Electronic Supplementary Information for

Tubular Microporous Organic Networks Bearing Imidazolium Salts and Their Catalytic CO₂ Conversion to Cyclic Carbonates

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Experimental Section

All SEM images were taken using a FE-SEM (JSM6700F). The TEM and EDS-mapped images were taken using a JEOL 2100F unit operated at 200kV. Solid phase ¹³C-NMR spectrum was recorded on a Varian 600 MHz solid state NOVA600 spectrometer at Korea Basic Science Institute (Daegu) operated at 150.9 MHz Larmor frequency. The spinning speed of 9.5 kHz was applied and the repetition delay time was 6.5 sec. Adsorption-desorption isotherm for N_2 (77 K) was recorded by using BELSORP II-mini volumetric adsorption equipment. Pore-size distribution was calculated based on density functional theory (DFT) method with a N_2 slit pore kernel at 77 K. Elemental analysis was performed on a CE EA1110 instrument. The TGA curve was obtained by Seiko Exstar 7300. ¹H-NMR and ¹³C-NMR spectra for model compound were recorded on a Varian 300MHz spectrometer. Mass spectrum of new compound was obtained using a JEOL JMS 700 spectrometer.

Preparation of model compound:

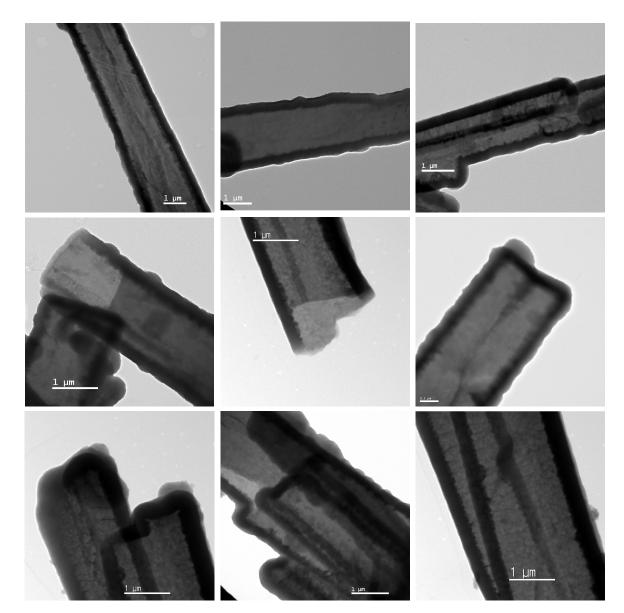
1,3-Bis(2,6-diisopropyl-4-iodophenyl)imidazolium chloride (0.50 g, 0.74 mmol), copper iodide (5.6 mg, 0.03 mmol), bis(triphenylphosphine) palladium dichloride (42 mg, 0.059 mmol), triphenylphosphine (31 mg, 0.12 mmol) and a mixture of anhydrous THF (30 mL) and diisopropylamine (10 mL) were added to the flame dried 50 mL Schlenk flask. To this reaction mixture, 1-ethynyl-4-methylbenzene (0.37 mL, 2.9 mmol) was added. The reaction mixture was heated to reflux for 12 h. After reaction, the solution was cooled to room temperature and poured into brine solution. The product was extracted with methylene chloride and solvent was evaporated to form dark brown powder. After recrystallization using the mixture of methylene chloride and hexane, a pure light-brown solid was obtained with 95% (0.46 g, 0.70 mmol) yield. Characterization data of model compound: ¹H NMR (300 MHz, acetone-d⁶): $\delta = 10.48$ (s, 1H), 8.53 (s, 2H), 7.67 (s, 4H), 7.50 (d, J = 8.1 Hz, 4H), 7.30 (d, J = 8.1 Hz, 4H), 2.67 (m, 4H), 2.39 (s, 6H), 1.35 (d, J = 6.9 Hz, 12 H), 1.32 (d, J = 6.9 Hz, 12 H) ppm; ¹³C NMR (75 MHz, acetone-d⁶): $\delta = 146.1$, 139.5, 131.8, 130.3, 129.6, 127.8, 127.3, 126.6, 119.7, 91.4, 87.8, 23.9, 23.0, 20.9 ppm; HRMS (FAB) [M]⁺ m/z, calc. for C₄₅H₄₉N₂ 617.3896, found 617.3894

Preparation of T-IM (Tubular organic networks bearing **IM**idazolium salts): Tetrakis(4ethynylphenyl)methane (50 mg, 0.12 mmol) and 1,3-bis(2,6-diisopropyl-4-iodophenyl)-imidazolium chloride (0.16 g, 0.24 mmol) were dissolved in a mixture of toluene (5 mL) and diisopropylamine (2 mL). After adding bis-(triphenylphosphine) palladium dichloride (10 mg, 0.014 mmol) and copper iodide (10 mg, 0.053 mmol), the reaction mixture was heated at 90 °C for 24 hours. During the heating, a solid was formed. After cooling to room temperature, the solid was retrieved by centrifugation, washed with excess acetone and methanol and then, Supplementary Material (ESI) for Chemical Communications This journal is (c) The Royal Society of Chemistry 2010

treated with Soxhlet extractor using refluxing methanol for 3 days. The resultant material (0.12 g, 70% yield based on imidazolium ion) was dried under vacuum for 24 h at 60 $^{\circ}$ C.

Representative procedure for catalytic reactions: **T-IM** (18 mg, 0.025 mmol imidazolium salt species) and epichlorohydrin (3.00 mL, 38.4 mmol) were added to 60 mL autoclave. Then, carbon dioxide (1 MPa) was charged. The autoclave was heated at 150 °C for 10 hours. After reaction, the autoclave was cooled to room temperature and carbon dioxide was discharged. The **T-IM** was retrieved by centrifugation and the solution was directly analyzed by NMR-spectroscopy.

Figure S1. Additional TEM images of T-IM showing tubular structure.



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Figure S2. Additional SEM images of T-IM showing tubular structure.

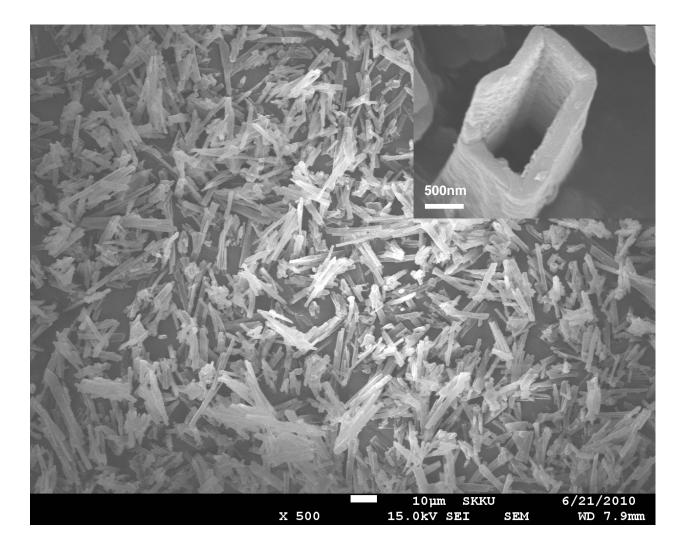


Figure S3. Photographs showing the comparison between T-IM and water.



Figure S4. Powder X-ray diffraction pattern of T-IM.

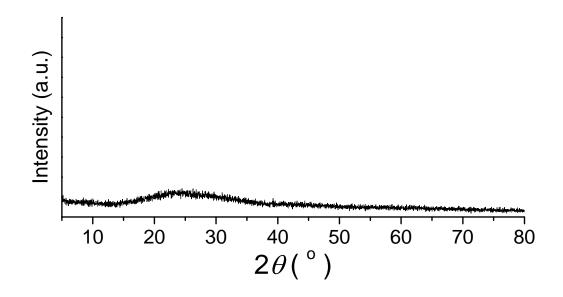


Figure S5. Solid-phase ¹H-CP/MAS NMR spectrum of the synthesized T-IM (with 22 kHz MAS rate).

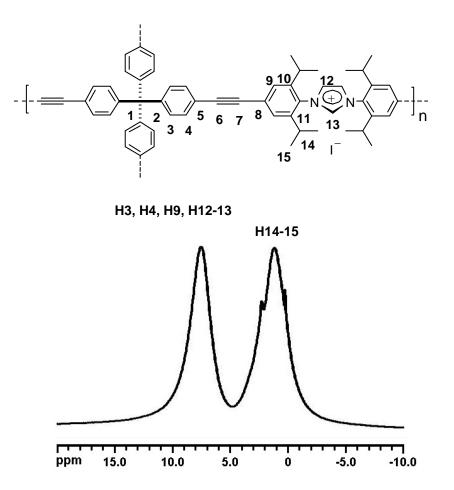


Figure S6. IR spectrum of T-IM.

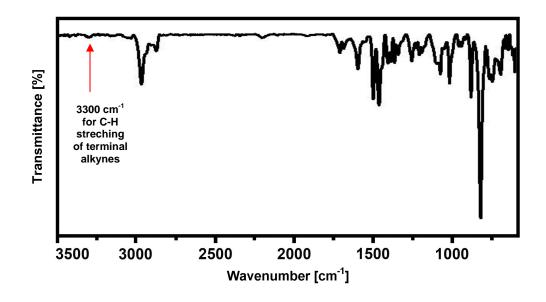


Figure S7. (a) Time-dependent SEM studies and typical TEM images; (b) a suggested formation mechansim of tubular organic networks (**T-IM**).

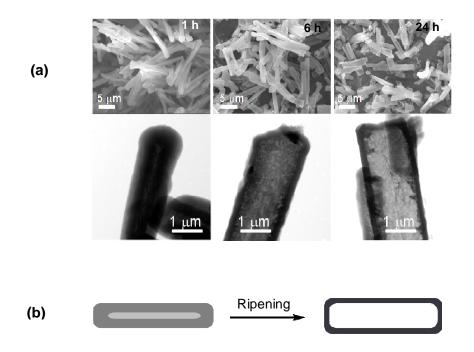
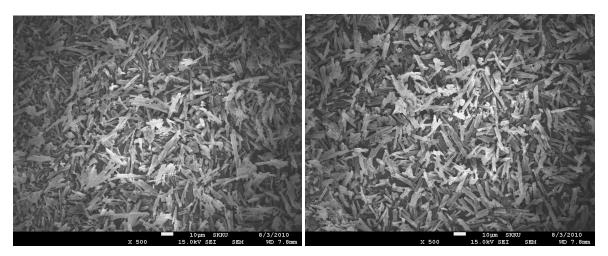


Figure S8. SEM images of the original **T-IM** (a) and the recovered **T-IM** (b) after reaction in entry 4 in table 1 (text).



(a)

