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A Novel Approach for Facilitating the Targeted Synthesis of Silicoaluminophosphates

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1. Experimental section

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References

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1. Experimental section

1.1 DNL-6 seed

Seed A: The typical DNL-6-DEA was synthesized based on the recipe in **Ref**. **1** and then was calcined under 600 ℃ for 4h in air.[1] The calcined sample was milled to a very low crystallinity using a planetary ball mill, denoted Seed A.

Seed B: Seed with crystal size ca. 200 nm was synthesized based on the method described in **Ref. 2** (a gel composition of 1.5 OSDA: 0.2 SiO_2: 0.4 P_2O_5: 0.5 Al_2O_3: 50 H_2O 0.2 CTAB, with a large amount of Seed A).[2] And then the as-made sample was calcined to remove organic structure direct agent (OSDA), denoted as Seed B.

If not emphasized, the seed used in this work was Seed B.

1.2 Initial tentative synthesis of DNL-6 using fourteen types of organic amines

Initial trials, verifying whether amines listed in Figure 2 have the ability to direct the synthesis of DNL-6, were based on the typical synthesis of DNL-6-DEA in **Ref. 1.**[1] The same gel composition of 1.0 OSDA: 0.2 SiO_2: 0.4 P_2O_5: 0.5 Al_2O_3: 50 H_2O 0.15 CTAB with a small amount of seeds (2-5wt%, based on Al_2O_3) was employed.

All trials were carried out by the conventional hydrothermal method. Phosphoric acid, amine, and deionized water were mixed and then vigorously stirred. And then tetraethyl orthosilicate (TEOS) and aluminum isopropoxide were added sequentially. After stirring overnight, hexadecyl trimethyl ammonium bromide (CTAB) and a certain amount of seeds were added into the homogeneous gel. Then thorough mixing gel was transported into a 35ml Teflon-lined autoclave and crystallized at 200℃ for 24h under the rotation state of 75 r/min. The final products were recovered by centrifugation, washed with distilled water repeatedly, and dried at 120℃ overnight.

1.3 Nine Optimized recipes of DNL-6s for the following structural analysis

The optimized synthesis process of the fourteen amines was similar to initial tentative synthesis.

For the nine amines which can synthesize well-crystallized DNL-6s, the detail synthetic information regarding raw materials and crystallization time was listed in Table S2.

It is challenging to synthesize pure DNL-6 samples using MIPA, TBEA, EBnA, BA, and PeA as OSDAs. And the best synthesis conditions and PXRD results were shown in Table S4, S5 and Figure S6.

1.4 Initial tentative synthesis of DNL-6s using triethylamine, tetraethylammonium hydroxide, and dimethylamine as OSDA

The gel composition for the tentative synthesis employing triethylamine, tetraethylammonium hydroxide, and dimethylamine as OSDAs is 1.0 OSDA: 0.2 SiO_2: 0.4 P_2O_5: 0.5 Al_2O_3: 50 H_2O 0.15 CTAB (the largest amount of seeds (40%, based on Al_2O_3) used). The preliminary PXRD results are shown in Figure S18.

1.5 Tentative synthesis for SAPO-42

The tentative synthesis of SAPO-42 was same to DNL-6. Represent synthesis recipes were listed in Table S6 and S7.

Seed C: The as-made sample SAPO-42-DPA-1 was calcined under 600 ℃ for 4h in air. denoted Seed C.

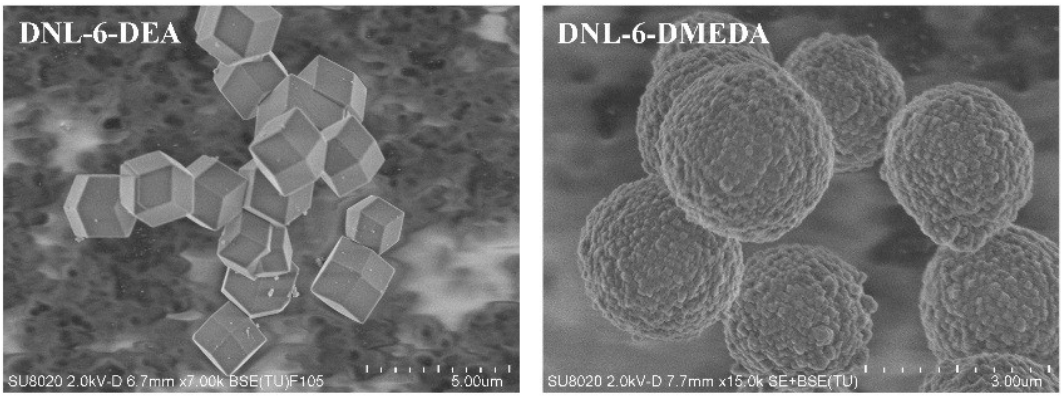

Figure S1. SEM images of DNL-6-DEA and DNL-6-DMEDA.

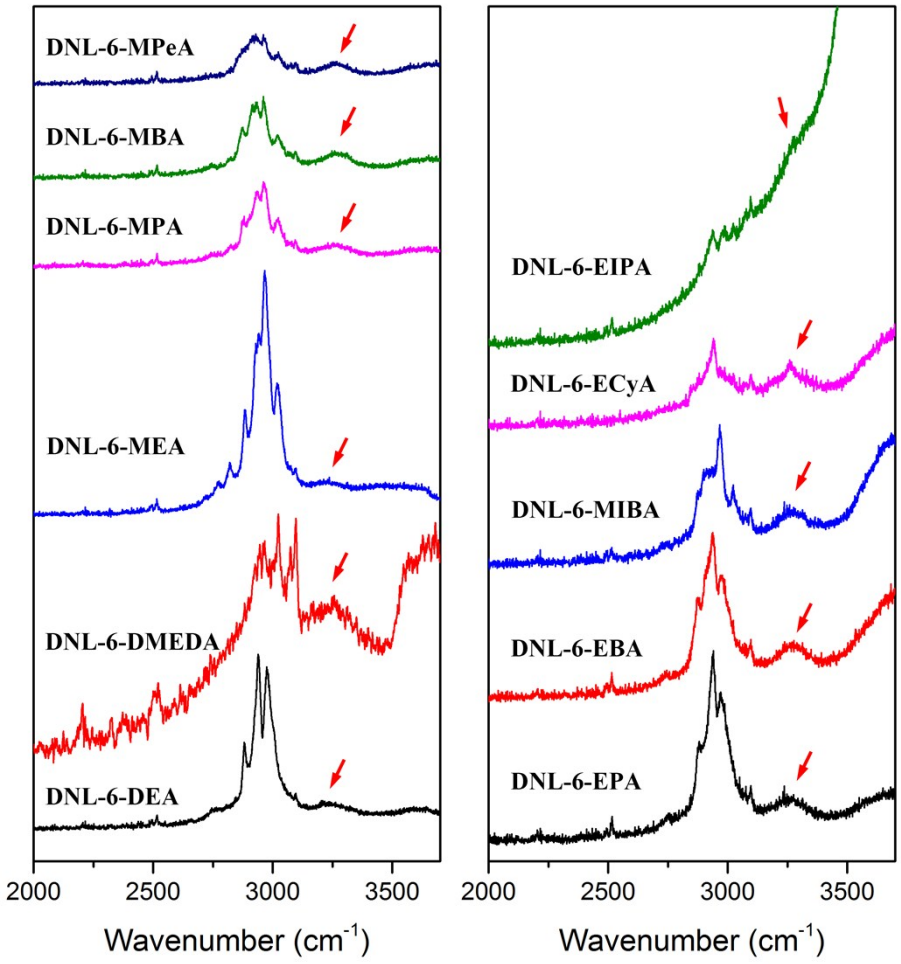

Figure S2. Raman spectra of DNL-6s.

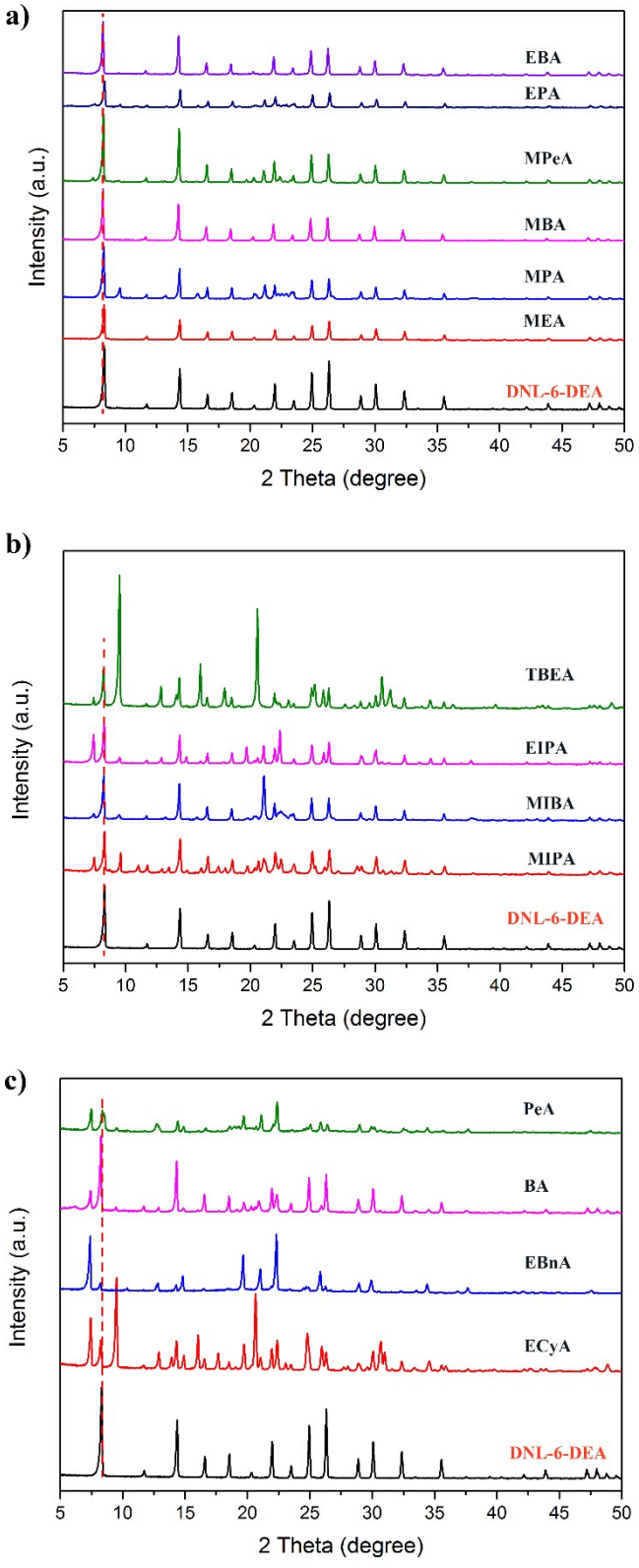

Figure S3. The PXRD results of the fourteen initial tentative synthesis with a gel composition 1.0 OSDA: 0.2 SiO_2: 0.4 P_2O_5: 0.5 Al_2O_3: 50 H_2O 0.15 CTAB. A small amount of seeds was added. For clarity, the OSDAs used were labeled as the abbreviation corresponding to Figure 2 in the main text.

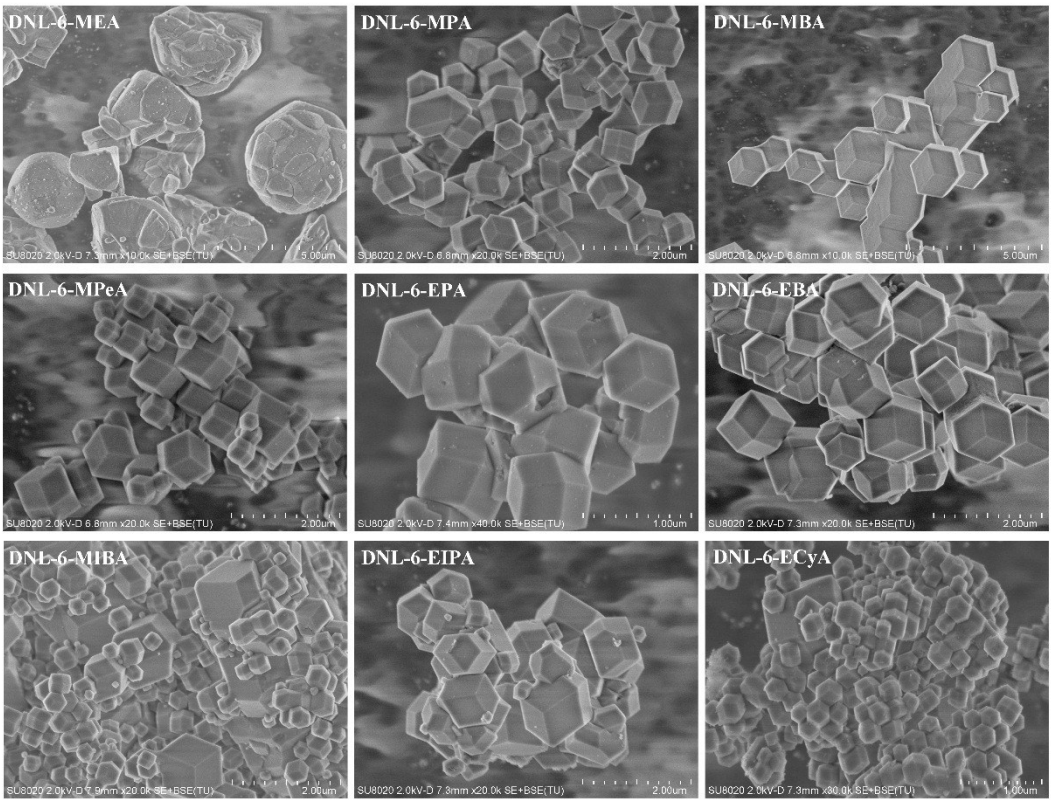

Figure S4. SEM images of DNL-6s synthesized by nine types of OSDAs listed in Table 1.

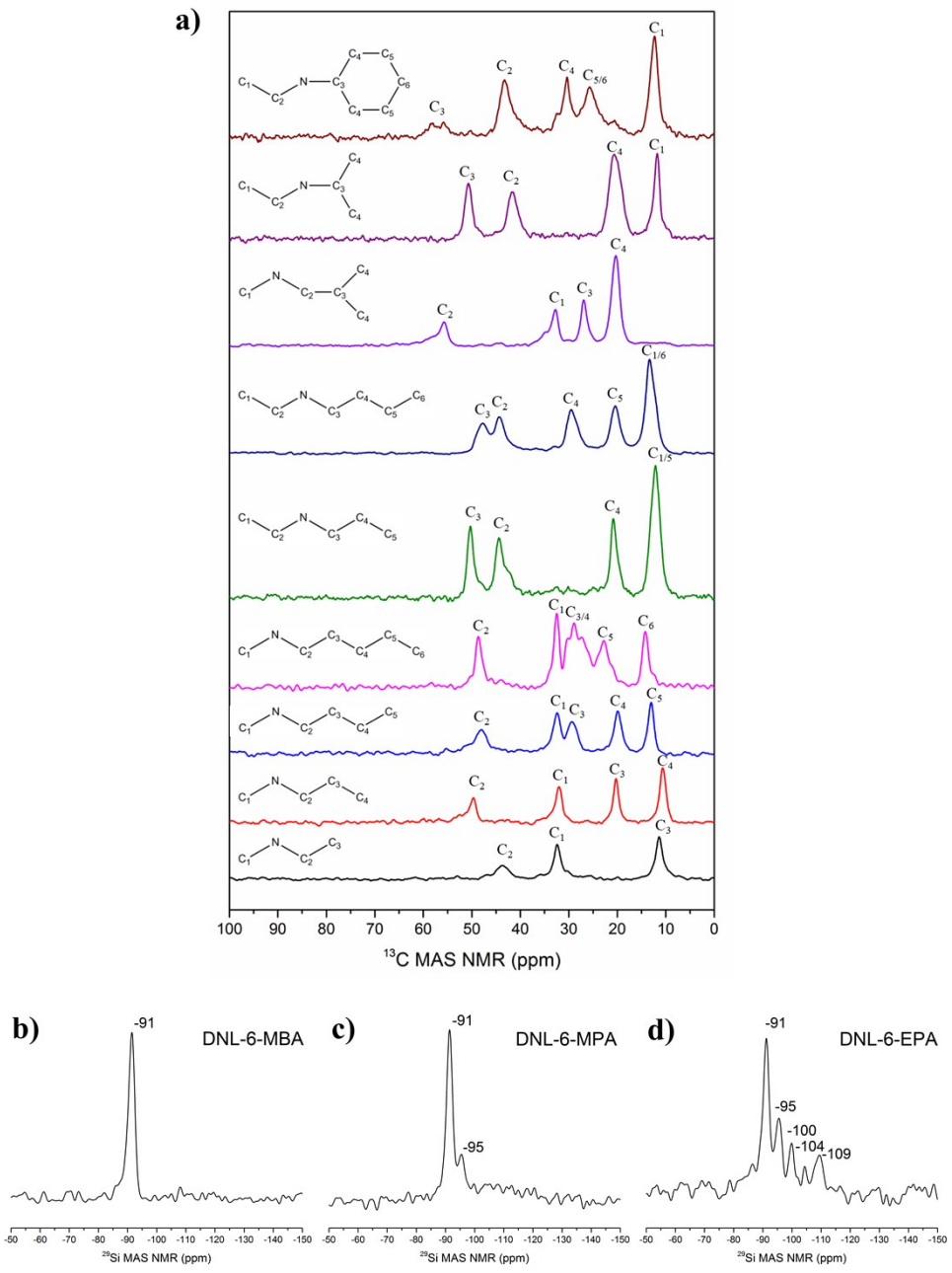

Figure S5. a) ^{13}C MAS NMR of DNL-6s synthesized by nine types of OSDAs listed in Table 1. b), c), and d) ^{29}Si MAS NMR of DNL-6-MBA, DNL-6-MPA and DNL-6-EPA, respectively.

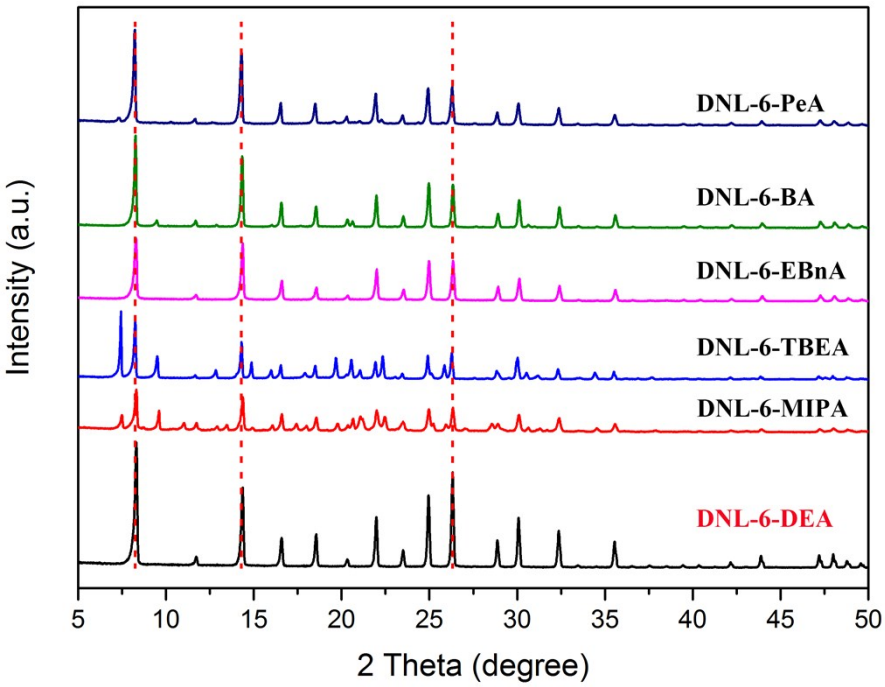

Figure S6. The PXRD results of five samples utilizing MIPA, TBEA, EBnA, BA, and PeA as OSDAs for DNL-6. Pure phase DNL-6 cannot be obtained, but with amorphous, SAPO-34 or/and SAPO-42.

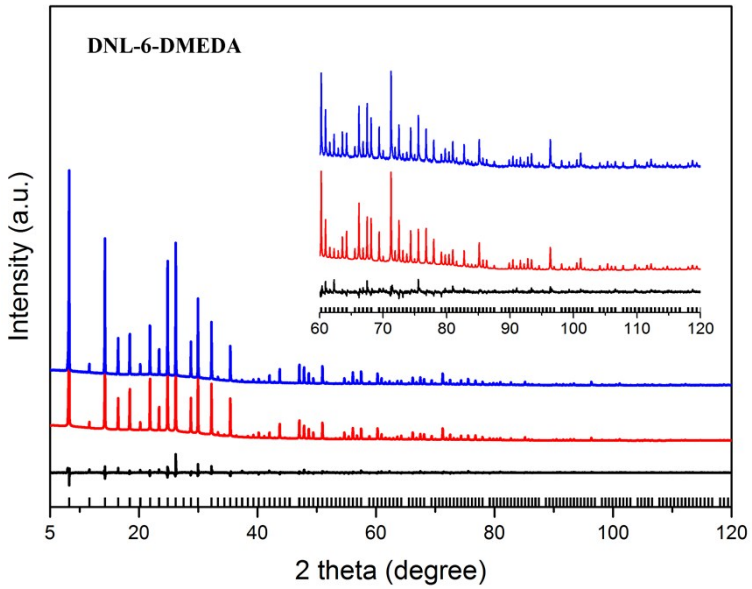

Figure S7. Final Rietveld refinement plots of DNL-6-DMEDA. The observed, calculated, and difference curves are in blue, red, and black, respectively. The vertical bars indicate the positions of Bragg peaks (Cu Kα1, λ = 1.5406 Å). The inset is the high angle part of the profiles. The PXRD data was collected in the 0.3 mm capillary.

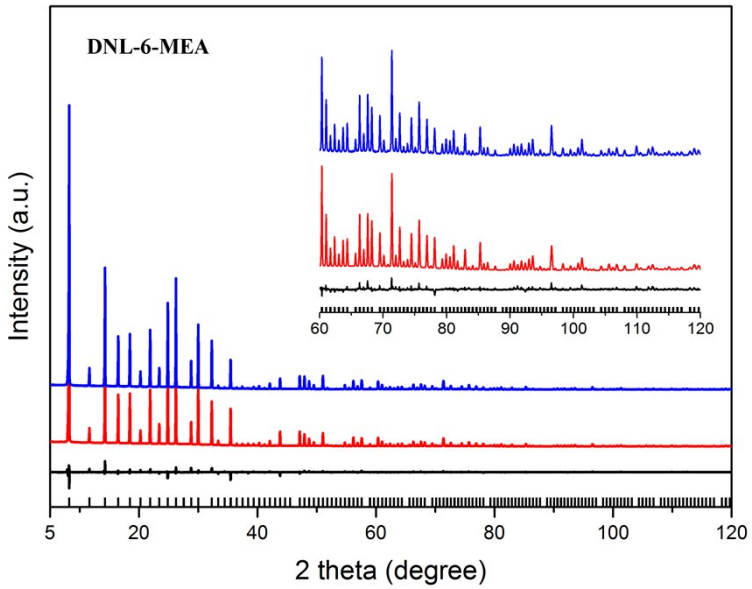

Figure S8. Final Rietveld refinement plots of DNL-6-MEA. The observed, calculated, and difference curves are in blue, red, and black, respectively. The vertical bars indicate the positions of Bragg peaks (Cu Kα1, λ = 1.5406 Å). The inset is the high angle part of the profiles. The PXRD data was collected in the 0.3 mm capillary.

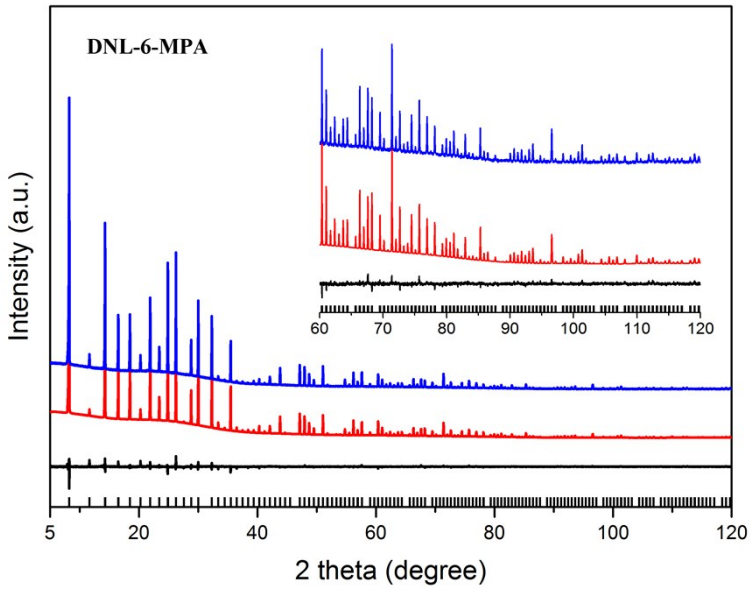

Figure S9. Final Rietveld refinement plots of DNL-6-MPA. The observed, calculated, and difference curves are in blue, red, and black, respectively. The vertical bars indicate the positions of Bragg peaks (Cu Kα1, λ = 1.5406 Å). The inset is the high angle part of the profiles. The PXRD data was collected in the 0.2 mm capillary.

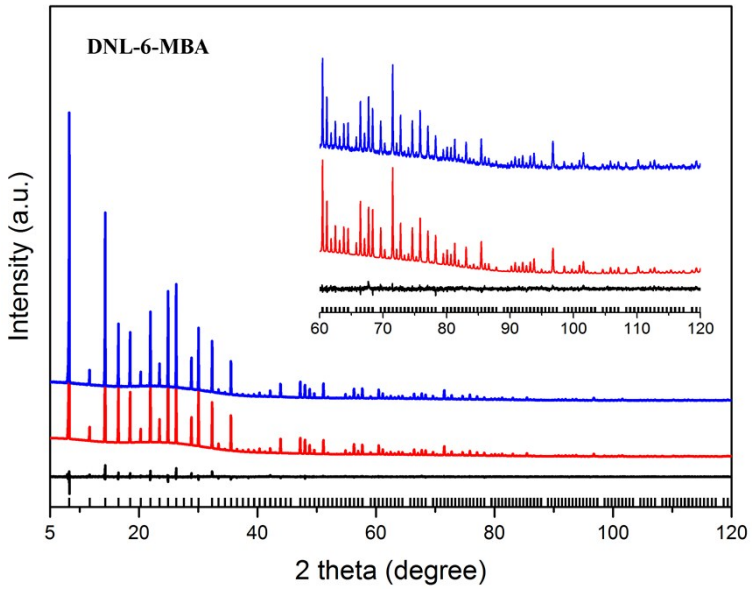

Figure S10. Final Rietveld refinement plots of DNL-6-MBA. The observed, calculated, and difference curves are in blue, red, and black, respectively. The vertical bars indicate the positions of Bragg peaks (Cu Kα1, λ = 1.5406 Å). The inset is the high angle part of the profiles. The PXRD data was collected in the 0.2 mm capillary.

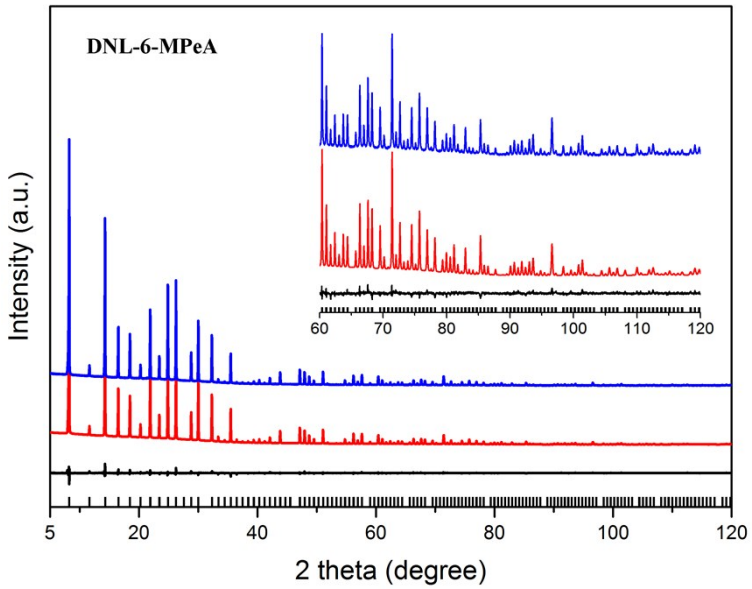

Figure S11. Final Rietveld refinement plots of DNL-6-MPeA. The observed, calculated, and difference curves are in blue, red, and black, respectively. The vertical bars indicate the positions of Bragg peaks (Cu Kα1, λ = 1.5406 Å). The inset is the high angle part of the profiles. The PXRD data was collected in the 0.3 mm capillary.

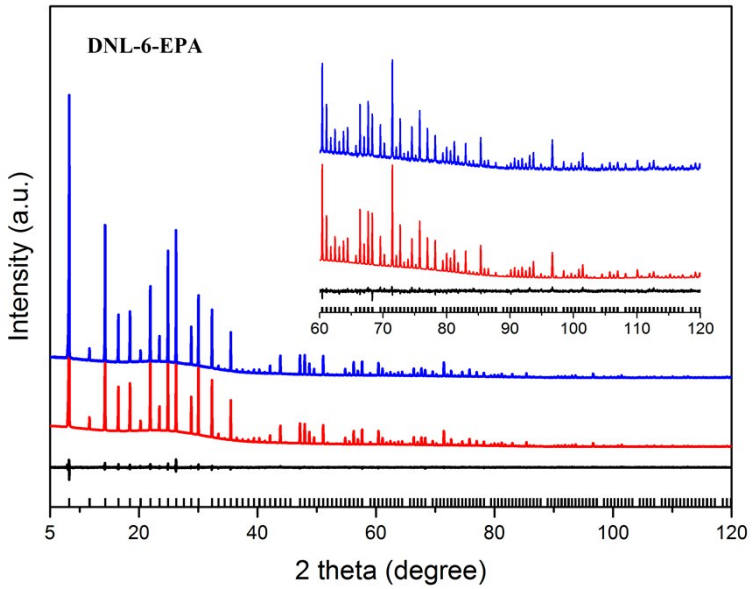

Figure S12. Final Rietveld refinement plots of DNL-6-EPA. The observed, calculated, and difference curves are in blue, red, and black, respectively. The vertical bars indicate the positions of Bragg peaks (Cu Kα1, λ = 1.5406 Å). The inset is the high angle part of the profiles. The PXRD data was collected in the 0.2 mm capillary.

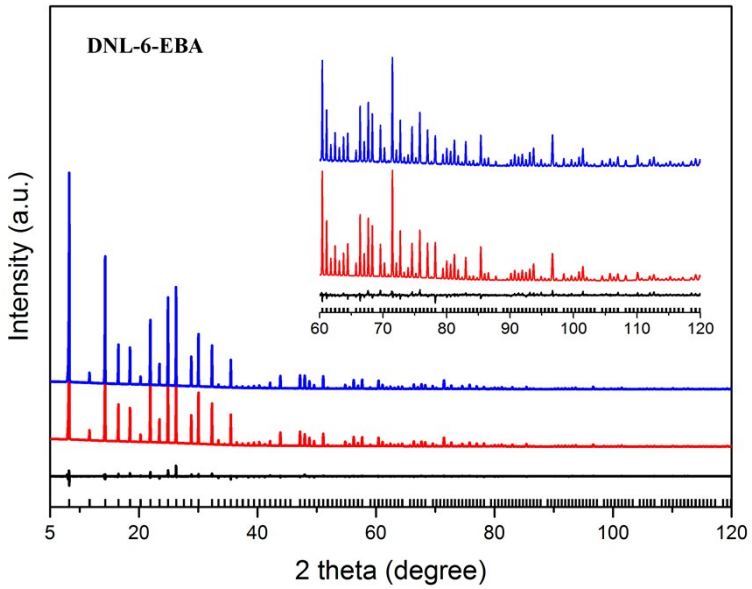

Figure S13. Final Rietveld refinement plots of DNL-6-EBA. The observed, calculated, and difference curves are in blue, red, and black, respectively. The vertical bars indicate the positions of Bragg peaks (Cu Kα1, λ = 1.5406 Å). The inset is the high angle part of the profiles. The PXRD data was collected in the 0.3 mm capillary.

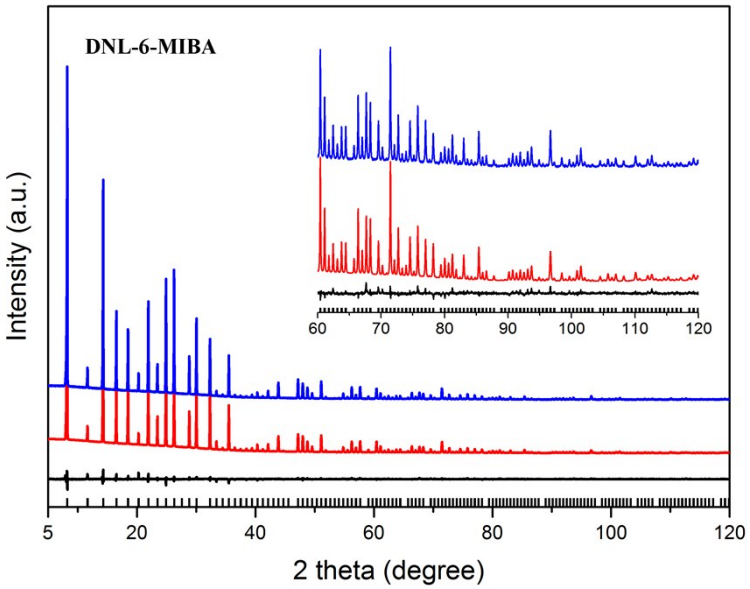

Figure S14. Final Rietveld refinement plots of DNL-6-MIBA. The observed, calculated, and difference curves are in blue, red, and black, respectively. The vertical bars indicate the positions of Bragg peaks (Cu Kα1, λ = 1.5406 Å). The inset is the high angle part of the profiles. The PXRD data was collected in the 0.3 mm capillary.

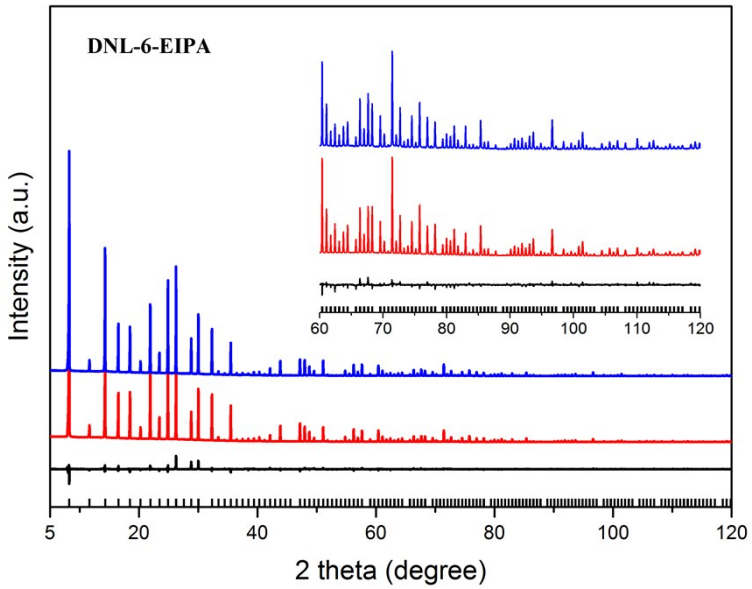

Figure S15. Final Rietveld refinement plots of DNL-6-EIPA. The observed, calculated, and difference curves are in blue, red, and black, respectively. The vertical bars indicate the positions of Bragg peaks (Cu Kα1, λ = 1.5406 Å). The inset is the high angle part of the profiles. The PXRD data was collected in the 0.3 mm capillary.

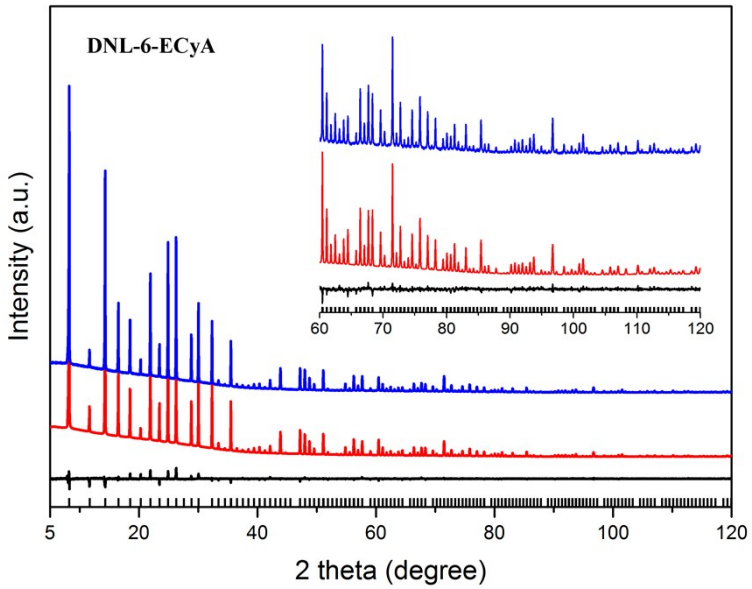

Figure S16. Final Rietveld refinement plots of DNL-6-ECyA. The observed, calculated, and difference curves are in blue, red, and black, respectively. The vertical bars indicate the positions of Bragg peaks (Cu Kα1, λ = 1.5406 Å). The inset is the high angle part of the profiles. The PXRD data was collected in the 0.3 mm capillary.

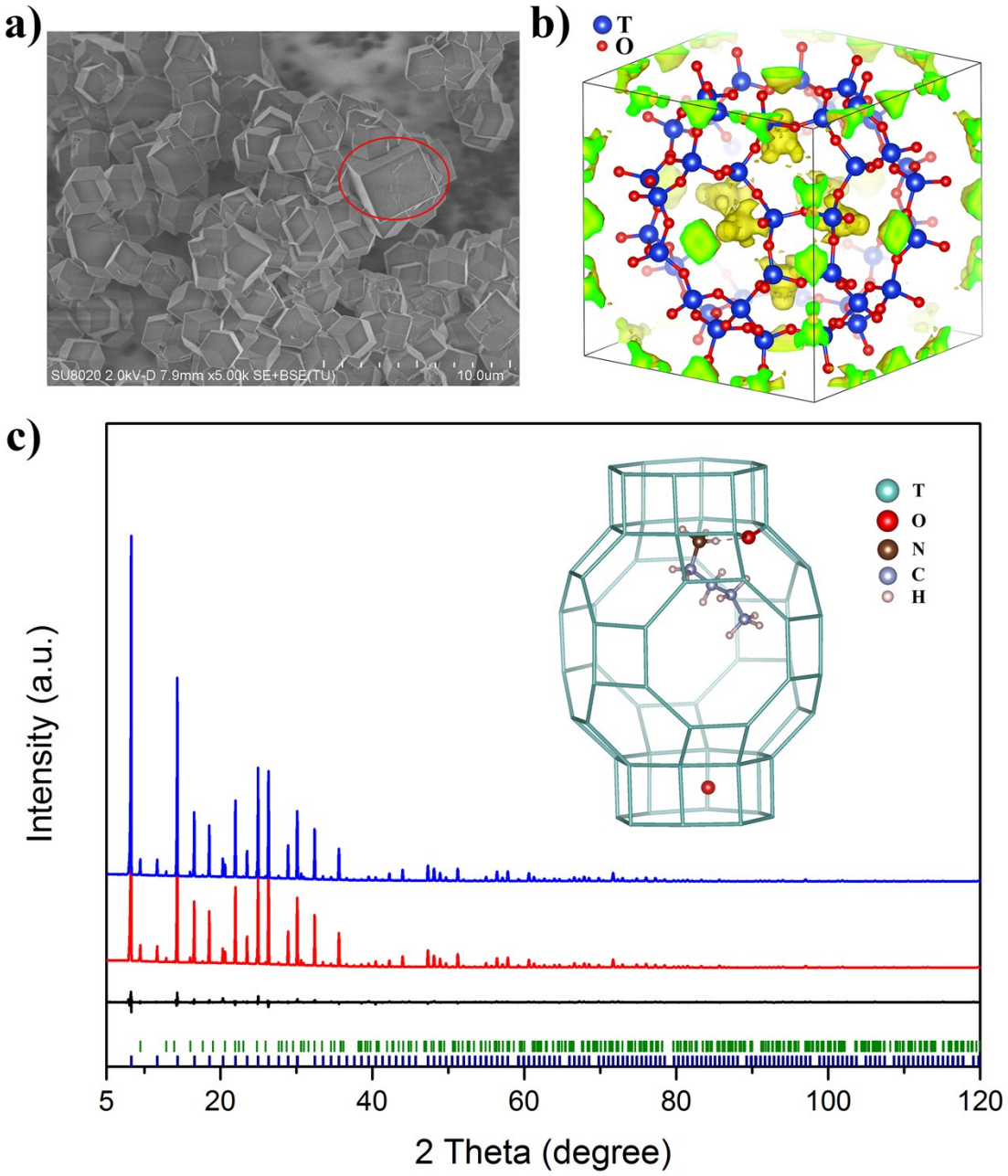

Figure S17. (a) The SEM image of sample DNL-6-BA and the impurity SAPO-34-BA highlighted in red circle. (b) The difference electron density map indicates the initial locations of BA and H_2O. (c) Final Rietveld refinement plots of DNL-6-BA. The observed, calculated, and difference curves are in blue, red, and black, respectively. The navy vertical bars indicate the positions of Bragg peaks (Cu Kα1, λ = 1.5406 Å) for DNL-6, while the olive one is SAPO-34. The insert is the locations of BA and H_2O and the host-guest interaction in DNL-6-BA. The unit cell composition of DNL-6 phase in DNL-6-BA sample is $|BA_{8.0}(H^+)_{8.3}(H_2O)_{5.7}|[Al_{23.7}Si_{8.9}P_{15.4}O_{96}]$. The ratio of Si, Al and P was determined by EDS, and the contents of BA and H_2O were refined value.

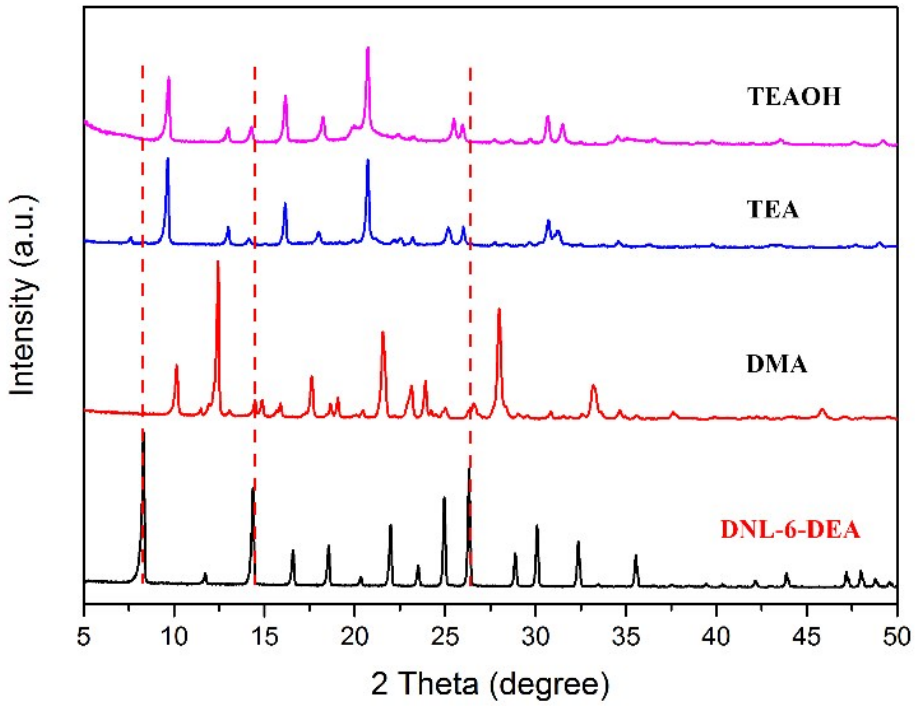

Figure S18. The PXRD results of the tentative synthesis using dimethylamine (DMA), triethylamine (TEA), tetraethylammonium hydroxide (TEAOH) as OSDAs with a gel composition 1.0 OSDA: 0.2 SiO_2: 0.4 P_2O_5: 0.5 Al_2O_3: 50 H_2O: 0.15 CTAB and 40% seed addition (based on Al_2O_3).

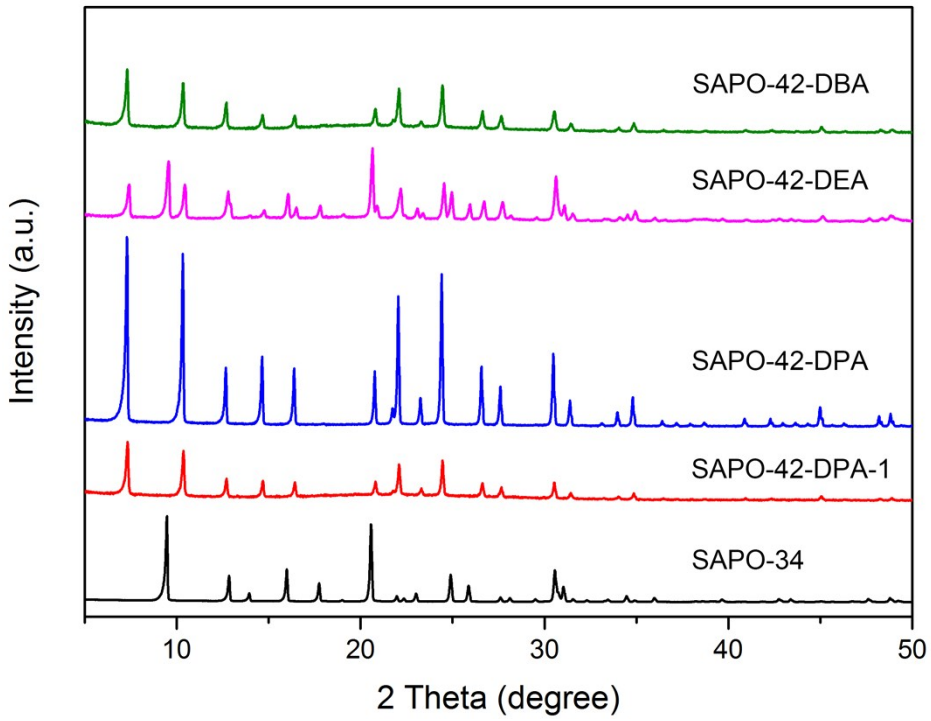

Figure S19. The PXRD results of sample in Table S6.

Table S1. Crystallographic details of Rietveld refinements of DNL-6 samples

Sample	DNL-6-DEA	DNL-6-DMEDA	DNL-6-MEA	DNL-6-MPA	DNL-6-MBA	DNL-6-MPeA
Space group	*I*432	*I*432	*I*432	*I*432	*I*432	*I*432
a(Å)	15.16970(10)	15.1935(2)	15.1700(2)	15.16710(10)	15.14540(10)	15.16300(10)
V(Å^3)	3490.85(4)	3507.30(8)	3491.06(8)	3489.05(4)	3474.10(4)	3486.23(4)
R_p	0.0165	0.0280	0.0397	0.0173	0.0176	0.0212
R_{wp}	0.0240	0.0424	0.0591	0.0262	0.0250	0.0308
R_{exp}	0.0161	0.0159	0.0141	0.0156	0.0171	0.0148
R_{bragg}	0.0110	0.0227	0.0445	0.0208	0.0174	0.0166
GOF	1.489	2.667	4.172	1.686	1.460	2.078
Reflections	299	302	299	299	299	299
Parameters	58	61	58	52	57	55
Restraints	4	5	4	4	4	4
Hydrogen bonding	3.265(17)	2.51(5)	2.94(4)	2.95(2)	3.04(4)	2.823(17)
CCDC number	1846955	1846956	1847057	1847060	1847056	1847059

Table S1. Crystallographic details of Rietveld refinements of DNL-6 samples (continued)

Sample	DNL-6-EPA	DNL-6-EBA	DNL-6-EIPA	DNL-6-ECyA	DNL-6-MIBA	DNL-6-BA
Space group	*I*432	*I*432	*I*432	*I*432	*I*432	*I*432
a(Å)	15.15680(10)	15.15430(10)	15.15880(10)	15.15030(10)	15.15450(10)	15.1119(2)
V(Å^3)	3481.95(4)	3480.23(4)	3483.33(4)	3477.47(4)	3480.37(4)	3451.10(8)
R_p	0.0154	0.0281	0.0409	0.0207	0.0245	0.0343
R_{wp}	0.0584	0.0445	0.0584	0.0307	0.0370	0.0510
R_{exp}	0.0157	0.0146	0.0142	0.0153	0.0150	0.0145
R_{bragg}	0.0211	0.0348	0.0506	0.0321	0.0206	0.0274
GOF	1.347	3.0377	4.119	2.005	2.468	3.515
Reflections	299	299	299	299	299	295
Parameters	59	58	54	53	57	84
Restraints	4	4	4	4	4	10
Hydrogen bonding	3.228(16)	2.735(17)	3.271(10)	3.270(14)	3.018(15)	2.94(2)
CCDC number	1847055	1847061	1847054	1847068	1847058	1846953

Table S2. Complementary synthetic information of nine recipes of DNL-6s described in Table 1

Sample	Raw materials		Crystallization time
	Silicon source[a]	Aluminum source[b]	(h)
DNL-6-MEA	TEOS	AiP	30
DNL-6-MPA	FS	PB	19.5
DNL-6-MBA	FS	AiP	14
DNL-6-MPeA	TEOS	AiP	22
DNL-6-EPA	FS	PB	41
DNL-6-EBA	TEOS	AiP	25
DNL-6-MIBA	FS	AiP	24
DNL-6-EIPA	CS	PB	72
DNL-6-ECyA	TEOS	AiP	44

Notes: a: FS, fumed silica; TEOS, tetraethylorthosilicate; CS, colloidal silica (30%).
b: PB, pseudo-boehmite; AiP, aluminum isopropoxide.

Table S3. The representative synthetic conditions and results with nine highlighted-in-green amines listed in Figure 2

OSDA	Sample	Gel composition OSDA: SiO_2: P_2O_5: Al_2O_3: H_2O: CTAB (seed[#])	Result*
N-Methylethylamine	MEA-1	2:0.3:0.4:0.5:50:0.15 (0)	DNL-6
	MEA-2	2:0.3:0.4:0.5:50:0 (20%)	DNL-6, unknown phase
	MEA-3	2:0.3:0.4:0.5:50:0 (0)	SAPO-43, DNL-6, AlPO-21
N-Methylpropylamine	MPA-1	1.5:0.4:0.4:0.5:50:0.2 (0)	DNL-6
	MPA-2	1.5:0.4:0.4:0.5:50:0 (20%)	DNL-6
	MPA-3	1.5:0.4:0.4:0.5:50:0 (0)	SAPO-34
N-Methylbutylamine	MBA-1	2:0.3:0.4:0.5:50:0.2 (10%)	DNL-6
	MBA-2	2:0.3:0.4:0.5:50:0.2 (2%)	DNL-6
	MBA-3	2:0.3:0.4:0.5:50:0.2 (0)	DNL-6
	MBA-4	2:0.3:0.4:0.5:50:0 (10%)	DNL-6
	MBA-5	2:0.3:0.4:0.5:50:0 (0)	SAPO-34
N-Methylpentylamine	MPeA-1	1.5:0.45:0.4:0.5:50:0.2 (0)	DNL-6, amorphous
	MPeA-2	1.5:0.45:0.4:0.5:50:0 (20%)	DNL-6
	MPeA-3	1.5:0.45:0.4:0.5:50:0 (0)	SAPO-34, DNL-6
N-Ethylpropylamine	EPA-1	2:0.6:0.4:0.5:50:0.2 (0)	DNL-6, amorphous
	EPA-2	2:0.6:0.4:0.5:50:0 (40%)	DNL-6
	EPA-3	2:0.6:0.4:0.5:50:0 (0)	SAPO-34, amorphous
N-Ethylbutylamine	EBA-1	1:0.55:0.4:0.5:50:0.2 (0)	DNL-6, amorphous
	EBA-2	1:0.55:0.4:0.5:50:0 (20%)	DNL-6, amorphous
	EBA-3	1:0.55:0.4:0.5:50:0 (0)	amorphous
N-Ethylisopropylamine	EIPA-1	2:0.45:0.4:0.5:50:0.2 (0)	DNL-6, SAPO-34
	EIPA-2	2:0.45:0.4:0.5:50:0 (40%)	SAPO-34, DNL-6
	EIPA-3	2:0.45:0.4:0.5:50:0 (0)	SAPO-34
N-Methylisobutylamine	MIBA-1	2.2:0.3:0.4:0.5:50:0.2 (0)	DNL-6, SAPO-34
	MIBA-2	2.2:0.3:0.4:0.5:50:0 (40%)	DNL-6, (SAPO-42, SAPO-34)
	MIBA-3	2.2:0.3:0.4:0.5:50:0 (0)	SAPO-34
N-Ethylcyclohexylamine	ECyA-1	2:0.55:0.4:0.5:50:0.2 (0)	DNL-6, (SAPO-34, SAPO-42)
	ECyA-2	2:0.55:0.4:0.5:50:0 (40%)	DNL-6, SAPO-34
	ECyA-3	2:0.55:0.4:0.5:50:0 (0)	SAPO-34

Notes: *: The product appearing first is the major phase, while the product obtained in a trace amount is given in parentheses.

[#]: The amount of seeds is based on the weight of Al_2O_3 in the gel throughout this article.

Table S4. Synthesis conditions of five amines (MIPA, TBEA, EBnA, BA, and PeA) utilized as OSDAs for DNL-6.

OSDA	Sample	Gel composition OSDA: SiO_2: P_2O_5: Al_2O_3: H_2O: CTAB (seed)	Results
N-Methylisopropylamine	DNL-6-MIPA	1.0:0.2:0.4:0.5:50:0.15 (5% seed A)	DNL-6, SAPO-34, SAPO-42
N-tert-Butylethylamine	DNL-6-TBEA	1.2:0.2:0.4:0.5:50:0.15 (5% seed A)	SAPO-42, DNL-6, SAPO-34
N-Ethylbenzylamine	DNL-6-EBnA	2.0:0.8:0.4:0.5:50:0.2 (40% seed B)	DNL-6, amorphous
N-Butylamine	DNL-6-BA	1.1:0.5:0.4:0.5:50:0.2 (40% seed B)	DNL-6, SAPO-34
N-Pentylamine	DNL-6-PeA	1.0:0.5:0.4:0.5:50:0.2 (40% seed B)	DNL-6, SAPO-42

Table S5. Complementary synthetic information of five recipes of DNL-6s described in Table S4

Sample	Raw materials		Crystallization time (h)
	Silicon source[a]	Aluminum source[b]	
DNL-6-MIPA	TEOS	AiP	24h
DNL-6-TBEA	TEOS	AiP	24h
DNL-6-EBnA	FS	PB	24h
DNL-6-BA	TEOS	AiP	24h
DNL-6-PeA	TEOS	AiP	22h

Notes: a: FS, fumed silica; TEOS, tetraethylorthosilicate.

b: PB, pseudo-boehmite; AiP, aluminum isopropoxide.

Table S6. Synthesis conditions for SAPO-42.

OSDA	Sample	Gel composition OSDA: SiO_2: P_2O_5: Al_2O_3: H_2O: CTAB (seed)	Results
dipropylamine (DPA)	SAPO-42-DPA-1	1.7:0.35:0.4:0.5:50:0.15 (no seed)	SAPO-42, amorphous
dipropylamine (DPA)	SAPO-42-DPA	2:0.35:0.4:0.5:50:0.15 (10% seed C)	SAPO-42
diethylamine (DEA)	SAPO-42-DEA	2.0:0.3:0.4:0.5:50:0.2 (40% seed C)	SAPO-34, SAPO-42
dibutylamine (DBA)	SAPO-42-DBA	2.0:0.3:0.4:0.5:50:0.15 (40% seed C)	SAPO-42, amorphous

Table S7. Complementary synthetic information of SAPO-42 in Table S6

Sample	Raw materials		Crystallization time (h)
	Silicon source[a]	Aluminum source[b]	
SAPO-42-DPA-1	TEOS	AiP	24h
SAPO-42-DPA	TEOS	AiP	24h
SAPO-42-DEA	TEOS	PB	47h
SAPO-42-DBA	TEOS	AiP	48h

Notes: a: TEOS, tetraethylorthosilicate.

b: PB, pseudo-boehmite; AiP, aluminum isopropoxide.

Table S8. Crystallographic details of Rietveld refinements of SAPO-42-DPA

Sample	SAPO-42-DPA
Space group	*Fm*-3*c*
a(Å)	24.14794(16)
R_p	0.0263
R_{wp}	0.0425
R_{exp}	0.0157
R_{bragg}	0.0443
GOF	2.6863
Reflections	504
Parameters	61
Restraints	9
CCDC number	1856120

Reference

1. Su, X. *et al.* Synthesis and characterization of DNL-6, a new silicoaluminophosphate molecular sieve with the RHO framework. *Microporous Mesoporous Mater.* **144,** 113–119 (2011).
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3. Smeets, S. *et al.* Locating Organic Guests in Inorganic Host Materials from X-ray Powder Diffraction Data. *J. Am. Chem. Soc.* **138,** 7099–7106 (2016).