

Supporting Information

for

A Highly Breathable Organic-Inorganic Barrier Material that Blocks the Passage of Mustard Agent Simulant Vapor

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Materials and General Procedures. All reagents were purchased from commercial suppliers (e.g., Sigma-Aldrich, Fisher Scientific, TCI America, and 3M) and used as received without further purification. The H₂O used for synthesis was purified and de-ionized, with resistivity greater than 12 MΩ cm¹. All chemical syntheses and manipulations did not require air- or water-free conditions, unless otherwise noted. Silica gel purification was performed using 230–400 mesh, normal-phase silica gel purchased from Sorbent Technologies.

Instrumentation. ¹H and ¹³C NMR spectra were obtained using a Bruker 300 Ultrashield™ (300 MHz for ¹H) or an Inova 400 (400 MHz for ¹H) spectrometer. Chemical shifts are reported in ppm relative to residual non-deuterated solvent. Fourier-transform infrared (FT-IR) spectroscopy measurements on thin films were performed using a Nicolet 6700 IR spectrometer with the attenuated total reflectance (ATR) attachment (Smart-ARK). High-resolution mass spectrometry (HRMS) analysis with electrospray (ES) was performed by the Central Analytical Facility in the Dept. of Chemistry and Biochemistry at the University of Colorado, Boulder. Photopolymerizations were conducted using a CL-1000 ultraviolet cross-linking oven (UVP, Inc.).

NaY particles.¹ Aluminum isopropoxide (98 wt %) (6.88 g, 33.7 mmol) was combined with tetramethylammonium hydroxide (25 wt % in H₂O) (29.83 g, 327.3 mmol) and deionized H₂O (40.15 g, 2.229 mol) in a 250-mL polypropylene bottle. This mixture was stirred until the solution became clear. Tetramethylammonium bromide (98 wt %) (2.39 g, 15.5 mmol) was then added to the clear solution with rigorous stirring, followed by NaOH (98 wt %) (0.0648 g, 1.62 mmol). To this clear solution, Ludox AS-40 (11.03 g, 183.6 mmol) was added drop-wise with rigorous stirring. The resulting reaction solution was then sealed and stirred at room temperature for 3 days. At the end of 3 days, the solution was transferred to an oil bath and heated at 100 °C for 4 days. The resulting milky solution was then centrifuged at 8000 rpm for 20 min and then decanted. The collected zeolite particles were re-dispersed in de-ionized H₂O (80 mL). This process dispersion, centrifugation, and decantation process was repeated three times. The isolated solid zeolite powder was then calcined at 600 °C for 8 h to remove the tetraalkylammonium structure-directing agents. Chemical and structural analysis of the prepared NaY particles were consistent with data in the literature.¹

1-(2,3-Dihydroxypropyl)-3-vinylimidazolium bis(trifluoromethanesulfon-imide) (2).² Synthesized from 1-vinylimidazole, 1-chloro-2,3-propanediol, and lithium bis(trifluoromethanesulfon-imide) (LiTf₂N) (i.e., Fluorad™ Lithium Trifluoromethane Sulfonimide from the 3M Company) as previously described in the literature.² Chemical

characterization data for the synthesized monomer were consistent with those reported in the literature.²

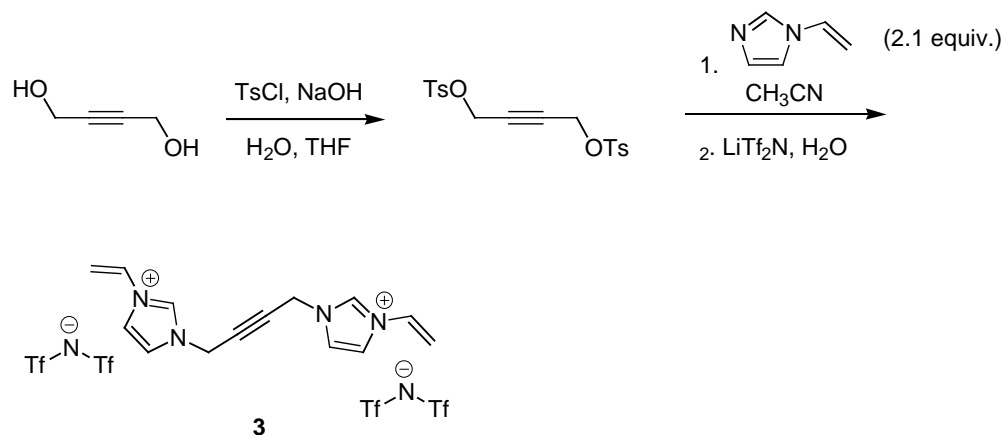


Figure S1. Reaction scheme for the preparation of cross-linking monomer **3**.

2-Butyne-1,4-diol ditosylate. 2-Butyne-1,4-diol (4.30 g, 50.0 mmol) was dissolved in THF (100 mL) and combined with NaOH (7.00 g, 175 mmol) dissolved in water (100 mL) in a round bottom flask. The flask was cooled to 0 °C in an ice bath, and a solution of *p*-toluenesulfonyl chloride (20.97 g, 110.0 mmol) in THF (150 mL) was added drop-wise. The resulting mixture was then stirred at 0 °C for 2 h. The product was then extracted with ethyl acetate (2 x 250 mL) and washed with saturated NaHCO₃ (3 x 100 mL), water (2 x 100 mL), and then brine (100 mL). The organic layer was dried over anhydrous MgSO₄, filtered, and then concentrated to give the product as a grey solid (19.5 g, 99%). ¹H NMR (400 MHz, CDCl₃): δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.39–7.34 (m, 2H), 4.59 (s, 2H), 2.46 (s, 3H).

2-Butyne-1,4-bis(vinyl-imidazolium) bis(trifluoromethanesulfon-imide) cross-linker (3). 2-Butyne-1,4-diol ditosylate (60.5 g, 153 mmol) was dissolved in CH₃CN (350 mL) and vinylimidazole (31.8 g, 337 mmol), and the mixture was heated to 60 °C and stirred for 20 h until the starting material was consumed, as determined by thin layer chromatography (1:1 v/v EtOAc/hexanes as the eluent). After cooling to room temperature, the solvent was removed in vacuo, and the resulting solid was re-dissolved in water (300 mL) and then washed with diethyl ether (3 x 100 mL). Lithium bis(trifluoromethanesulfonyl)imide (96.7 g, 337 mmol) was then added to the aqueous portion and stirred for 24 h at room temperature. The product was extracted with CH₂Cl₂ (500 mL) and washed with water (3 x 250 mL), dried over anhydrous MgSO₄, and then filtered. Activated carbon (~ 5 g) was added to the collected CH₂Cl₂ fractions, stirred overnight, and then filtered through a plug of Celite before concentrating in vacuo. The resulting oil was washed with hot diethyl ether (3 x 300 mL) and then dried thoroughly in vacuo at room temperature to afford the product as a yellow solid (99.0 g, 81%). ¹H NMR (300 MHz, DMSO-*d*₆): δ 9.55 (t, *J* = 1.6 Hz, 1H), 8.27 (t, *J* = 1.8 Hz, 1H), 7.99 (t, *J* = 1.7 Hz, 1H), 7.33 (dd, *J* = 15.6, 8.9 Hz, 1H), 6.00 (dd, *J* = 15.6, 2.5 Hz, 1H), 5.47 (dd, *J* = 8.7, 2.5 Hz, 1H), 5.35 (s, 2H).

Note: Cross-linking monomer **3** had to be used with diol-RTIL monomer **2** to prepare cross-linked **1** because divinylbenzene, a conventional hydrophobic cross-linker (used to prepare cross-linked polymer **4**), is not miscible with **2**.

Cross-linked 1/NaY Composite Films. The appropriate amount of NaY zeolite particles was ground up to obtain a fine powder using a mortar and pestle. The NaY powder was then suspended in the diol-RTIL monomer **2** and stirred at room temperature for 12–24 h. Bis(vinylimidazolium) cross-linker **3** (5 mol % relative to monomer **2**) and 2-hydroxy-2-methylpropiophenone photoinitiator (1 wt %) were added to the zeolite/**2** mixture and stirred for 23 min. This mixture was then poured onto a Rain-X[®]-coated glass plate and a second coated plate was placed on top to form a thin liquid film. The plate stack was placed in the UV oven and cured for a minimum of 6 h on each side. The cured film was then carefully removed from the glass plates using a razor blade. Supported membranes were prepared in a similar manner, but the monomer/zeolite particle suspension was poured onto a microporous (Supor[®]) (i.e., 100 μm polysulfone) support, pressed between glass plates, and photopolymerized as described above. FT-IR spectroscopy was used to confirm a high degree (80%) of double bond conversion after photopolymerization by monitoring the decrease in intensity of the out-of-plane vinyl C–H bending bands (922 and 953 cm^{-1}) and using the heteroaromatic γ -C–H bending bands of the imidazolium rings (842 and 861 cm^{-1}) as internal sample standards.

Cross-linked poly[1-(2,3-dihydroxypropyl)-3-vinylimidazolium bis(trifluoromethanesulfon-imide)] (cross-linked 1; control sample). Prepared from the same proportions of monomer **2** and cross-linker **3** as described above for the cross-linked **1**/NaY films, except that no NaY was present.

Cross-linked 4/H-SAPO-34 composite (control sample).⁴ A composite film composed of 72/18/10 (w/w/w) cross-linked **4**/1-ethyl-3-methylimidazolium bis(trifluoromethane)sulfon-imide (an RTIL)/H-SAPO-34 was prepared as previously described in the recent literature.⁴ In this procedure, the appropriate amounts of H-SAPO-34 zeolite particles, the RTIL monomer (styrylmethylimidazolium bis(trifluoromethyl)sulfon-imide), a small amount of divinylbenzene cross-linker (2 wt % relative to monomer), and a small amount of RTIL (added as a liquid interfacial wetting agent between polymer **4** and the zeolite) were combined into film form and radically photo-cross-linked in situ, as previously described.⁴ Characterization data for this cross-linked **4**/RTIL/H-SAPO-34 composite were consistent with those previously reported in the literature.⁴

Cross-linked 4/NaY composite (control sample). A composite film composed of 72/18/10 (w/w/w) cross-linked **4**/1-ethyl-3-methylimidazolium bis(trifluoromethane)sulfon-imide /NaY) was prepared as described above,⁴ except that 10 wt % NaY was used as the zeolite instead of 10 wt % H-SAPO-34. Characterization data for this cross-linked **4**/RTIL/zeolite composite were similar to that of the cross-linked **4**/RTIL/H-SAPO-34 composite previously reported in the literature.⁴

Cross-linked 1/H-SAPO-34 composite (additional control sample). The appropriate amount of H-SAPO-34 zeolite particles was ground up to obtain a fine powder using a mortar and pestle. The H-SAPO-34 powder was then suspended in the diol-RTIL monomer **2** and stirred at room temperature for 12–24 h. Bis(vinylimidazolium) cross-linker **3** (1 mol % relative to monomer **2**) and 2-hydroxy-2-methylpropiophenone photoinitiator (1 wt %) were added to the zeolite/**2** mixture and stirred for 23 min. This mixture was then poured onto a Rain-X[®]-coated glass plate and a second coated plate was placed on top to form a thin liquid film. The plate stack was placed in the UV oven and cured for a minimum of 6 h on each side. The cured film was then carefully removed from the glass plates using a razor blade.

Cross-linked 4 without zeolite (additional control sample). A film composed of 80/20 (w/w) cross-linked 4/1-ethyl-3-methylimidazolium bis(trifluoromethane)sulfoni-mide) was prepared as described above,⁴ except that no zeolite was used.

Water Vapor Permeation Studies. Figure S2 shows the test configuration used at the U.S. Army Natick Soldier Research, Development and Engineering Center (Natick, MA) for determining the “breathability” of the membrane films.⁵ Air with relative humidity (RH) of 95% and 5% flowed over the top and bottom of the sample respectively; the humidity detectors were used to measure how much water vapor was transported through the sample. The measurement was conducted at a constant humidity gradient, but the mean RH was increased at each set-point. Mean RH was the average of the incoming humidity on the two sides of the sample. Higher mean RH values meant that a hydrophilic membrane contained more water than at a lower mean RH. Results were reported in terms of water vapor flux ($\text{g m}^{-2} \text{ day}^{-1}$).

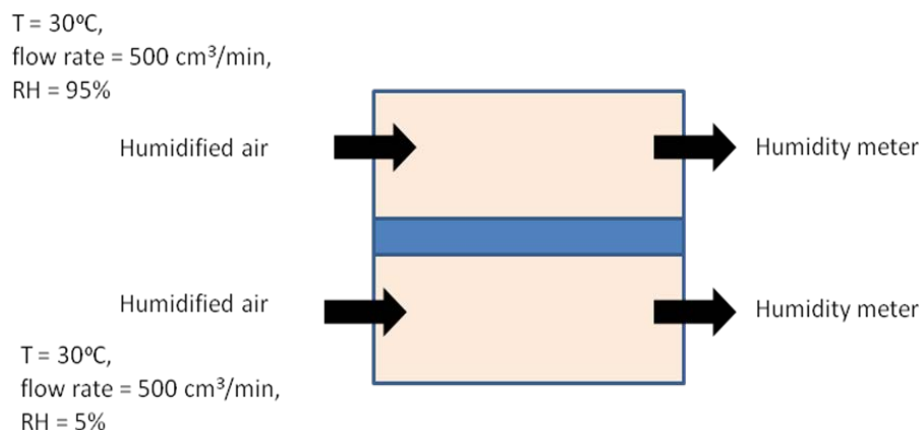


Figure S2. Schematic of the direct moisture permeation cell set-up at the U.S. Army Natick Soldier Research, Development, and Engineering Center.⁵ The sample test area size for the water vapor permeation studies using this apparatus was 5.00 cm².

CEES Vapor Permeation Studies. Figure S3 shows the test configuration used at the U.S. Army Natick Soldier Research, Development and Engineering Center (Natick, MA) for determining the degree of CEES vapor penetration through the membrane films.⁶ Drops of CEES were placed on a glass fiber filter suspended above the test sample. This glass filter layer was used to wick and spread the droplets of the liquid evenly for the vapor diffusion test. A stainless steel screen supported the filter paper, and prevented liquid from wicking into the test sample by separating the upper surface of the test sample from the filter paper. The top opening of the diffusion cell was closed with a stopper, and the test began with an air sweep of the underside of the sample to a flame ionization detector. The closed test cell volume above the test sample had no ventilating air flow, and was a small-volume stagnant air space that became saturated with the test liquid (3 mL of CEES (3.2 mg)) and served as a vapor source for the top surface of the test sample. The air sweep was controlled to a RH value of 80%, a temperature of 30 °C and a flow rate of 100 cm³ min⁻¹ (0.002156 g s⁻¹). Prior to the application of the CEES liquid to the test cell, the sample was allowed to equilibrate in the humidified sweep flow for a period of 1 to 10 h, depending on its anticipated water content as determined previously from the measured water vapor sorption isotherm.

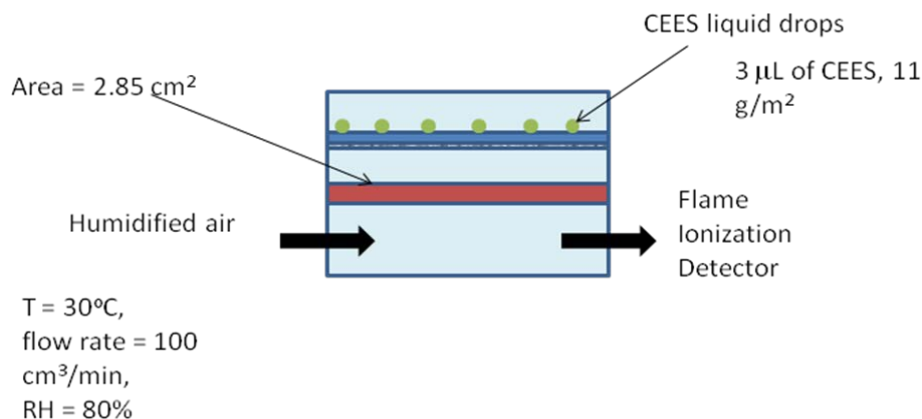


Figure S3. Schematic of the cross-flow CEES vapor permeation testing system used at the U.S. Army Natick Soldier Research, Development, and Engineering Center.⁶ The sample test area size for the CEES vapor permeation studies using this apparatus was 2.85 cm².

Preparation of cross-linked **1 and cross-linked **1**/NaY film exposed to additives for FT-IR analysis.** The cross-linked **1** or cross-linked **1**/NaY film samples were exposed to CEES and diethylsulfide for FT-IR analysis by placing a 1–2 mL of each liquid on each film and placing the resulting film in a sealed vial overnight at room temperature to equilibrate. The excess liquid was then removed by dabbing the film with a Kim-Wipe. In the case of aq. NaCl, a saturated solution of NaCl in de-ionized water was prepared, and the aforementioned procedure was followed. The resulting film samples were then characterized by FT-IR ATR analysis.

Additional FT-IR control studies on neat cross-linked **1 films exposed to water, dry NaCl, and (NaCl + water):**

Neat cross-linked **1.** Preparation of the neat cross-linked **1** control samples began by immersion in liquid nitrogen. The solid was subsequently crushed to a powder with a mortar and pestle. The powder was then dried in vacuo for 48 h to remove any remaining water. The FT-IR spectrum of the neat, dry, diol-RTIL polymer **1** sample was recorded using the same IR spectrometer and settings as previously described (see Figure S4 below).

Cross-linked **1 exposed to water vapor.** The neat, dry, cross-linked **1** polymer was placed in a vial and inserted into a beaker of 50 °C water with a lid to ensure water vapor contact with the polymer. The polymer was contacted with the water vapor for 10 min. Upon contact with water vapor, the polymer became more rubbery. The FT-IR spectrum of the cross-linked **1** + water vapor sample was recorded using the same FT-IR spectrophotometer and settings as previously described (see Figure S4 below).

Cross-linked **1 blended with dry NaCl.** The neat, dry, cross-linked **1** polymer (100 mg) was crushed together with dry NaCl (100 mg) with a mortar and pestle. The FT-IR spectrum of the dry cross-linked **1** + dry NaCl sample was recorded using the same FT-IR spectrometer and settings as previously described (see Figure S4 below).

Cross-linked **1 with NaCl and water vapor.** The dry cross-linked **1** (100 mg) + dry NaCl (100 mg) sample from the previous experiment was placed in a vial and inserted into a beaker of 50 °C water with a lid to ensure water vapor contact with the composite. The cross-linked **1**/NaCl

composite was contacted with the water vapor for 10 min. Upon contact with water vapor, the composite sample became more rubbery. The FT-IR spectrum of the cross-linked **1** + NaCl + water vapor sample was recorded using the same FT-IR spectrometer and settings as previously described (see Figure S4 below).

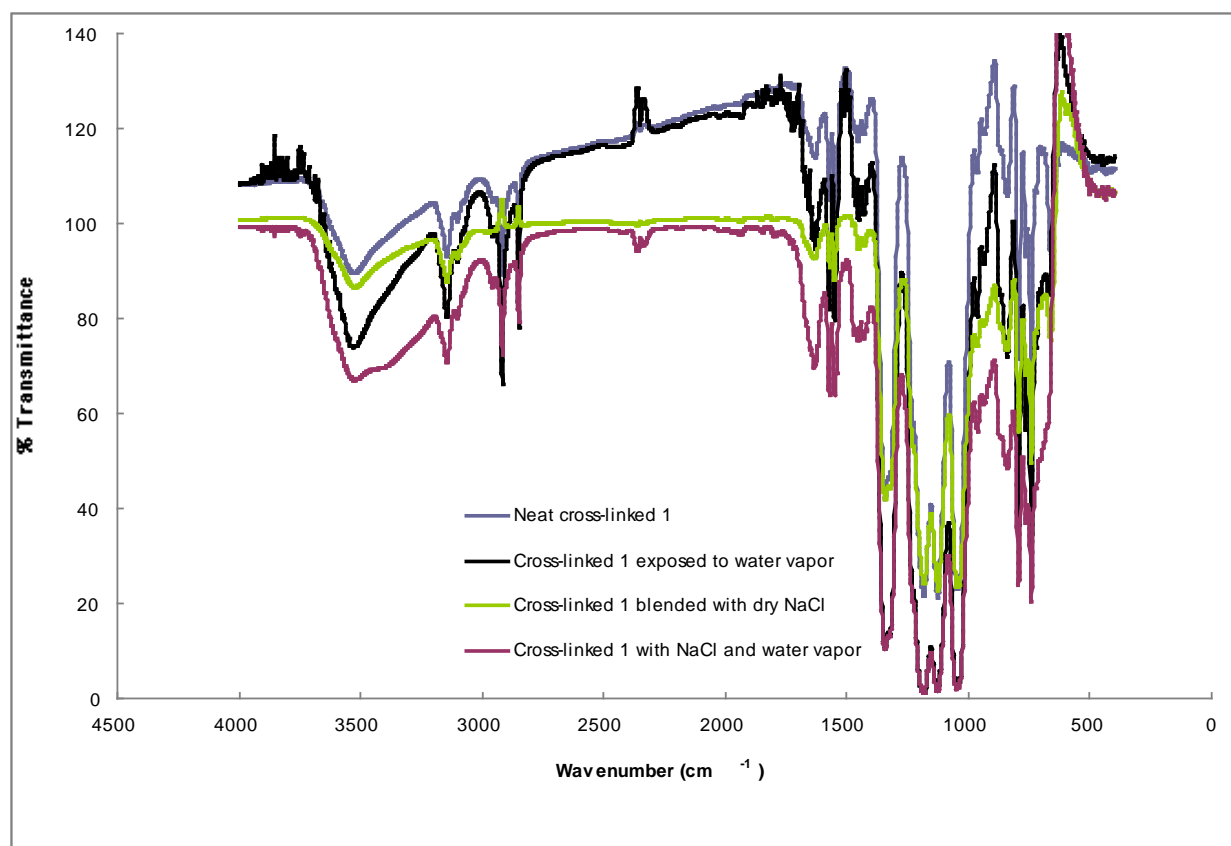


Figure S4. FT-IR spectra of additional control samples of cross-linked **1** films neat and exposed to water vapor, dry NaCl, and dry NaCl + water vapor.

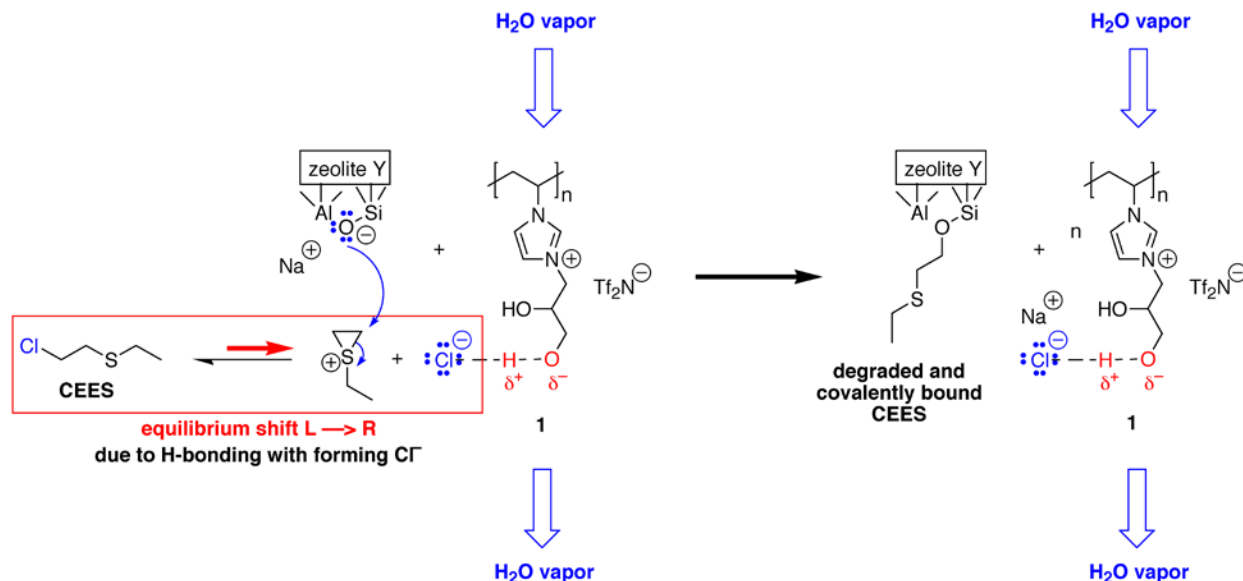


Figure S5. Reaction scheme showing the *proposed* interaction of OH groups on cross-linked polymer **1** with free/solvated Cl⁻ anions formed from CEES in the cross-linked **1**/NaY composite film, as inferred from FT-IR evidence.

References for the Supporting Information:

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