Supplemental Information for

Restriction of $CaCO_3$ polymorph by NH···O hydrogen-bonded poly(methacryloylaminocarboxylate) ligands; induced polymorph change by strength and/or formation manner of hydrogen bond

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Experimental Section

Materials. Triphenylacetic acid was obtained from Sigma-Aldrich Co. Other reagents were commercially obtained and solvents were used after distillation. All synthetic procedures were performed under Ar atmosphere.

3-Methyl-2-(methacryloylamino)-butyric Acid 2-Oxo-2-phenyl-ethyl Ester (MA-Val-OPac). H-Val-OPac•HCl (3.0 g, 11 mmol) and triethylamine (3.06 mL, 22 mmol) in 40 mL of CH_2Cl_2 was added methacryloyl chloride (1.08 mL, 11 mmol) dropwise on ice-water bath with shade and stirred at room temperature. After 12 hours, the solution was washed with pure water (1 time), 3.5% HCl aqueous solution (1 time), pure water (1 time) and 4% $NaHCO_3$ aqueous solution (3 times), respectively. The organic layer was dried over Na_2SO_4 and concentrated to give an orange powder. Yield, 51%. m.p. = 334 K ~ 336 K. ^{1}H NMR (303 K, chloroform-*d*); δ 7.91 (2H, d, *o*-CH), 7.62 (1H, t, *p*-CH), 7.50 (2H, t, *m*-CH), 6.29 (1H, d, NH), 5.76 (1H, t, *trans*-CH), 5.53 (1H, d, CH_2), 5.39 (1H, m, *cis*-CH), 5.28 (1H, d, CH_2), 4.80 (1H, d, Val α-CH), 2.41 (1H, m, Val β-CH), 2.00 (3H, d, CH_3), 1.08 (6H, d, Val CH_3). Anal Calcd for $C_{17}H_{21}N_1O_4$: C, 67.31; H, 6.98; N, 4.62. Found: C, 67.14; H, 6.98; N, 4.61.

Poly(MA-Val-OPac). ^{1}H NMR (303 K, chloroform-*d*); δ 7.85 (2H, br, *o*-CH), 7.57 (1H, br, *p*-CH), 7.45 (2H, br, *m*-CH), 6.39 (1H, br, NH), 5.48 (1H, br, Pac-CH_2), 5.10 (1H, br, Pac-CH_2), 4.40 (1H, br, Val α-CH), 2.17 (1H, br, Val β-CH), 1.74 (2H, br, CH_2), 0.95 (9H, br, Val CH_3 and CH_3).

Poly(MA-Val-OH) (1H). ^{1}H NMR (303 K, Me_2SO-d_6); δ 12.8 (1H, br, COOH), 5.40 (1H, br, NH), 4.05 (1H, br, Val α-CH), 1.90 (1H, br, Val β-CH), 1.23 (2H, br, CH_2), 0.87 (9H, br, CH_3).

3-(Methacryloylamino)-propionic Acid Benzyl Ester (MA-β-Ala-OBzl). H-β-Ala-OBzl•*p*-tosylate (5.00 g, 14 mmol) and triethylamine (3.96 mL, 28 mmol) in 100 mL of CH_2Cl_2 was added methacryloyl chloride (1.39 mL, 14 mmol) dropwise on an ice-water bath and stirred at room temperature and kept out of direct sunlight. After 12 hours, the solution was washed with 3.5% HCl aqueous solution (1 time), pure water (1 time) and 4% $NaHCO_3$ aqueous solution (3 times), respectively. The organic layer was dried over Na_2SO_4 and concentrated to give a yellow solution. Yield, 2.48 g (71%). ^{1}H NMR (303 K, chloroform-*d*): δ 7.39-7.31 (5H, m, phenyl), 6.39 (1H, br, NH), 5.63 (1H, t, *trans*-CH), 5.30 (1H, m, *cis*-CH), 5.15 (2H, s, CH_2), 3.60 (2H, q, H^β), 2.63 (2H, t, H^α), 1.92 (3H, t, CH_3).

Poly(MA-β-Ala-OBzl). ^{1}H NMR (303 K, chloroform-*d*): δ 7.30 (5H, br, phenyl), 6.36 (1H, br, NH), 5.09 (2H, br, CH_2), 3.34 (2H, br, H^β), 2.52 (2H, br, H^α), 1.79-1.65 (2H, br, CH_2), 0.92 (3H, br, CH_3). ^{1}H NMR (303 K, Me_2SO-d_6): δ 7.29 (6H, br, Ar and NH), 5.03 (2H, br, Bzl-CH_2), 3.18 (2H, br, H^β), 2.49 (2H, br, H^α), 1.61 (2H, br, CH_2), 0.89-0.75 (3H, br, CH_3).

Poly(MA-β-Ala-OH) (2H). ^{1}H NMR (303 K, Me_2SO-d_6): δ 12.1 (1H, br, COOH), 7.40 (1H, br, NH), 3.15 (2H, br, H^β), 2.44 (2H, br, H^α), 1.55 (2H, br, CH_2), 0.88-0.72 (3H, br, CH_3).

4-(Methacryloylamino)-butyric Acid Benzyl Ester (MA-γ-Abu-O^{t}Bu). H-γ-Abu-O^{t}Bu•HCl (1.00 g, 3.8 mmol) and triethylamine (1.06 mL, 7.6 mmol) in 100 mL of CH_2Cl_2 was added methacryloyl chloride (0.370 mL, 3.8 mmol) dropwise on an ice-water bath and stirred at room temperature and kept out of direct sunlight. After 12 hours, the solution was washed with 3.5% HCl aqueous solution (1 time), pure water (1 time) and 4% $NaHCO_3$ aqueous solution (3 times), respectively. The organic layer was dried over Na_2SO_4 and concentrated to give a yellow solution. Yield, 830 mg (71%). ^{1}H NMR (303 K, chloroform-*d*): δ 6.75 (1H, br, NH), 5.62 (1H, s, *trans*-CH), 5.22 (1H, s, *cis*-CH), 3.25 (2H, q, H^γ), 2.21 (2H, t, H^α), 1.67 (3H, s, CH_3), 1.76 (2H, m, H^β), 1.36 (9H, s, ^{t}Bu).

Poly(MA-γ-Abu-O^{t}Bu). ^{1}H NMR (303 K, chloroform-*d*): δ 6.13 (1H, br, NH), 3.14 (2H, br, H^{γ}), 2.27 (2H, br, H^{α}), 1.77 (2H, br, H^{β}), 1.45 (9H, br, ^{t}Bu), 1.53 (2H, br, CH_2), 1.2-0.9 (3H, br, CH_3). ^{1}H NMR (303 K, Me_2SO-d_6): δ 7.24 (1H, br, NH), 3.26 (2H, br, H^{γ}), 2.92 (2H, br, H^{α}), 2.15 (2H, br, H^{β}), 1.59 (2H, br, CH_2), 1.39 (9H, s, ^{t}Bu-CH_3), 0.91-0.76 (3H, br, CH_3).

Poly(MA-γ-Abu-OH) (3H). ^{1}H NMR (303 K, Me_2SO-d_6): δ 12.0 (1H, br, COOH), 7.28 (1H, br, NH), 3.58 (2H, br, H^{γ}), 2.93 (2H, br, H^{α}), 2.18 (2H, br, H^{β}), 1.61 (2H, br, CH_2), 0.91-0.77 (3H, br, CH_3).

Isotactic-rich Poly(MA-β-Ala-OBzl). ^{1}H NMR (303 K, chloroform-*d*): δ 7.35-7.26 (5H, br, phenyl), 6.90 (1H, br, NH), 5.09 (2H, br, CH_2), 3.34 (2H, br, H^{β}), 2.52 (2H, br, H^{α}), 1.8-1.6 (2H, br, CH_2), 1.3-0.8 (3H, br, CH_3).

Isotactic-rich Poly(MA-β-Ala-OH) (2^{iso}H). ^{1}H NMR (303 K, Me_2SO-d_6): δ 12.1 (1H, br, COOH), 7.30 (1H, br, NH), 3.14 (2H, br, H^{β}), 2.38 (2H, br, H^{α}), 1.87-1.74 (2H, br, CH_2), 1.50-0.86 (3H, br, CH_3).

Triphenylacetyl chloride. Triphenylacetic acid (5.0 g, 17.3 mmol) in 4.1 mL of thionyl chloride (51.9 mmol) was stirred at 363 K. After 2 hours, the solution was concentrated to give yellow powder. Yield, 5.3 g (~ 100%). ^{1}H NMR (303 K, chloroform-*d*): δ 7.37-7.26 (15H, m, Ar).

3-Methyl-2-(2,2,2-triphenyl-acetylamino)-butyric Acid Benzyl Ester (Ph_3CCO-Val-OBzl). H-Val-OBzl•HCl (795 mg, 3.3 mmol) in 10 mL of CH_2Cl_2 was added triethylamine (0.90 mL, 6.6 mmol) and the solution was stirred. The solution was added triphenylacetyl chloride (1.0 g, 3.3 mmol) in 10 mL of CH_2Cl_2 on an ice-water bath and stirred at room temperature. After 12 hors, the solution was washed with pure water, 3.5% HCl *aq*., 4% $NaHCO_3$ *aq*. and conc. NaCl *aq*., respectively, and dried with Na_2SO_4. The organic layer was concentrated to give a yellow powder and the obtained powder was dried over P_2O_5 under reduced pressure. Yield, 635 mg (40%). ^{1}H NMR (303 K, chloroform-*d*): δ 7.34-7.23 (20H, m, Ar), 6.18 (1H, d, NH), 5.14 (2H, dd, Bzl-CH_2), 4.65 (1H, dd, H^{α}), 2.15 (1H, m, H^{β}), 0.81 and 0.63 (6H, d, H^{γ}).

3-Methyl-2-(2,2,2-triphenyl-acetylamino)-butyric Acid (4H). Ph_3CCO-Val-OBzl (635 mg, 1.33 mmol) in 50 mL of MeOH was stirred under Ar atmosphere during 30 minutes, and the solution was added Pd-C (64 mg) and stirred under Ar atmosphere. After 30 minutes, H_2 gas was bubbled to the solution for 4 hours and the solution was filtrated to remove Pd. The mother liquor was concentrated and the residue was suspended to ether. The solution was concentrated and added *n*-hexane to give white powder. The powder was collected by filtration and dried over P_2O_5 under reduced pressure. Yield, 222 mg (43%). M.p. = 399 ~ 401 K. ^{1}H NMR (303 K, chloroform-*d*): δ 7.30-7.23 (15H, m, Ar), 6.22 (1H, d, NH), 4.45 (1H, d, H^{α}), 2.17 (1H, m, H^{β}), 0.88 and 0.69 (6H, d, H^{γ}). FT-IR (10 mM, in chloroform-*d*, at r.t.): ν(NH) = 3435 cm^{-1}, ν(CO) = 1755 and 1672 cm^{-1} (COOH and CONH, respectively). Anal. Calcd for $C_{25}H_{25}NO_3$: C, 77.49; H, 6.50; N, 3.61. Found: C, 76.66; H, 6.51; N, 3.63.

Tetramethylammonium 3-Methyl-2-(2,2,2-triphenyl-acetylamino)-butyrate ($4NMe_4$). **4H** (100 mg, 258 μmol) in 5 mL of MeOH was added 25 % NMe_4OH methanol solution (108.8 μL, 258 μmol) and the mixed solution was stirred for several minutes. The solution was concentrated and the residue was washed with ether to give a white powder. ^{1}H NMR (303 K, chloroform-*d*): δ 7.37-7.20 (15H, m, Ar), 6.64 (1H, d, NH), 4.26 (1H, d, H^{α}), 2.26 (1H, m, H^{β}), 0.93 and 0.77 (6H, d, H^{γ}). FT-IR (10 mM, in chloroform-*d*, at r.t.): ν(NH) = 3377 cm^{-1}, ν(CO) = 1597 and 1652 cm^{-1} (COO^- and CONH, respectively).

3-(2,2,2-Triphenyl-acetylamino)-propionic Acid Benzyl Ester (Ph_3CCO-β-Ala-OBzl). H-β-Ala-OBzl•*p*-tosylate (573 mg, 1.63 mmol) in 10 mL of CH_2Cl_2 was added triethylamine (0.454 mL, 3.26 mmol) and the mixed solution was stirred. The solution was added triphenylacetyl chloride (500 mg, 1.63 mmol) in 10 mL of CH_2Cl_2 on an ice-water bath and stirred at room temperature. After 12 hors, the solution was washed with pure water, 3.5% HCl *aq*., 4% $NaHCO_3$ aq. and conc. NaCl *aq*., respectively, and dried with Na_2SO_4. The organic layer was concentrated and the residue was suspended to ether. The solution was concentrated and added *n*-hexane to give a white powder. The

obtained powder was collected by filtration and dried over P_2O_5 under reduced pressure. Yield, 281 mg (38%). ^{1}H NMR (303 K, chloroform-*d*): δ 7.34-7.20 (20H, m, Ar), 6.26 (1H, br, NH), 5.03 (2H, s, Bzl-CH_2), 3.59 (2H, q, H^β), 2.58 (2H, t, H^α).

3-(2,2,2-Triphenyl-acetylamino)-propionic Acid (5H). Ph_3CCO-β-Ala-OBzl (281 mg, 647 μmol) in 5 mL of hot EtOH was added NaOH (40.0 mg, 1.00 mmol) in 2 mL aqueous solution. The solution was stirred at 353 K during a day and concentrated to remove EtOH. The residue was suspended to a pure water and the solution was stirred at 353 K. After a day, 3.5% HCl *aq*. was added to the solution to give white powder, and the powder was collected by filtration and dried over P_2O_5 under reduced pressure. Yield, 200 mg (86%). M.p. = 441 ~ 443 K. ^{1}H NMR (303 K, chloroform-*d*): δ 7.31-7.22 (15H, m, Ar), 6.31 (1H, br, NH), 3.59 (2H, m, H^β), 2.60 (2H, t, H^α). FT-IR (10 mM, in chloroform-*d*, at r.t.): ν(NH) = 3437 cm^{-1}, ν(CO) = 1749 and 1663 cm^{-1} (COOH and CONH, respectively). Anal. Calcd for $C_{23}H_{21}NO_3$: C, 76.86; H, 5.89; N, 3.90. Found: C, 75.67; H, 5.81; N, 3.92.

Tetramethylammonium 3-(2,2,2-Triphenyl-acetylamino)-propionate ($5NMe_4$). 5H (100 mg, 278 μmol) in 5 mL of MeOH was added 25% NMe_4OH methanol solution (117.2 μL, 278 μmol) and the mixed solution was stirred for several minutes. The solution was concentrated and the residue was washed with ether to give a white powder. The powder was crystallized with the mixed solution of MeCN and ether. ^{1}H NMR (303 K, chloroform-*d*): δ 7.32-7.18 (15H, m, Ar), 7.07 (1H, br, NH), 3.57 (2H, m, H^β), 2.32 (2H, t, H^α). FT-IR (10 mM, in chloroform-*d*, at r.t.): ν(NH) = 3019 cm^{-1}, ν(CO) = 1578 and 1653 cm^{-1} (COO^- and CONH, respectively).

4-(2,2,2-Triphenyl-acetylamino)-butyric Acid Benzyl Ester (Ph_3CCO-γ-Abu-OBzl). H-γ-Val-OBzl•*p*-tosylate (1.00 g, 3.26 mmol) in 10 mL of CH_2Cl_2 was added triethylamine (0.91 mL, 6.52 mmol) and the solution was stirred. The solution was added triphenylacetyl chloride (1.19 g, 3.26 mmol) in 10 mL of CH_2Cl_2 on an ice-water bath and stirred at room temperature. After 12 hors, the solution was washed with pure water, 3.5% HCl *aq*., 4 % $NaHCO_3$ *aq*. and conc. NaCl *aq*., respectively, and dried with Na_2SO_4. The organic layer was concentrated to give a white powder and the obtained

powder was dried over P_2O_5 under reduced pressure. Yield, 536 mg (35%). ^{1}H NMR (303 K, chloroform-*d*): δ 7.29-7.14 (20H, m, Ar), 5.80 (1H, br, NH), 4.99 (2H, s, Bzl-CH_2), 3.28 (2H, m, H^{γ}), 2.21 (2H, t, H^{α}), 1.73 (2H, m, H^{β}).

4-(2,2,2-Triphenyl-acetylamino)-butyric Acid (6H). Ph_3CCO-γ-Abu-OBzl (528 mg, 1.14 mmol) in 10 mL of MeOH was added 1 M NaOH *aq*. (1.2 mL, 1.20 mmol) and the solution was stirred at 313 K. After 12 hours, the solution was concentrated to remove MeOH and the residue was added 3.5% HCl *aq*. to give a white powder. The white powder was collected by filtration and washed with pure water, and dried over P_2O_5 under reduced pressure. Yield, 381 mg (89%). M.p. = 433 ~ 437 K. ^{1}H NMR spectra (303 K, chloroform-*d*): δ 9.62 (1H, br, COOH), 7.32-7.23 (15H, m, Ar), 5.94 (1H, br, NH), 3.39 (2H, m, H^{γ}), 2.27 (2H, t, H^{α}), 1.79 (2H, m, H^{β}). FT-IR (10 mM, in chloroform-*d*, at r.t.): ν(NH) = 3435 cm^{-1}, ν(CO) = 1746 and 1664 cm^{-1} (COOH and CONH, respectively). Anal. Calcd for $C_{24}H_{23}NO_3$: C, 77.19; H, 6.21; N, 3.75. Found: C, 77.26; H, 6.11; N, 3.48.

Tetramethylammonium 4-(2,2,2-Triphenyl-acetylamino)-butyrate (6NMe_4). 6H (100 mg, 268 μmol) in 5 mL of MeOH was added 25% NMe_4OH methanol solution (112.8 μL, 268 μmol) and the mixed solution was stirred for several minutes. The solution was concentrated and the residue was washed with ether to give a white powder. ^{1}H NMR spectra (303 K, chloroform-*d*): δ 7.46-7.34 (15H, m, Ar), 6.13 (1H, br, NH), 2.30 (2H, m, H^{γ}), 1.89 (2H, t, H^{α}), 1.03 (2H, m, H^{β}). FT-IR (10 mM, in chloroform-*d*, at r.t.): ν(NH) = 3011 cm^{-1}, ν(CO) = 1570 and 1656 cm^{-1} (COO^- and CONH, respectively).

Deuteration of Amide Proton of 5NMe_4 and 6NMe_4 (7 and 8, respectively). The detuteration of the amide NH of **5NMe_4** was performed by an exchange reaction with methanol-d_1 (CH_3OD). Tetramethylammonium 3-(2,2,2-triphenyl-*N*-deuterium-acetylamino)-propionate (**7**) was obtained as white powder by concentration of the CH_3OD solution of **6NMe_4**. Tetramethylammonium 4-(2,2,2-triphenyl-*N*-deuterium-acetylamino)-butyrate (**8**) was prepared by the same procedure.

Crystallization of $CaCO_3$ Composites in the Presence of Model Carboxylate Ligands. Crystalline model ligand–$CaCO_3$ composites were obtained by the same procedures in the case of polymer ligands.

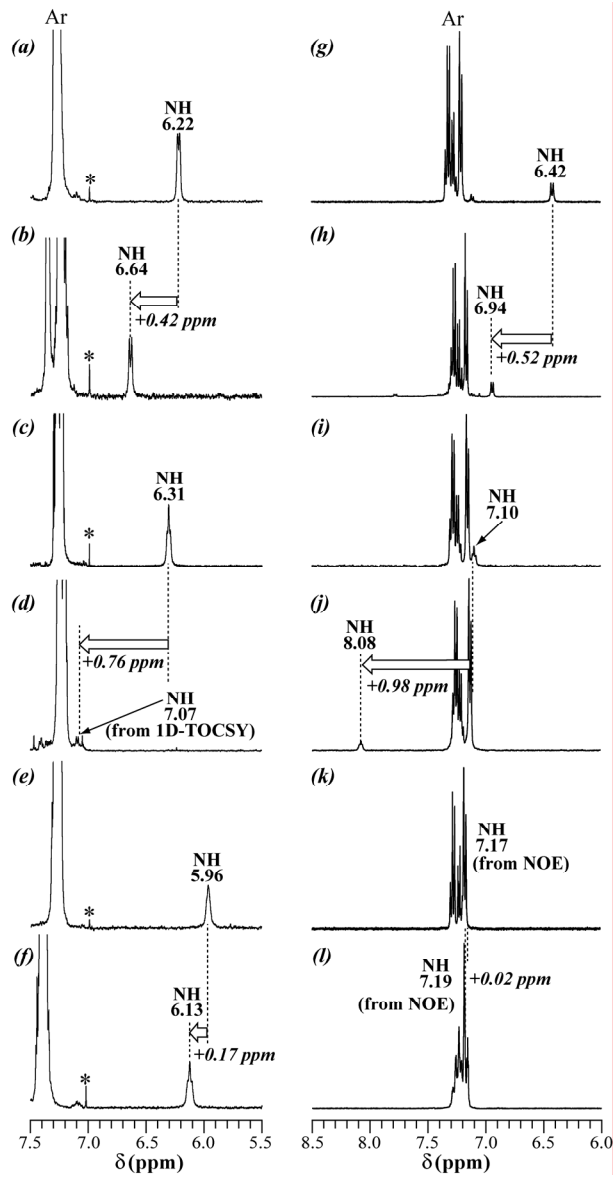

Fig. S1. ^{1}H NMR spectra of (a) **4H**, (b) **4NMe$_4$**, (c) **5H**, (d) **5NMe$_4$**, (e) **6H**, and (f) **6NMe$_4$** (303 K, chloroform-*d*), and (g) **4H**, (h) **4NMe$_4$**, (i) **5H**, (j) **5NMe$_4$**, (k) **6H**, and (l) **6NMe$_4$** (303 K, Me_2SO-d_6).

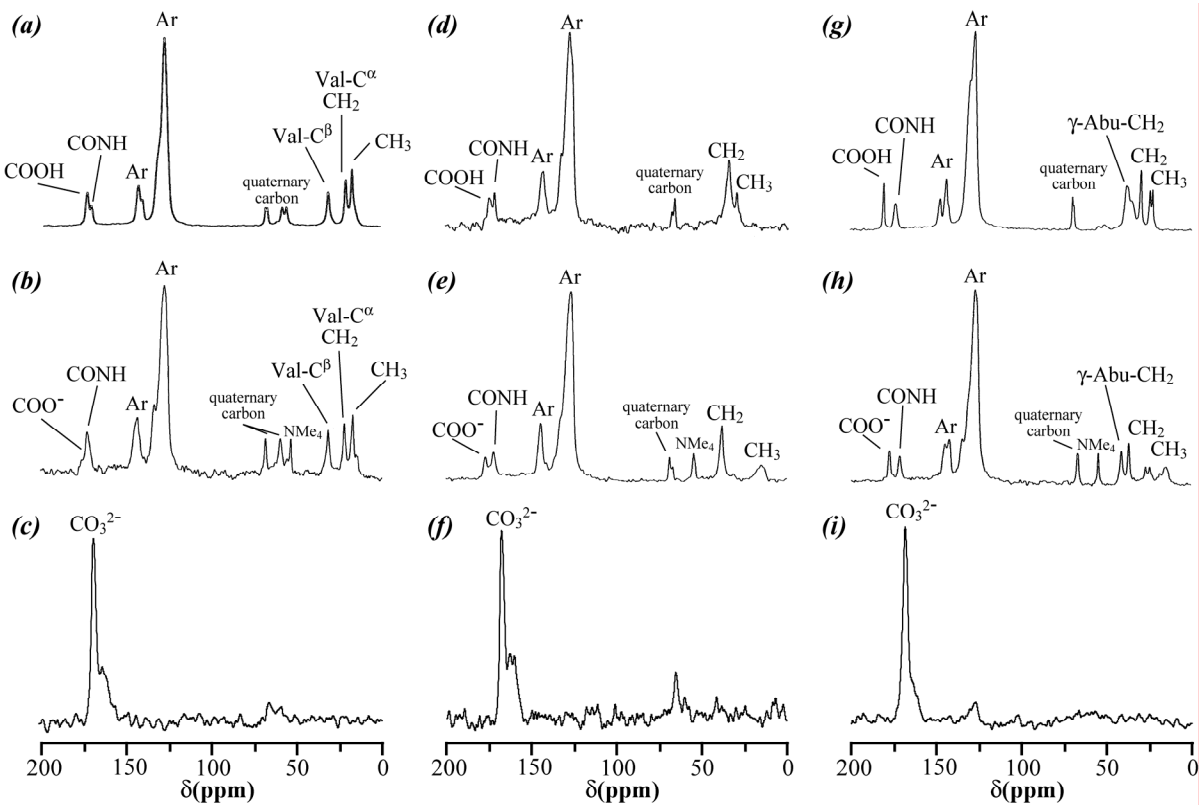

Fig. S2. Solid-state ^{13}C CP/MAS NMR spectra of (a) **4H**, (b) **4NMe$_4$**, (c) $CaCO_3$ composite in the presence of **4**, (d) **5H**, (e) **5NMe$_4$**, (f) $CaCO_3$ composite in the presence of **5**, (g) **6H**, (h) **6NMe$_4$**, and (i) $CaCO_3$ composite in the presence of **6**. The model ligands were easily dislodged from $CaCO_3$ crystal during the washing process. The spectra in (c), (f), and (i) were obtained after the washing process.

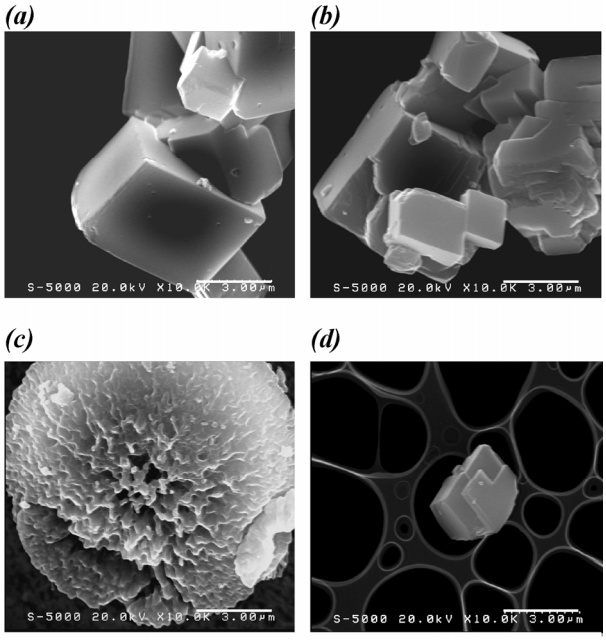

Fig. S3. FE/SEM images of (a) $CaCO_3$ composite in the presence of **4**, (b) $CaCO_3$ composite in the presence of **5**, (c) $CaCO_3$ composite in the presence of **6**, and (d) $CaCO_3$ composite in the absence of model ligands. The model ligands were easily dislodged from $CaCO_3$ crystal during the washing process. These images were obtained after the washing process (20 kV accelearation voltage, × 10,000). The scale bars in these images show 3 mm.

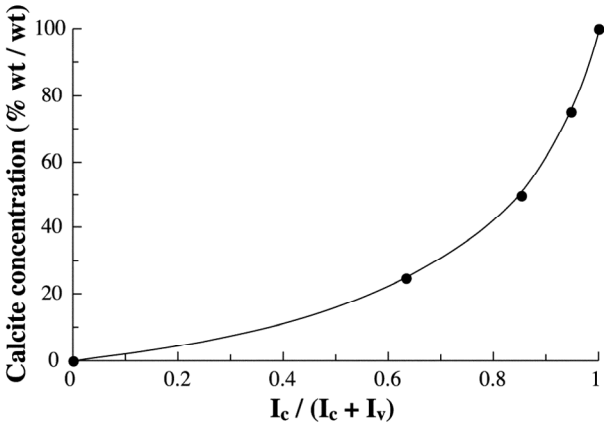

Fig. S4. A calibration curve for determining the component ratio of calcite and vaterite by the XRD analysis. The calcite content is plotted as a function of the relative intensitiy $I_c/(I_c + I_v)$ between the (104) calcite peak, I_c, and the (101) vaterite peak, I_v.