**Electronic Supplementary Material**

# Design and synthesis of micro-meso-macroporous polymers with versatile active sites and excellent activities in production of biofuels and fine chemicals

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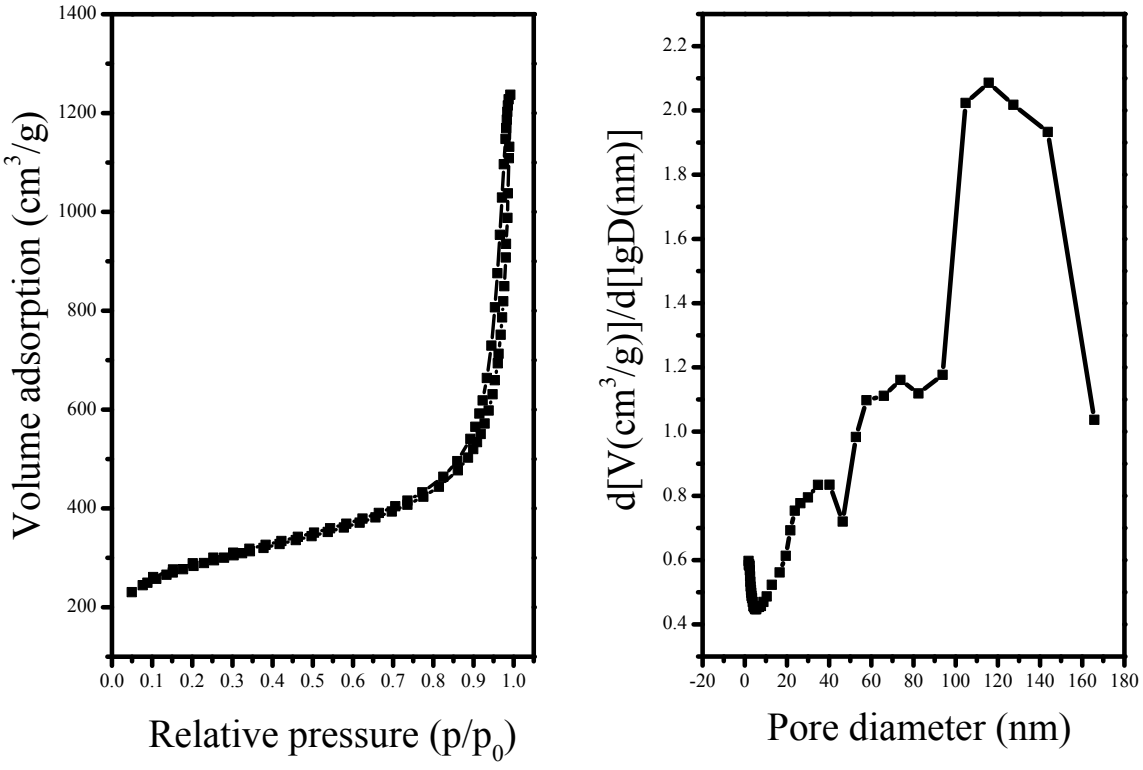


**Fig. S1** $N_2$ adsorption-desorption isotherm and pore size distribution of MOP-benzene.

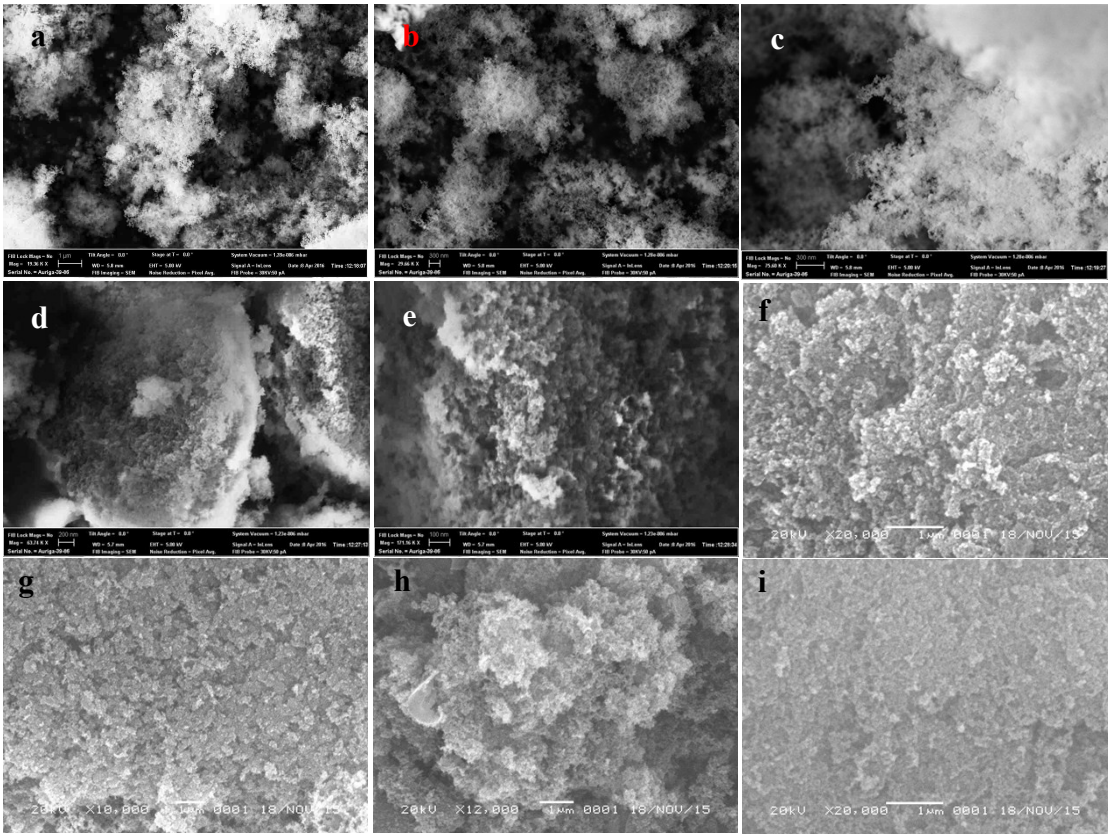


**Fig. S2** SEM images of (a,b) MOP-P(Ph)$_3$, (c) MOP-ethylbenzene-$SO_3H$, (d,e) MOP-pyridine, (f) MOP-benzene, (g) MOP-phloroglucinol, (h) MOP-triazole and (i) MOP-aniline.

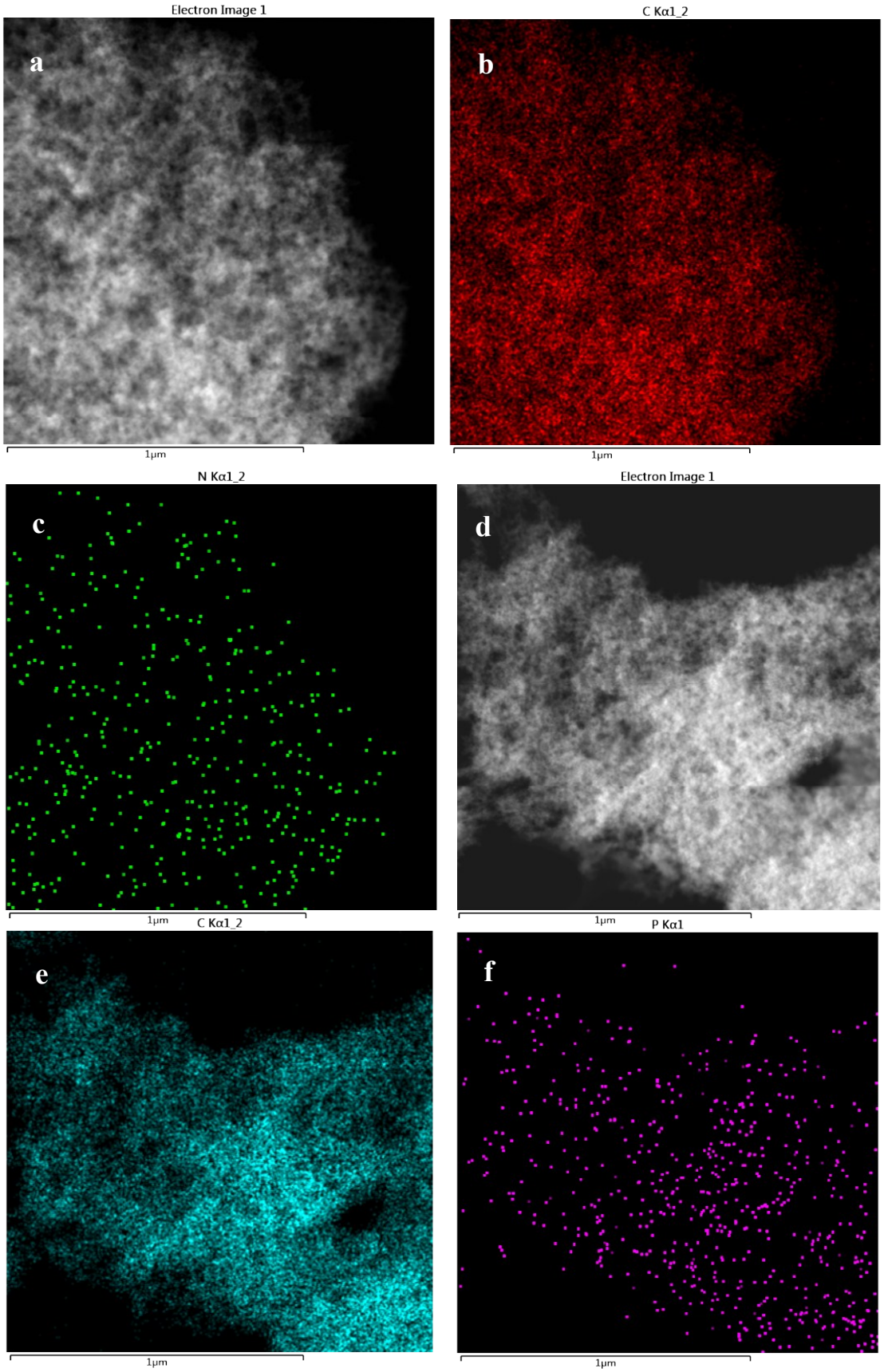


**Fig. S3** Scanning transmission electron microscope (STEM) images and element maps of (a-c) MOP-triazole and (d-f) MOP-P(Ph)$_3$.

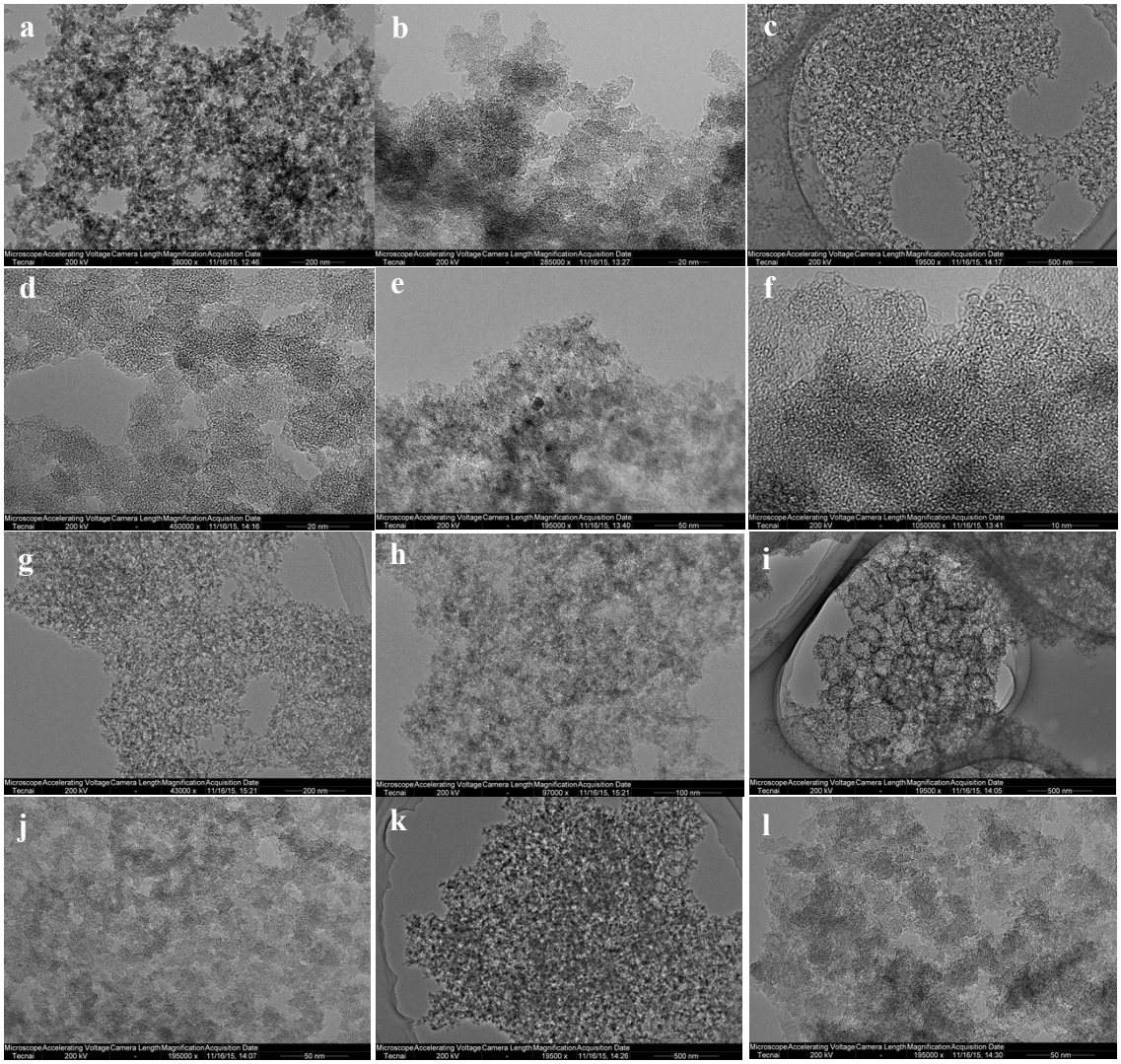


**Fig. S4** TEM images of (a, b) MOP-ethylbenzene-$SO_3H$, (c, d) MOP-pyridine, (e, f) MOP-$P(Ph)_3$-Pd, (g, h) MOP-triazole, (i, j) MOP-aniline, and (k, l) MOP-benzene .

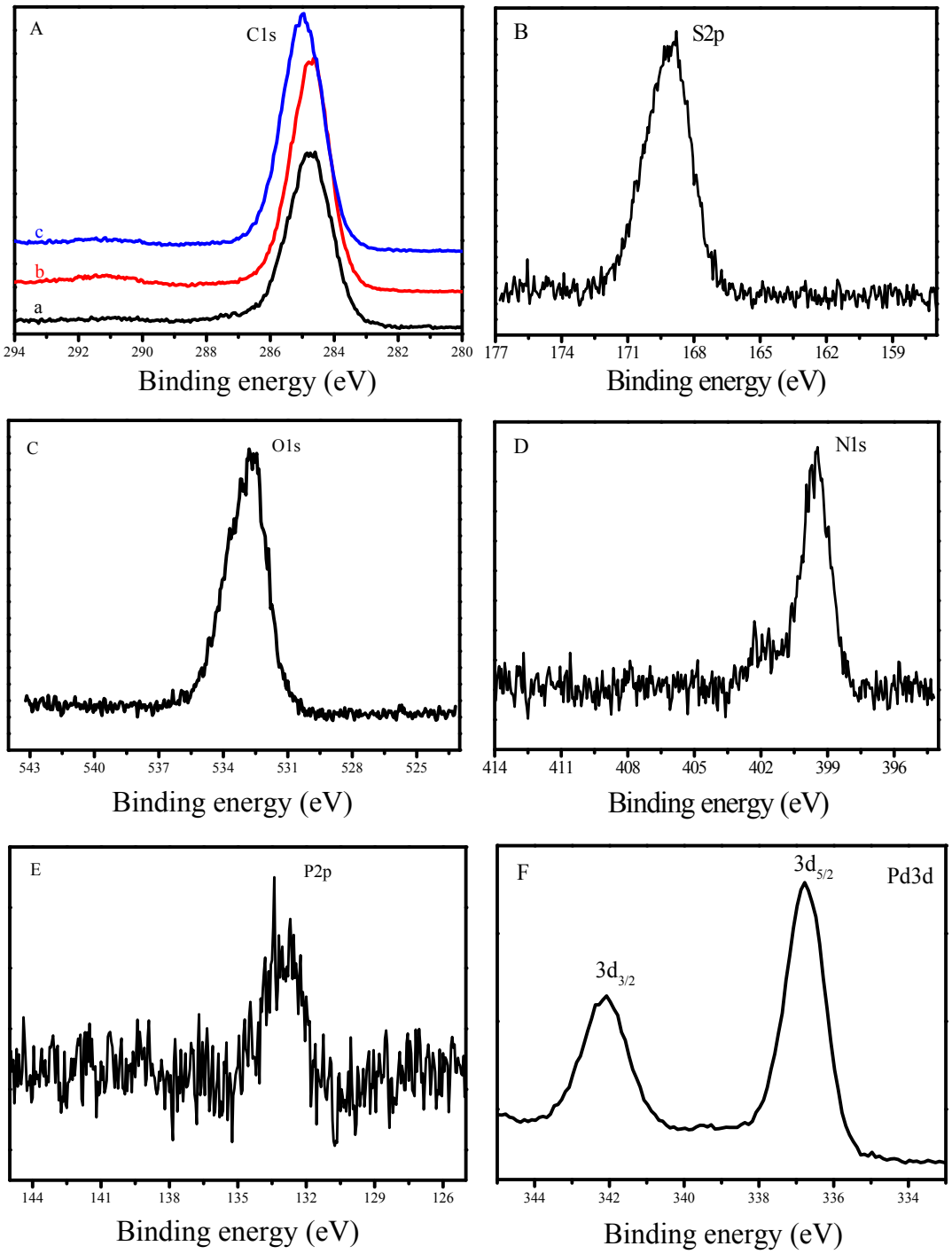


**Fig. S5** XPS spectra of (A) C1s of (a) MOP-ethylbenzene-$SO_3H$, (b) MOP-aniline and (c) MOP-$P(Ph)_3$-Pd; (B) S2p and (C) O1s of MOP-ethylbenzene-$SO_3H$; (D) N1s of MOP-aniline; (E) P2p and (F) Pd3d o f MOP-$P(Ph)_3$-Pd.

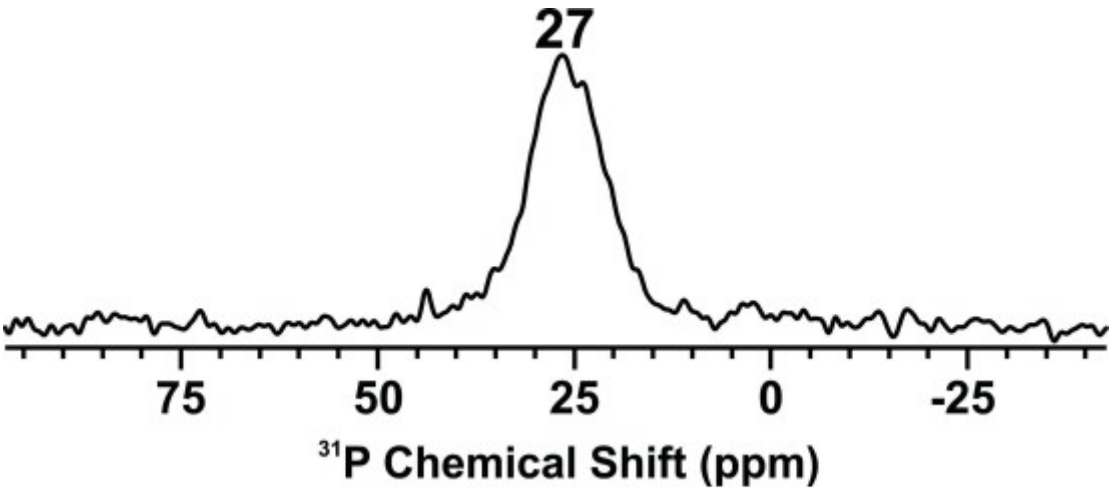


**Fig. S6** $^{31}P$ solid state nuclear magnetic resonance (NMR) spectrum of MOP-P$(Ph)_3$-Pd.

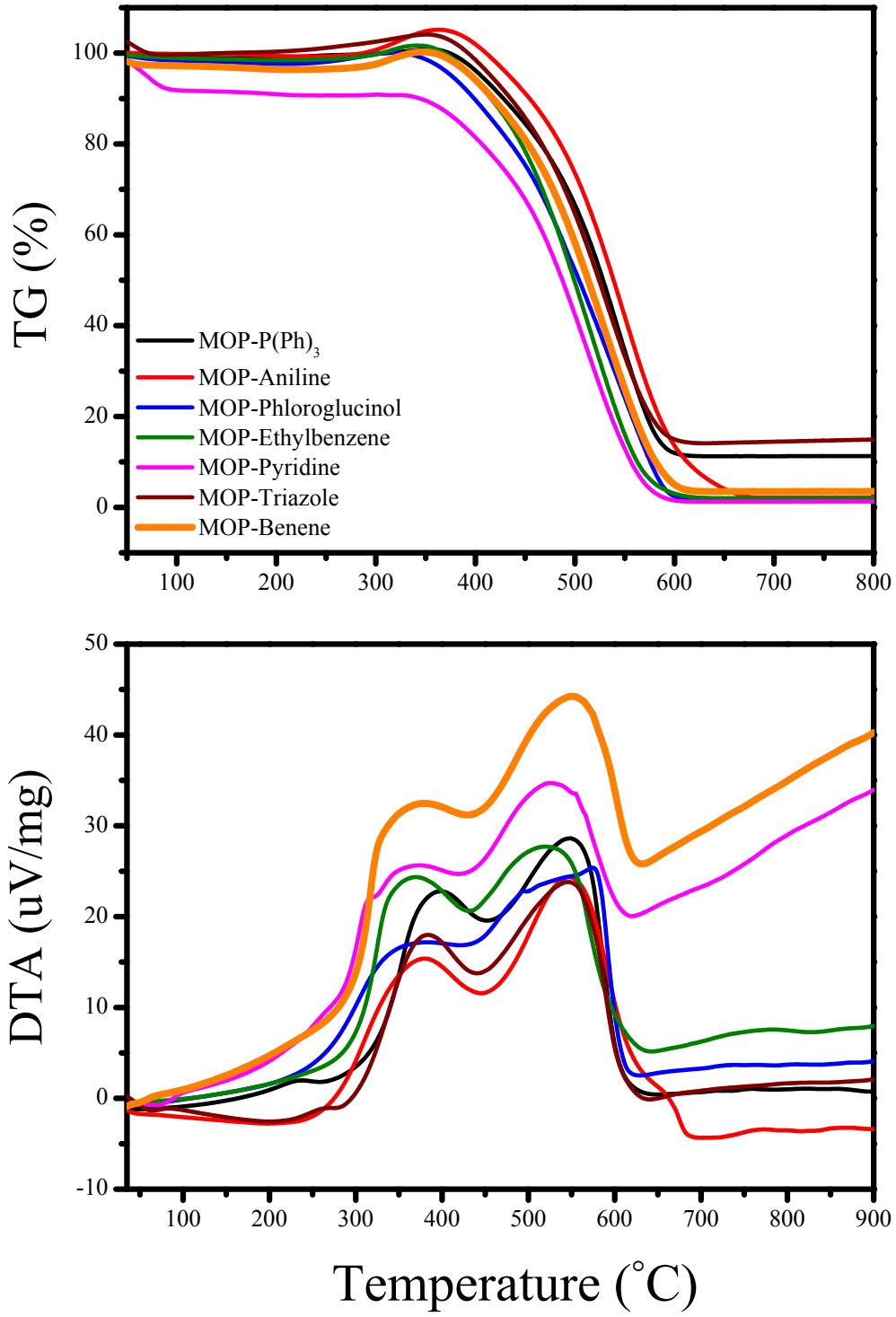


**Fig. S7** TG-DTA curves of various MOPs materials.

Figure S7 showed TG-DTA curves of various samples. Notably, all the samples showed relative good thermal stability of both functional groups and polymer

networks. For example, all of MOPs showed mainly two weight loss steps ranged from 360~460, and 460~600°C, which should be attributed decomposition of functional groups and polymer networks. Correspondingly, the DTA curves gave two peaks associated with deposition of different functional groups and polymer networks were ranged from 350~400°C, and 530~550°C, in agreement with TG results. Besides MOP-phloroglucinol, nearly no weight loss could be observed before 350°C in other MOPs samples, which indicate very limited adsorption of $H_2O$ in air due to their controllable hydrophobic networks. Notably, the aromatic structures of functional groups in MOPs exhibit good thermal stabilities, highly crosslinked network partially protects functional groups and abundant nanopores could enhance heat diffusion at high temperatures, these characteristics may result in relatively good stabilities of functional groups in MOPs. On the other hand, the decomposition temperatures of polymeric networks of these samples were all higher than 500°C because of high cross linking degree in various MOP materials.