New Insights of Di-*n*-propylamine (DPA) Molecule as an Organic Structural Directing Agent (OSDA) in the Crystallization of $AlPO_4$-11 Molecular Sieve

Na Sheng,[a] Yueying Chu,[b] Shaohui Xin,[b] Qiang Wang,[b] Xiaolong Liu,[b] Jun Xu,[b] Feng-Shou Xiao,*[a] and Feng Deng*[b]

[a] Department of Chemistry, Zhejiang University, Hangzhou 310028, China.

[b] State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics and Mathematics, the Chinese Academy of Sciences, Wuhan 430071, China.

Characterization. The ^{31}P-{^{27}Al} PT-*J*-HMQC MAS NMR experiments were performed on an 11.7 T Bruker AVANCE-III spectrometer using commercial 4 mm outer diameter rotors at the spinning frequency of 12.5 kHz, tuning and matching to ^{1}H, ^{31}P and ^{27}Al Larmor frequencies (500.6 MHz, 202.6 MHz and 130.5 MHz, respectively). An initial ^{1}H-^{31}P CP transfer was used with a contact time of 3 ms and rf-field of $\nu_{31P,\ CP}$ =43.03 kHz and $\nu_{1H,\ CP}$ =55.68 kHz. The ^{31}P-{^{27}Al} PT-*J*-HMQC pulse sequence with CT selective π/2 pulses and π pulses were employed on ^{27}Al and ^{31}P channels with $\tau_{\pi/2,\ 27Al} = \tau_{\pi,\ 27Al}/2$= 8.5 us and $\tau_{\pi/2,\ 31P} = \tau_{\pi,\ 31P}/2$= 4.5 us, respectively. Continuous-wave proton decoupling with amplitude of 70.42 kHz was used at the end of CP transfer. The Population transfer enhancement of between ^{31}P and ^{27}Al was achieved with a sideband-selective (SS) WURST-80 irradiation on ^{27}Al with a length of 75 us that used a sweep frequency range of ν_R. The values for peak RF amplitude and offset of WURST-80 were optimized with respect to the different samples: (ν_1^{max} ,

ν_{offset}) = (10, 170) kHz on ^{27}Al channel. 30 t_1 increments of 80 μs were acquired in the first dimension and a total of 1000 scans were accumulated with a recycle time of 1.5 s.

The 2D ^{31}P-^{31}P DQ-SQ MAS NMR experiments were performed on an 9.4 T Bruker AVANCE-III spectrometer using commercial 4 mm outer diameter rotors at the spinning frequency of 10 kHz, tuning and matching to ^{1}H, ^{31}P Larmor frequencies (399.3 MHz and 161.6 MHz, respectively). ^{1}H-^{31}P CP experiments with a contact time of 4 ms and rf-field of $\nu_{31P, CP}$ =86.27 kHz and $\nu_{1H, CP}$ =55.93 kHz was employed to prepare the initial ^{31}P signal. RFDR homonuclear recoupling was used on the ^{31}P channel with $\nu_{nut,31P}$ =20.83 kHz. continuous-wave ^{1}H decoupling with an amplitude of 67.02 kHz was used at the end of CP transfer, while a TPPM proton decoupling with an amplitude of 44.66 kHz was used during acquisition. The increment in the indirect dimension (t_1) was set to 100 μs, and 2048 scans were acquired for each t_1 increment.

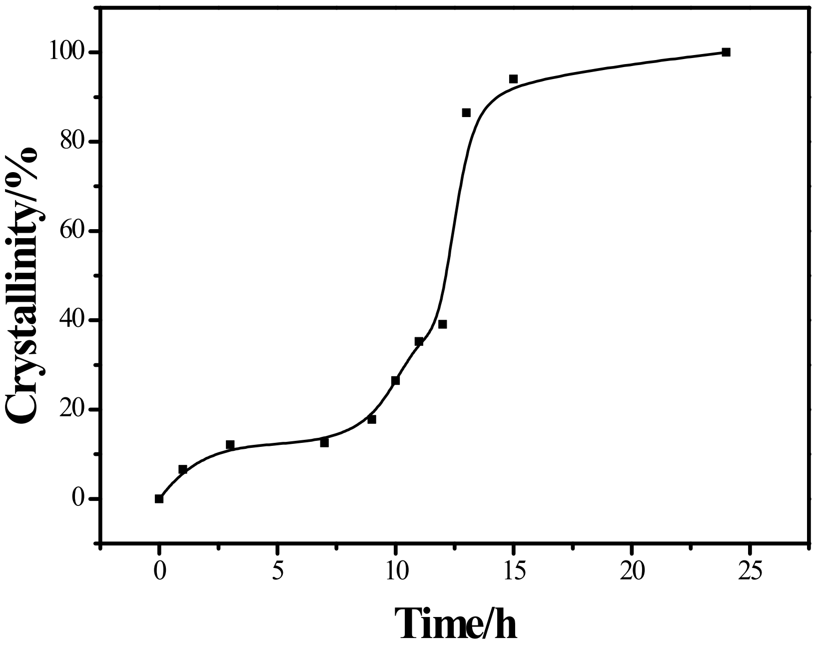

Figure S1. The dependence of S-$AlPO_4$-11 crystallinity on the crystallization time.

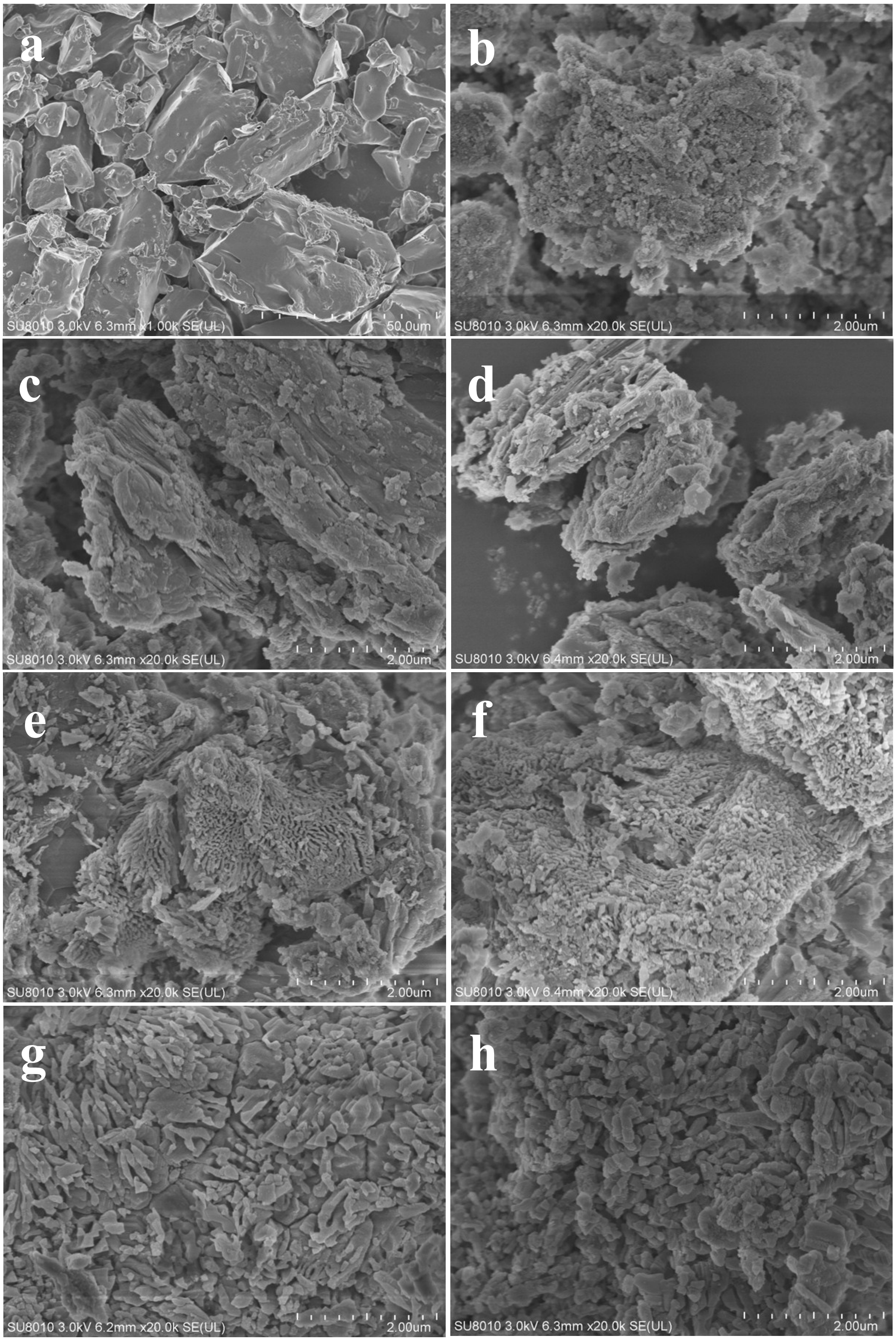

Figure S2. The SEM images of S-$AlPO_4$-11 at crystallization time of (a) 0, (b) 1, (c) 3, (d) 7, (e) 9, (f) 10, (g) 13, and (h) 24 h, respectively.

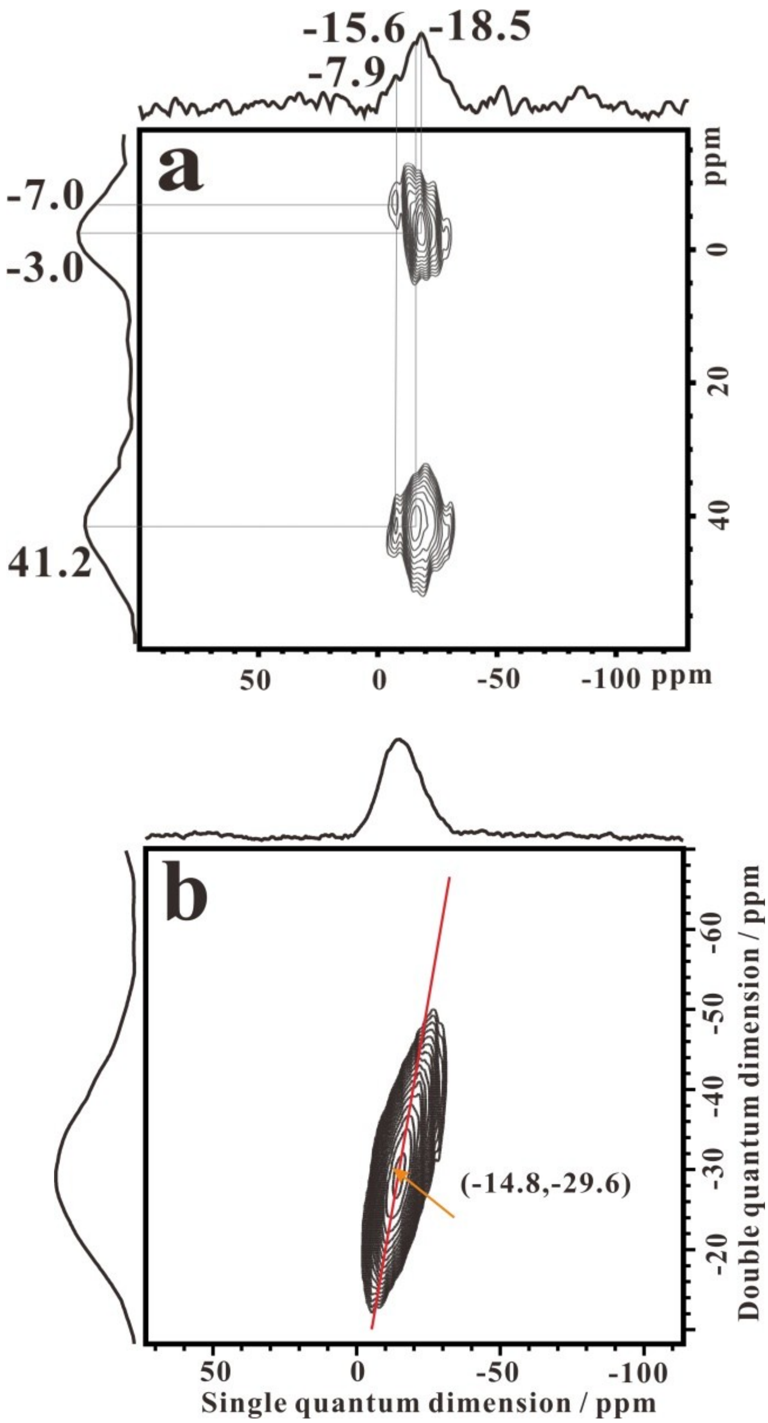

Figure S3. (a) ^{31}P-{^{27}Al} PT-*J*-HMQC and (b) ^{31}P-^{31}P 2D DQ-SQ MAS NMR spectra of S-AlPO$_4$-11 sample crystallization at 2 h.

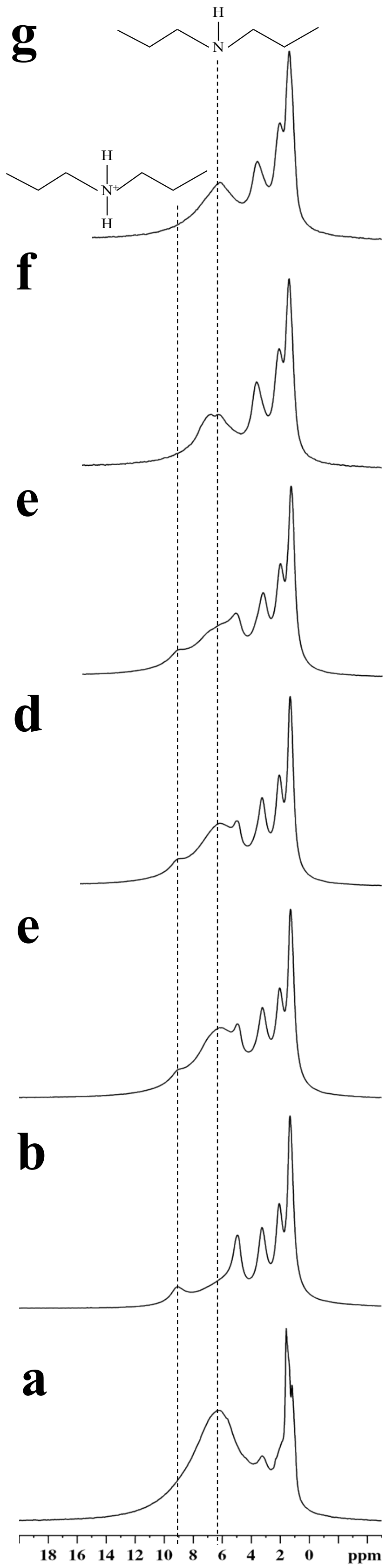

Figure S4. ^{1}H MAS spectra of S-AlPO$_4$-11 samples crystallized at (a) 1, (b) 3, (c) 7, (d) 9, (e) 11, (f) 15, and (h) 24 h, respectively.

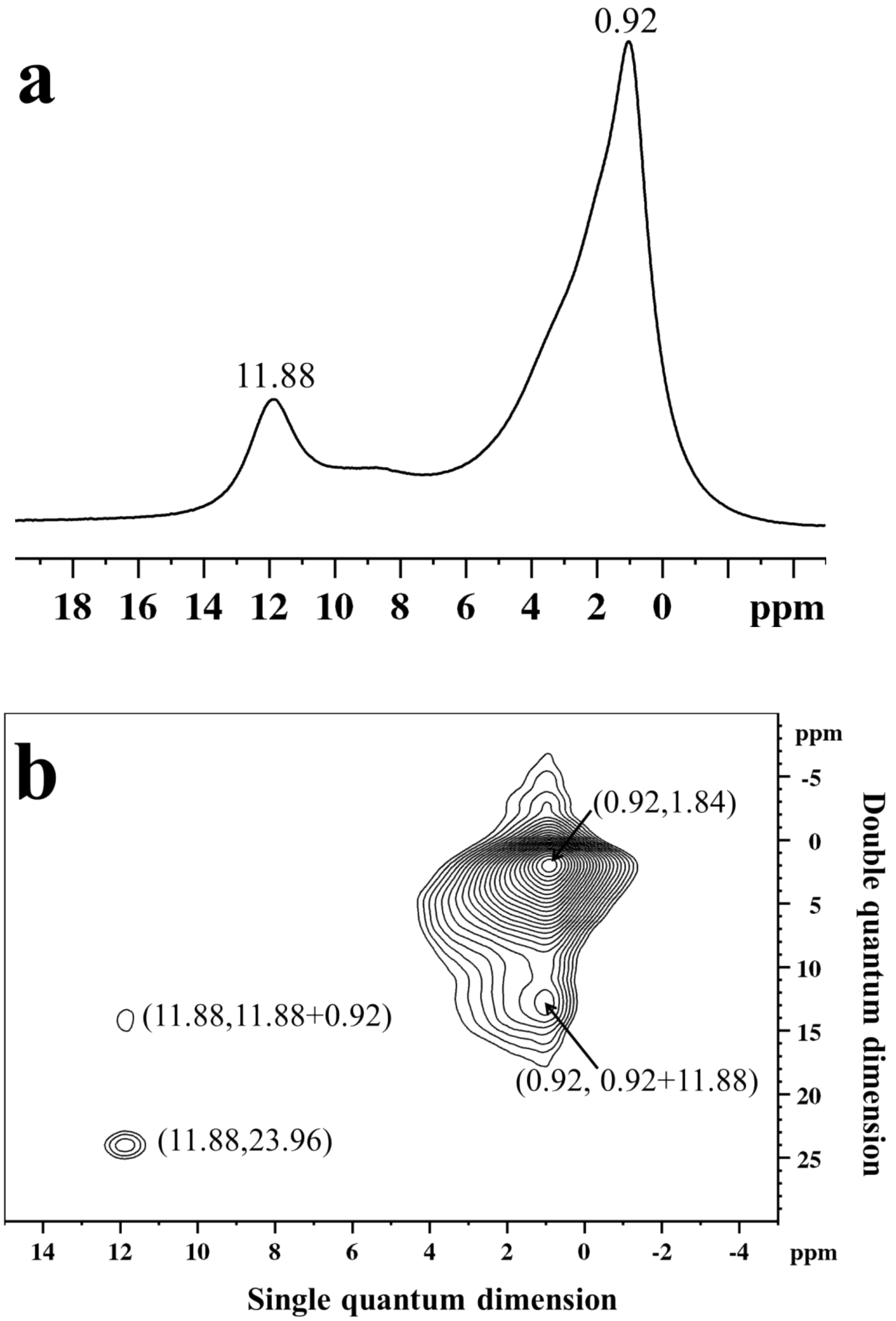

Figure S5. (a) ^{1}H MAS and (b) 2D ^{1}H DQ-SQ MAS spectra of DPA·H_3PO_4.

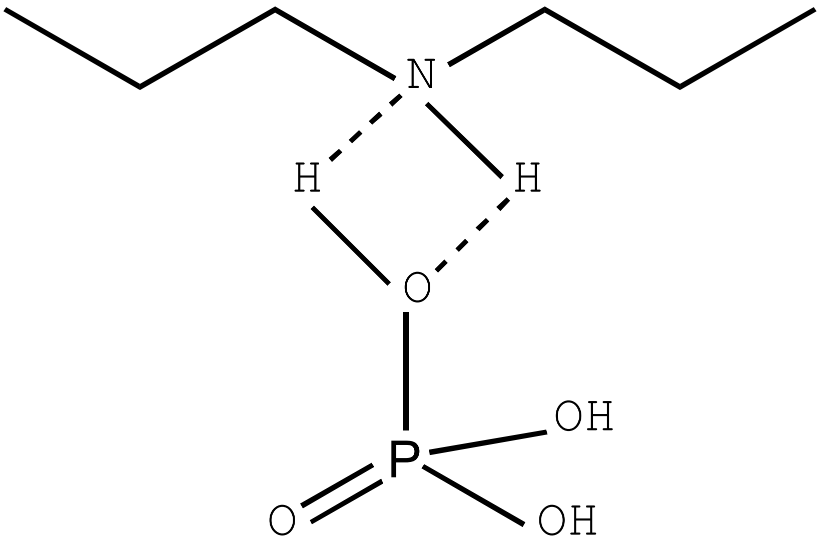

Figure S6. Schematic structure of DPA·H_3PO_4.

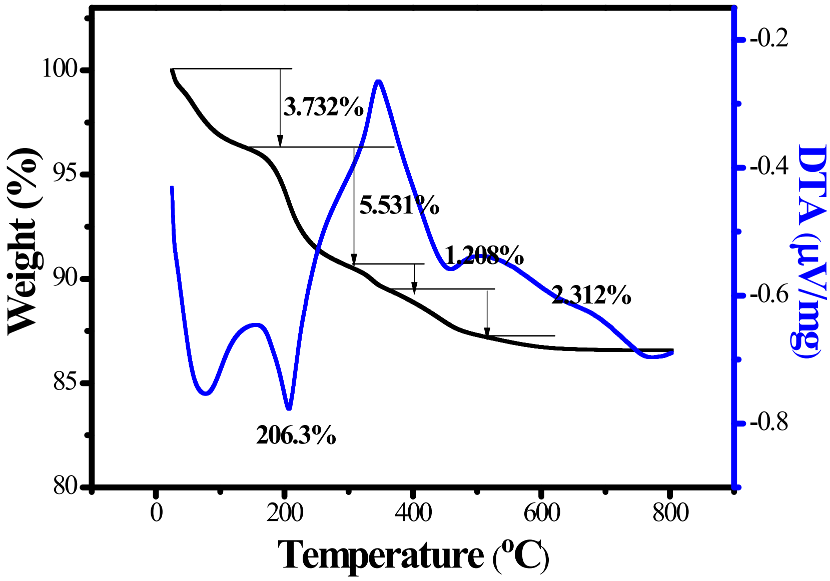

Figure S7. TG-DTA curves of S-$AlPO_4$-11 sample crystallized at 24h.