

## Supporting information

### Electron-Withdrawing Ability Tunable Polyphosphazene Frameworks as Novel Heterogeneous Catalysts for Efficient Biomass Upgrading

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#### Materials:

Fructose was purchased from Sigma-Aldrich. Hexachlorocyclotriphosphazene (HCCP), 4,4'-sulfonyldiphenol (BPS), 4,4'-(hexafluoroisopropylidene) diphenol (BPAF), 4,4'-diaminodiphenyl ether (ODA), benzoyl chloride, and dihydroxyacetone were purchased from Aladdin Chemistry Co. Ltd (China). Acetonitrile (AN) (GC > 99.9%) was purchased from Shanghai Lingfeng Chemical Reagent Company and was used without further purification. Acetone, tetrahydrofuran (THF), triethylamine (TEA) and DMSO (analytical grade) were obtained from Shanghai Chemical Reagents Company and used without further purification. Dimethyl sulfoxide-D<sub>6</sub> for NMR measurements was obtained from Cambridge Isotope Laboratories, Inc.

#### Preparation of poly(cyclotri-phosphazene-co-4,4'-sulfonyldiphenol) nanoparticles (PZS-NPs):

The typical preparation was carried out as follows: TEA (0.52 g, 5.14 mmol), HCCP (0.2 g, 0.575 mmol), and BPS with different feed ratios were added in a glass flask and dissolved in acetonitrile (50 mL) under ultrasonic irradiation, then the reaction was completed after 2 h at room temperature. The precipitated polymer nanoparticles were separated by filtration, and then washed with acetone, ethanol and deionized water, respectively. The final products were dried in vacuum at 40 °C to a constant weight.

#### Preparation of poly(cyclotriphosphazene-co-(4,4'-(hexafluoroisopropylidene) diphenol)) nanoparticles (PZAF-NPs):

The preparation of PZAF-3.5 was carried out as follows (as shown in Scheme S1): TEA (0.52 g, 5.14 mmol), HCCP (0.1 g, 0.288 mmol), and BPAF (0.34 g, 1.008 mmol) were added in a glass flask and dispersed in acetonitrile (50 mL) under ultrasonic irradiation. The reaction was completed after 3 h at room temperature. The precipitated polymer nanoparticles were recovered by filtration, washed with acetone, ethanol and deionized water, and then dried in vacuum at 40 °C to a constant weight.

### **Preparation of poly(cyclotriphosphazene-co-(4,4'-diaminodiphenyl ether)) nanoparticles (PZODA-NPs):**

The preparation of PZODA-3.5 was carried out as follows (as shown in Scheme S2): TEA (0.52 g, 5.14 mmol), HCCP (0.1 g, 0.288 mmol), and ODA (0.202 g, 1.008 mmol) were added to a glass flask and dispersed in acetonitrile (50 mL) under ultrasonic irradiation. The reaction was completed after 8 h at 60 °C. The precipitated polymer nanoparticles were recovered by filtration, washed with acetone, ethanol and deionized water, and then dried in vacuum at 40 °C to a constant weight.

### **Catalytic performance tests:**

In a typical reaction procedure for the dehydration of D-fructose, 12.5 g fructose/DMSO solution (3 wt %) was charged into a 50 mL three-necked flask, followed by the addition of the catalyst (0.2 g). The reaction was performed at 90 °C for 2 h with magnetic stirring, and an oil bath was used for keeping the temperature which was elevated to the setting point before the reaction. During the reaction, the mixture was sampled (about 0.5 ml) at predefined time intervals and filtered with a PTFE syringe filter (40 µm) and diluted 20 times with water before HPLC analysis. Before each reaction, a control sample for HPLC analysis was taken from the 3 wt% fructose/DMSO solution and diluted 20 times with water.

### **Catalyst recycling experiments:**

12.5 g of 10 wt% fructose/DMSO was mixed with 0.67 g PZS-2.0 in a 50 mL flash equipped with magnetic stirring, and the reaction was kept in oil bath at 90 °C for 0.5 h. After that, the nanoparticle catalyst was separated by centrifugation and purified for three times by repeating ultra-centrifugation (12,000 rpm for 10 min) / re-dispersion cycles in acetonitrile with ultrasonic bathing and was dried in a vacuum at 45 °C overnight. It was then used directly for the next run.

### **Typical separation procedure for HMF :**

After the dehydration reaction of fructose, the reaction mixture was centrifugation and then filtration to separate the polymer catalyst, then the liquid was transferred into a flask and was distilled under reduced pressure to remove the DMSO solvent. The remaining mixture was extracted with ethyl acetate (20 mL × 5) after water (20 mL) was added, and then the organic phase was collected. After drying with anhydrous sodium sulfate, the organic layer was distilled under reduced pressure to obtain pure HMF as the main product. The purity was good from NMR analysis.

Separated HMF: <sup>1</sup>H NMR spectrum (400 MHz, [D<sub>6</sub>] DMSO, δ ppm): 4.481-4.496 (d, 2 H, *J* = 6.000), 5.548–5.562 (t, 1 H, *J* = 5.600), 6.573–6.582 (d, 1 H, *J* = 3.600), 7.455–7.465 (d, 1 H, *J* = 4.000), 9.519 (s, 1H); <sup>13</sup>C NMR spectrum (100 MHz, [D<sub>6</sub>] DMSO, δ ppm): 56.6, 110.3, 125.1, 152.4, 162.8, 178.6.

### **Characterization:**

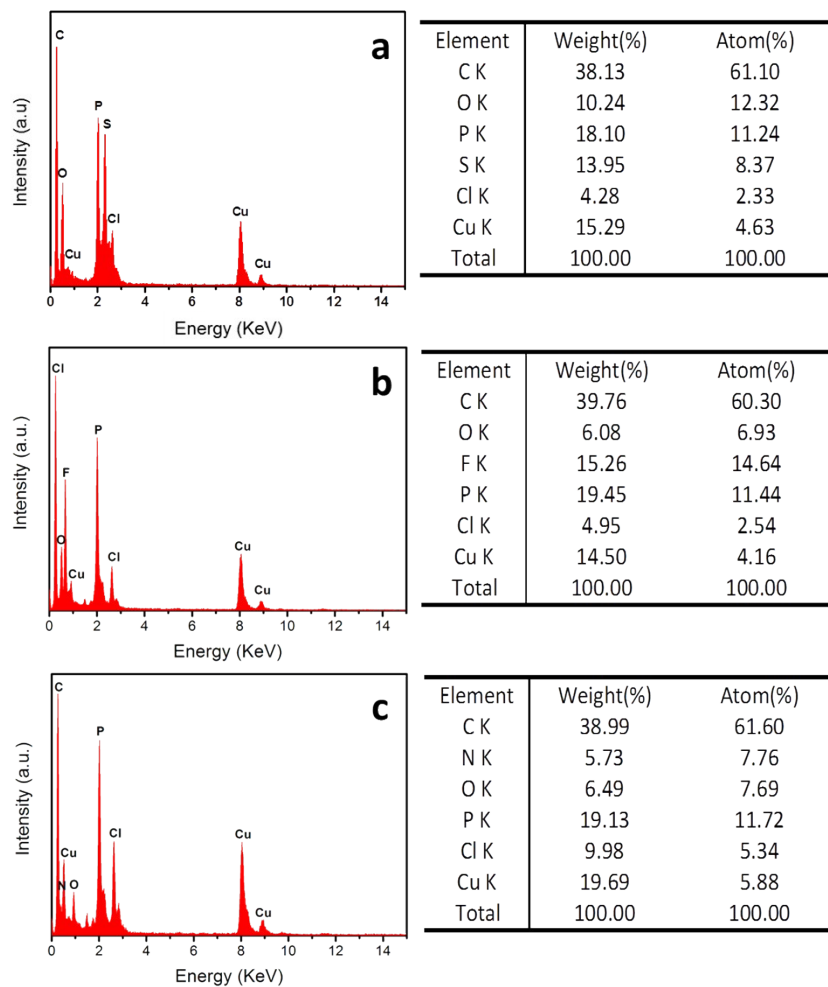
Field emission scanning electron microscopy (FE-SEM) was performed on a Hitachi S-4800 Scanning electron microscope at an accelerating voltage of 20 kV. The sample was prepared by drop-casting an ethanol suspension onto mica substrate and then coated with gold. Transmission electron microscope (TEM) was by a JEOL 1230 transmission electron microscope at an accelerating voltage of 75 kV. Samples dispersed at an appropriate concentration were cast onto a carbon-coated copper grid.

Energy dispersive X-ray spectroscopy (EDX) was taken on a JEM-2100F transmission electron microscope at an accelerating voltage of 200 kV. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were obtained on a Mercury plus 400 MHz spectrometer with D<sub>6</sub>-DMSO as the solvent and tetramethylsilane (TMS) as the internal standard. Fourier transform infrared spectra (FT-IR) were recorded on a NEXUS-470 Fourier transform infrared spectrophotometer. Thermal gravimetric analysis (TGA) was run on a Pyris 1 TGA instrument. The TGA curves were

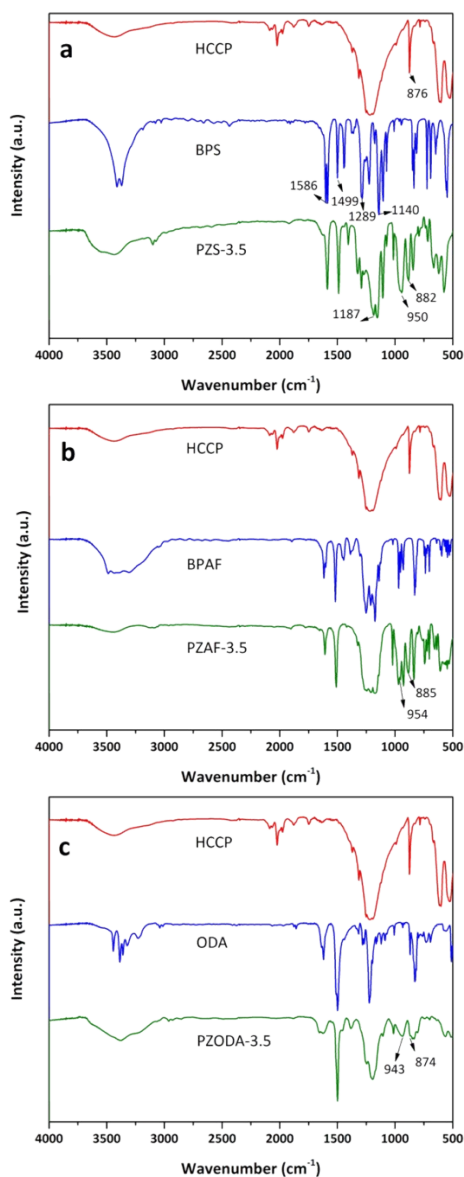
measured under N<sub>2</sub> by heating the samples from 50 to 800 °C at a rate of 20 °C min<sup>-1</sup>. All measurements were taken under a constant flow of nitrogen of 40 mL/min. Gas chromatography-mass spectrometry (GC-MS) were conducted with a Finnigan Voyager GC-MS equipped with a HP-5MS capillary column (30 m×0.25 mm×0.25 μm) and the corresponding GC/MS spectra. The elemental analysis was taken on a vario EL III analyzer (Elementar Company in Germany) in Shanghai Institute of Organic Chemistry (SIOC), Chinese Academy of Sciences.

High performance liquid chromatography (HPLC) measurements are conducted using a Shimadzu Class-VP HPLC with RID-10A Refractive Index detector. A shodex SH1011 sugar column (300 × 8 mm, 6 μm) is used to separate the products. General HPLC conditions for analysis of products: column temperature: 50 °C; rate of fluid: 0.8 mL / min; injection amount: 5 μL.

**Experimental Data:**



**Fig. S1** Energy dispersive X-ray spectroscopy data of (a) PZS-3.5, (b) PZAF-3.5 and (c) PZODA-3.5.



**Figure S2.** FTIR spectra of (a) PZS-3.5, (b) PZAF-3.5 and (c) PZODA-3.5 with the spectra of monomers.

The characteristic peak of HCCP monomer (P-N) is located at  $876\text{ cm}^{-1}$ . For BPS monomer, the characteristic peaks of (C=C(Ph)) are located at  $1586\text{ cm}^{-1}$  and  $1499\text{ cm}^{-1}$ , while the characteristic peaks of (O=S=O) are located at  $1289\text{ cm}^{-1}$  and  $1140\text{ cm}^{-1}$ , respectively. For PZS-3.5, the product shows new characteristic peaks of (P-O(Ph)) located at  $945\text{ cm}^{-1}$ , which verified the polymerization successfully. The retained characteristic peaks of (P=N) at  $1187\text{ cm}^{-1}$  and (P-N) at  $882\text{ cm}^{-1}$ , and other characteristic peaks of BPS monomer, verify the PZS-3.5 has the fundamental structure of HCCP and BPS units. The slight shift vibration frequency of (P-N) in HCCP from  $876\text{ cm}^{-1}$  to  $882\text{ cm}^{-1}$  should be ascribed to the inductive effect of substituted BPS co-monomer.

For the sample of PZAF-3.5, the characteristic peaks originated from HCCP and BPAF can be found in a range of  $500 \sim 1700\text{ cm}^{-1}$ , which indicates the basic components in PZAF framework. Furthermore, the vibration frequency of (P-N) in HCCP moiety shifts to  $885\text{ cm}^{-1}$  and the vibration frequency of newly formed (P-O(Ph)) in PZAF might be located at  $954\text{ cm}^{-1}$ . There might be a stronger inductive effect on the P-O bonding compared with that of PZS framework, which is caused by the  $-\text{CF}_3$  group containing co-monomer BPAF with a strong electron-withdrawing capability.

For the sample PZODA-3.5, the characteristic peaks originated from HCCP and BPAF can also be found in a range of  $500 \sim 1700\text{ cm}^{-1}$ , indicating the basic components in PZODA framework. And the vibration peak located at  $943\text{ cm}^{-1}$  should be attributed to the bond formation (P-N(Ph)) after the polymerization. However, the vibration peak at  $874\text{ cm}^{-1}$ , which can be regarded as the vibration of (P-N) in HCCP, slightly shifts to the lower frequency by comparing that of PZS and PZAF, and this might be due to the conjugated effect in ODA co-monomer with an electron-donating ability.

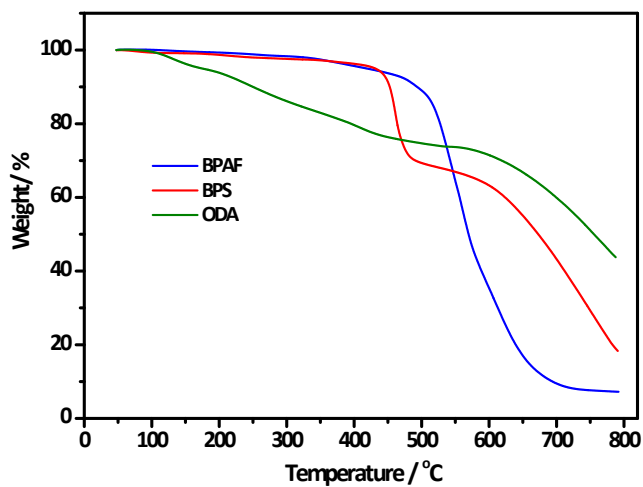


Fig. S3 The TGA profiles of co-monomers BPS, BPAF and ODA.

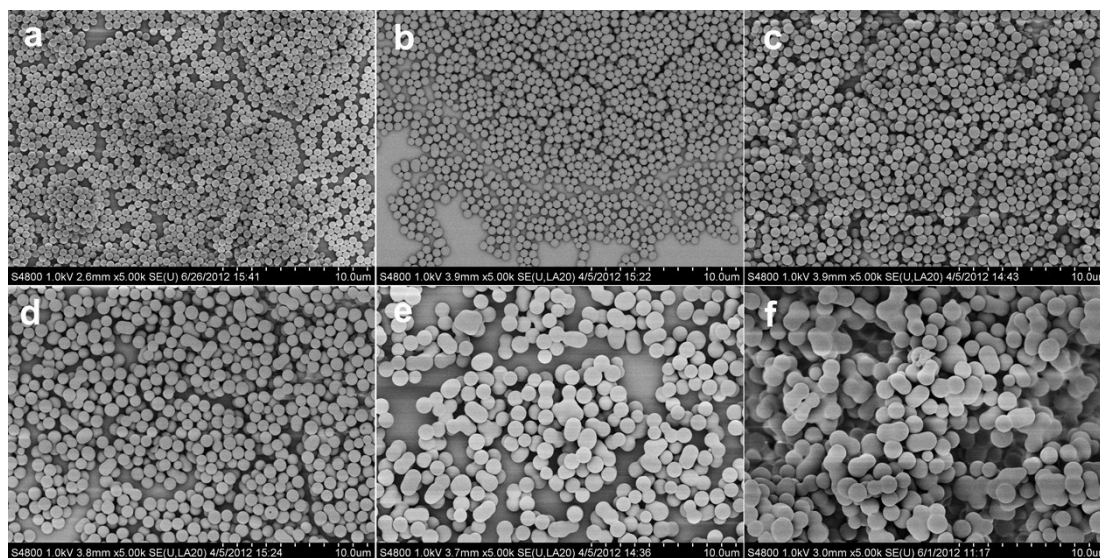


Fig. S4 FE-SEM images of PZS polyphosphazene nanoparticles with different BPS : HCCP molar ratio (a) 2/1, (b) 3/1, (c) 3.5/1, (d) 4.5/1, (e)5.5/1, (f) 7/1.

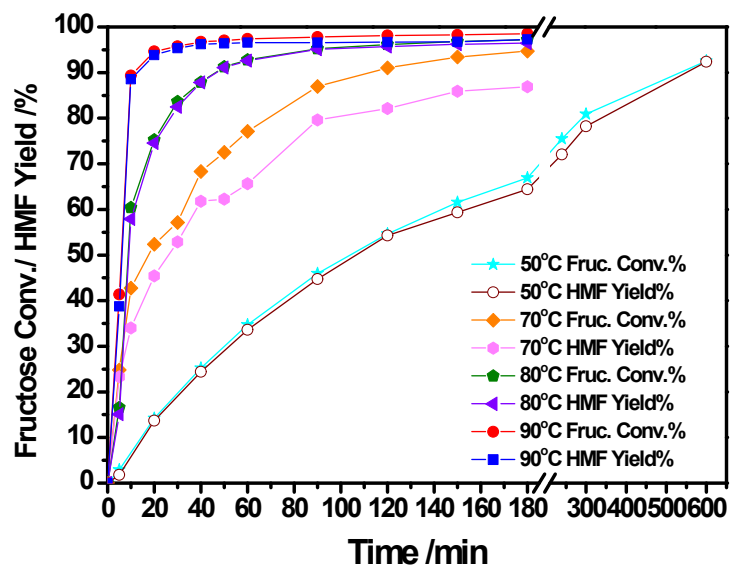


Fig. S5 The catalysis real-time data of PZS-3.5 with different reaction temperatures. Reaction conditions: 3 % D-fructose in DMSO, 0.2 g of catalyst, 3 – 10 h of reaction time.

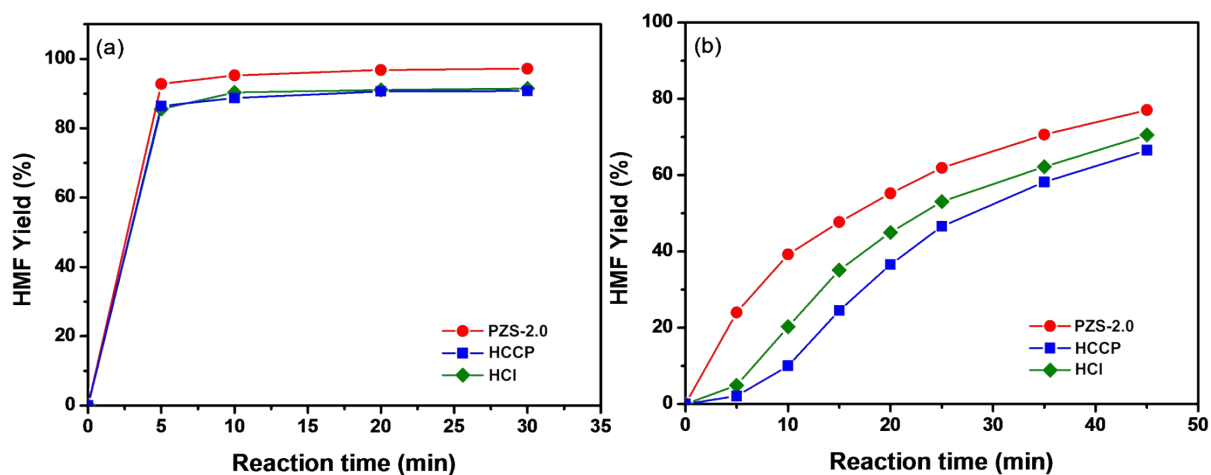
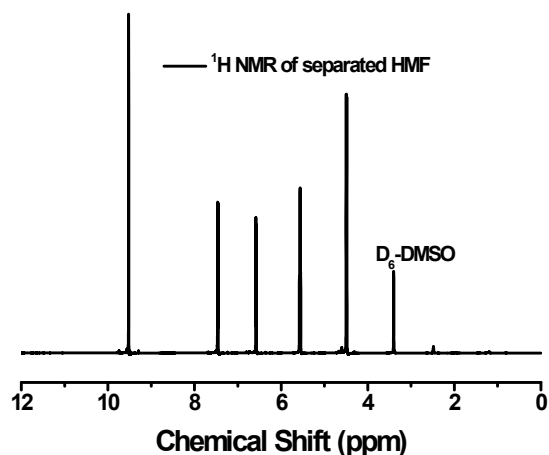


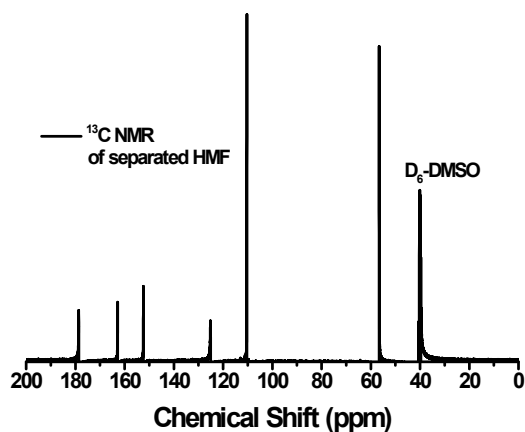
Fig. S6. Effect of reaction temperatures on conversion of fructose to HMF catalyzed by PZS-2.0, HCCP and HCl at (a) 90 °C and (b) 60 °C in 3 wt% fructose solution.

**Table S1.** Elemental Analysis (EA) results of PZS-NPs with different HCCP: BPS molar ratios.

sample	C /%	H /%	N /%	Cl /%
PZS-2.0	41.09	2.61	5.83	12.09
PZS-3.5	46.22	3.24	4.78	3.25
PZS-5.5	47.97	3.18	4.42	2.74
PZS-7.0	48.38	4.32	3.36	2.68

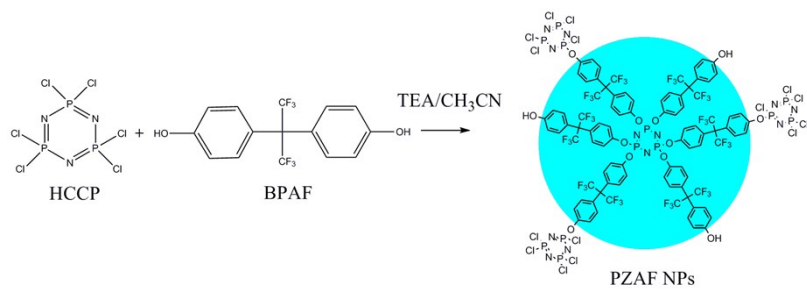


**Fig. S7**  $^1\text{H}$  NMR spectra of the separated HMF after reaction (PZS-2.0 1.25 g, fructose 1.25 g, DMSO 11.25 g, 90°C, 2h).  $^1\text{H}$  NMR spectrum (400 MHz,  $[\text{D}_6]$  DMSO,  $\delta$  ppm): 4.481-4.496 (d, 2 H,  $J = 6.000$ ), 5.548-5.562 (t, 1 H,  $J = 5.600$ ), 6.573-6.582 (d, 1 H,  $J = 3.600$ ), 7.455-7.465 (d, 1 H,  $J = 4.000$ ), 9.519 (s, 1H).

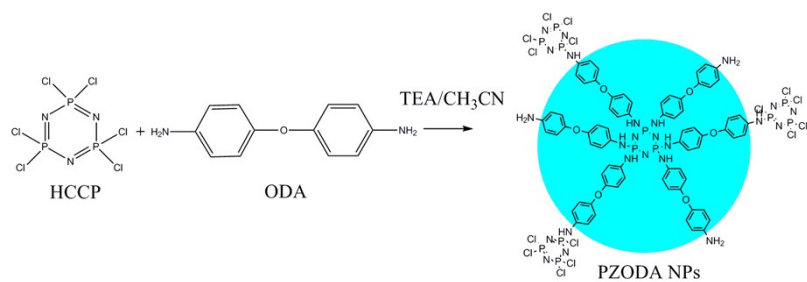


**Fig. S8**  $^{13}\text{C}$  NMR spectra of the separated HMF after reaction (PZS-2.0 1.25 g, fructose 1.25 g, DMSO 11.25 g, 90°C, 2h).  $^{13}\text{C}$  NMR spectrum (100 MHz,  $[\text{D}_6]$  DMSO,  $\delta$  ppm): 56.6, 110.3, 125.1, 152.4, 162.8, 178.6.





**Scheme S1.** The scheme illustrates the preparation of poly(cyclotriphosphazene-co-(4,4'-(hexafluoroisopropylidene)diphenol)) nanoparticles (PZAF-NPs).



**Scheme S2.** The scheme illustrates the preparation of poly(cyclotriphosphazene-co-(4,4'-diaminodiphenyl ether)) nanoparticles (PZODA-NPs).