

All chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd and used without further purification. The constituents were confirmed based on GC or LC analysis (comparison with an authentic sample). Gas chromatography (GC) analysis was performed on an Agilent GC-6820 equipped with a 30 m×0.32 mm × 0.5 μm HP-Innowax capillary column and a flame ionization detector. LC analysis was performed on a Shimadzu LC-20 equipped with SPA-20 UV-detector, a mixture of methanol and water was used as the mobile phase. FT-IR was recorded on Bruker Vietor22. SEM was recorded on JEOLJSM-6380LV. BET surface area was recorded on Quantachrome NOVA1000 with N₂ adsorption method.

Preparation of Amphiphilic Salts: Amphiphilic salt was synthesized according to the procedure in the literature [28]. One gram of [Bmim]Br was dissolved in 50 mL of deionized water, and a given amount of HPAs was dissolved in 30 mL of deionized water. The [Bmim]Br solution was added dropwise into the HPAs solution, yielding a white precipitate (H₃PMo₁₂O₄₀ is yellowish green). The resulting suspension was stirred for 2 h at room temperature, and the solid product was separated by filtration, washed with deionized water, and then dried overnight at 100 °C.

Preparation of supported Amphiphilic Salts: Supported [Bmim]_xPAs was prepared by a co-precipitation method. One gram of carrier (SiO₂, Al₂O₃, or TiO₂) was dispersed in 50 mL of deionized water, and [Bmim]Br (0.029 – 0.175 g) was added dropwise to the slurry and stirred for 1 h. Then, 30 mL of the aqueous solution of HPAs (0.081 – 0.486 g) was added dropwise. The resulting slurry was stirred for 2 h at room temperature, and the solid product was separated by filtration, washed with deionized water, and then dried at 100 °C for 12h. The SiO₂-supported [Bmim]₃PW₁₂O₄₀ catalyst was denoted as Si-PW. Then Si-SiW, Si-PMo, Al-PW and Ti-PW stands for [Bmim]₄SiW₁₂O₄₀/SiO₂, [Bmim]₃PMo₁₂O₄₀/SiO₂, [Bmim]₃PW₁₂O₄₀/Al₂O₃, and [Bmim]₃PW₁₂O₄₀/TiO₂ respectively.

Nitration: In a typical aromatic nitration process, to a vigorously stirred mixture of a given amount of catalyst and substrate (10 mL), 67% nitric acid was added dropwise at room temperature. The reaction was warmed up to a higher temperature which is indicated in Table 3. After 3 h, the solution was extracted by filtration at negative pressure. The organic phase was isolated and washed with saturated sodium bicarbonate (5 mL), water (5 mL×3), and brine (5 mL), dried over Na₂SO₄, and analyzed by GC or LC.

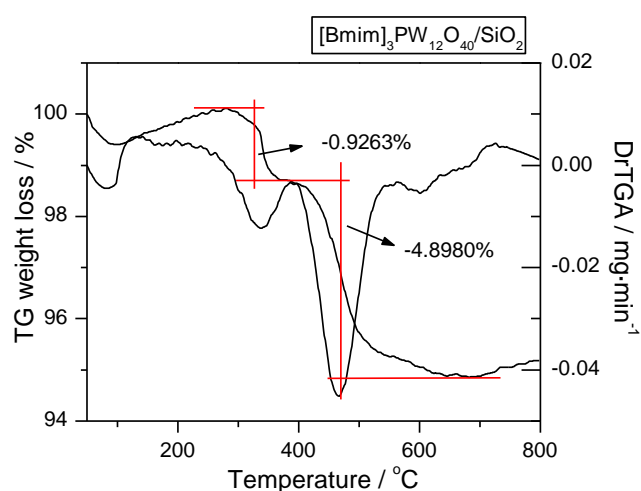


Fig. s1 TG weight loss of [Bmim]₃PW₁₂O₄₀/SiO₂ (calculated 8% loading).

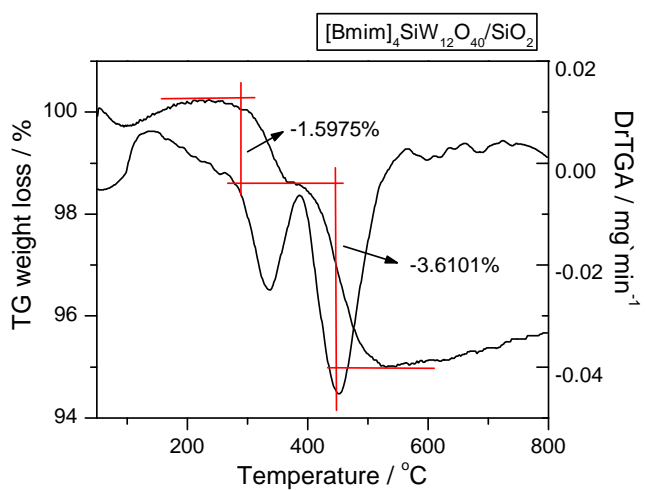


Fig. s2 TG weight loss of $[\text{Bmim}]_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ (calculated 10% loading).

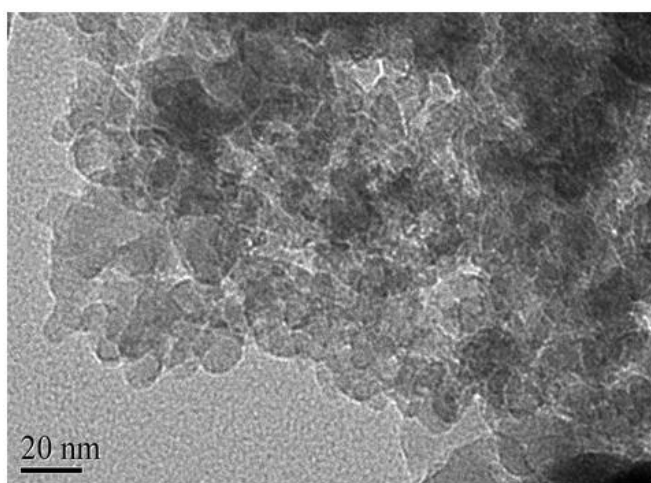


Fig. s3 HRTEM of $[\text{Bmim}]_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$

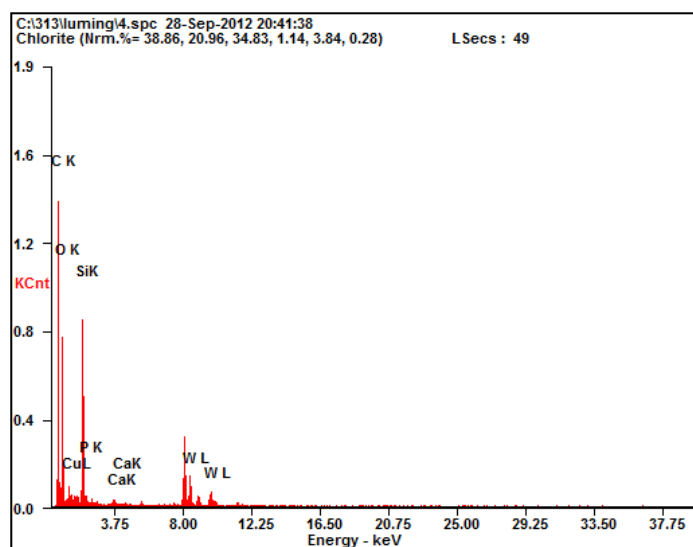


Fig. s4 EDX of $[\text{Bmim}]_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$

Table s1 IR bands of BmimBr, [Bmim]₃[PW₁₂O₄₀] and [Bmim]₃P W₁₂O₄₀/SiO₂

Wavenumber (cm ⁻¹)			Vibration
BmimBr	[Bmim] ₃ P W ₁₂ O ₄₀	[Bmim] ₃ P W ₁₂ O ₄₀ /SiO ₂	
1630	1630	1630	O-H bending
1572, 1563	--	1572, 1563	Imidazole ring
1168	--	1168	1. Imidazole C-C-H 2. H-C-N bending
--	1079	1079	ν (P-O) in PW ₁₂ O ₄₀
--	978	978	ν (W-O) in PW ₁₂ O ₄₀
--	973	973	ν (W-O) in SiW ₁₂ O ₄₀
--	890	893	ν (W-O _b -W) in PW ₁₂ O ₄₀
--	890	916	ν (W-O _b -W) in SiW ₁₂ O ₄₀
--	795	800-810	ν (W-O _c -W) in PW ₁₂ O ₄₀
--	788	788	ν (W-O _c -W) in SiW ₁₂ O ₄₀
840	--	--	In-plane imidazole ring bending
752	--	--	1. Out-of-plane C ₆ H 2. Bending of imidazole ring
620	--	620	Imidazole C-N-C bending