SUPPORTING INFORMATION

Insights of the Crystallization Process of Molecular Sieve $AlPO_4$-5 Prepared by Solvent-free Synthesis

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KEYWORDS: Solvent-free; J-HMQC $^{27}Al/^{31}P$ double-resonance NMR; Zeolite crystallization process; $AlPO_4$-5.

Computational Method:

The 20T 4MR (Figure S6), 18T 6MR (Figure S7) and 28T 4MR-6MR (Figure 5) chains extracted from the $AlPO_4$-5 crystallographic data,[1] was applied to represent the intermediate species during $AlPO_4$-5 synthesis. The terminal O atoms are saturated with hydrogen atoms, and the hydrogen atoms were positioned on the vector from the O atom to the Al (P) atom that the hydrogen atom was replacing. The ωB97XD/6-31G(d, p) was utilized for geometries optimization. During the structure optimizations, all of the framework atoms were relaxing while the terminal H atoms were fixed to preserve the integrity of the chains structures. Based on the optimized structures, the ^{31}P and ^{27}Al NMR chemical shifts were calculated at the level of ωB97XD/6-311G(d, p). The calculated ^{31}P and ^{27}Al NMR chemical shifts were referenced to the experiment results of the $(P\text{-}O\text{-}Al)_n$ chain (^{31}P, -12.2 ppm; ^{27}Al, -1.0 ppm). All the calculations were performed by using the Gaussian 09 package.[2]

REFERENCES

(1) http://www.iza-structure.org/databases/.

(2) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.;Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian09, revision B.01; Gaussian, Inc.: Wallingford, CT, **2010**.

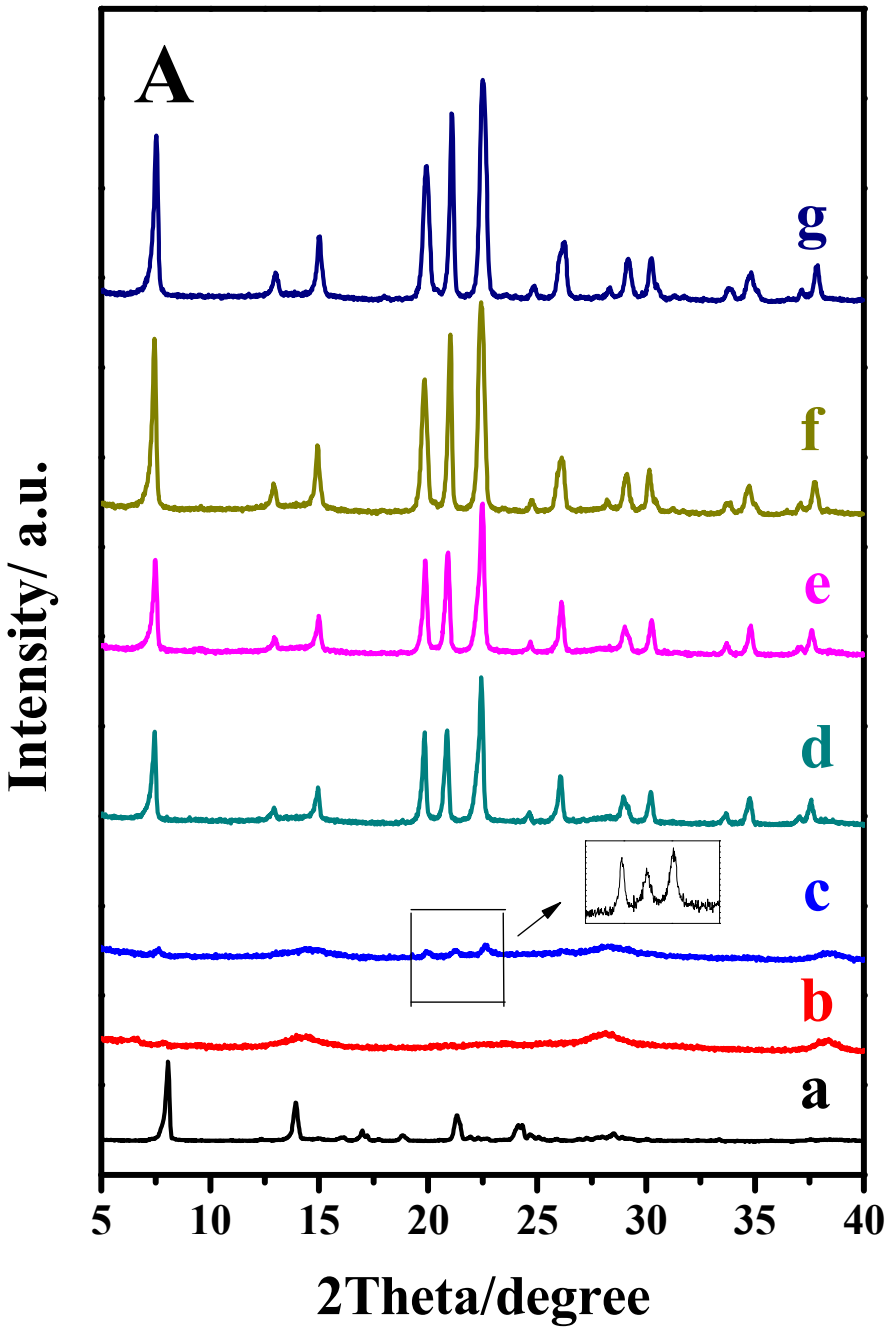

Figure S1A. XRD patterns of washed S-APO-5 samples synthesized at crystallization time of (a) 0 h, (b) 1 h, (c) 1.5 h, (d) 2 h, (e) 3 h, (f) 4 h, and (g) 24 h.

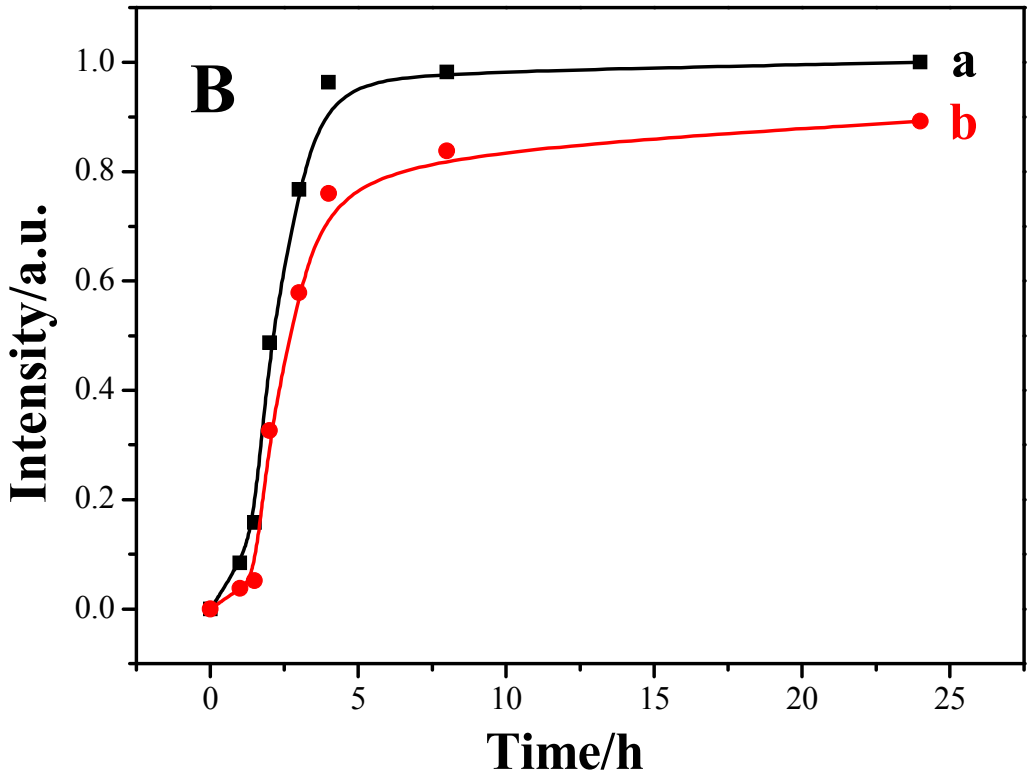

Figure S1B. The dependences of S-APO-5 (a) crystallinity and (b) solid yield on the crystallization time.

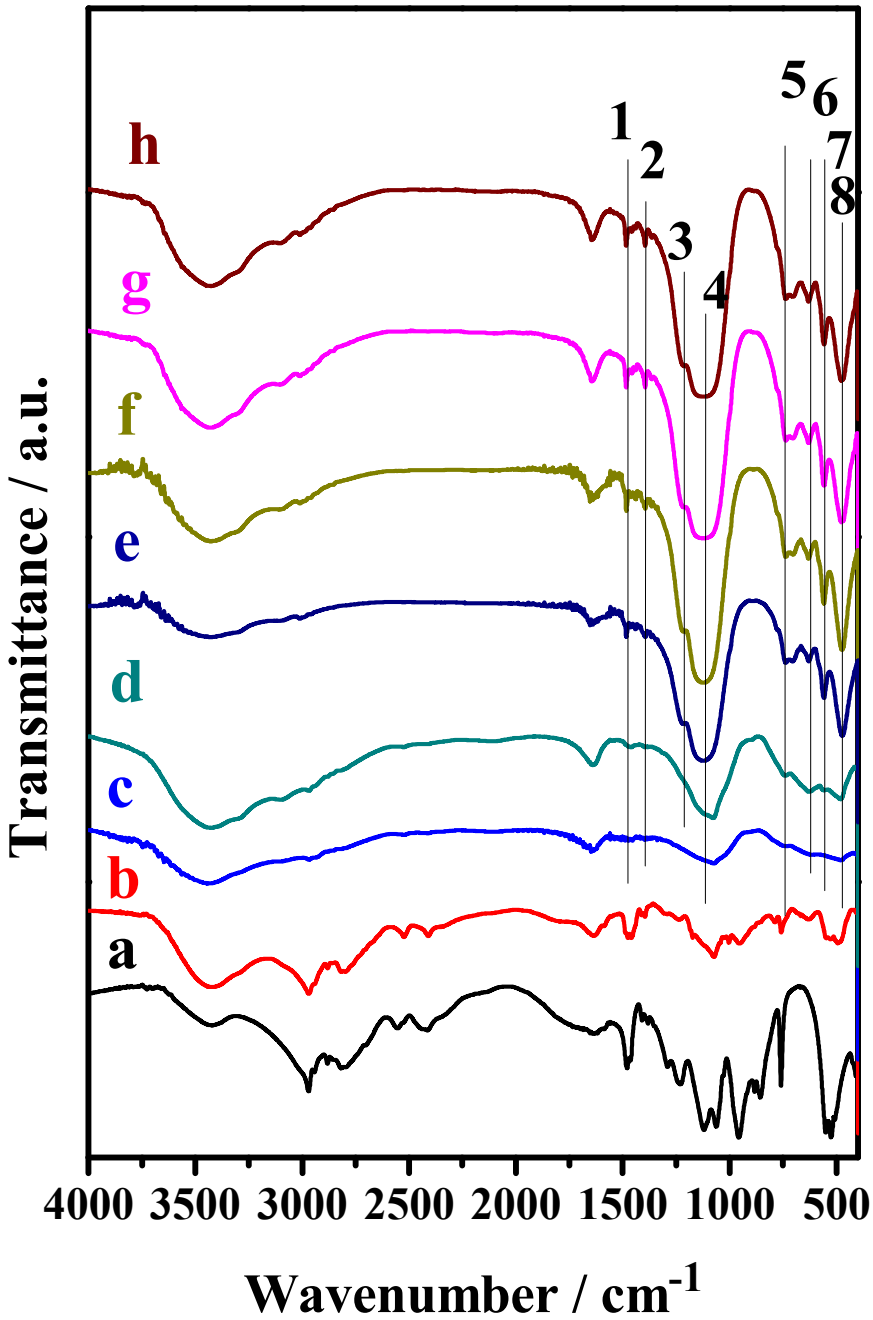

Figure S2. FT-IR spectra of washed S-APO-5 samples synthesized at crystallization time of (a) DPA·H_3PO_4 , (b) 0 h, (c) 1 h, (d) 1.5 h, (e) 2 h, (f) 3 h, (g) 4 h, and (h) 24 h (1: 1470 cm^{-1}, 2: 1400 cm^{-1}; 3: 1216 cm^{-1}; 4: 1123 cm^{-1}; 5: 739 cm^{-1}; 6: 627 cm^{-1}; 7: 550 cm^{-1}; 8: 499 cm^{-1}).

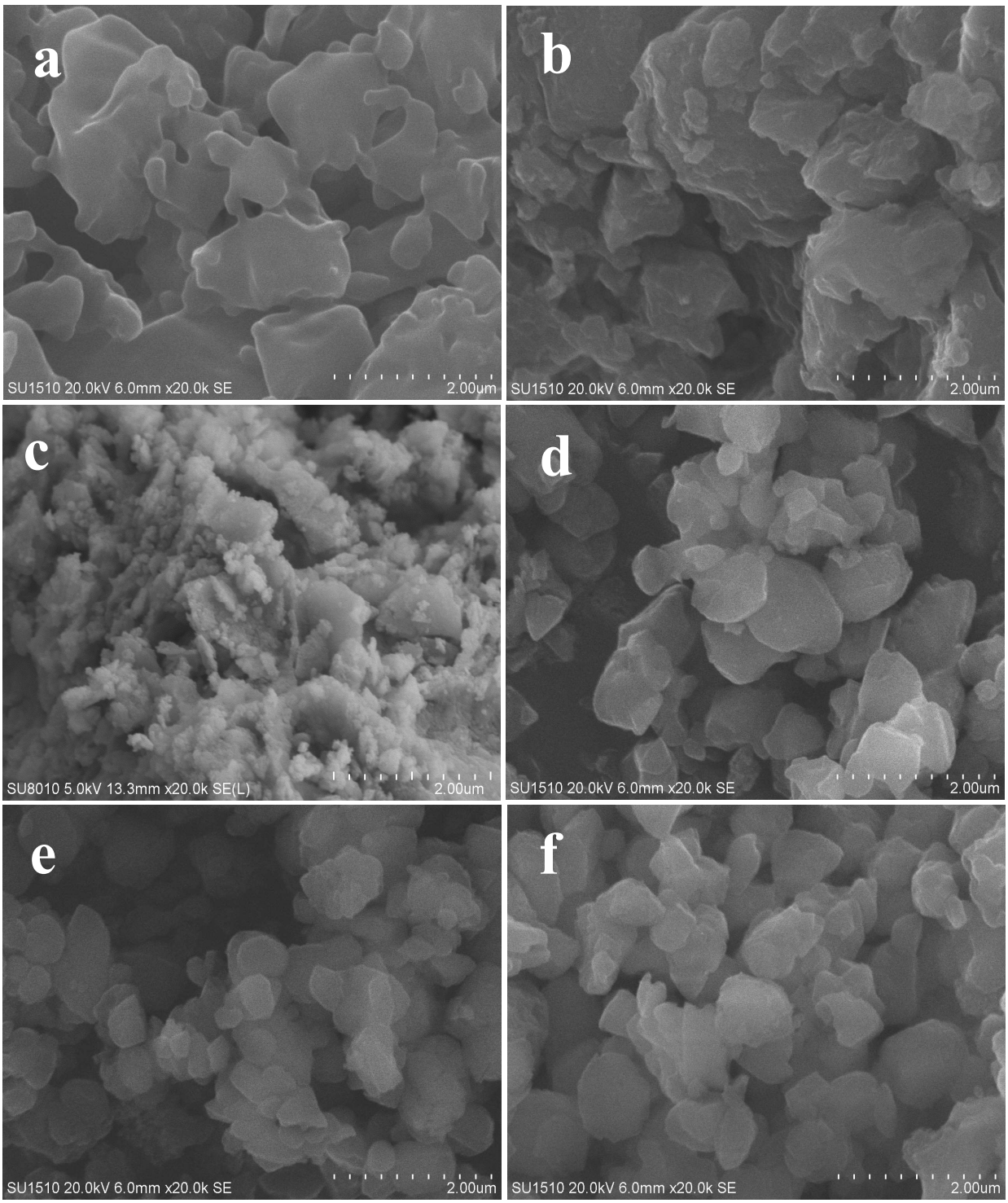

Figure S3. The SEM images of S-APO-5 at different crystallization time of (a) 0 h, (b) 1 h, (c) 1.5 h, (d) 2 h, (e) 3 h and (f) 24 h.

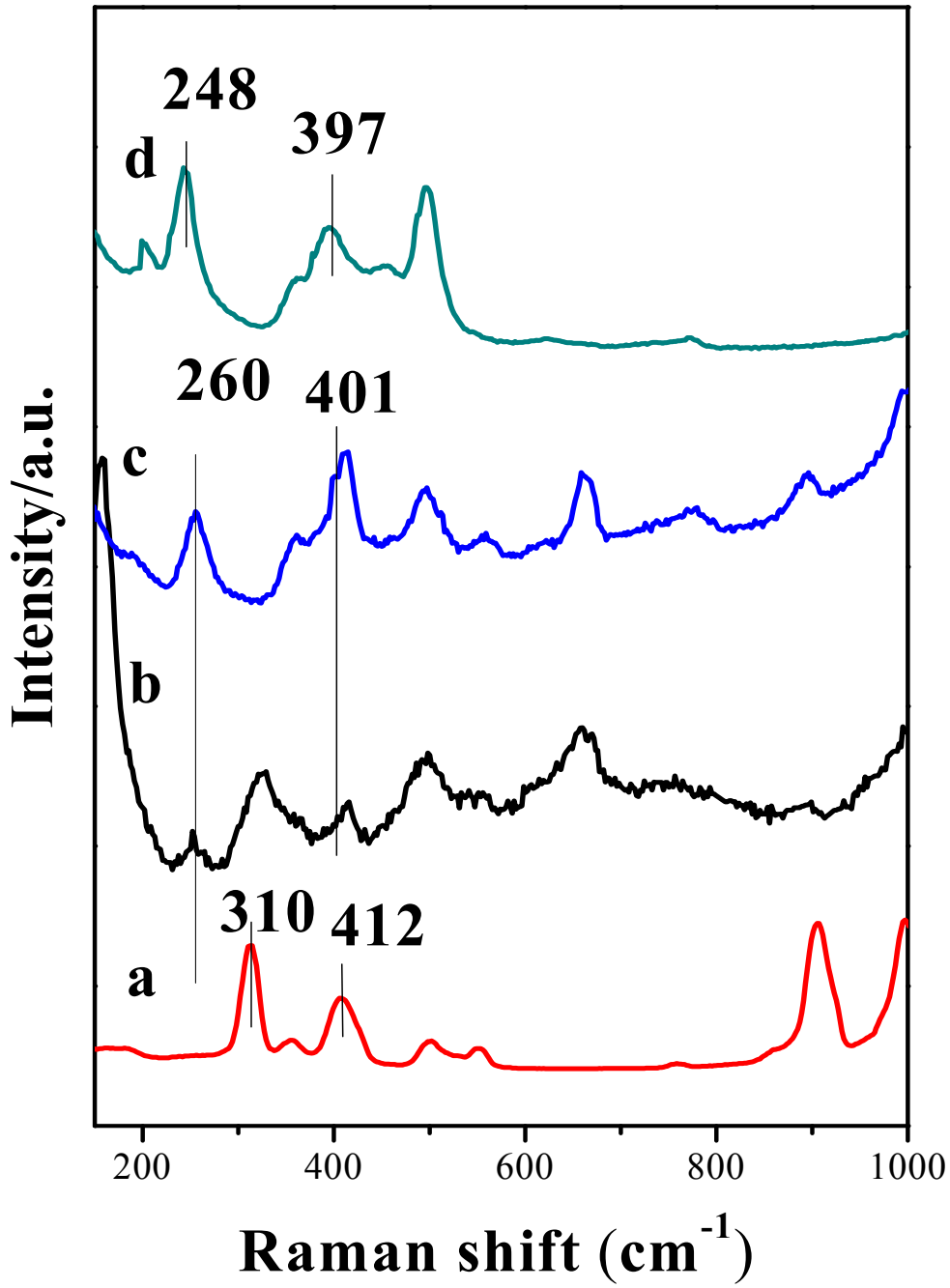

Figure S4. UV-Raman spectra of (a) DPA·H_3PO_4 as well as (b) as-synthesized, (c) washed, and (d) calcined S-APO-5 samples crystallization time at 24 h.

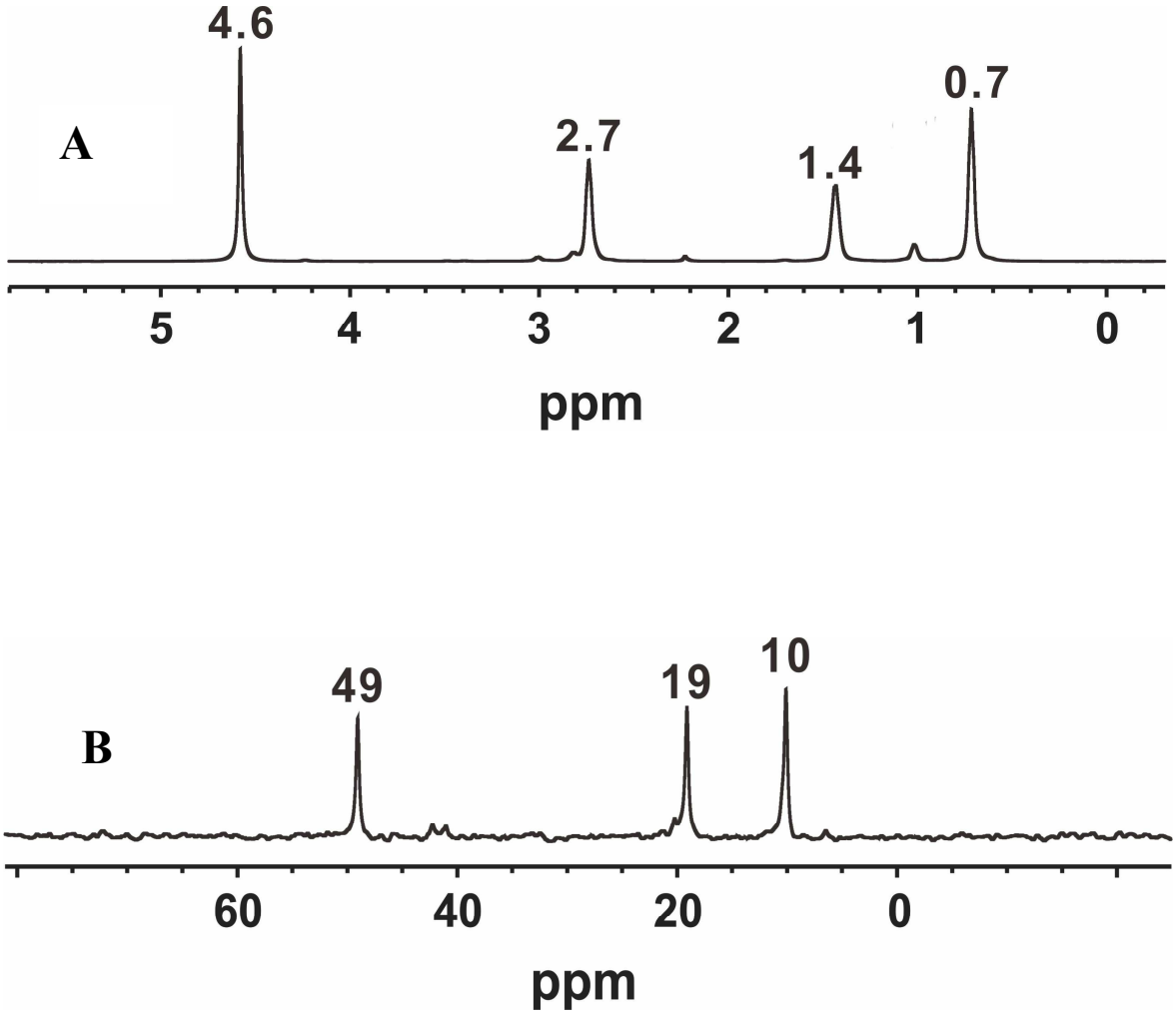

Figure S5. (A) ^{1}H NMR spectra and (B) ^{13}C NMR spectra of the filtrates of fully crystallized samples with crystallization time of 24 h.

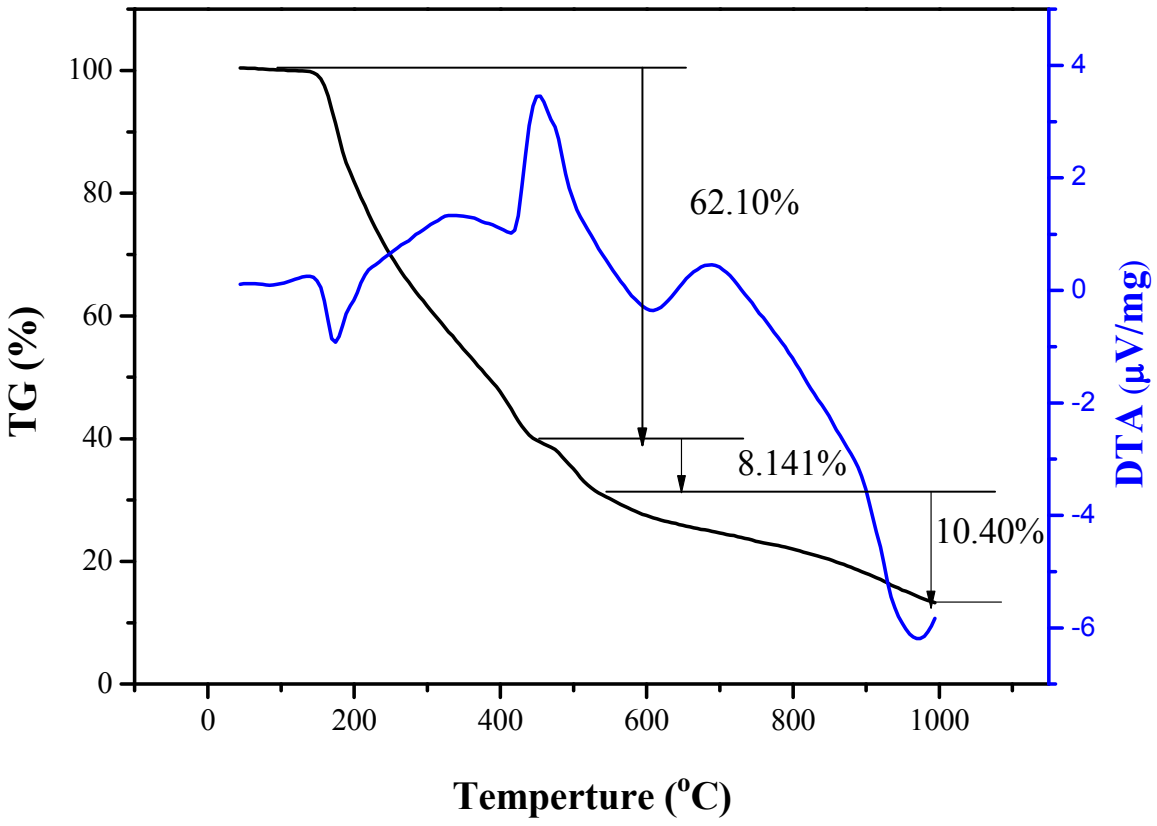

Figure S6. TG-DTA curve of the as-synthesized DPA·H_3PO_4.

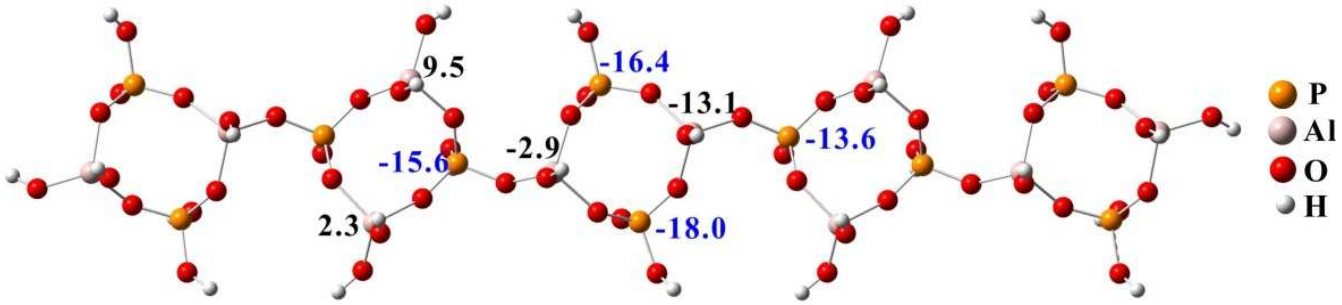

Figure S7. The optimized 4MR chain structure [The calculated ^{31}P (blue) and ^{27}Al (black) NMR labeled in ppm].

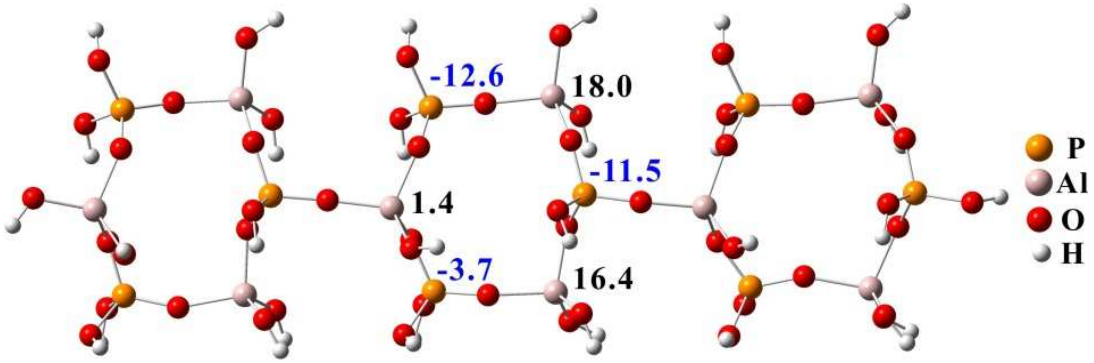

Figure S8. The optimized 6MR chain structure [The calculated ^{31}P (blue) and ^{27}Al (black) NMR labeled in ppm].