Supplementary Material (ESI) for Chemical Communications
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Supporting Information

Intrinsically fluorescent nanoparticles with excellent stability based on highly crosslinked organic-inorganic hybrid polyphosphazene material

Wei Liu, Xiaobin Huang,* Hao Wei, Xiaozhen Tang and Lu Zhu

Experimental Materials

Crosslinked polyphosphazene fluorescent nanoparticles were prepared as follows: triethylamine (TEA) (20 μL) was added to a solution of cyclotriphosphazene (CP) (10.0 mg) and 4,4'-sulfonyldiphenol (BPS) (21.6 mg) in acetonitrile (50 mL). Subsequently, the solution reacted in an ultrasonic bath (150 W) at room temperature for about 2 min, 3 min, and 4 min to obtain FNPs with mean diameters of 17 nm, 46 nm, and 104 nm, respectively. The resultant particles were obtained by centrifugation and then washed with tetrahydrofuran and deionized water three times.

Crosslinked polyphosphazene fluorescent nanotubes were prepared as follows: 1 mL of TEA was added to a solution of CP (0.50 g) and BPS (1.08 g) in tetrahydrofuran (100 mL). Subsequently, the solution reacted in an ultrasonic bath (100 W) at room temperature for 3 h. The resultant product was filtrated and then washed with tetrahydrofuran and deionized water three times.

Crosslinked polyphosphazene fluorescent microspheres were prepared as follows: 1 mL of TEA was added to a solution of CP (0.25 g) and BPS (1.08 g) in 100 mL of acetone. The reaction mixture was stirred with magnetic stirrer at room temperature for 3 h. The resultant product was obtained by centrifugation and then washed with tetrahydrofuran and deionized water three times.

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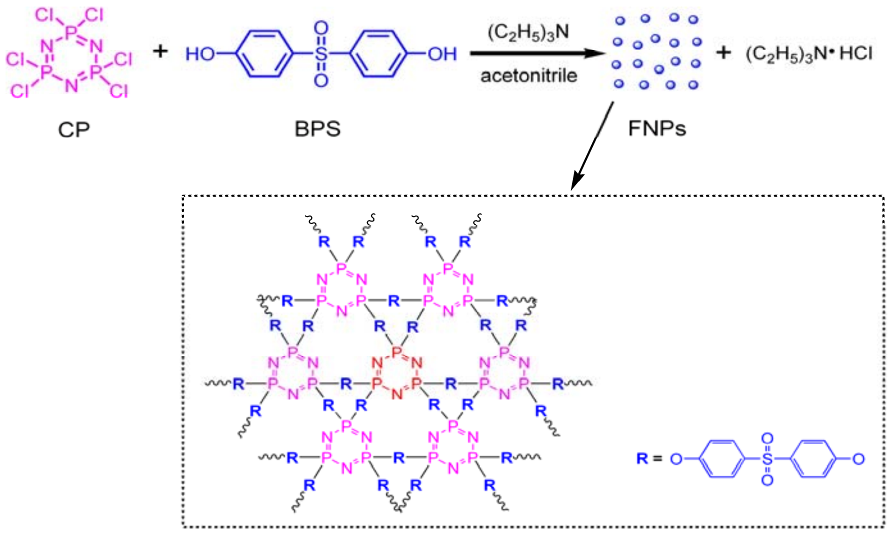

Fig. S1 Formation mechanism of crosslinked polyphosphazene fluorescent nanoparticles (FNPs).

The formation mechanism[18] of crosslinked polyphosphazene fluorescent nanoparticles (FNPs) is shown in Fig. S1. With the aid of an acid acceptor (triethylamine), FNPs were formed due to the nucleophilic replacement reaction between hydroxyl groups of BPS and P-Cl bonds of CP. At the very beginning, BPS substituted the Cl atoms of CP through a nucleophilic attack to form covalent branches. Then the BPS branches were projected above and below CP plane and thus produced a rigid spherical core. As polymerization proceeding, the spherical core grew gradually to form crosslinked nanoparticles. Meanwhile, HCl was generated during the reaction, which was subsequently absorbed by triethylamine to afford $(C_2H_5)_3N{\cdot}HCl$. This combination spontaneously accelerated the crosslinking reaction.

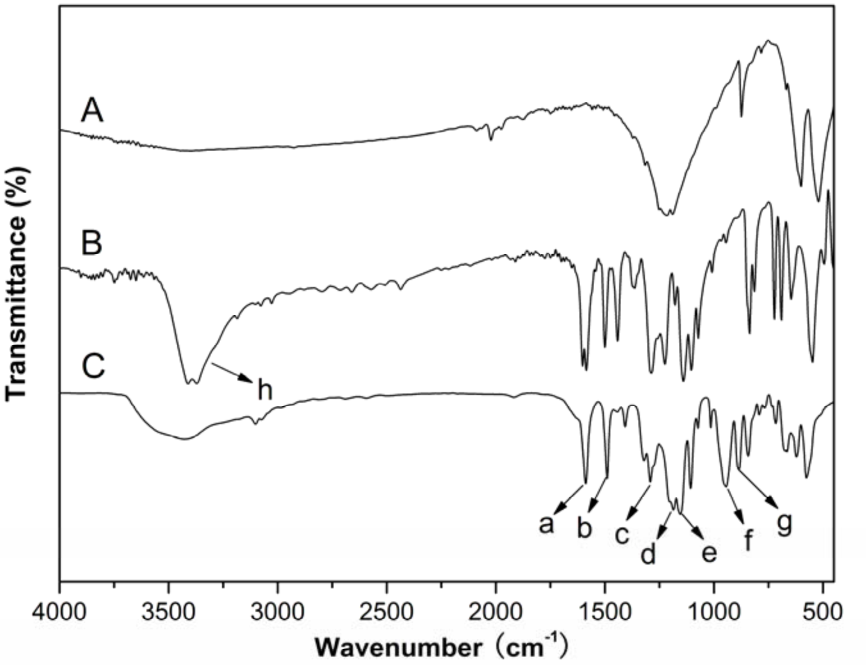

Fig. S2 FTIR spectra of CP (A), BPS (B) and FNPs (C).

The chemical structure of FNPs was characterized by FTIR measurements. As shown in Fig. S2, the peaks at 1590 cm^{-1} (a) and 1490 cm^{-1} (b), correspond to the phenyl absorption of sulfonyldiphenol units. The characteristic peaks of O=S=O group can be seen at 1290 cm^{-1} (c) and 1150 cm^{-1} (e). The bands at 1190 cm^{-1} (d) and 885 cm^{-1} (g) are attributed to the P=N and P–N characteristic absorption of CP, respectively. The analysis above can make a conclusion that the products contain the structure units of CP and BPS. Furthermore, a broad strong absorption peak of the phenolic hydroxyl group of BPS ranging from 3100 to 3500 cm^{-1} (h) (Fig. S2B) obviously reduces after the polycondensation (Fig. S2C). Meanwhile, a new absorption peak at 940 cm^{-1} (f) is assigned to the P–O–Ph band. Thus we could reasonably assume that FNPs were synthesized by the crosslinking reaction between CP and BPS.

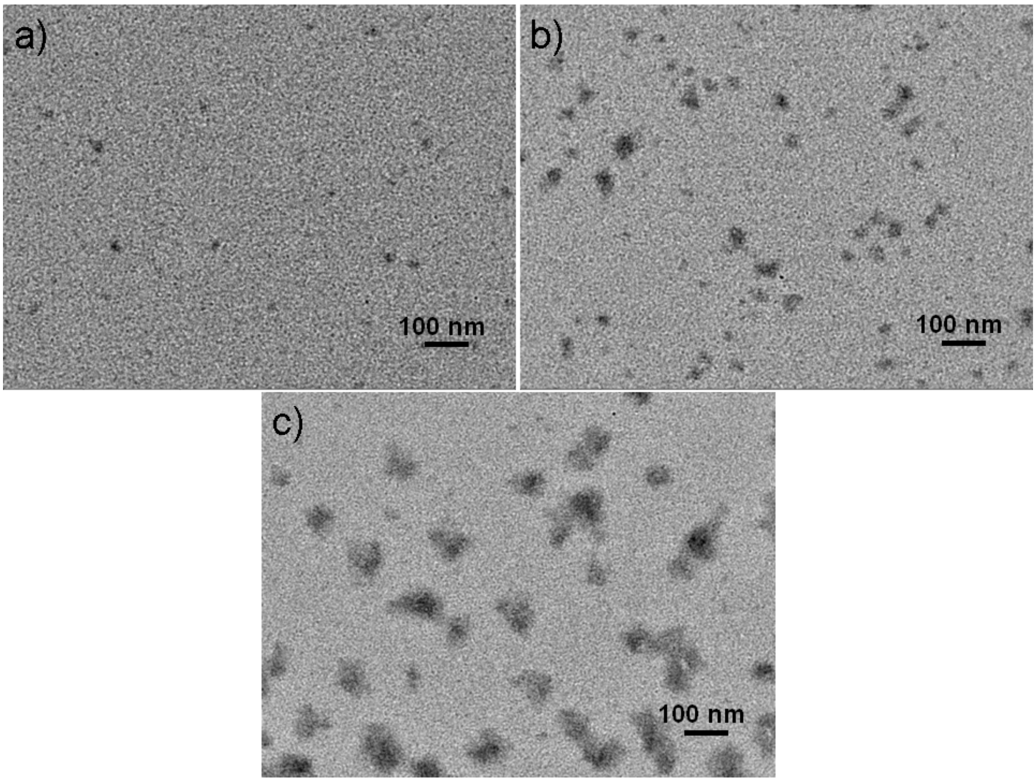

Fig. S3 TEM micrographs of FNPs with mean diameter of 17 nm (a), 46 nm (b), and 104 nm (c).

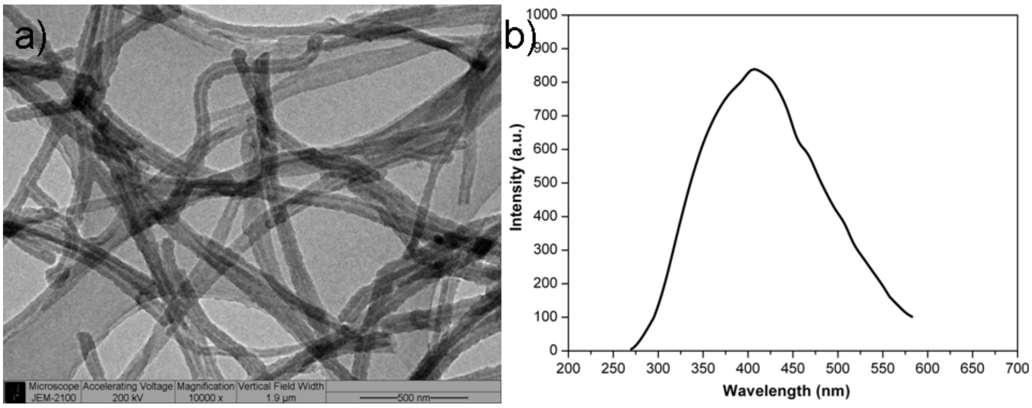

Fig. S4 a) TEM micrograph of crosslinked polyphosphazene nanotubes. The scale bar is 500 nm; b) Fluorescent emission spectrum of crosslinked polyphosphazene nanotubes ($\lambda_{ex} = 290$ nm).

Fig. S4a shows the TEM micrograph of crosslinked polyphosphazene nanotubes. Typically, the nanotubes are several micrometers in length. Most of them have an outer diameter of about 50 nm. The TEM micrograph also reveals that the nanotubes possess hollow tubular structures with an average inner diameter of about 5–10 nm. From Fig. S4b, we can see that the nanotubes have strong fluorescent intensity at around 400 nm.

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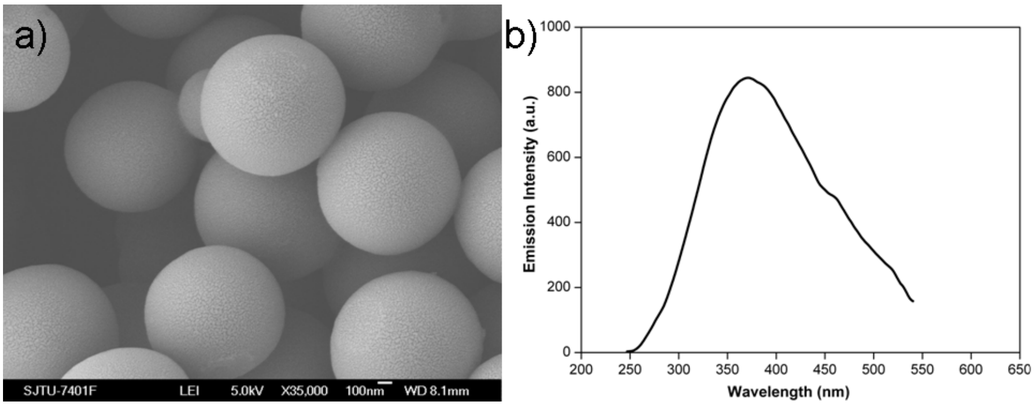

Fig. S5 a) SEM micrograph of crosslinked polyphosphazene microspheres. The scale bar is 100 nm; b) Fluorescent emission spectrum of crosslinked polyphosphazene microspheres (λ_{ex} = 290 nm).

Fig. S5a shows the SEM micrograph of crosslinked polyphosphazene microspheres. Typically, the microspheres have a mean diameter of several hundred nanometers. From Fig. S5b, we can see that the microspheres have strong fluorescent intensity at around 380 nm.