Supporting Information

Boron–π–nitrogen-based Conjugated Porous Polymers with Multi-Function

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General Methods

All starting materials were purchased from Aladdin and Aldrich. All air-sensitive reactions were carried out under nitrogen atmosphere and performed using Schlenk techniques. All solvents were dried before use. Tetrahydrofuran (THF) was refluxed with sodium. Triethylamine (TEA) and dichloromethane were refluxed with calcium hydroxide. 4-(dimesitylboryl)-N,N-diphenylaniline were synthesized according to the reported procedures. ¹H nuclear magnetic resonance (NMR) spectra were recorded on a Mercury Plus 400 (400 MHz for proton) spectrometer with tetramethylsilane as the internal reference using CDCl₃ as solvent in all cases.

Materials synthesis and characterization

Synthesis of 4-(dimesitylboryl)-N,N-diphenylaniline (B1N1)

To the solution of 4-bromo-N,N-diphenylaniline (0.5 g, 1.54 mmol) in dry Et₂O (30 mL) added n-BuLi (1.62 mmol, 1.6 M) at RT. After 10 min stirring, solution of Mes₂BF (0.83 g, 3.09 mmol) in Et₂O
(5 mL) was added dropwise and reaction mixture was refluxed for 1 h. After cooling to room temperature, reaction was quenched by addition of water (20 mL) and organic phase was separated by extraction. Collected organic phase was dried over MgSO₄ and the solvent was removed under reduced pressure. Upon addition of acetonitrile to the crude mixture, pale yellow solid precipitated out. It was collected by filtration. Pure product was obtained (0.51 g, 75%). 1H NMR (400 MHz, CDCl₃, ppm): δ 7.35 (d, J=8.22 Hz, 2H), 7.30-7.267 (m, 4H) 7.15 (d, J=7.64 Hz, 4H), 7.10-7.06 (m, 2H), 6.90 (d, J=8.32 Hz, 2H), 6.79 (s, 4H), 2.28 (s, 6H), 2.05 (s, 12H).

**Synthesis of porous polymer NN-ph**

![Chemical Structure](image)

4,4,4-(Tri(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl))triphenylamine (388.0 mg, 0.62 mmol) and tris(4-bromophenyl)amine (300.0 mg, 0.62 mmol) were dissolved in 35 mL of CsCO₃/THF solution. The reaction mixture was degassed for 30 min, tetrakis(triphenylphosphine)palladium was then added to the reaction mixture and heated to 75°C for 72 h under nitrogen atmosphere. The mixture was cooled to room temperature, and the insoluble precipitated network polymer was filtered and washed four times with chloroform (3×50 mL), water (3×50 mL), methanol (3×50 mL), and acetone (3×50 mL) to remove any un-reacted monomers or catalyst residues. Further purification of the polymer was carried out by Soxhlet extraction with methanol for 24 h. The product was then dried under vacuum for 24 h at 60 °C to give grey powder in 83% yield.

Elemental analysis calcd for NN-ph: C, 96.94; N, 2.34; H, 1.72. Found: C, 95.03; N, 3.15; H, 1.82.
Fig. S1 (a) XRD pattern of BN-ph and BN-ph-ae

Fig. S2 SEM images of (a) BN-ph and (b) BN-ph-ae.

Table. S1 Pore structure properties of BN-ph and BN-ph-ae.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{\text{BET}}$ (m$^2$/g)$^a$</th>
<th>$S_{\text{Lang}}$ (m$^2$/g)$^b$</th>
<th>$S_{\text{micro}}$ (m$^2$/g)$^c$</th>
<th>$V_{\text{micro}}$ (cm$^3$/g)$^d$</th>
<th>$V_{\text{total}}$ (cm$^3$/g)$^e$</th>
<th>$P_{\text{NL-DFT}}$ (nm)$^f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BN-ph</td>
<td>1279</td>
<td>2307</td>
<td>884</td>
<td>0.54</td>
<td>0.81</td>
<td>1.54</td>
</tr>
<tr>
<td>BN-ph-ae</td>
<td>634</td>
<td>824</td>
<td>498</td>
<td>0.23</td>
<td>0.30</td>
<td>1.61</td>
</tr>
</tbody>
</table>

$^a$Surface areas calculated from the N$_2$ adsorption isotherm using the BET method. $^b$The Langmuir surface area calculated from the N$_2$ adsorption isotherm by application of the Langmuir equation. $^c$Micropore surface area calculated from the N$_2$ adsorption isotherm using the t-plot method. $^d$Micropore volume derived using the t-plot method based on the Halsey thickness equation. $^e$Total pore volume at P/P$_0$ =0.99. $^f$Pore size calculated from N$_2$ adsorption isotherms using non-local density functional theory (NL-DFT).
Fig. S3 (a) UV-vis and (b) Normalized fluorescence ($\lambda_{ex} = 300$ nm) of BN-ph-ae; (c) Luminescence photographs of BN-ph-ae in different solvents under UV irradiation ($\lambda_{ex} = 365$ nm).

Fig. S4 (a) UV-vis and (b) Normalized fluorescence ($\lambda_{ex} = 386$ nm) of NN-ph; (c) Luminescence photographs of NN-ph in different solvents under UV irradiation ($\lambda_{ex} = 365$ nm).

References