Supporting Information

Polytriazine Porous Networks for Effective Iodine Capture

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Section A. Materials and methods

\(N^2,N^4, N^6\)-Tris(4-bromophenyl)-1,3,5-triazine-2,4,6-triamine (TBTT) was purchased from Shanghai YuKang company. 2,4,6-Triaminotriazine was purchased from Shanghai Macklin biochemical company. 4,4''-Diamino-\(p\)-terphenyl, benzidine and \(p\)-Phenylenediamine were purchased from Aladdin. Bis(dibenzylideneacetone)palladium (0) was purchased from Energy Chemical. Sodium tert-butoxide and 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl were purchased from san bang chemical. All solvents used were purchased from Aladdin.

Fourier transform Infrared (FT-IR) spectra were recorded on a Perkin-elmer model FT-IR-frontier infrared spectrometer. For all FT-IR tests, a small amount of sample can be directly mixed with potassium bromide and ground into a powder, and then compressed, and the pressed product can be directly tested. The UV-visible analyzer was used for JASCO V-770ST. For the UV test, the blank sample test is first carried out with the solid barium sulfate powder as the background, and then the holder with solid samples of CMPs was mounted onto the window of the integration sphere. Solid-state \(^{13}\)C CP/MAS NMR measurements was recorded using a Bruker AVANCE III 400 WB spectrometer at a MAS rate of 5 kHz and a CP contact time of 2 ms. X-ray photoelectron spectra (XPS) were recorded on an ESCALAB250Xi electron spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA). Field-emission scanning electron microscopy (FE-SEM) images were performed on a JEOL model JSM-6700 operating at an accelerating voltage of 5.0 kV. High-resolution transmission electron microscopy (HR-TEM) images were obtained on a JEOL model JEM-3200 microscopy. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku model RINT Ultima III diffractometer by depositing powder on glass substrate, from \(2\theta = 1.5^\circ\) up to \(60^\circ\) with \(0.02^\circ\) increment. TGA analysis data were carried out using a Q5000IR analyser (TA Instruments) with an automated vertical overhead thermobalance. Before measurement, the samples were heated for 12 h at a rate of 5 °C min\(^{-1}\) under a nitrogen atmosphere.

Nitrogen sorption isotherms were measured at 77 K with ASIQ (iQ-2) volumetric adsorption analyzer. Carbon dioxide sorption isotherms were measured at 318 K and 70 bar with a iSorbHP2 analyzer, respectively. Before measurement, the samples were also degassed in vacuum at 120 °C more than 10 h.
Section B. Synthetic procedures

Synthesis of TBTT-CMP@1

Firstly, $N^2,N^4,N^6$-Tris(4-bromophenyl)-1,3,5-triazine-2,4,6-triamine (TBTT) (44.4 mg, 0.075 mmol), $p$-phenylenediamine (12.2 mg, 0.113 mmol), 2-dicyclohexylphosphino-2,4,6-trisopropylbiphenyl (21.5 mg, 0.046 mmol), bis(dibenzylideneacetone)palladium (17.3 mg, 0.03 mmol), and sodium tert-butoxide (192.2 mg, 2 mmol) were added to the two-necked bottle in turn. Next, the 4 mL of anhydrous toluene and 2 mL of anhydrous $n$-butanol were separately added into a 50 mL two-necked flask, then the flask was exchanged 3 cycles under vacuum/N$_2$. After evacuating three times, it was filled with nitrogen gas, and then the reaction was heated to 120 °C for 48 h. After completion of the reaction, the obtained product was cooled to room temperature, and washed with water, methanol and chloroform for three times, respectively, to give TBTT-CMP@1 as black powder (71% yield).

Synthesis of TBTT-CMP@2-3

Similar method was used for the preparation of TBTT-CMP@1, when the monomer $p$-phenylenediamine was changed to benzidine (20.82 mg, 0.113 mmol) finally obtained TBTT-CMP@2 as black powder (73% yield). When the monomer $p$-phenylenediamine was changed to 4,4′-diaminoterphenyl (29.41 mg, 0.113 mmol) to give TBTT-CMP@3 as black powder (75% yield).
Section C. FT-IR spectra

Fig. S1 (a) FT-IR spectra of monomer TBTT (green), TBTT-CMP@1 (black), TBTT-CMP@2 (red), and TBTT-CMP@3 (blue). (b) FT-IR spectra of TBTT (green), TBTT-CMP@1 (black), TBTT-CMP@2 (red), and TBTT-CMP@3 (blue) in 1850-1240 cm⁻¹.
### Section D. The elemental analysis

**Table S1.** Elemental analysis data of TBTT-CMP@1, TBTT-CMP@2, and TBTT-CMP@3

<table>
<thead>
<tr>
<th>wt%</th>
<th>C</th>
<th>H</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBTT-CMP@1</td>
<td>Anal. calcd.</td>
<td>70.57</td>
<td>5.92</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>72.36</td>
<td>5.28</td>
</tr>
<tr>
<td>TBTT-CMP@2</td>
<td>Anal. calcd.</td>
<td>76.41</td>
<td>5.77</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>78.97</td>
<td>5.11</td>
</tr>
<tr>
<td>TBTT-CMP@3</td>
<td>Anal. calcd.</td>
<td>79.97</td>
<td>5.68</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>81.67</td>
<td>5.04</td>
</tr>
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</table>
Section E. The solid-state $^{13}$C NMR spectra
Fig. S2 The solid-state $^{13}\text{C}$ CP-MAS NMR of (a) TBTT-CMP@1, (b) TBTT-CMP@2, and (c) TBTT-CMP@3. The peaks at 157.3 marked by the red arrow are the characteristic peaks of the C=N.
Section F. Powder X-ray diffraction patterns

Fig. S3 Powder X-ray diffraction profiles of TBTT-CMP@1, TBTT-CMP@2 and TBTT-CMP@3.
Section G. The Solid-UV spectra

**Fig. S4** The normalized solid state UV/Vis spectra of TBTT (black), TBTT-CMP@1 (blue), TBTT-CMP@2 (green) and TBTT-CMP@3 (red), respectively.
Section H. TEM images

Fig. S5 TEM images of TBTT-CMP@1, TBTT-CMP@2 and TBTT-CMP@3 (10 nm width).
Section I. TGA curves

Fig. S6 TGA curves of TBTT-CMP@1 (red), TBTT-CMP@2 (black) and TBTT-CMP@3 (blue).
Table S2. Summary of iodine capacity of porous materials.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>$S_{\text{BET}}$ (m$^2$ g$^{-1}$)</th>
<th>$V_{\text{total}}$ (cm$^3$ g$^{-1}$)</th>
<th>Iodine Uptake (wt.%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBTT-CMP@1</td>
<td>58.84</td>
<td>0.45</td>
<td>442</td>
<td></td>
</tr>
<tr>
<td>TBTT-CMP@2</td>
<td>64.23</td>
<td>0.38</td>
<td>357</td>
<td>This work</td>
</tr>
<tr>
<td>TBTT-CMP@3</td>
<td>14.98</td>
<td>0.29</td>
<td>352</td>
<td></td>
</tr>
<tr>
<td>TTPPA</td>
<td>512.39</td>
<td>0.2997</td>
<td>490</td>
<td></td>
</tr>
<tr>
<td>TTDAB</td>
<td>1.643</td>
<td>0.004</td>
<td>313</td>
<td>S1</td>
</tr>
<tr>
<td>Tm-MTDAB</td>
<td>2.778</td>
<td>0.007</td>
<td>304</td>
<td></td>
</tr>
<tr>
<td>TPT-BD</td>
<td>109</td>
<td>0.3</td>
<td>543</td>
<td></td>
</tr>
<tr>
<td>TPT-DHBD$\text{_{25}}$</td>
<td>188</td>
<td>0.32</td>
<td>465</td>
<td>S2</td>
</tr>
<tr>
<td>TPT-DHBD$\text{_{50}}$</td>
<td>124</td>
<td>0.19</td>
<td>430</td>
<td></td>
</tr>
<tr>
<td>TPT-DHBD$\text{_{75}}$</td>
<td>157</td>
<td>0.19</td>
<td>412</td>
<td></td>
</tr>
<tr>
<td>TPT-DHBD</td>
<td>297</td>
<td>0.54</td>
<td>403</td>
<td></td>
</tr>
<tr>
<td>SIOC-COF-7</td>
<td>618</td>
<td>0.41</td>
<td>481</td>
<td>S3</td>
</tr>
<tr>
<td>TTTBT</td>
<td>222.25</td>
<td>0.1271</td>
<td>443</td>
<td>S4</td>
</tr>
<tr>
<td>Azo-Trip</td>
<td>520</td>
<td>0.47</td>
<td>238</td>
<td>S5</td>
</tr>
<tr>
<td>BDP-CPP-1</td>
<td>635</td>
<td>0.78</td>
<td>283</td>
<td></td>
</tr>
<tr>
<td>BDP-CPP-2</td>
<td>235</td>
<td>0.18</td>
<td>223</td>
<td>S6</td>
</tr>
</tbody>
</table>
Section J. Pore size distribution curves

Fig. S7 Pore size distribution curves for the TBTT-CMPs networks.
Section K. Iodine capture analyses
Fig. S8 (a) The standard curve of iodine in cyclohexane solution (Inset is the fitting curve of Abs value vs concentration of iodine in cyclohexane solution, the value of $R^2$ indicated that the curve with the relatively good linearity satisfies Lambert-Beer Law. The iodine adsorption capacity of TBTT-CMPs was calculated according to the standard curve); (b-d) the UV/Vis spectra upon immersion of 30 mg TBTT-CMPs in cyclohexane solution of I$_2$ (6 mg/mL). All experiments were performed at ambient temperature and pressure.
Sorption Kinetic Studies:
The linear form of the pseudo-first-order kinetic model:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t$$

Where $Q_t$ and $Q_e$ are the mass percent of iodine adsorbed at time $t$ and equilibrium (%), $k_1$ is the pseudo-first-order rate constant of adsorption process (h$^{-1}$).

The linear form of the pseudo-second-order kinetic model:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}$$

Where $Q_t$ and $Q_e$ are the mass percent of iodine adsorbed at time $t$ and equilibrium (%), $k_2$ is the pseudo-second-order rate constant of adsorption process ((% h)$^{-1}$).

Table S3. Parameters of the different isotherm models extracted from the pseudo-first-order model and the pseudo-second-order model for TBTT-CMP@1, TBTT-CMP@2 and TBTT-CMP@3.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Pesudo-first-order</th>
<th>Pesudo-second-order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_1$ (1/h)</td>
<td>$Q_e$ (%)</td>
</tr>
<tr>
<td>TBTT-CMP@1</td>
<td>0.1278</td>
<td>98.58434</td>
</tr>
<tr>
<td>TBTT-CMP@2</td>
<td>0.12808</td>
<td>96.90864</td>
</tr>
<tr>
<td>TBTT-CMP@3</td>
<td>0.10672</td>
<td>101.82767</td>
</tr>
</tbody>
</table>
Fig. S9 The iodine adsorption kinetic was analyzed by the pseudo-first-order model.
Fig. S10 The iodine adsorption kinetic was analyzed by the pseudo-second-order model.
Fig. S11 Deconvoluted XPS spectra for I$_3$d$_3$ and I$_5$d$_5$ in the (a) I$_2$@TBTT-CMP@1, (b) I$_2$@TBTT-CMP@2 and (c) I$_2$@TBTT-CMP@3, respectively.
Fig. S12 Deconvoluted C 1s spectra of (a) I$_2$@TBTT-CMP@1, (b) I$_2$@TBTT-CMP@2 and (c) I$_2$@TBTT-CMP@3, respectively.
Fig. S13 Deconvoluted N 1s spectra of (a) I$_2$@TBTT-CMP@1, (b) I$_2$@TBTT-CMP@2 and (c) I$_2$@TBTT-CMP@3, respectively.
Fig. S14 Photographs showing progress of the iodine release from I$_2$@TBTT-CMP@1, I$_2$@TBTT-CMP@2 and I$_2$@TBTT-CMP@3, respectively, when the containing iodine polymer networks were immersed in ethanol.
Section N. Reusability of the CMPs

Fig. S15 Reusabilities of the TBTT-CMP@1-3 polymers for iodine adsorption by vapor sublimation.
Section O. CO₂ adsorption isotherms

**Fig. S16** CO₂ adsorption isotherms of TBTT-CMP@1-3 collected at 318 K at 70 bar.
Section P. References