Supporting Information

Confinement of the Polysulfides within the Bi-functional Metal-Organic Framework for High Performance Lithium-Sulfur battery

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Figure S1. PXRD patterns of sulfur and Cu-TDPAT after ground (left) and after heated at 155°C (right).

Figure S2. Adsorption isotherms of different size of nano Cu-TDPAT and S@Cu-TDPAT.

Table S1. Pore characterization results given by nitrogen adsorption measurement at 77K and the calculated sulfur contents in the composites.

<table>
<thead>
<tr>
<th>Size</th>
<th>$S_{BET}$ (m$^2$/g)$^a$</th>
<th>Pore size (nm)</th>
<th>$V$ (cm$^3$/g)$^b$</th>
<th>S/MOF (g/g)$^c$</th>
<th>S content (%)$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100nm</td>
<td>1473</td>
<td>1.7645</td>
<td>0.55</td>
<td>1.001</td>
<td>50.0</td>
</tr>
<tr>
<td>200nm</td>
<td>1532</td>
<td>1.8662</td>
<td>0.62</td>
<td>1.128</td>
<td>53.0</td>
</tr>
<tr>
<td>500nm</td>
<td>1618</td>
<td>1.7766</td>
<td>0.63</td>
<td>1.146</td>
<td>53.4</td>
</tr>
<tr>
<td>1µm</td>
<td>1564</td>
<td>1.6832</td>
<td>0.61</td>
<td>1.110</td>
<td>52.6</td>
</tr>
</tbody>
</table>

$^a$Fitting range : 0.005 < $p/p_0$ < 0.05

$^b$Calculated based on the adsorption volumes at $p/p_0$=0.05

$^c$S/MOF=(density of molten sulfur, 1.82g/cm$^3$) × (pore volume at $p/p_0$=0.05)

$^d$The largest amount of sulfur loading in the cage.
Figure S3. SEM and EDS mapping of S@Cu-TDPAT with different size (a) ~100nm; (b) ~200nm; (c) ~500nm; (d) ~1μm S@Cu-TDPAT.

Figure S4. EIS plots of the S@Cu-TDPAT composite cathodes with different size before cycles.
Figure S5. Cycling stability of S@Cu-TDPAT-100nm cathode at 0.1 C for 200 cycles.

Figure S6. Cycling stability of S@Cu-TDPAT-100nm cathode at 1 C for 500 cycles (the capacity calculation based on the whole electrode including binder and electrolyte).
Figure S7. The cyclic voltammetry curves of S@Cu-TDPAT composites with different particle sizes: (a) 100nm; (b) 200nm; (c) 500nm; (d) 1µm.

Figure S8. The galvanostatic discharge/charge profiles at different current rates of S@Cu-TDPAT with different size: (a) 100nm; (b) 200nm; (c) 500nm; (d) 1µm.
Figure S9. Comparison of the cycle performance of the reported partial sulfur/MOFs composite cathode materials.

Figure S10. DFT optimized adsorption configuration. (a) Cu-TDPAT crystal cell containing 960 atoms. (b) a segment containing 104 atoms of Cu$_2$(TDPAT)$_2$. 
Figure S11. The interactions between polysulfide anions and Cu-TDPAT in the cage A. (a) Cu-TDPAT and Li$_2$S$_8$; (b) Cu-TDPAT and Li$_2$S$_6$; (c) Cu-TDPAT and Li$_2$S$_4$; (d) Cu-TDPAT and Li$_2$S$_2$.

Figure S12. Calculated adsorption energy between Li$_2$S$_x$ and Cu$_2$(TDPAT)$_2$. 
Figure S13. Calculated adsorption energy between Li$_2$S$_x$ and Cu-TDPAT in the cage A.

Figure S14. PXRD patterns of S@Cu-TDPAT after cycling at 0.5C.