Supporting Information (JA0270569)

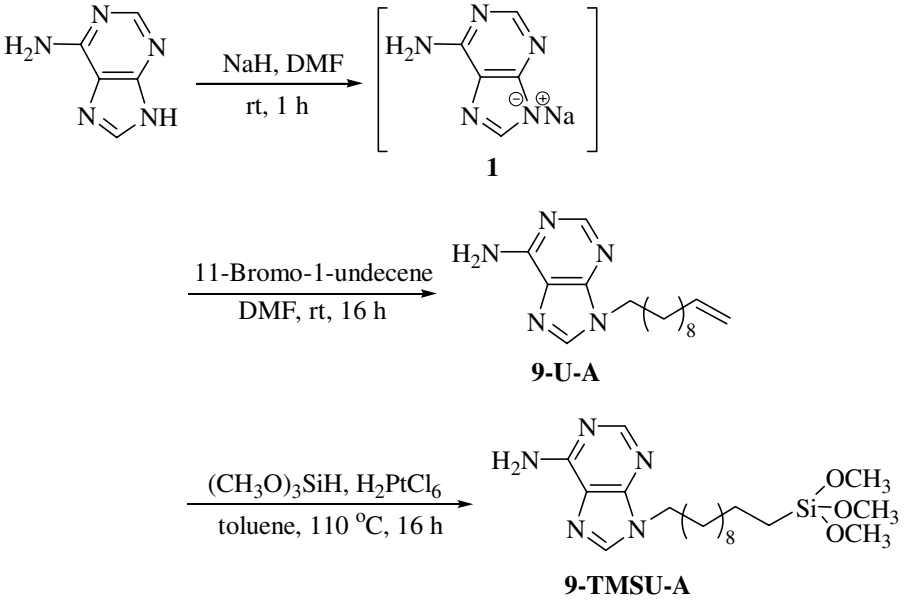
Organization of Microcrystals on Glass by Adenine-Thymine Hydrogen Bonding

Supporting Information

Synthesis of Zeolite-A. The zeolite-A used in this study was synthesized from a gel whose composition was AIP:TEOS:TMAOH:NaCl:H_2O = 0.7:3:1.85:0.74:300, where, AIP, TEOS, and TMAOH represent aluminum isopropoxide, tetraethyl orthosilicate, and tetramethylammonium hydroxide, respectively. Distilled water (70 mL) was introduced into a plastic beaker containing TMAOH (Aldrich, 33.6 g, 25 wt%). AIP (Acros, 7.5 g) and TEOS (Acros, 33 g) were sequentially added to the aqueous solution of TMAOH and then stirred for 2 h for hydrolysis. An aqueous solution of sodium chloride (1.15 g NaCl dissolved in 90 mL of H_2O) was subsequently added into the solution and then stirred for 12 h. The top of the plastic beaker was wrapped by using a piece of plastic film and a rubber band, and the plastic beaker was placed in an oven whose temperature was maintained at 100 °C. After elapse of 7 d, the beaker was removed from the oven and fresh sodium chloride solution (1.15 g NaCl dissolved in 90 mL of H_2O) was added into the plastic beaker while the turbid solution was vigorously stirred. After wrapping the top, the plastic beaker was also placed for 3 d in the oven at 100 °C. The resulting nearly monodisperse zeolite A crystals were purified by repeated washing and sedimentation cycle.

Synthesis of ZSM-5. ZSM-5 crystals were synthesized from a gel consisting of TEOS, TPAOH, $NaAlO_2$, and H_2O with the molar ratio of TEOS:TPAOH:$NaAlO_2$:H_2O = 0.8:0.1:0~0.08:50, where the composition of $NaAlO_2$ was Na_2O = 31~35% and Al_2O_3 = 34~39%. TEOS was first hydrolyzed in the TPAOH solution. Sodium aluminate solution was subsequently added into the clear gel. The final clear gel was further stirred for additional 12 h and transferred into a Teflon container placed in an autoclave. The hydrothermal reaction was carried out with stirring at 160 °C for 40 h. The obtained ZSM-5 crystals were thoroughly washed with copious amounts of water and dried at 120 °C for 3 h prior to use.

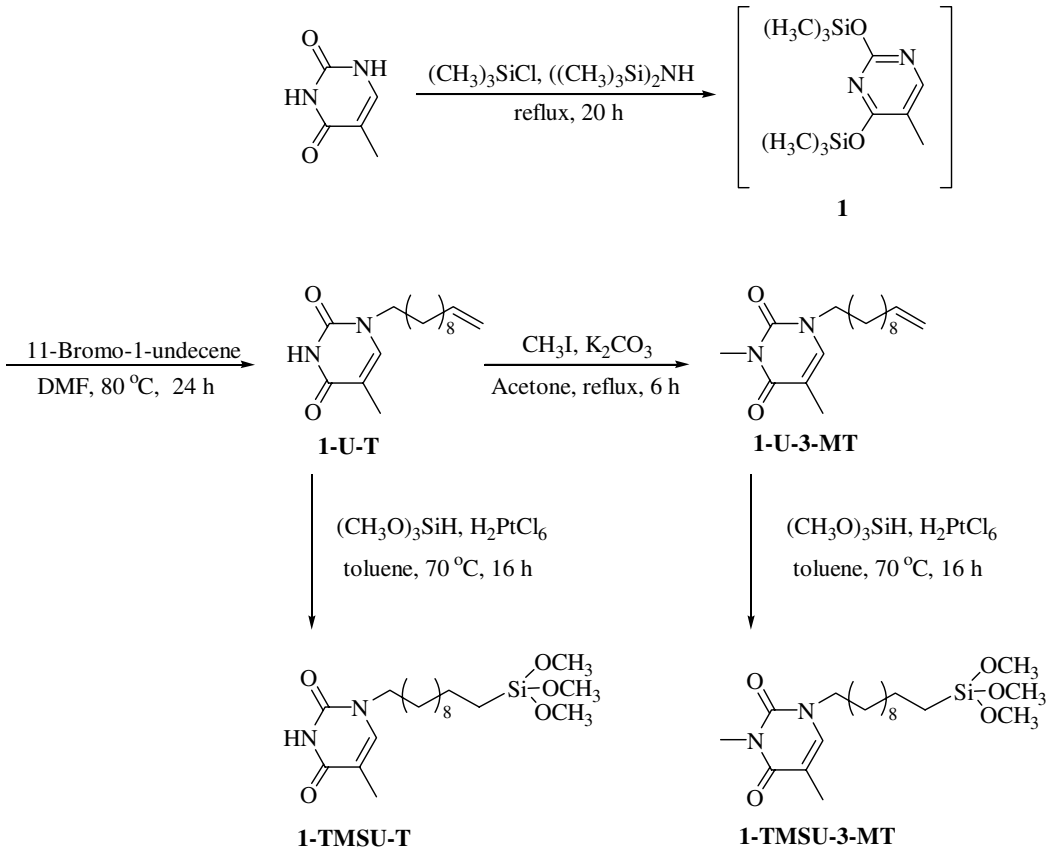
Preparation of 9-TMSU-A. 9-TMSU-A was synthesized according to the following scheme.



Preparation of 9-Undecylenyladenine (9-U-A). Adenine (2.73 g, 0.020 mol) and NaH (0.81 g, 0.53 mmol) were introduced into a two-necked round-bottomed flask (50 mL) charged with anhydrous DMF (30mL). Stirring the heterogeneous mixture for 1 h led to formation of a white suspension of **1**. 11-Bromo-1-undecene (3.1 g, 0.013 mol) was slowly added into the heterogeneous mixture with the help of a hypodermic syringe over a period of 5 min, and the reaction mixture was stirred for 16 h at room temperature. The reaction mixture was passed through a glass frit, and the collected clear yellow solution was concentrated by rotary evaporation to afford a yellow solid. Recrystallization from CH_3OH afforded 9-U-A as a white solid**.** $C_{16}H_{25}N_5$ 287.41: yield 3.06 g (55 %), ^{1}H NMR ($CDCl_3$, δ/ppm); 8.36 (s, 1H, CH), 7.79 (s, 1H, CH), 5.84 (m, 1H, CH), 5.59 (bs, 2H, NH_2), 4.95 (m, 2H, -CH=CH_2), 4.17 (t, 2H, J=6 Hz, NCH_2), 2.05 (m, 2H, CH_2), 1.90 (m, 2H, CH_2), 1.2~1.1 (m, 12H, -CH_2-).

Preparation of 9-Trimethoxysilylundecyladenine (9-TMSU-A). Anhydrous toluene (5 mL) and hydrogen hexachloroplatinate(IV) hydrate (catalytic amount, ~10 mg) were introduced into a round-bottomed flask containing 9-U-A (287 mg, 1 mmol) under argon. Subsequently, trimethoxysilane (0.3 mL, 293 mg, 2.4 mmol) was introduced into the mixture using a hypodermic syringe and the mixture was refluxed for 16 h. After cooling to room temperature, the mixture was immediately filtered through cotton fiber filter by applying argon pressure. Upon concentrating the filtrate, 9-TMSU-A was obtained as pale yellow oil. $C_{19}H_{35}O_3N_5Si$ 409.60: yield 266 mg (65 %), ^{1}H NMR ($CDCl_3$, δ/ppm); 8.36 (s, 1H, CH), 7.79 (s, 1H, CH), 5.87 (bs, 2H, NH_2), 4.17 (t, 2H, J=6 Hz, NCH_2), 3.56 (s, 9H, CH_3O), 1.90 (m, 2H, CH_2), 1.2~1.1 (m, 14H, -CH_2-), 0.85 (m, 2H, CH_2CH_2Si), 0.62 (m, 2H, CH_2Si).

Preparation of 1-TMSU-T and 1-TMSU-3-MT. 1-TMSU-T and 1-TMSU-3-MT were synthesized according to the following scheme.



Preparation of 1-Undecylenylthymine (1-U-T): Thymine (3.1 g, 25 mmol), 1,1,1,3,3,3-hexamethyldisilazane (16 mL, 76 mmol), and chlorotrimethylsilane (1.6 mL, 12 mmol) were introduced into a two-necked, round-bottomed flask (50 mL). The frothy mixture was refluxed for 20 h, during which NH_4Cl collected in the condenser. After cooling to room temperature, the excess disilazane was removed under vacuum to afford thymine bis(tri-methylsilyl) ether (**1**) as colorless oil. DMF (10 mL) and 11-Bromo-1-undecene (17.5 g, 0.075 mol) were introduced into the flask containing the oil under a counter flow of argon. The resulting solution was heated at 80 ^oC for 24 h. Subsequently, ice water (150 mL) was added into the solution, and the mixture was stirred for 30 min, and the organic product was extracted with 200 mL portions of CH_2Cl_2. The organic phase was then dried over $MgSO_4$, filtered, and concentrated by rotary evaporation to yield yellow oil. The oil was triturated with ca. 15 mL of pentane at –20 ^oC to afford a yellow solid. Recrystallization from $CHCl_3$ and pentane or hexane afforded 1-U-T (**2**) as fine pale yellow crystals. $C_{16}H_{26}O_2N_2$ 278.39: yield 4.18 g (60 %), ^1H NMR ($CDCl_3$, δ/ppm); 8.16 (bs, 1H, NH), 6.95 (s, 1H, CH), 5.84 (m, 1H, CH), 4.95 (m, 2H, -CH=CH_2), 3.65 (t, 2H, J = 6 Hz, CH_2), 2.0~1.25 (m, 19H, -CH_2-).

Preparation of 1-Trimethoxysilylundecylthymine (1-TMSU-T): Anhydrous toluene (5 mL) was introduced into a round-bottomed flask charged with 1-U-T (278 mg, 1 mmol) and hydrogen hexachloroplatinate (IV) hydrate (~10 mg) under argon. Trimethoxysilane (0.3 mL, 293 mg, 2.4 mmol) was introduced into the mixture under argon using a hypodermic syringe and the mixture was stirred at 70 ^oC for 16 h. After cooling to room temperature, the mixture was immediately filtered through cotton fiber by applying argon pressure. Upon concentrating the filtrate, 1-TMSU-T was obtained as pale yellow oil. $C_{19}H_{36}O_5N_2Si$ 400.59: yield 280 mg (70 %), ^1H NMR ($CDCl_3$, δ/ppm); 8.16 (s, 1H, NH), 6.95 (s, 1H, CH), 3.68 (t, 2H, J=6 Hz, NCH_2), 3.56 (s, 9H, CH_3O), 1.60 (s, 3H, CH_3), 1.92~1.3 (m, 16H, -CH_2-), 0.9 (m, 2H, CH_2CH_2Si), 0.83 (t, 2H, J=8 Hz, CH_2Si).

Preparation of 1-Undecylenyl-3-methylthymine (1-U-3-MT): Dry K_2CO_3 (166 mg, 1.2 mmol) and CH_3I (0.25 mL, 4 mmol) were added to a solution of dry acetone (10 mL) dissolved with 1-U-T (278 mg, 1 mmol). After the reaction mixture was refluxed for 6 h, the mixture was concentrated to dryness. The residue was dissolved in ethyl acetate (30 mL) and washed with brine (2 x 30 mL). The organic layer was dried ($MgSO_4$), filtered, and evaporated to dryness. The residue was purified by flash column chromatography (2:1 hexane/ethyl acetate) to afford 1-U-3-MT as colorless liquid. $C_{17}H_{28}O_2N_2$ 292.42 yield 219.32 mg (75 %), ^1H NMR ($CDCl_3$, δ/ppm); 6.95 (s, 1H, CH), 5.84 (m, 1H, CH), 4.95 (m, 2H, -CH=CH_2), 3.65 (t, 2H, J = 6 Hz, CH_2), 3.35 (s, 3H, CH_3), 2.0~1.25 (m, 19H, -CH_2-).

Preparation of 1-Trimethoxysilylundecyl-3-methylthymine (1-TMSU-3-MT): Anhydrous toluene (5 mL) and hydrogen hexachloroplatinate (IV) hydrate (~10 mg) were introduced into a round-bottomed flask containing 1-U-MT (292 mg, 1 mmol) under argon. Trimethoxysilane (0.3 mL, 293 mg, 2.4 mmol) was introduced into the mixture under argon using a hypodermic syringe and the mixture was stirred at 70 ^oC for 16 h. After cooling to room temperature, the mixture was immediately filtered through double pads of cellite and charcoal by applying argon pressure. Upon concentrating the filtrate, 1-TMSU-3-MT was obtained as pale yellow liquid. $C_{20}H_{38}O_5N_2Si$ 414.62: yield 290 mg (70 %), ^1H NMR ($CDCl_3$, δ/ppm); 6.95 (s, 1H, CH), 3.68 (t, 2H, J=6 Hz, NCH_2), 3.56 (s, 9H, CH_3O), 3.35 (s, 3H, CH_3), 1.60 (s, 3H, CH_3), 1.92~1.3 (m, 16H, -CH_2-), 0.9 (m, 2H, CH_2CH_2Si), 0.83 (t, 2H, J=8 Hz, CH_2Si).

Preparation of A-Tethering Glass Plates (A-GL). A Teflon support mounting ten pieces of glass plate (1.8 × 1.8 × 0.2 mm) was placed in a round-bottomed flask charged with a toluene solution of 9-TMSU-A (1 mM, 30 mL), and the solution was refluxed for 1 h. After cooling to room temperature the glass plates were removed from the flask, successively washed with copious amounts of toluene and ethanol, and dried by blowing a gentle stream of pure nitrogen.

Preparation of T- or 3-MT-Tethering Zeolite Crystals Zeolite-A or ZSM-5 (100 mg) was introduced into a round-bottomed flask charged with toluene (30 mL) and the heterogeneous mixture was sonicated for 10 min to thoroughly disperse zeolite crystals in the solvent. Into the toluene suspension of zeolite crystals 11 μL of the stock solution of 9-TMSU-T or 9-TMSU-3-MT in toluene (274 mM) was introduced and the heterogeneous mixture was refluxed for 1 h under argon. After cooling to room temperature the zeolite crystals were isolated by centrifugation, and washed with fresh anhydrous toluene. The centrifugation-wash cycle was repeated for additional 4 times, and the cycle was repeated for 5 times by employing ethanol as the solvent. The resulting zeolite crystals were finally dried under

vacuum.

Demonstration of the Presence of A, T, and 3-MT on Glass and Zeolite Crystals by UV-vis Spectrophotometry.

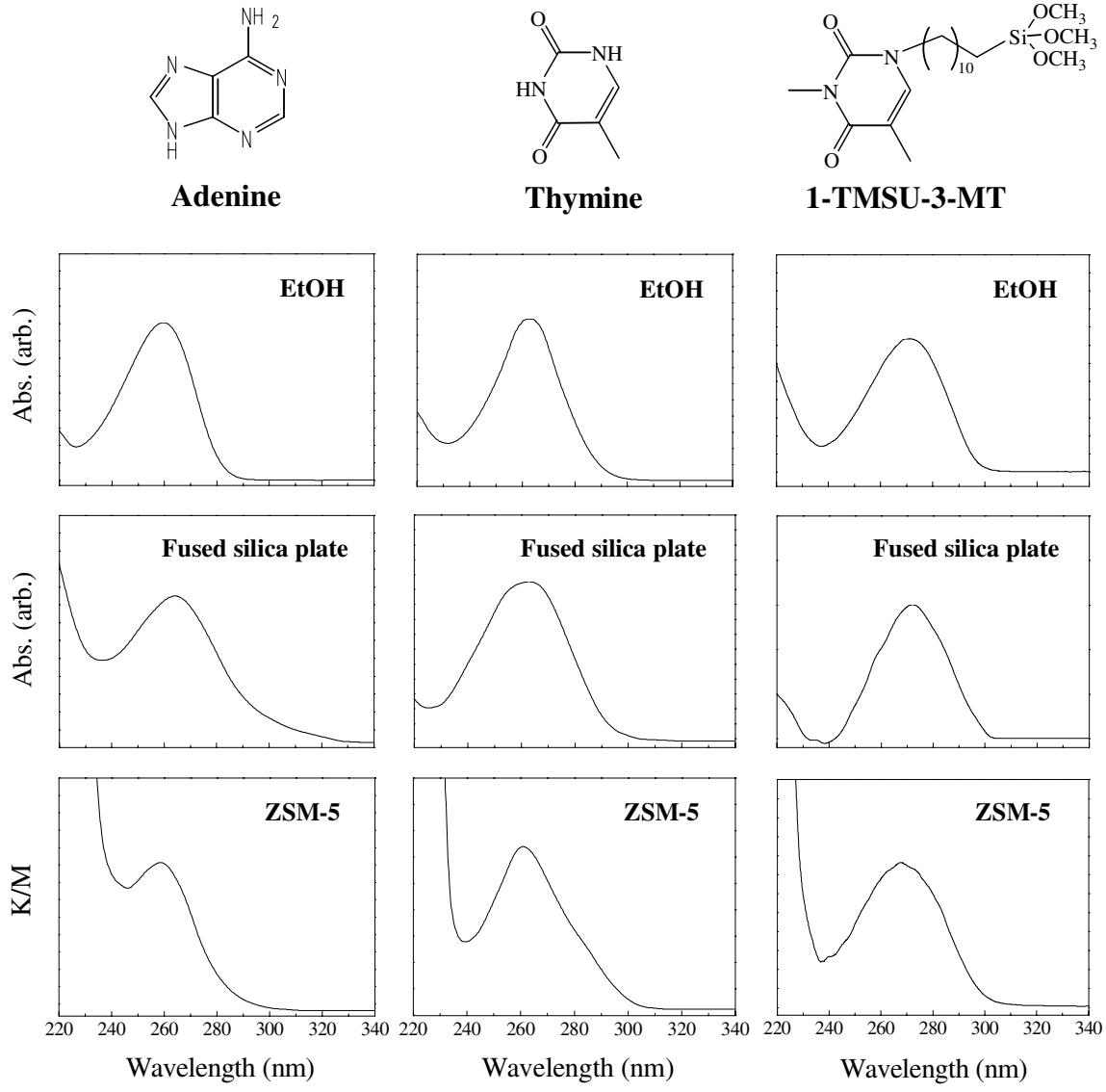


Figure SI-1. UV-vis spectra of (top) ethanol solutions of A, T, and 1-TMSU-3-MT and (middle) fused silica plates treated with 9-TMSU-A, 1-TMSU-T, and 1-TMSU-3-MT, respectively, and (bottom) diffuse reflectance UV-vis spectra of ZSM-5 crystals treated with 9-TMSU-A, 1-TMSU-T, and 1-TMSU-3-MT, respectively (as indicated). The similarity between the spectra of the corresponding DNA base and modified DNA base in solution and on solid supports demonstrates that A, T, and 3-MT groups are readily tethered on the surfaces of fused silica (glass) plates and zeolite crystals upon reaction with TMSU-tethering A, T, and 3-MT, respectively, under the experimental conditions given

in the main text.

Demonstration of The Essentiality of A-T Hydrogen Bonding for the Monolayer Assembly of T-ZSM-5 on A-GL.

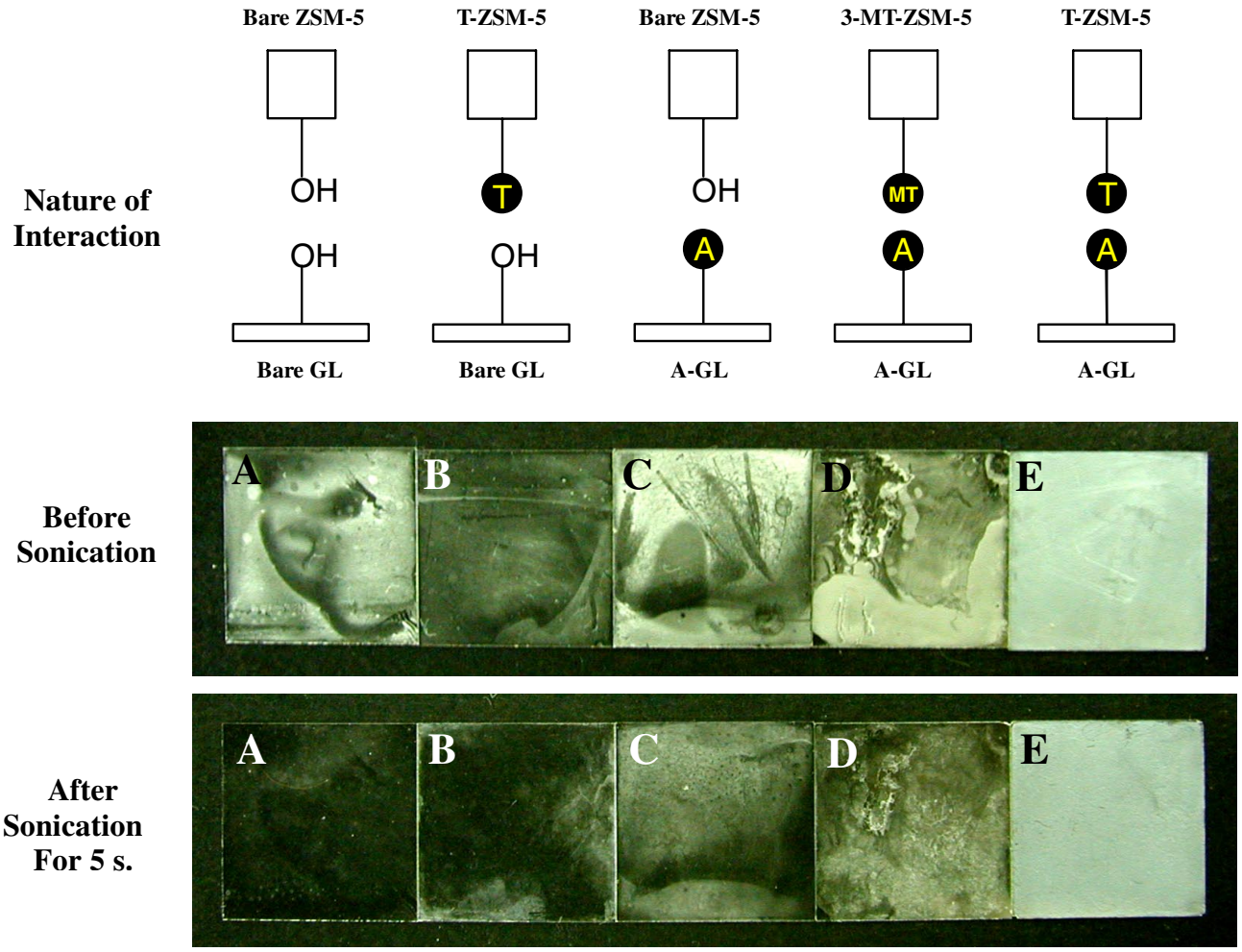


Figure SI-2. Digital camera images of various glass plates with two different types of surface modification (as indicated) that were removed after gentle shaking for 3 h in the corresponding aqueous solution dispersed with either bare ZSM-5, T-ZSM-5, or 3-MT-ZSM-5 crystals (as indicated) before and after 5-s sonication (as indicated). The result clearly shows that the presence of T on ZSM-5 and A on GL is essential for the monolayer assembly of zeolite microcrystals on glass. (3-MT group was much more hydrophobic than A and T. As a result, unlike T-ZSM-5 crystals, 3-MT-ZSM-5 crystals tended to float on top of water for more than 3 h upon keeping it still at room temperature. Although reluctantly, the zeolite crystals dispersed into water upon prolonged shaking. Therefore, for the above control experiment, we employed a thoroughly dispersed aqueous solution of 3-MT-ZSM-5 crystals. The measured water contact angles of the glass plates were bare glass; < 5°, A-GL; 75°, T-

GL; 68°, and 3-MT-GL; 96°.)

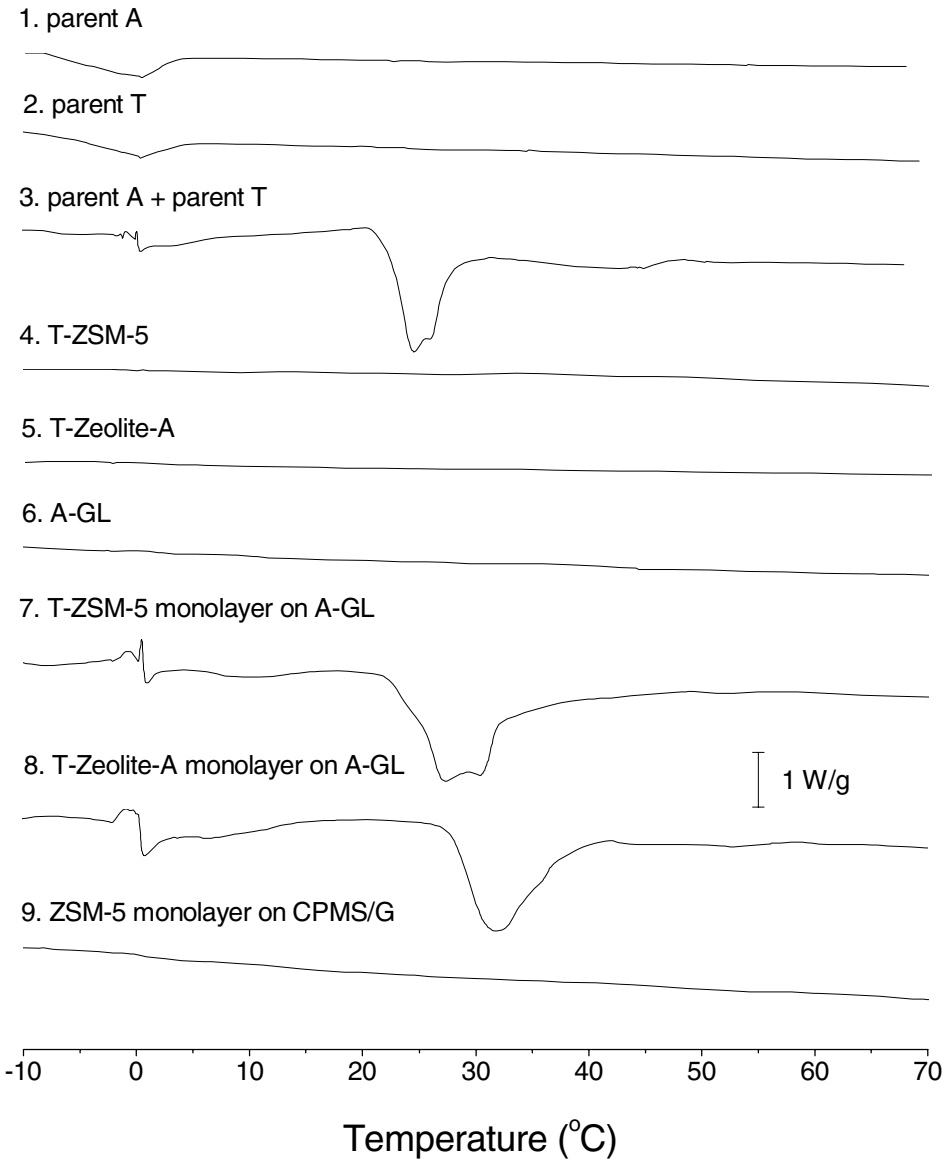


Figure SI-3. DSC curves of (1) parent, unmodified A powder, (2) parent, unmodified T powder, (3) the mixture of parent A and parent T powders, (4) T-ZSM-5, (5) T-zeolite-A, (6) A-GL, the glass plate (A-GL) covered by a monolayer of (7) T-ZSM-5 and (8) T-zeolite-A crystals, respectively, and (9) the glass plate covered by a monolayer of ZSM-5 crystals assembled on the glass plate by propyl ether covalent linkage prepared according to the method described in ref 4d in the main text. The curves were obtained from a TA instrument (Model DSC 2010) and each sample (total weight of ~20 mg) was loaded in the dry state into an aluminum sample cup (Al Hermetic cell) and an empty cup was used as

the reference. The temperature was increased at a rate of 5 °C min^{-1}.