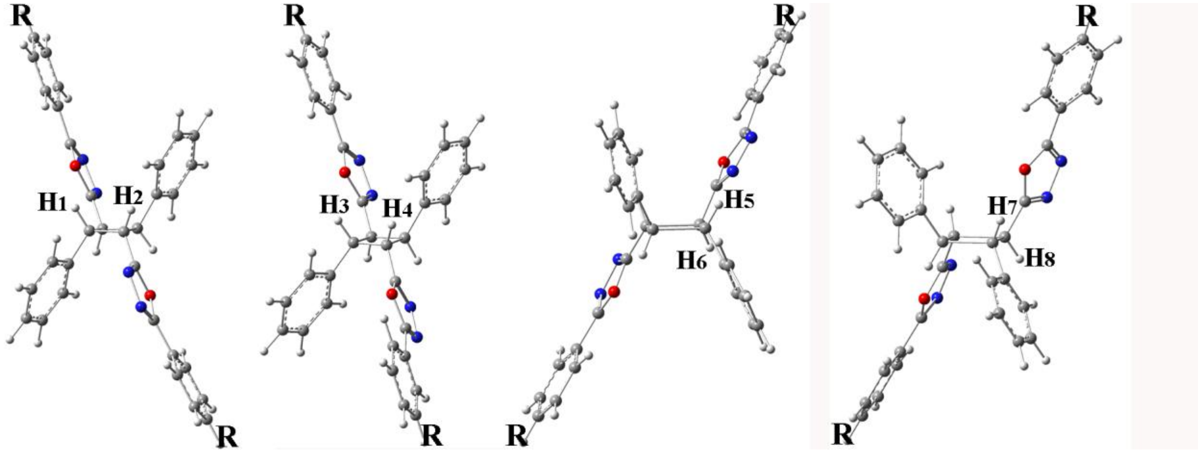


Fig. S10 The possible structures of several stereo-isomers resulted from the photoreaction in solution.

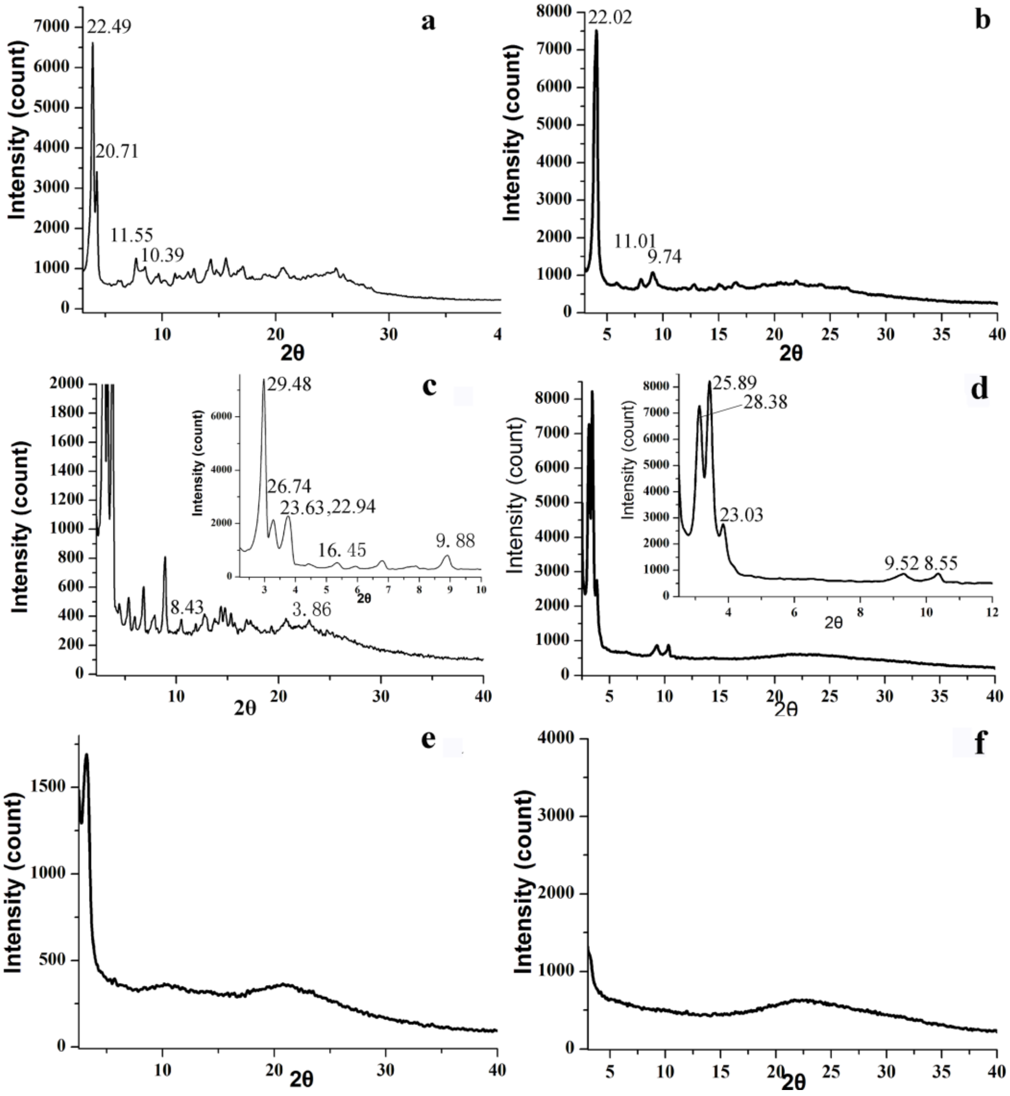


Fig. S11 XRD patterns of HSCP bulk powder materials (a,b), microbelts (c,d), and microflower-like particles (e,f). (a,c,e) before and (b,d,f) after irradiation.

XRD spectrum. The structures of the bulk powder, microbelts, and microflower-like particles, as well as their solid-state photoreaction properties were also investigated by XRD analysis (Figure S11). The photoreaction samples for XRD analysis were prepared under the same conditions. The samples were cast on clean glass slides and then photo-irradiated with a 400 W high-pressure mercury lamp (350–400 nm) at 25 °C from a distance of 20 cm for 2 h. As shown in Figures S11a and 11b, after photoreaction, the largest d-spacing of HSCP bulk powder decreased from 22.49 Å to 20.2 Å, the peak of d = 20.71 Å disappeared, and the 2θ peaks greater than 10 weakened. Compared with HPCP powder, more peaks of the microbelts were observed at small 2θ angles (Figure S11c). The largest d-spacing of HSCP nanobelts was 29.48 Å, which was much higher than that of HSCP powder, indicating that the molecules of the microbelts were more stretched. After photo-irradiation, the diffraction peak positions of the microbelts only slightly changed, and the relative intensity of the maximum peak significantly decreased. Almost all 2θ peaks greater than 12° disappeared (Figure S11d). Figure S11e shows the XRD spectra of the microflower-like particles obtained at 1.5 mmol/L HSCP. Only one obvious diffraction peak at 3.26° (2θ) and two packaged peaks at 10° and 20° were observed, indicating that the microflower-like particles had a low degree of crystallinity. After exposure, the peaks at 3.26° and 10° disappeared, indicating that the self-assembled microflower-like particles had also undergone photochemical reaction, and more thoroughly.

References

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