

Supporting Information

For New Journal of Chemistry

Ribbon-like Ultramicroporous Conjugated Polycarbazole Network for Gas Storage and Separation

Shanlin Qiao^{‡a,b}, Huan Wei^{‡a,b}, Ting Wang^b, Wei Huang^b, Chunyang Gu^b,
Renqiang Yang^{b*} and Xiaoyun Li^{a*}

^a Institute of Chemical Industry and Pharmaceutical Engineering, Hebei University
of Science and Technology, Shijiazhuang 050000, China

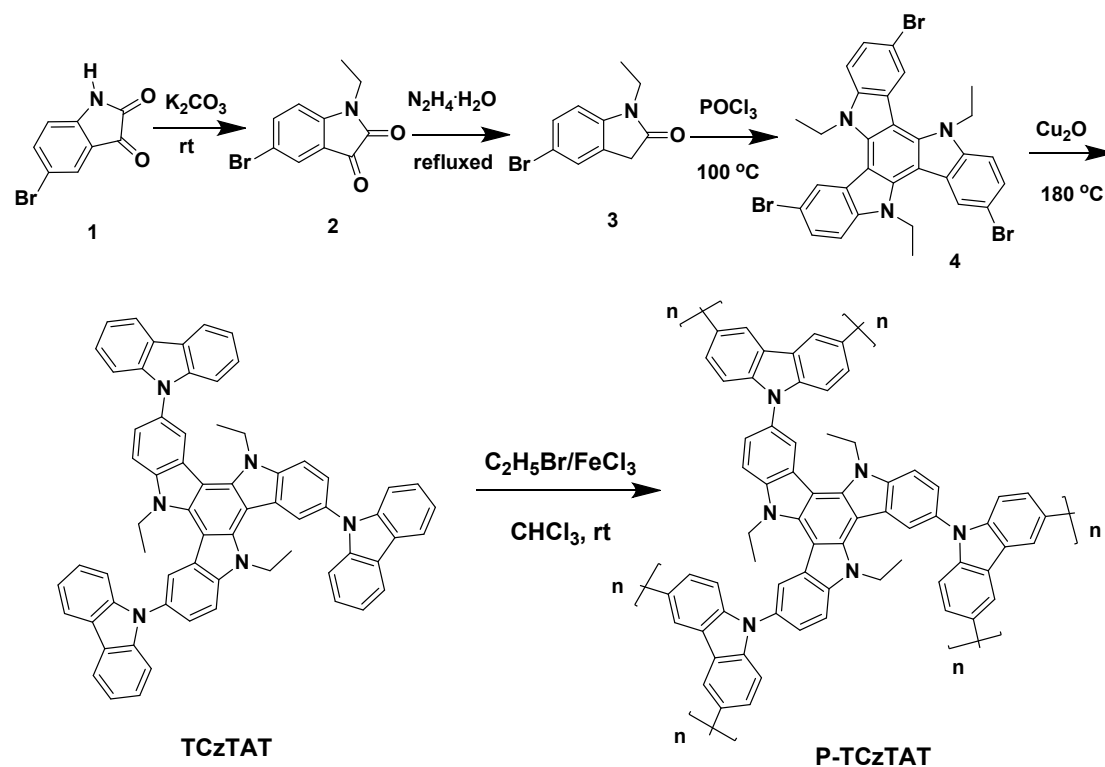
E-mail: lixiaoyun@hebust.edu.cn

^b CAS Key Laboratory of Bio-based Materials, Qingdao Institute of Bioenergy and
Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China

E-mail: yangrq@qibebt.ac.cn

[‡] These authors contributed equally to this work.

Experimental section



Scheme S1. Synthetic route of the carbazole based network P-TCzTAT.

5-Bromo-N-ethylisatin (2)

A mixture of 5-bromoisatin (1) (6.78 g, 30 mmol), potassium carbonate (K_2CO_3) (12.42 g, 90 mmol), C_2H_5Br (5.34 mL, 36 mmol), and N,N-dimethylformamide (DMF) (30 mL) was stirred at room temperature for 12 h under argon protection. After the reaction the mixture was poured into water, and extracted with dichloromethane, the combined organic layers were dried with anhydrous $MgSO_4$ and evaporated to dryness, the residue was purified by column chromatography (petroleum ether/dichloromethane, 3:1) to give orange solid (6.26 g, 72%). 1H NMR (600 MHz, $CDCl_3$): δ (ppm) = 8.20 (d, 1H); 8.03 (s, 1H); 7.37 (d, 1H); 3.60 (m, 1H); 2.12 (m, 2H), 0.9 (t, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) = 179.9, 160.1, 147.1, 145.3, 119.9, 119.2, 117.5, 133.6, 42.5, 13.7.

5-Bromo-N-ethyloxindole (3)

A mixture of compound **2** (3.16 g, 10 mmol), 1,2-diethoxyethane (7 mL), and hydrazine hydrate (80%) was stirred and refluxed for 12 h under argon protection. The reaction mixture was allowed to cool to room temperature, the resulted precipitates were collected to obtain yellow solid (2.75 g, 93%). ¹H NMR (600 MHz, CDCl₃): δ (ppm) = 7.71-7.5 (d, 1H); 7.33 (s, 1H); 7.06 (d, 1H); 3.75 (s, 2H), 3.66 (m, 1H); 2.06-2.04 (m, 2H); 0.95-0.91 (t, 3H). ¹³C NMR (150 MHz, CDCl₃): δ (ppm) = 174.7, 143.9, 134.8, 134.6, 128.1, 119.2, 117.3, 43.8, 35.1, 13.7.

3, 8, 13-Tribromo-5, 10, 15-triethyl-triazatruxene (4)

A mixture of compound **3** (2.0 g, 8.3 mmol) and POCl₃ (10 mL) was heated at 100 °C for 8 h. Then the reaction mixture was poured into ice and neutralized carefully with KOH until pH 7–8. After neutralization, the precipitate was filtered to give the crude product as a brown solid. The latter was dissolved in methanol, adsorbed onto silica gel and purified by flash chromatography (ethyl acetate/*n*-hexane, 15:85) to give pure **4** as a white solid (884 mg, 48 %). ¹H NMR (600 MHz, CDCl₃): δ (ppm) 8.32 (s, 3H), 7.54-7.52 (d, 3H), 7.47-7.46 (d, 6H), 4.81-4.78 (m, 3H), 1.57-1.54 (t, 9H). ¹³C NMR (150 MHz, CDCl₃): δ (ppm) 139.25, 138.95, 125.75, 124.89, 124.00, 113.17, 111.64, 102.34, 41.79, 15.40.

TCzTAT

A mixture of compound **4** (667 mg, 1 mmol), carbazole (800 mg, 5 mmol), Cu₂O (719 mg, 5.0 mmol), and dimethylacetamide (20 mL) were added sequentially to a sealed tube under argon protection and heated at 180 °C in oil bath for 24 h. Then the

mixture was cooled to room temperature and filtered. The filtrate was poured into H₂O (200 mL) and stirred for 20 min. The solid was collected by filtration and was purified by chromatography (silica gel, petroleum ether/CH₂Cl₂, 1:2, v/v) to give white solid (450 mg 49%). ¹H NMR (600 MHz, CDCl₃): δ (ppm) 8.53 (s, 3H), 8.23-8.22 (d, 6H), 7.78-7.76 (d, 3H), 7.62-7.61 (d, 3H), 7.52-7.51 (d, 6H), 7.46-7.44 (t, 6H), 7.34-7.31 (t, 6H), 5.03-5.00 (m, 6H), 1.54-1.52 (t, 9H). ¹³C NMR (150 MHz, CDCl₃): δ (ppm) = 139.9, 137.7, 136.6, 136.5, 133.8, 129.4, 126.6, 122.7, 121.4, 119.8, 112.2, 111.7, 111.4, 109.5, 45.9, 14.5.

P-TCzTAT

The solution of monomer TCzTAT (200 mg, 0.22 mmol) dissolved in 30 mL of anhydrous chloroform was dropwise transferred to a suspension of ferric chloride (470 mg, 1.76 mmol) in 20 mL of anhydrous chloroform. The solution mixture was stirred for 24 h at room temperature under nitrogen protection, and then 100 mL of methanol was added to the above reaction mixture. The resulting precipitate was collected by filtration and washed with methanol and concentrated hydrochloric acid solution. After extracted in a Soxhlet extractor with methanol for 24 h, and then with tetrahydrofuran for another 24 h extraction, the desired polymer was collected and dried in vacuum oven at 80 °C overnight to give yellowish powder, yield in 95%. Anal. Calcd. for C₆₆H₄₈N₆: C, 85.69%; N, 9.08%; H, 5.23%. Found: C, 67.45%; N, 4.9%; H, 3.89%.

Thermogravimetric analysis

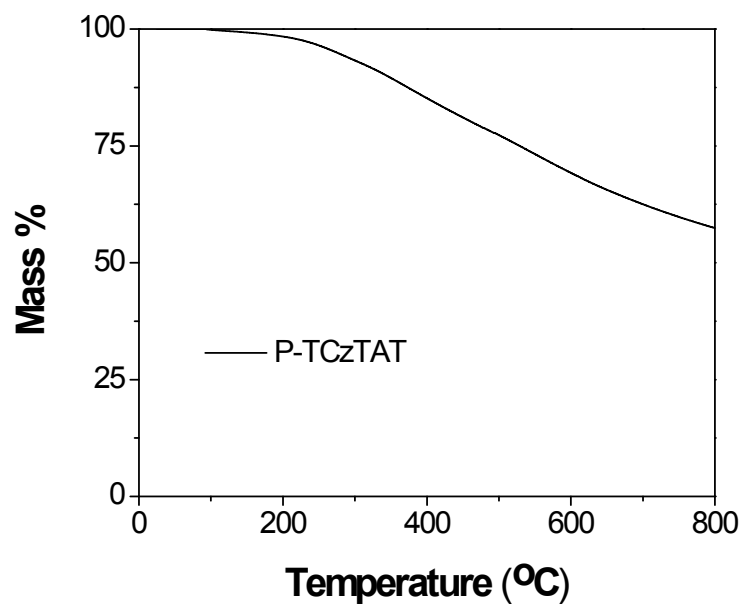


Fig. S1 Thermogravimetric analysis curve of P-TCzTAT network.