Supporting Information

Constructing Polymer towards Two-Dimensional Nanosheets with Dual Mesopores and Intrinsic Photoactivity

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1. Experimental Section

Preparation of 2D mPTAPB nanosheets: Firstly, block co-polymer (BCP) of PS\textsubscript{90}-b-PEO\textsubscript{114} was synthesized according to the previous reports everywhere. Then, 0.050 g of PS\textsubscript{90}-b-PEO\textsubscript{114} was dissolved in 1 mL THF and add 8 mL H\textsubscript{2}O for generating the spherical micellar aggregate under stirring condition for 1 h. 0.024 g perfluorooctadecanoic acid solution (1.3 wt\% in ethanol) was added, then 20 mg monomer of 1, 3, 5-Tris (4-aminophenyl) benzene (TAPB) was dissolved in 1 ml hydrochloric acid (2 M) and added into the above mixing solution, which subsequently polymerized triggered by ammonium persulfate (APS, 0.076 g in 1 mL H\textsubscript{2}O). After continuous stirring, the solution gradually turns to dark purple, indicating the polymerization completed. By repeatedly removing soft template, excess oligomer and salt by washing with THF, ethanol and H\textsubscript{2}O. The final samples can collect by centrifugation and free-dry for avoiding accumulation of nanosheets. For each experiment, we can obtain 12 mg of pure porous nanosheets with a yield of 60\%. Our experiment can also be scaled up to 8 times proportionately, and the yield and morphology were not almost affected.
2. Characterization of 2D mPTAPB nanosheets.

The morphology and structure of the mPTAPB nanosheet samples were investigated by transmission electron microscopy (JEM-ARM300F), scanning electron microscopy (SEM, JSM-7800F&HITACHI-S4700), the powder samples are suspended in ethanol under ultrasonic treatment for 2 minutes, then a drop of the supernatant drops on a holey carbon film supported on 200 mesh copper grid and washed silicon wafer respectively, which is dried overnight at room temperature before analysis. Powder XRD patterns were recorded on a Bruker X-ray diffractometer (D8 Advance) equipped with Cu-Ka radiation (40 kV, 20 mA) at a rate of 2° min⁻¹ over the range 2–60 (2θ). Raman spectra were recorded with a Jobin-Yvon LabRAM HR Evolution spectrometer (laser wavelength 532 nm) by irradiating the surface of a solid powder on a glass sheet. The solvent dispersion sample was placed in a quartz cuvette, and measured at 519 nm by a UV-Vis spectrophotometer (UV-2600, Thermo) to get a UV absorption spectra and fluorescence analysis were achieved by HORIBA FluoroMax-4/Plus fluorescence spectrometer, respectively. Infrared spectra were recorded on a FT-IR Spectrometer (Nicolet iS50 FTIR, Thermo) by mixing the solid sample with KBr and grinding, pressing mixture powder into a tablet. Nitrogen absorption isotherms were measured at 77 K on a Quantachrome 9ASIQMUTV02UT-6. Prior to measurements, all samples were degassed at 120 °C for at least 12 h. Specific surface area was determined by standard Barrett–Emmett–Teller (BET) method in the relative pressure range of 0.05–0.9 P/P₀ and pore size distribution was analyzed by Density functional theory (DFT). Atomic force microscopy (AFM) images were recorded in air on a customized HORIBA JobinYvon AFM/BXFM in semicontact mode, and sample preparation method is similar to SEM.
3. Dynamic simulation of the fluorescence sensing process of 2D mPTAPB nanosheets.

Materials Studio software was used to simulate the sensing process and mechanism of 2D mPTAPB fluorescent probe in terms of quantum chemistry and dynamics, in which triphenylazo triphenyl benzene were selected as the model compound, regarding as the large molecule size of 2D mPTAPB nanosheets. The related parameter settings are the following,

The frontier molecular orbitals:

**Step1. Forcite Geometry Optimization**

- Ensemble: NVE
- Quality: Ultra-fine
- Forcefield: COMPASS II
- Charges: Forcefield assigned
- Quality: Ultra-fine
- Summation method: Electrostatic: atom based; Van der waals: atom based
- Orbital cutoff quality Fine
- Energy 1.0e-5
- Max. force 0.002 Ha/Å
- Max. displacement 0.05 Å
- Max. iterations: 50
- Max. step size: 0.3 Å
- Functional: GGA-BLYP
- Use symmetry

**Step2. DMol3 Geometry Optimization**

- Ensemble: NVE
- Quality: Ultra-fine
- Forcefield: COMPASS II
- Charges: Forcefield assigned
- Quality: Ultra-fine
- Summation method: Electrostatic: atom based; Van der waals: atom based
- Energy 1.0e-5
- Intergration accuracy: Fine
- SCF tolerance Fine
- Core treatment All Electron
- Basis set DNP
- Properties: Optics (TDDFT); Orbitals
- Occupation: thermal 0.0050
- Pseudopotential: none
- Property: Optics (TDDFT)
- Iteration: 10
- Convergence: 0.0000063 Ha

Dynamics simulation:

**Step 1. Forcite Dynamics**

- Ensemble: NVE
- Quality: Ultra-fine
- Forcefield: COMPASS II
- Charges: Forcefield assigned
- Quality: Ultra-fine
- Summation method: Electrostatic: atom based; Van der waals: atom based
- Temperature: 298.00 K
- Timestep: 1.00 fs
- Number of steps: 500000
- Duration: 500 ps

**Step 2. Forcite Geometry Optimization**

- Ensemble: NPT
- Total simulation time: 500ps
- Quality: Ultra-fine
- Forcefield: COMPASS II
- Charges: Forcefield assigned
- Quality: Ultra-fine
- Summation method: Electrostatic: atom based; Van der waals: atom based
- Temperature: 298.00 K
- Timestep: 1.00 fs
- Number of steps: 500000
- Duration: 500 ps
4. Supplementary Figures and Tables.

**Supplementary Figure 1.** $^1$H NMR spectrum of PS$_{90}$-$b$-PEO$_{114}$. The degree of polymerization (DP) was calculated by the formula,

$$\text{DP} = \frac{I_a/5}{I_b/4} \times 114 \approx 90$$
Supplementary Figure 2. FT-IR spectra of the as-made 2D mesoporous PTAPB nanosheets synthesized with block copolymer PS$_{90}$-b-PEO$_{114}$ and C$_{18}$-PFCA, and the control PTAPB samples (PTAPB-blank) without any templates. The Fourier-transform infrared (FT-IR) spectra (Figure S2, Supporting Information) demonstrated the complete removal of templates, because characteristic peaks of –COOH of PFCA and PEO/PS of BCP in the resultant 2D mPTAPB nanosheets were not detected. The appearance of new bands at 1444 cm$^{-1}$ and 1400 cm$^{-1}$ can be attributed to asymmetric vibration of the N=N bonds, manifesting the formation of azo groups of PTAPB polymers. The almost identical signals across the frequency bands of 500–4000 cm$^{-1}$ in the FT-IR spectra of 2D mPTAPB nanosheets with the controlled PTAPB samples (synthesized without any templates, denoted as PTAPB-blank) further proved the removal of the organic templates.
Supplementary Figure 3. Raman spectra of as-made 2D mPTAPB nanosheets. The azo-linkage formation was further confirmed by the Raman spectra because of the presence of typical N=N stretching modes of PTAPB at 1450 cm\(^{-1}\).
Supplementary Figure 4. XRD patterns of the as-made 2D mPTAPB nanosheets, which revealed a featureless diffraction pattern, suggesting that the resultant polymeric backbones were amorphous.
Supplementary Figure 5. UV–vis absorption spectra of the PTAPB-blank and 2D mPTAPB nanosheet samples.
Supplementary Figure 6. SEM images of the control PTAPB irregular particles (denoted as PTAPB-blank) synthesized without the PFCA and BCP templates.
Supplementary Figure 7. SEM images of the 2D mPTAPB nanosheets (A) dispersed in ethanol solvent for 15 days, (B) 10K, (C) 50K magnification of expanding the experiment eightfold proportionately. (D) TEM images of the 2D mPTAPB nanosheets.
Supplementary Figure 8. The stability of samples dispersed in different solvents (left column) and samples with different concentrations (0.5 g/L, 1 g/L, 2 g/L and 4 g/L) in ethanol (right column).
**Supplementary Figure 9.** Nitrogen adsorption–desorption isotherm (left) and pore size distributions (right) of the 2D mPTAPB nanosheets and PTAPB-blank. The isotherms of the 2D mPTAPB nanosheet samples are offset vertically by 40 cm$^3$ g$^{-1}$ STP.
Supplementary Figure 10. The fluorescence intensities of 2D mPTAPB nanosheets in CH$_3$OH at different concentration.
Supplementary Figure 11. (a) The fluorescence quenching curves of 2D mPTAPB nanosheets and PTAPB-blank in different volumes of triphenylphosphine and (b) their fluorescence (Solvent-CH₃OH; concentration of 2D mPTAPB-0.1 mg/mL; concentration of triphenylphosphine-1000 ppm).
Supplementary Figure 12. Dynamics diagram of the interactions between trimethylphosphine and 2D mPTAPB nanosheets before and after 500 ps NPT dynamics process.
Supplementary table 1. Porous properties of as-synthesized and carbonized samples of 2D mPTAPB nanosheets.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Surface area$^a$ [m² g⁻¹]</th>
<th>Pore volume [cm³ g⁻¹]</th>
<th>micropore size$^b$ [nm]</th>
<th>mesopore size$^c$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>mPTAPB</td>
<td>268</td>
<td>0.69</td>
<td>2.6</td>
<td>15</td>
</tr>
<tr>
<td>PTAPB-blank</td>
<td>106</td>
<td>0.17</td>
<td>2.5</td>
<td>---</td>
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</tbody>
</table>

Note: $^a$ Surface area was obtained based on the Brunauer–Emmett–Teller (BET) method. $^b, c$ The micropore size was obtained from DFT calculation by BET test and the mesopore size was obtained from TEM characterization and averaged at least 20 points.