Supplementary Information

Porous Macromolecular Dihydropyridyl Frameworks Exhibiting Catalytic and Halochromic Activity

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(1) Spectroscopic Measurements

Figure S1. 1H-NMR (DMSO-d6) spectrum of 3,3'-benzene-1,4-diylbis(3-aminoprop-2-enenitrile).

Figure S2. FTIR spectrum of 3,3'-benzene-1,4-diylbis(3-aminoprop-2-enenitrile).
Figure S3. Solid-state UV-vis spectra of protonated and deprotonated PMF materials (black: protonated; red: deprotonated). The protonated PMFs are yellow turns red on deprotonation with OH. This protonation/deprotonation reaction is reversible.
(2) Gas Adsorption Studies

_Nitrogen Adsorption_

Isotherms for nitrogen adsorption and desorption at 77 K on PMF-NOTT-1 and PMF-NOTT-2 (black squares: adsorption; open squares: desorption) and DFT/Monte-Carlo pore size distributions (slit pore model; liquid N$_2$ density: 0.808 g cm$^{-3}$) are shown in Figures S4 and S5, respectively.

**Figure S4.** Isotherms of nitrogen adsorption and desorption on PMF-NOTT-1 and PMF-NOTT-2 at 77 K (black squares: adsorption; open squares: desorption).

**Figure S5.** DFT/Monte-Carlo pore size distributions (slit pore model; liquid N$_2$ density: 0.808 g cm$^{-3}$).
Dubinin-Radushkevich (D-R) Graphs for CO$_2$ adsorption

The D-R plots of CO$_2$ adsorption isotherms on PMF-NOTT-1 and PMF-NOTT-2 are given in Figure S6. It is evident that the D-R graphs overlap when plotted on a relative pressure (p/p$^0$) basis.

a)

![Graph for PMF-NOTT-1](image1)

b)

![Graph for PMF-NOTT-2](image2)

**Figure S6.** Dubinin-Radushkevich graphs of CO$_2$ adsorption isotherms at 273-303 K on a) PMF-NOTT-1 and b) PMF-NOTT-2.
Virial Equation Analysis

a)

PMF-NOTT-1
CO₂ adsorption at 273K

Y = A + B*10^X

Parameter Value Error
A -15.6058 0.0226
B1 -1.1491 0.3304
B2 83830.1381 863.9238

R-Square: 0.9564
SD 0.00056

b)

PMF-NOTT-1
CO₂ adsorption at 273K

Y = A + B*10^X

Parameter Value Error
A -15.7289 0.0143
B -1170.1635 12.2140

R SD
0.9976 0.0044

c)

PMF-NOTT-1
CO₂ adsorption at 283K

Y = A + B*10^X

Parameter Value Error
A -15.6029 0.0326
B1 -1.1491 0.3304
B2 83830.1381 863.9238

R-Square: 0.9564
SD 0.00056

d)

PMF-NOTT-1
CO₂ adsorption at 283K

Y = A + B*10^X

Parameter Value Error
A -15.1327 0.0369
B -1170.1635 12.2140

R SD
0.99919 0.02905

e)

PMF-NOTT-1
CO₂ adsorption at 303K

Y = A + B*10^X

Parameter Value Error
A -17.1002 0.0362
B1 -1.2310265 15.7614
B2 123580.9114 4963.1912

R-Square: 0.9871
SD 0.03235

f)

PMF-NOTT-1
CO₂ adsorption at 303K

Y = A + B*10^X

Parameter Value Error
A -17.1321 0.0369
B -1170.1635 12.2140

R SD
0.99862 0.0278
Figure S7. Virial graphs (polynomial: $\ln(n/p) = A_0 + A_1 n + A_2 n^2$ and linear: $\ln(n/p) = A_0 + A_1 n$, for CO$_2$ adsorption isotherms of PMF-NOTT-1 and PMF-NOTT-2 at 273, 283 and 303 K. 
a) PMF-NOTT-1 (273 K) (Polynomial Equation), b) PMF-NOTT-1 (273 K) (Linear Equation), 
c) PMF-NOTT-1 (283 K) (Polynomial Equation), d) PMF-NOTT-1 (283 K) (Linear Equation), 
e) PMF-NOTT-1 (303 K) (Polynomial Equation), f) PMF-NOTT-1 (303 K) (Linear Equation), 
g) PMF-NOTT-2 (273 K) (Polynomial Equation), h) PMF-NOTT-2 (273 K), (Linear Equation) 
i) PMF-NOTT-2 (283 K) (Polynomial Equation), j) PMF-NOTT-2 (283 K) (Linear Equation), 
k) PMF-NOTT-2 (303 K) (Polynomial Equation), l) PMF-NOTT-2 (303 K) (Linear Equation).

The isosteric adsorption heat at zero coverage ($q^{\text{st},0}$) was calculated from the gradient of plotting $A_0$ against $1/T$ i.e. $\partial A_0 / \partial (1/T) = q^{\text{st},0} / R$ ($R = 8.314$ J K$^{-1}$ mol$^{-1}$).

Figure S8. Variation of virial parameter $A_0$ with $1/T$ for a) PMF-NOTT-1 and b) PMF-NOTT-2. The isosteric heat ($q^{\text{st},0}$) of adsorption at zero surface coverage was calculated from the gradient of the straight line. The polynomial fitting of $\ln(n/p) \sim n$ gives values for PMF-NOTT-1 of $33.09 \pm 3.26$ kJ mol$^{-1}$ and for PMF-NOTT-2 of $31.86 \pm 1.35$ kJ mol$^{-1}$; as a comparison, linear fitting gives PMF-NOTT-1: $33.74 \pm 2.44$ kJ mol$^{-1}$, PMF-NOTT-2: $30.45 \pm 0.51$ kJ mol$^{-1}$. 
Figure S9. Variation of isosteric heat of adsorption \( (q^{st}) \) with amount of CO\(_2\) adsorbed a) PMF-NOTT-1 and b) PMF-NOTT-2.
Figure S10. Adsorption isotherms for H₂ in a) PMF-NOTT-1 and b) PMF-NOTT-2 at 77 and 87 K (closed symbols: adsorption; open symbols: desorption).

Figure S11. Virial graphs for equation \( \ln (n/P) = A_0 + A_1 n \) for H₂ adsorption for a) PMF-NOTT-1 (77 K) b) PMF-NOTT-1 (87 K), c) PMF-NOTT-2 (77 K), d) PMF-NOTT-2 (87 K)
The isosteric heat of adsorption at zero coverage \((q_{st,0})\) was calculated from the gradient of the graph of \(A_0\) against \(1/T\) i.e. \(\frac{\partial A_0}{\partial (1/T)} = \frac{q_{st,0}}{R}\) \((R = 8.314 \text{ JK}^{-1}\text{mol}^{-1})\) (for PMF-NOTT-1: \(q_{st,0} = 9.46 \text{ kJ mol}^{-1}\); for PMF-NOTT-2: \(q_{st,0} = 8.85 \text{ kJ mol}^{-1}\)).

(3) Catalysis Studies

Table S1. Data for different runs of the Knoevenagel condensation between aldehydes and malonitriles using PMF-NOTT-1 and PMF-NOTT-2 catalysts. a

<table>
<thead>
<tr>
<th>Run</th>
<th>Entry</th>
<th>Aldehyde</th>
<th>Catalyst</th>
<th>Time (h)</th>
<th>Conversion (%)b</th>
<th>Selectivity (%)b</th>
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<tbody>
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<td>1</td>
<td>7a</td>
<td>Benzaldehyde</td>
<td>PMF-NOTT-1</td>
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<td>68</td>
<td>98</td>
</tr>
<tr>
<td>2</td>
<td>7a</td>
<td>Benzaldehyde</td>
<td>PMF-NOTT-1c</td>
<td>54</td>
<td>66</td>
<td>98</td>
</tr>
<tr>
<td>3</td>
<td>7a</td>
<td>Benzaldehyde</td>
<td>PMF-NOTT-1d</td>
<td>54</td>
<td>63</td>
<td>98</td>
</tr>
<tr>
<td>4</td>
<td>7a</td>
<td>Benzaldehyde</td>
<td>PMF-NOTT-2</td>
<td>54</td>
<td>36</td>
<td>98</td>
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<tr>
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<td>PMF-NOTT-1</td>
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<td>64</td>
<td>97e</td>
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<tr>
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<td>7d</td>
<td>4-methylbenzaldehyde</td>
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<td>93</td>
<td>97e</td>
</tr>
</tbody>
</table>

a Reaction conditions: aldehyde (1 mmol), malonitrile (1 mmol), toluene (4 mL), catalyst (20 mg), 110 °C. b Determined by GC. c First reuse; d Second reuse; e 2 % of corresponding acid was observed.

(4) Scanning Electron Micrographs

![Scanning Electron Micrographs](image)

Figure S12. SEM images show the spherical morphology of PMF-NOTT-1 and PMF-NOTT-2.