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Synthesis of Pure Silica MFI Zeolites Using Imidazolium-based Long Dications. A Comparative Study of Structure-directing Effects Derived from a Further Spacer Length Increase

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Index

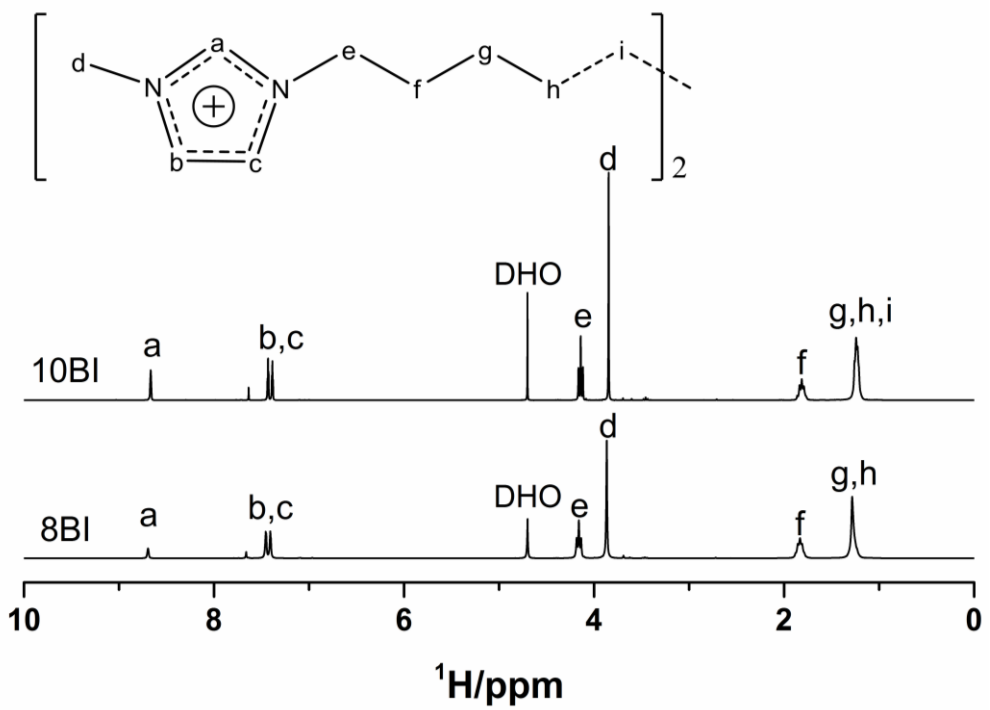

Figure S1. ^{1}H NMR in D_2O of the organic dications used in this work.

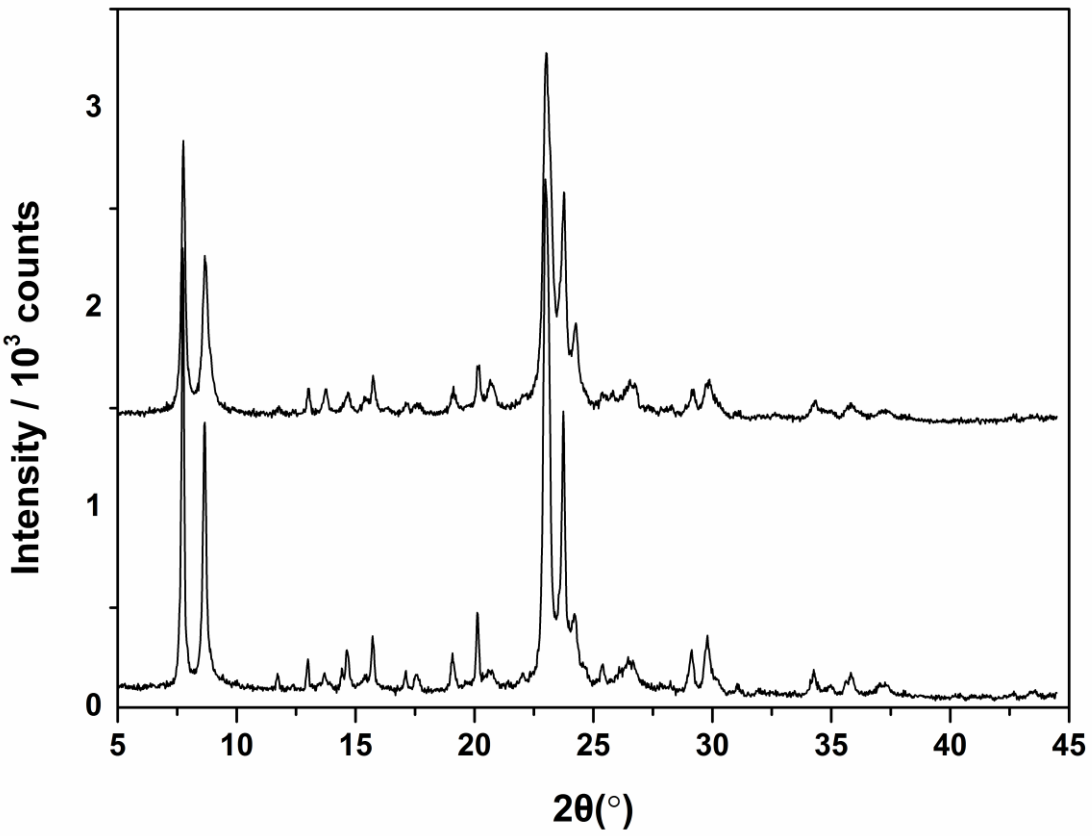

Figure S2. XRD patterns of as-made 8BI-MFI (bottom) and 10BI-MFI (top) zeolites synthesized at 175 ℃ and 150 ℃ with synthesis time of 9 and 10 days and water/silica ratio of 2.6 and 3.0, respectively.

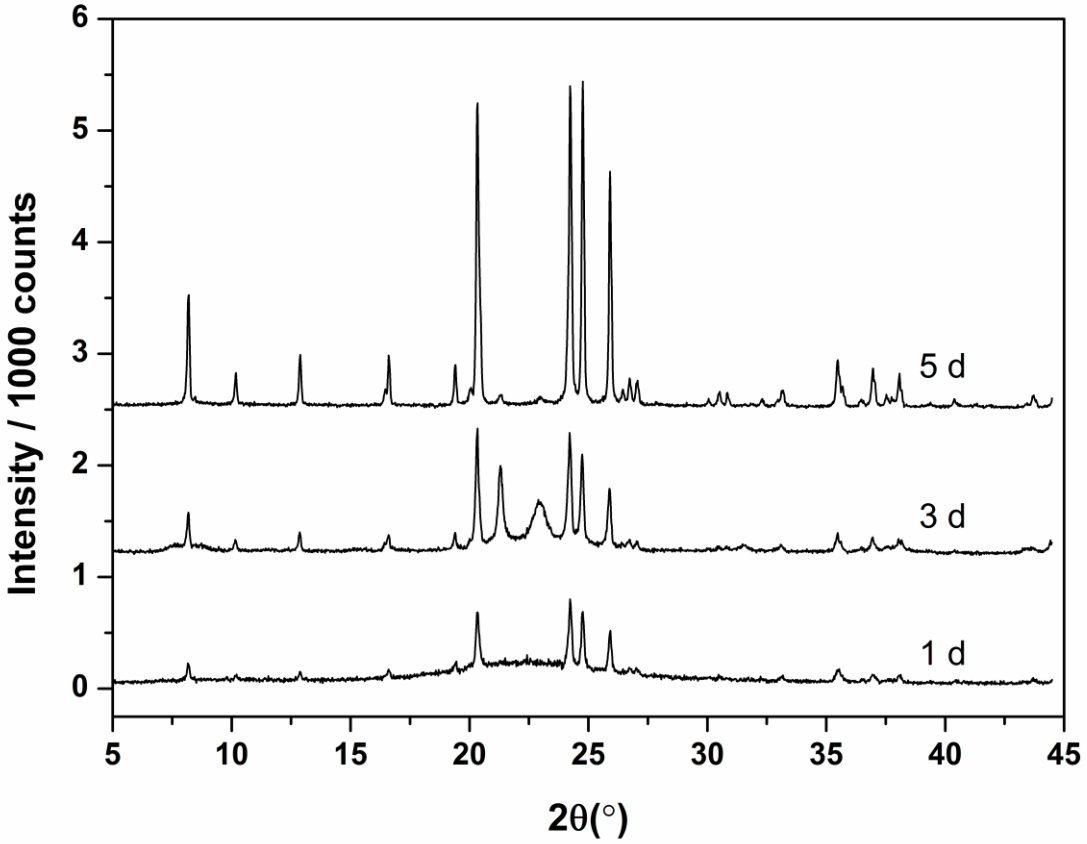

Figure S3. XRD patterns of as-made materials synthesized at different times with 8BI at 175 ℃ and a water/silica ratio of 8. The main phase obtained at 5 days is zeolite TON.

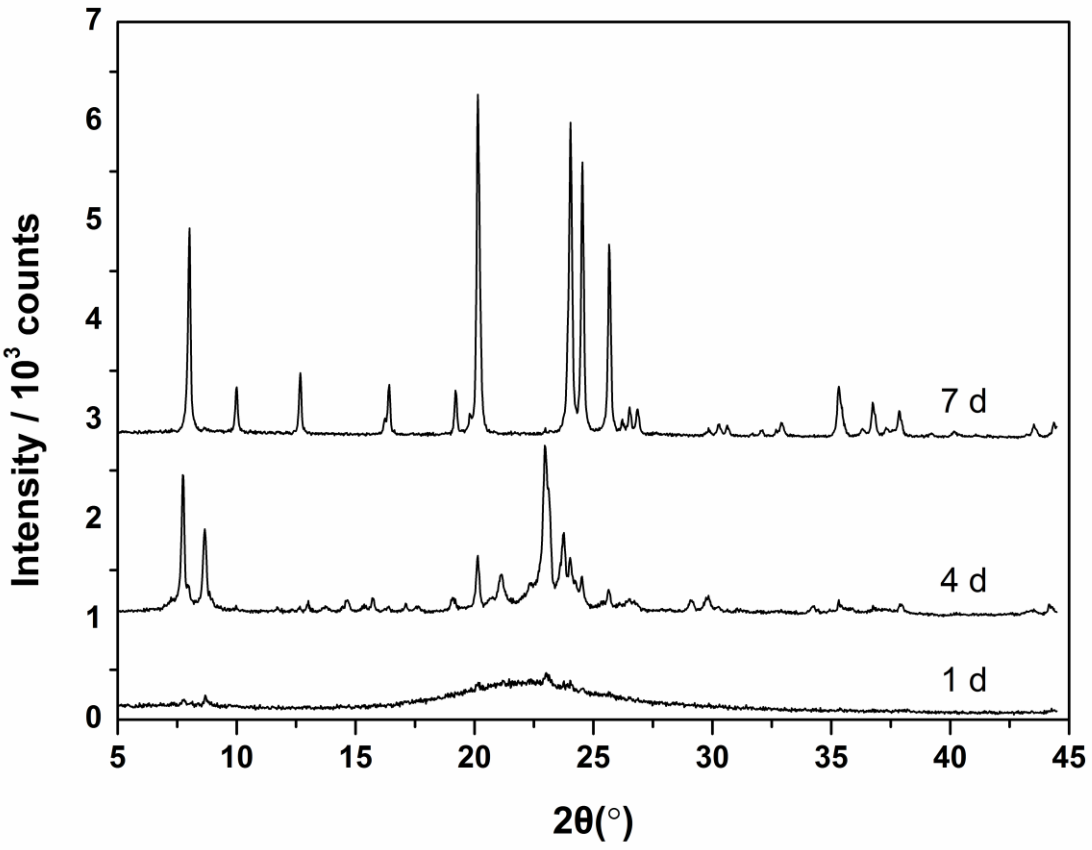

Figure S4. XRD patterns of as-made materials synthesized at different times with 10BI at 175 ℃ and a water/silica ratio of 8. The phase obtained at 7 days is zeolite TON.

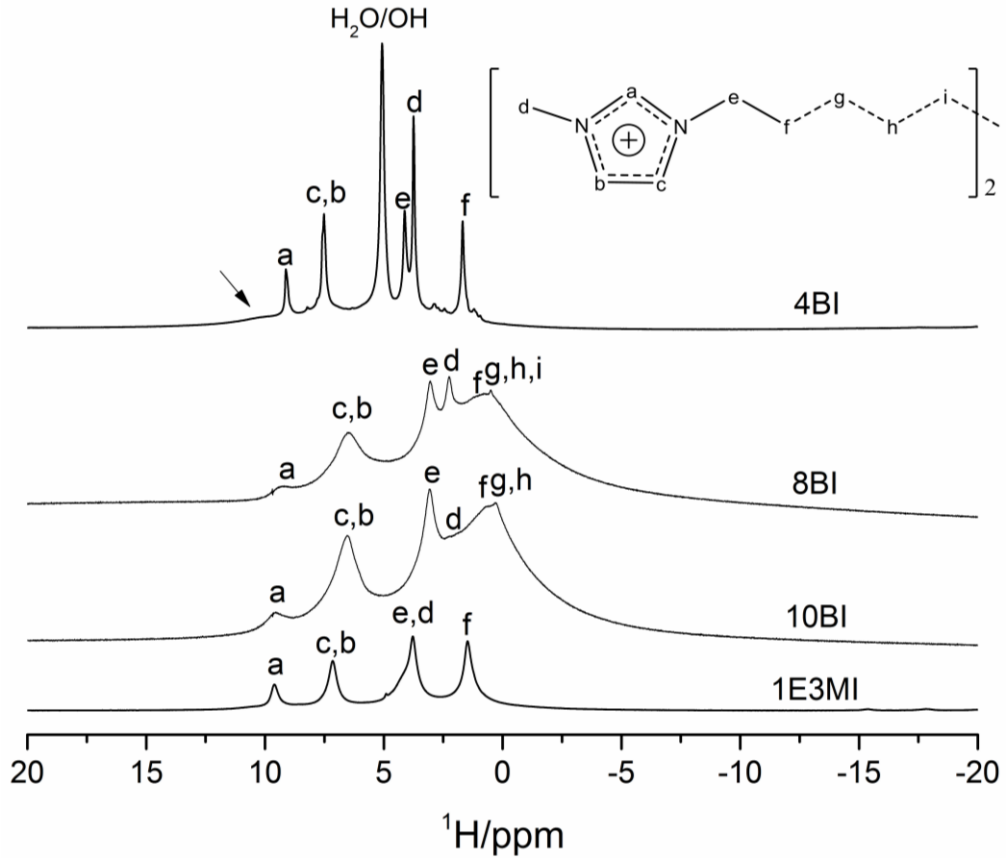

Figure S5. ^{1}H MAS NMR spectra of MFI zeolites synthesized with (from top to bottom): 4BI, 8BI, 10BI and 1E3MI. The arrow points to a broad signal at 10.2 ppm related to silanol-silanolate hydrogen bonding. The top and bottom traces correspond to reference [1].

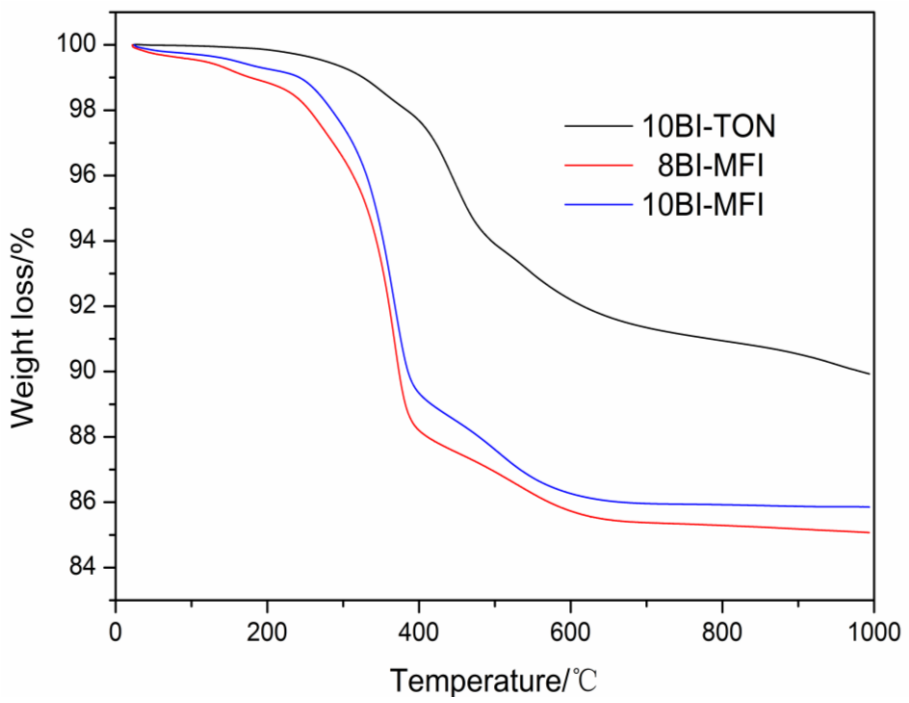

Figure S6. Thermogravimetric analysis of the as-made zeolites obtained in this work.

The porous properties of the calcined MFI zeolites were determined by N_2 adsorption-desorption. The two samples demonstrated almost identical isotherms except for several minor differences (Figure S6). Both exhibited a steep uptake at low relative pressure ($P/P_0 < 0.1$) indicative of existence of micropores and also a distinctive uptake stage in the region $0.1 < P/P_0 < 0.2$, which could be due to the completeness of monolayer coverage and multilayer adsorption about to begin.[2] The hysteresis loops appeared for both samples, though is more obvious for 8BI-MFI suggesting the presence of mesopores. Indeed, abundant mesopores were calculated in both samples, and 8BI-MFI has a much higher mesopore volume (0.16 cm^3/g) than 10BI-MFI (0.11 cm^3/g) (Table S1). However, we perceive that these mesopores are inter-crystal mesopores indicating the loosely packed pattern of the rod-like crystals.

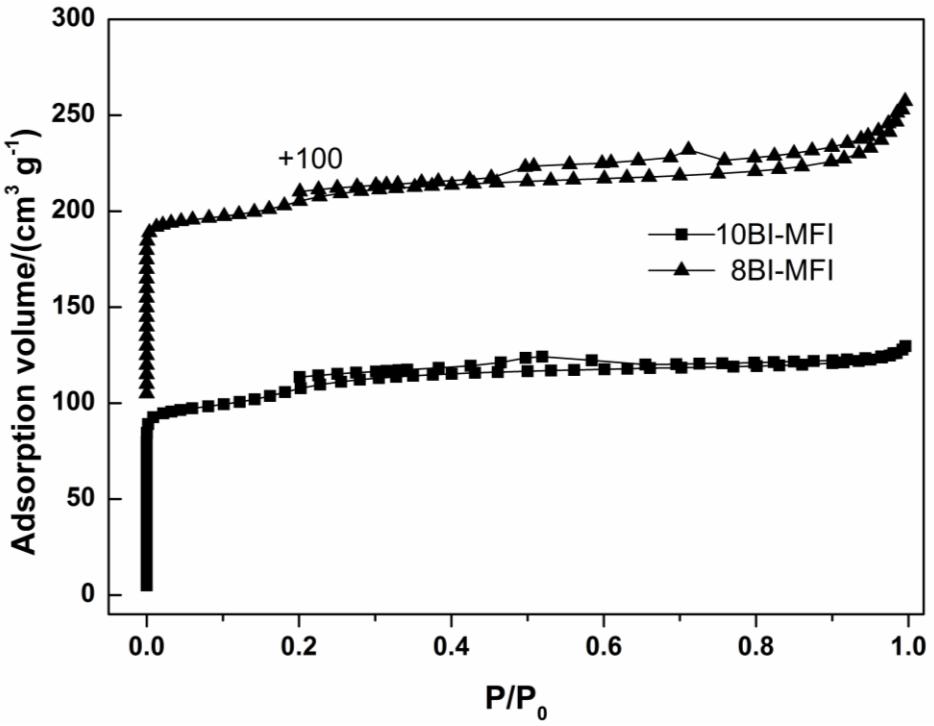

Figure S7. N_2 sorption isotherms of the calcined MFI zeolites.

Table S1. Porous properties of the calcined MFI zeolites

Sample	Surface area (m^2/g)			Pore volume (cm^3/g)			[g]Pore width (Å)
	[a]S_{total}	[b]S_{micro}	[c]S_{ext}	[d]V_{total}	[e]V_{micro}	[f]V_{meso}	
8BI-MFI	335	161	174	0.24	0.08	0.16	5.0
10BI-MFI	341	169	172	0.20	0.09	0.11	4.9

[a]BET surface area. [b]t-plot micropore surface area. [c]t-plot external surface area. [d]V_{total} was determined from adsorbed volume at $P/P_0 = 0.99$. [e]t-plot micropore volume. [f]V_{meso} (mesopore volume) = $V_{total} - V_{micro}$. [g]The median pore width derived for H-K pore size distribution.

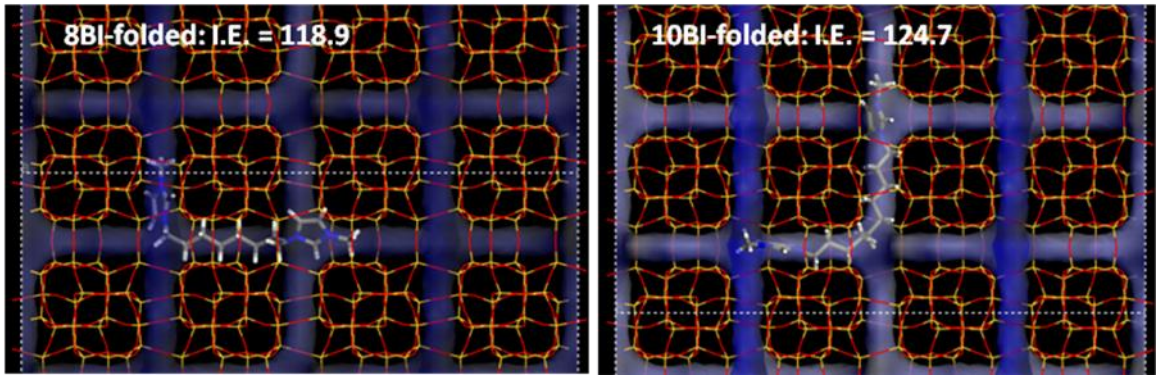

Figure S8. Location of 8BI (left) and 10BI (right) dications in a folded conformation, occupying both types of channels.

References:

[1] A. Rojas, L. Gomez-Hortiguela, M.A. Camblor, Zeolite structure direction by simple bis(methylimidazolium) cations: the effect of the spacer length on structure direction and of the imidazolium ring orientation on the 19F NMR resonances, Journal of the American Chemical Society, 134 (2012) 3845-3856.

[2] K.S.W. Sing, Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity (Recommendations 1984), Pure and Applied Chemistry, Pure and Applied Chemistry, 1985, pp. 603-619.