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Supplementary Information

Fluoride-free synthesis of high-silica, medium-pore zeolites PST-22 and PST-30

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Table S1 Representative products from zeolite syntheses using 14DMP-C_4^{2+} or 13DMP-C_4^{2+} as an OSDA in the presence of K^+ Ions

R[a]	KOH/SiO_2	Product[b]
14DMP-C_4^{2+}	0.20	Amorphous
	0.25	Amorphous
	0.30	Amorphous
	0.35	Amorphous
	0.40	Amorphous
13DMP-C_4^{2+}	0.20	Amorphous
	0.25	Amorphous
	0.30	Amorphous + PST-30 + SUZ-4
	0.35	SUZ-4
	0.40	SUZ-4

[a] The composition of the synthesis mixture was $0.125RBr_2 \cdot xK_2O \cdot 1.0SiO_2 \cdot 0.05Al_2O_3 \cdot 30H_2O$, where R is 14DMP-$C_4^{2+}$ or 13DMP-C_4^{2+} and x is varied between $0.10 \leq x \leq 0.20$. All syntheses were performed under rotation (60 rpm) at 175 °C for 7 days. [b] The product appearing first is the major phase.

Table S2 Crystallographic and experimental parameters for the Rietveld refinement of as-made PST-22(OH) synthesized with 14DMP-C_4^{2+} and Na^+ ions

Chemical unit cell formula	$\|(14DMP\text{-}C_4^{2+})_{1.7}(H_2O)_{0.7}(Na^+)_{0.3}(OH^-)_{0.4}\|[Al_{3.3}Si_{36.7}O_{80}]$
Refined unit cell formula	$\|(14DMP\text{-}C_4^{2+})_2\|[Si_{40}O_{80}]$
Crystal system	monoclinic
Space group	*C*2/*c* (no. 15)
a (Å)	20.42404(18)
b (Å)	11.69690(9)
c (Å)	11.03974(10)
β (°)	118.1157(5)
Unit cell volume (Å^3)	2326.155(34)
X-ray source	9B beamline, PAL
Wavelength (Å)	1.5167
Step size (°)	0.01
2*θ* scan range (°)	5-125.5
No. of total reflections	1971
No. of restraints	54
No. of parameters	89
R_{wp} (%)	7.36
R_F^2 (%)	5.13
χ^2	5.63

Table S3 Atomic coordinates and thermal parameters for as-made PST-22(OH)

Atom	*x*	*y*	*z*	Occupancy	U_{iso} (× 100 Å^2)	Multiplicity
Si1	0.84150(9)	0.65365(16)	0.37005(16)	1	0.885(11)	8
Si2	0.71334(9)	0.57440(16)	0.43573(17)	1	0.885(11)	8
Si3	0.82952(9)	0.58494(16)	0.75317(17)	1	0.885(11)	8
Si4	0.91722(9)	0.74669(17)	0.65885(18)	1	0.885(11)	8
Si5	0.72830(10)	0.32497(15)	0.36582(17)	1	0.885(11)	8
O1	0.76526(8)	0.63326(21)	0.37749(18)	1	1.462(30)	8
O2	0.86207(12)	0.53885(14)	0.31492(22)	1	1.462(30)	8
O3	0.90787(12)	0.68302(21)	0.52140(16)	1	1.462(30)	8
O4	0.83130(13)	0.75795(17)	1.26815(18)	1	1.462(30)	8
O5	0.76036(13)	0.57209(24)	0.60170(16)	1	1.462(30)	8
O6	0.63804(9)	0.64470(16)	0.38646(25)	1	1.462(30)	8
O7	0.69368(12)	0.44543(13)	0.37842(23)	1	1.462(30)	8
O8	0.89507(9)	0.65872(17)	0.74687(18)	1	1.462(30)	8
O9	0.80263(8)	0.65009(21)	0.85127(17)	1	1.462(30)	8
O10	0.5	0.28942(30)	0.75	1	1.462(30)	4
O11	0.75	0.25	0.5	1	1.462(30)	4
N1	0.52088(23)	0.33786(30)	0.32678(23)	0.5	1.74(13)	8
N2	0.50463(24)	0.23621(24)	0.26882(32)	0.5	1.74(13)	8
C1	0.46673(22)	0.24866(30)	0.13096(30)	0.5	1.74(13)	8
C2	0.45982(25)	0.36430(34)	0.10040(26)	0.5	1.74(13)	8
C3	0.49695(24)	0.41720(22)	0.2267(4)	0.5	1.74(13)	8
C4	0.42243(32)	0.4200(6)	-0.0345(4)	0.5	1.74(13)	8
C5	0.52381(29)	0.12692(31)	0.3356(6)	0.5	1.74(13)	8
C6	0.55826(25)	0.3666(5)	0.47089(27)	0.5	1.74(13)	8
C7	0.53878(19)	0.4766(5)	0.5208(8)	0.5	1.74(13)	8

Table S4 Selected bond lengths and angles for as-made PST-22(OH)

Bond length (Å)		Bond angle (°)	
Si1-O1	1.6151(27)	O1-Si1-O2	109.01(16)
Si1-O2	1.6096(29)	O1-Si1-O3	109.74(16)
Si1-O3	1.6164(20)	O1-Si1-O4	109.76(15)
Si1-O4	1.6051(27)	O2-Si1-O3	109.09(14)
Si2-O1	1.6292(30)	O2-Si1-O4	109.87(17)
Si2-O5	1.6192(22)	O3-Si1-O4	109.36(15)
Si2-O6	1.5967(25)	O1-Si2-O5	107.73(14)
Si2-O7	1.6117(24)	O1-Si2-O6	110.46(16)
Si3-O2	1.6051(24)	O1-Si2-O7	109.19(18)
Si3-O5	1.6086(21)	O5-Si2-O6	110.88(19)
Si3-O8	1.6217(29)	O5-Si2-O7	109.50(16)
Si3-O9	1.6173(31)	O6-Si2-O7	109.06(13)
Si4-O3	1.6189(29)	O2-Si3-O5	110.01(16)
Si4-O6	1.6141(26)	O2-Si3-O8	108.25(15)
Si4-O8	1.6192(31)	O2-Si3-O9	110.12(17)
Si4-O10	1.5867(19)	O5-Si3-O8	110.09(16)
Si5-O4	1.6084(22)	O5-Si3-O9	109.34(15)
Si5-O7	1.6116(27)	O8-Si3-O9	109.01(15)
Si5-O9	1.6264(29)	O3-Si4-O6	108.37(15)
Si5-O11	1.5940(18)	O3-Si4-O8	109.10(16)
Si1-O1	1.6151(27)	O3-Si4-O10	111.04(16)
Si1-O2	1.6096(29)	O6-Si4-O8	109.51(18)
Si1-O3	1.6164(20)	O6-Si4-O10	109.21(18)
Si1-O4	1.6051(27)	O8-Si4-O10	109.58(13)
Si-O (Avg.)	1.6118	O4-Si5-O7	109.44(14)
N1-N2	1.316500(10)	O4-Si5-O9	109.50(17)
N1-C3	1.346300(10)	O4-Si5-O11	110.17(13)
N1-C6	1.443040(10)	O7-Si5-O9	108.64(16)
N2-C1	1.351440(10)	O7-Si5-O11	110.00(16)
N2-C5	1.435020(10)	O9-Si5-O11	109.07(11)
C1-N2	1.351440(10)	O-Si-O (Avg.)	109.47
C1-C2	1.385080(10)	N1-N2-C1	109.2340(4)
C2-C3	1.380110(10)	N2-C1-C2	108.54750(10)
C2-C4	1.467630(10)	C1-C2-C3	104.3240(4)
C3-N1	1.346300(10)	C2-C3-N1	109.5252(7)
C6-C7	1.524(7)	C3-N1-N2	108.2232(6)
C7-C7	1.528(9)	N1-N2-C5	127.5559(6)
		N2-N1-C6	128.87550(10)
		C1-N2-C5	123.19980(20)
		C1-C2-C4	128.71460(20)
		C3-N1-C6	122.8981(5)
		C3-C2-C4	126.9595(6)
		N1-C6-C7	120.18(30)
		C6-C7-C7	127.2(6)

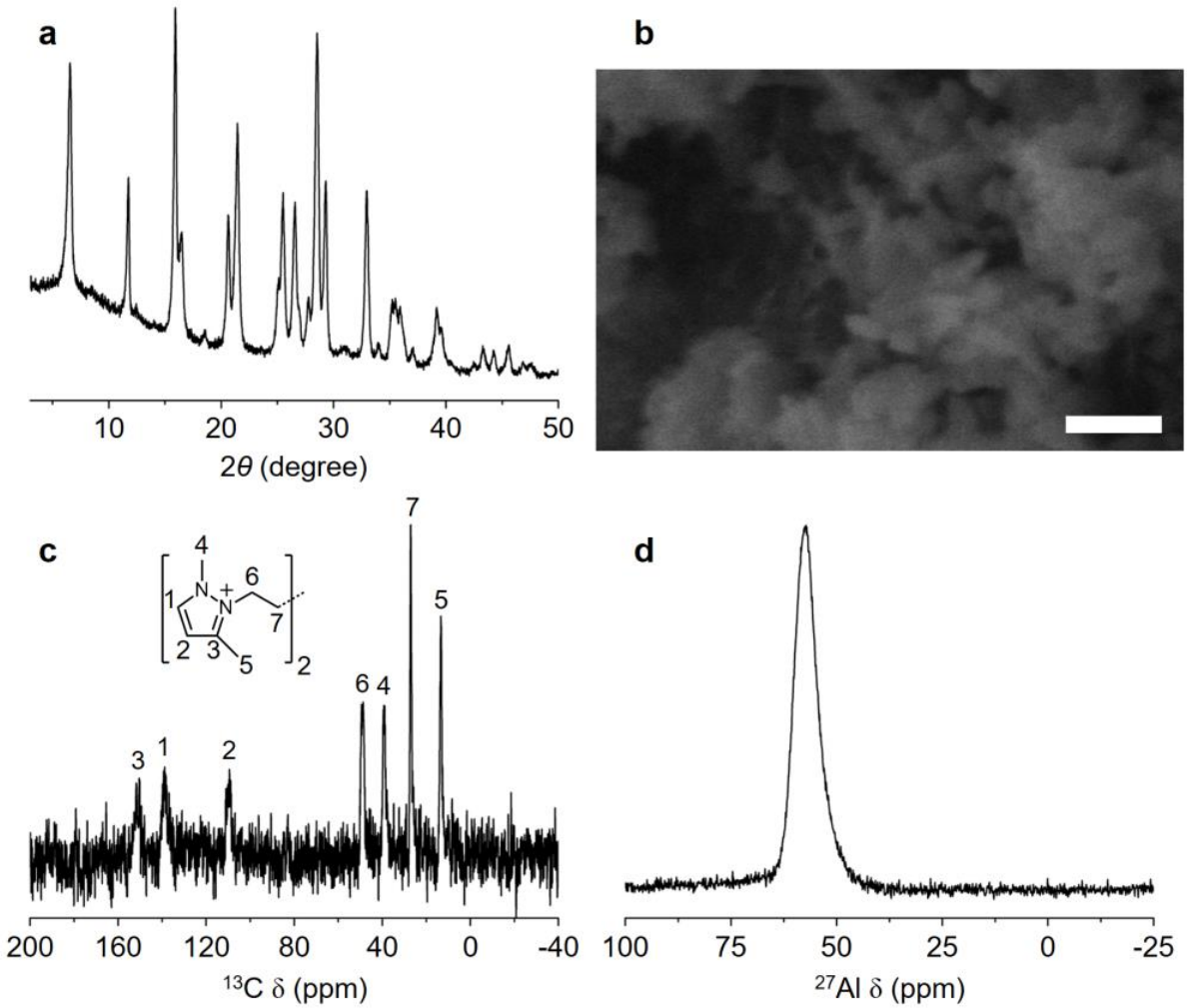

Fig. S1 (a) PXRD pattern, (b) SEM image (scale bar, 1 μm), and (c) ^{1}H-^{13}C CP and (d) ^{27}Al MAS NMR spectra of as-made SUZ-4 synthesized using 13DMP-C_4^{2+} as an OSDA, together with K^+.

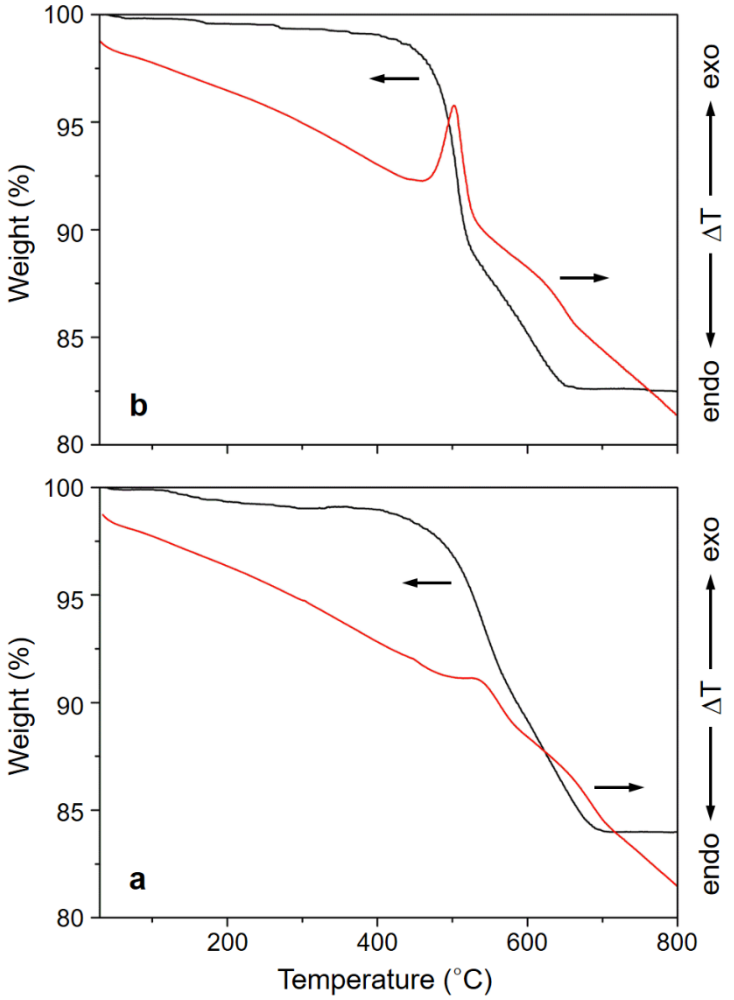

Fig. S2 TGA/DTA profiles of as-made (a) PST-22(OH) and (b) PST-30(OH) synthesized in this study.

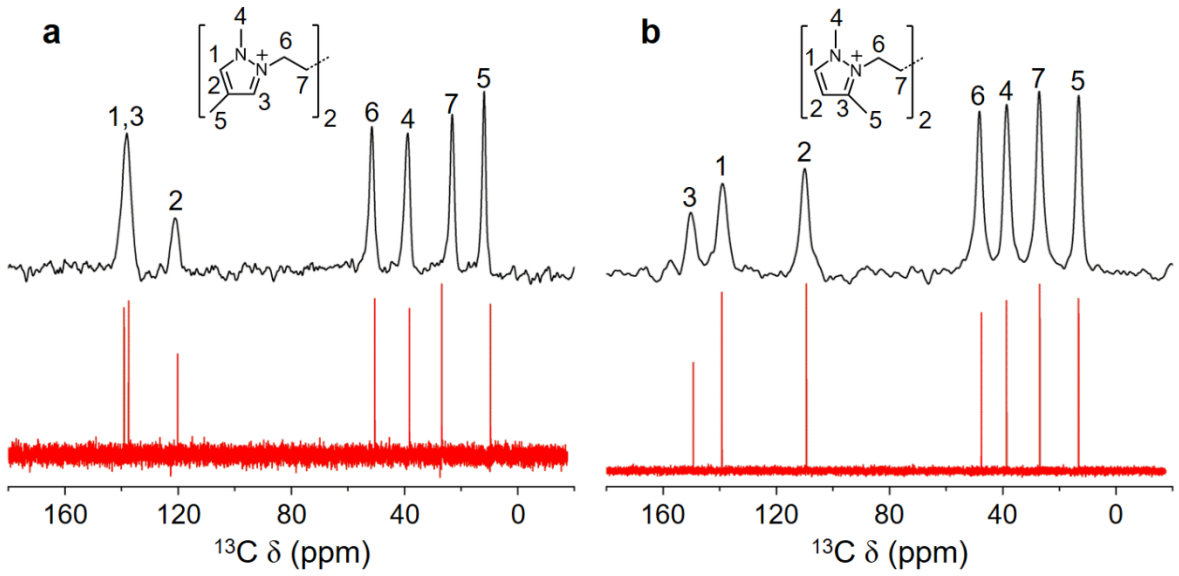

Fig. S3 ^{1}H-^{13}C CP MAS NMR spectra (a) of as-made PST-22(OH) and (b) PST-30(OH). The bottom traces in red are the solution ^{13}C NMR spectra of the dibromide salt of 14DMP-C_4^{2+} and 13DMP-C_4^{2+} in D_2O, which were used as an OSDA in the synthesis of these two zeolites, respectively.

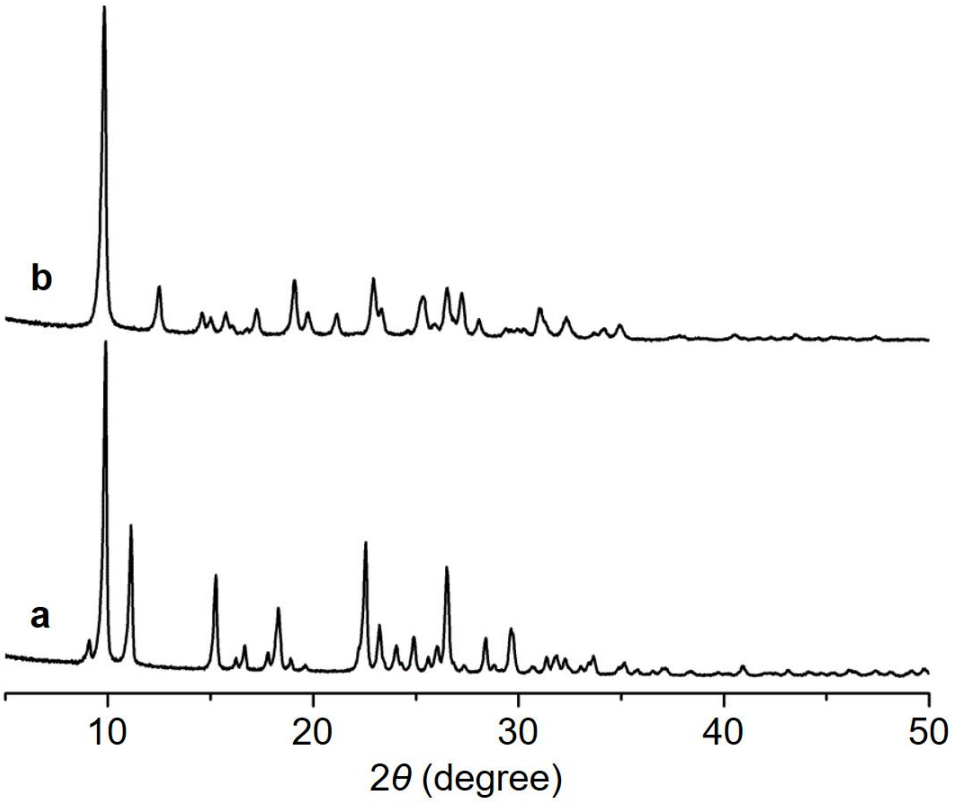

Fig. S4 PXRD patterns of the proton form of (a) PST-22(OH) and (b) PST-30(OH) synthesized using 14DMP-C_4^{2+} and 13DMP-C_4^{2+} as an OSDA in hydroxide media, respectively.

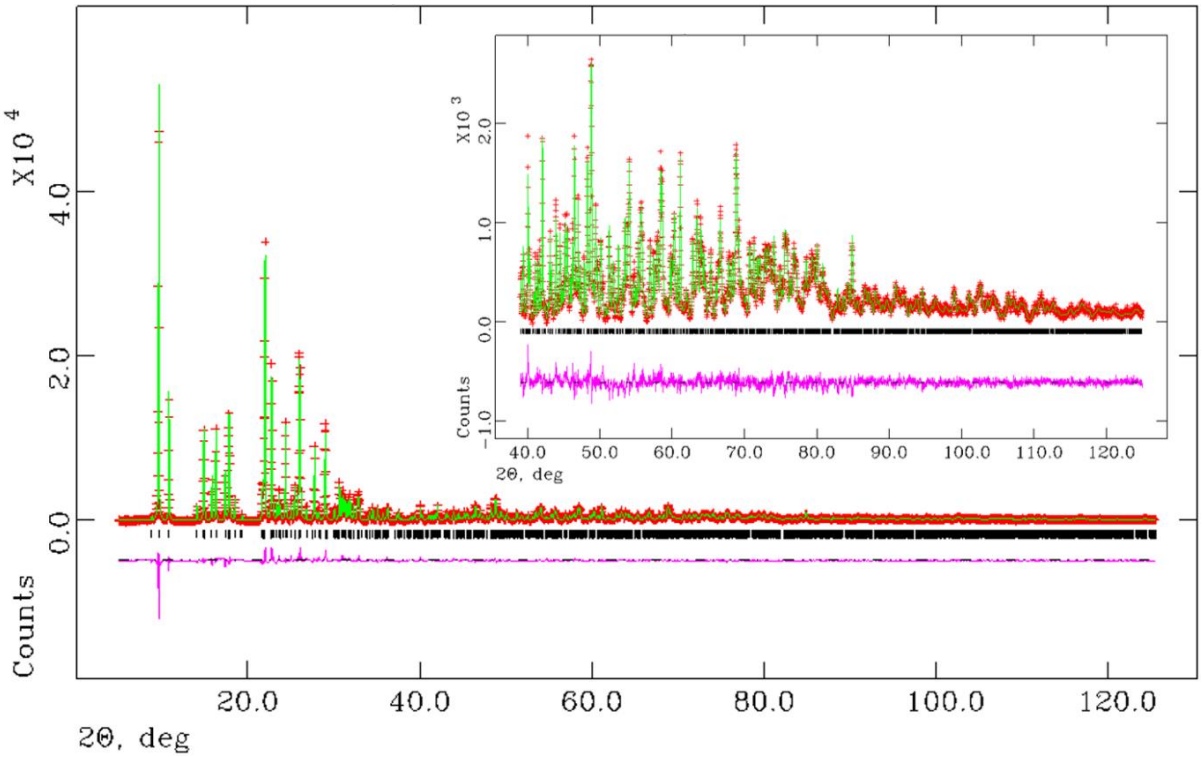

Fig. S5 Rietveld plot for as-made PST-22(OH): observed data (+), calculated fit (solid line), and difference plot (lower trace). The tick marks represent the positions of allowed reflections.

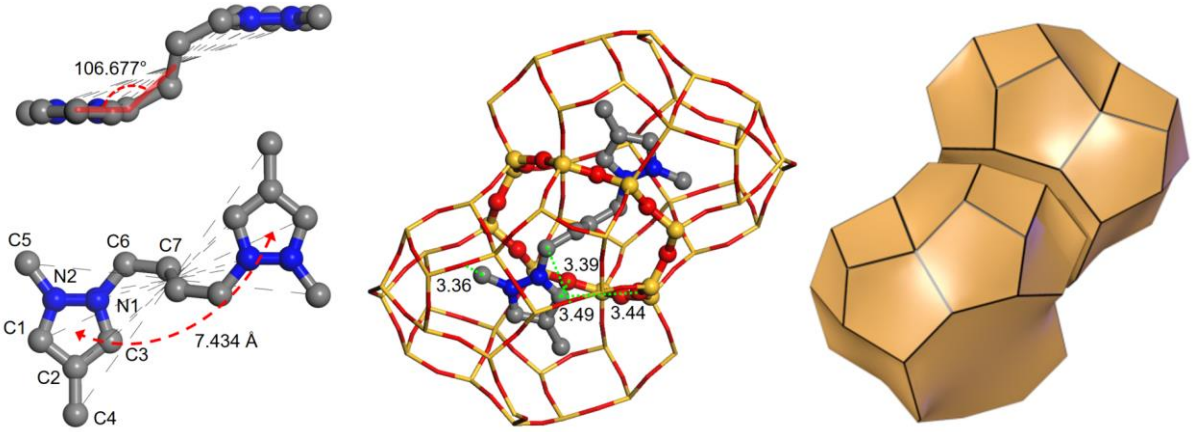

Fig. S6 The crystallographically determined conformation (left and middle) of 14DMP-C_4^{2+} encapsulated within two adjacent 18-hedral *t-pww* ([$4^6.5^8.8^2.10^2$]) cages (right) of as-made PST-22(OH). The inversion center of 14DMP-C_4^{2+} is guided with dashed lines (left). The 10-ring window connecting two *t-pww* cages is indicated by ball and stick model (middle). The distances between the host cage and the guest OSDA molecule, shorter than 3.5 Å, are also given: C2-O7, 3.39 Å; C3-O10, 3.44 Å; C5-O2, 3.36 Å; C6-O7, 3.49 Å.

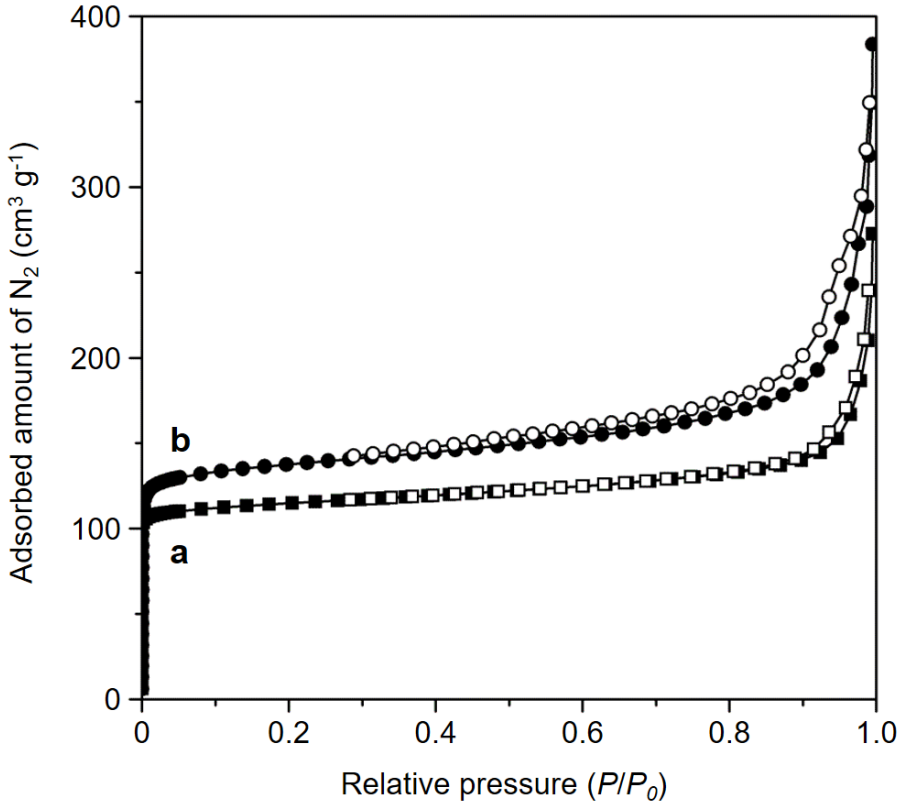

Fig. S7 N_2 adsorption and desorption isotherms of (a) H-PST-22 (OH) and (b) H-PST-30(OH). Their BET surface areas were calculated to be 460 (microporous, 405; external, 55) and 545 (microporous, 460; external, 85) $m^2\ g^{-1}$, giving micropore volumes of 0.15 and 0.17 $cm^3\ g^{-1}$, respectively.