Supporting Information

Guest Controlled Pillar[5]arene and Polyoxometalate Based Two-Dimensional Nanostructures toward Reversible Iodine Capture

Mengyan Zeng †, Junyan Tan ‡, Kun Chen †, Dejin Zang †, Yang Yang †, Jie Zhang * ‡ and Yongge Wei * †

† Key Lab of Organic Optoelectronics & Molecular Engineering of Ministry of Education, Department of Chemistry, Tsinghua University, Beijing 100084 (P.R. China). E-mail: yonggewei@tsinghua.edu.cn

‡ Key Lab of Polymer Chemistry and Physics of Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871 (P. R. China). E-mail: jz10@pku.edu.cn

Figure S1. Solution transmittance of P5A-POM-SDS complex at different SDS ratio with the fixed concentration of the system SDS@P5A-POM at ~ 2 mg / L and the testing UV-Vis absorbance wavelength was at 550 nm.
**Figure S2.** Morphologies of SDS@P5A-POM with different equivalent SDS in system under TEM observations. (a) 1-SDS@P5A-POM; (b) 2-SDS@P5A-POM; (c) 3-SDS@P5A-POM; (d) 4-SDS@P5A-POM; (e) 5-SDS@P5A-POM; (f) 6-SDS@P5A-POM; (g) 7-SDS@P5A-POM; (h) 8-SDS@P5A-POM; (i) 9-SDS@P5A-POM.
Figure S3. Morphologies of control experiments under TEM observations. (a) P5A; (b) 1-SDS@P5A; (c) 2-SDS@P5A; (d) 3-SDS@P5A; (e) 4-SDS@P5A; (f) 5-SDS@P5A.

Figure S4. 8 equivalent of SDS in SDS@P5A-POM system (a) TEM image. (b)HRTEM image. (c) HRTEM element mapping. There are only Br, Na, S, O, N, C elements. (d) N kα1 (f) O kα1 (e) S kα1. Scale bar: (a) 5 μm; (b), (c), (d), (e), (f) 100 nm.
Figure S5. 30 equivalent of SDS in SDS@P5A-POM system (a) TEM image. (b) HRTEM image. (c) HRTEM element mapping. There are only Br, Na, S, O, N, C elements. (d) N kα1 (f) O kα1 (e) S kα1. Scale bar: (a), (b), (c), (d), (e), (f) 500 nm.

Figure S6. TEM images of 6 equivalent of SDS in SDS@P5A-POM system. Scale bar: 100 nm.
**Figure S7.** SEM images of nanobones (1-SDS@P5A-POM).

**Figure S8.** The EDX mapping images of nanobones (1-SDS@P5A-POM).

**Figure S9.** The AFM image of nanobones (1-SDS@P5A-POM) with width about 150 nm.
**Figure S10.** The HAADF-STEM images of nanosheets (5-SDS@P5A-POM).

**Figure S11.** The SEM image of nanosheets (5-SDS@P5A-POM).

**Figure S12.** The AFM image of nanosheets (5-SDS@P5A-POM) with width about 2.2nm.
**Figure S13.** The EDX mapping image of nanosheets (5-SDS@P5A-POM).

**Figure S14.** The TEM image of SDS@P5A-PO\(_4^3-\) with no assemblies in this system.
Figure S15. The XPS spectrum of nanobones (blue line) and nanosheets (red line).

Table S1. Summary of nanobones (1-SDS@P5A-POM) and nanosheets (5-SDS@P5A-POM) elemental analysis characterized by ICP-OES and elemental analysis.

<table>
<thead>
<tr>
<th>Nanobones</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>Cr</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na_{0.80}(P5A@SDS_{1.14})</td>
<td>Found</td>
<td>26.86</td>
<td>7.09</td>
<td>2.64</td>
<td>3.35</td>
</tr>
<tr>
<td></td>
<td>Calcd.</td>
<td>26.85</td>
<td>7.11</td>
<td>2.64</td>
<td>3.16</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Nanosheets</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>Cr</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na_{0.81}(P5A@SDS_{1.69})</td>
<td>Found</td>
<td>28.34</td>
<td>7.64</td>
<td>2.64</td>
<td>3.14</td>
</tr>
<tr>
<td></td>
<td>Calcd.</td>
<td>28.04</td>
<td>7.63</td>
<td>2.64</td>
<td>2.98</td>
</tr>
</tbody>
</table>
Figure S16. The DFT calculation of P5A with the outer cavity of ~ 10 Å and the height of ~ 17 Å.

Figure S17. Time-dependent iodine vapor loading at 85 °C by POM, SDS, P5A, Et-P5A, nanobones and nanosheets solids.
Figure S18. TGA analysis of nanobones and nanosheets and after iodine adsorption.
Figure S19. TEM images of nanosheets and nanobones before and after treatments with different solvents for one day.
Figure S20. $N_2$ adsorption isotherm of nanobones: Adsorption, closed symbols; desorption, open symbols.

Figure S21. $N_2$ adsorption isotherm of nanosheets: Adsorption, closed symbols; desorption, open symbols.
Figure S22. UV-Vis spectra of I$_2$ capture in cyclohexane after adding nanobones (a) and nanosheets (b). The images (c) and (d) showing the color changing when added the nanobones (10.0 mg) and nanosheets (10.0 mg) immersed in 1 mM I$_2$ / 2 mL cyclohexane solution.

Figure S23. The images showing the color changing when added nanobones (10.0 mg) and nanosheets (10.0 mg) immersed in 1 mM I$_2$ / 5 mM KI / 2 mL aqueous solution (a) 1 mM I$_2$ / 2 mL chloroform solution (b).
Figure S24. Time-dependent UV spectra of the I$_2$ released with 1.0 mg nanomaterials immersed in 8 mL DMSO solvent: (a) nanobones@I$_2$ and (b) nanosheets@I$_2$.

Figure S25. The XPS spectrum obtained after soaking in I$_2$ cyclohexane solution.
Figure S26. IR spectrum of nanobones, nanobones@I$_2$, nanosheets, nanosheets@I$_2$. 
Figure S27. Cycled I$_2$ adsorption and desorption efficiency using nanobones (30.2 mg) performed in I$_2$ n-hexane solution. Inset: images of the nanomaterials and nanomaterials@I$_2$ in cycle 1 and 5, respectively. The adsorption capability is 5.8 mg / 30.2 mg.

Figure S28. Cycled I$_2$ adsorption and desorption efficiency using nanosheets (63.5 mg) performed in I$_2$ n-hexane solution. Inset: images of the nanomaterials and nanomaterials@I$_2$ in cycle 1 and 5, respectively. The adsorption capability is 23.2 mg / 63.5 mg.