Supporting Information for

One-Pot Structural Conversion of Magadiite into MFI Zeolite Nanosheets Using Mononitrogen Surfactants as Structure and Shape-Directing Agents

Jérémy Dhainaut,^{*a,b*} T. Jean Daou^{*} Yannick Bidal,^{*b,c*} Nicolas Bats,^{*a*} Bogdan Harbuzaru,^{*a*} Grégory Lapisardi,^{*a*} Hélène Chaumeil,^{*c*} Albert Defoin,^{*c*} Loïc Rouleau^{*a*} and Joël Patarin^{*b*}

^a IFP Energies nouvelles, Etablissement de Lyon, Solaize, France.

^b Univ de Haute Alsace (UHA), CNRS, Équipe Matériaux à Porosité Contrôlée (MPC), Institut de Science des Matériaux de Mulhouse (IS2M) UMR 7361, Mulhouse, France.

E-mail: jean.daou@uha.fr

^c Univ de Haute Alsace (UHA), Laboratoire de Chimie Organique et Bioorganique (COB), EA 4566, ENSCMu, Mulhouse, France.

1. Synthesis of mononitrogen surfactants

1.1 Synthesis of C₂₂NPr₃ (C₂₂H₄₅-N⁺(C₃H₇)₃, Br⁻)

To a solution of bromodocosane (1.0 g, 2.56 mmol) in proprionitrile (20 mL) was added tri-N-propylamine (1 mL, 2 equiv.) and sodium carbonate (0.32g, 0.12 equiv.). The reaction mixture was stirred at reflux overnight. The organic layer was recovered after centrifugation and the solvent was evaporated under reduced pressure. The crude solid was then co-evaporated three times with toluene (3 mL) and washed three times with anhydrous diethylether (3 mL). Recrystallization in ethyl acetate (20 mL) afforded the pure derivative (1.69 g, 60%).



¹H NMR (δ, J) : (CDCl₃, 400 MHz, 295 K) : 0.88 (t, 3H), 1.07 (t, 9 H), 1.25 (s, 38H), 1.65 (m, 4H, N⁺CH₂(2)), 1.79 (m, 4H, N⁺CH₂(2)), 3.39 (m, 8H, N⁺CH₂(1)).

1.2 Synthesis of $C_{22}NPr_2C_6 (C_{22}H_{45}-N^+(C_3H_7)_2-C_6H_{13}, Br^-)$

To a solution of bromodocosane (2.0 g, 5.13 mmol) in proprionitrile (20 mL) was added di-Npropylamine (1.42 mL, 2 equiv.) and sodium carbonate (1.36 g, 2.5 equiv.). The reaction mixture was stirred at reflux overnight. The organic layer was recovered after centrifugation and the solvent was evaporated under reduced pressure. The crude solid was then co-evaporated three times with toluene (3 mL) and washed three times with anhydrous diethylether (3 mL). A 5 M hydrogen chloride solution in diethyl ether (1.02 mL, 1 equiv.) was added to the organic layer. A pink solid precipitated and was recovered by centrifugation.



¹**H NMR (δ, J) : (CDCl₃, 400 MHz, 295 K) :** 0.88 (t, 3H), 1.01 (t, 9 H, NPr(3)), 1.25 (s, 38H), 1.80 (m, 2H, CH₂(2)), 1.87 (m, 6H, NPr(2)), 2.96 (m, 8H, CH₂(1)).

To the previous hydrochloride (1.08 g, 2.44 mmol) in diethylether (10 mL) was added an aqueous solution of sodium carbonate (0.127 mL/0.127 g, 1.22 mmol). The reaction mixture was stirred at ambient temperature for 1h. The obtained organic layer was dried over magnesium sulfate and evaporated under reduced pressure to afford the desired amine (1.0 g). To a solution of this amine (1.0 g) in proprionitrile (10 mL) was added bromohexane (0.7 mL, 2 equiv.) and sodium carbonate (0.32 g, 0.12 equiv.). The reaction mixture was stirred at reflux during 24 h. The organic layer was recovered after centrifugation and the solvent was evaporated under reduced pressure. The crude solid was then co-evaporated three times with toluene (3 mL) and washed three times with diethylether (3 mL). Recrystallization in ethyl acetate afforded the pure derivative as a beige compound (0.465 g, 40%).



¹H NMR (δ , J) : (CDCl₃, 400 MHz, 295 K) : 0.88 (t, 3H), 0.90 (t, 3H, Me(6)), 1.07 (t, 9 H, N⁺Pr(3)), 1.25 (s, 38H), 1.34 (m, 2H, C₆(4)), 1.42 (m, 2H, C₆(3)), 1.79 (m, 8H, N⁺CH₂(2)), 3.39 (m, 8H, N⁺CH₂(1)).

Tab. S1 Silicon to aluminum ratio of as-synthesized zeolites obtained after 5 days at 150° C in the presence of the two mononitrogen surfactants, determined from the unit cell (u.c.) parameters evaluated by X-ray diffraction.¹

Mononitrogen surfactant	a (Å)	b (Å)	c (Å)	V u.c. (Å ³)	Al u.c.	Si/Al
C_{22} -N(C_{3}) ₃	20.13	19.91	13.44	5386	3.8	24
C_{22} -N(C_3) ₂ C_6	20.14	19.91	13.44	5388	3.8	24

(1) J.L. Guth, J. L.; Delmotte, L.; Soulard, M.; Brunard, N.; Joly, J. F.; Espinat, D. Zeolites 1992, 12, 929.



Fig. S1 Wide-angle powder XRD patterns of as-synthesized materials obtained after 5 days (a) and 15 days (b) at 130°C without the use of any organic compound. A pure magadiite material is obtained.



Fig. S2 Thermal analyses of the as-synthesized MFI-type materials obtained after 5 days at 150°C in the presence of C_3 -N(C_3)₃ (cross), C_{22} -N(C_3)₃ (triangle) and C_{22} -N(C_3)₂ C_6 (rhombus).