Supplementary Information

For

A covalent triazine-based framework from tetraphenylthiophene and 2,4,6-trichloro-1,3,5-triazine motifs for sensing o-nitrophenol and effective I\textsubscript{2} uptake

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Experimental section

Chemicals

2,3,4,5-Tetraphenylthiophene (98%) was purchased from J&K China Chemical Ltd. Co. (Shanghai) and used as received. 2,4,6-trichloro-1,3,5-triazine (TCT) and anhydrous aluminium chloride, methane-sulfonic acid were purchased from Aladdin reagent Co., Ltd. (Shanghai) and used as received. Unless otherwise noted, all other reagents and solvents were of analytical grade and used as supplied without further purification.

Physical characterization

Fourier transform infrared (FT-IR) spectra were performed on a Thermo Nicolet Nexus 380 in KBr pellets. Solid-state $^{13}\text{C}$ cross polarization magic angle spinning ($^{13}\text{C}$ CP/MAS) NMR spectrum was obtained on a Bruker Avance III 400 NMR spectrometer. The spectrum was obtained by using a contact time of 2.0 ms and a relaxation delay of 10.0 s. Elemental analysis (CHN) was performed on an analyzer (model VarioELIII). Powder X-ray diffraction (PXRD) data were collected over the 20 range 5–60° on a RINT Ultima III diffractometer equipped with Ni-filtered Cu Kα radiation (40 kV, 100 mA) at room temperature with a scan speed of 5° min⁻¹. Thermogravimetric analysis (TGA) were carried out using a Mettler ATA409PC thermogravimetric analysis instrument in a flowing N₂ atmosphere with a heating rate of 10° C
min\(^{-1}\) from r.t. to 800 °C. The dry state polymer surface area and pore size distribution was tested using a Bel Japan Inc. model BELSORP-mini II sorption analyzer by nitrogen adsorption and desorption at 77 K. The pore parameters, including BET specific surface area, pore size, and pore volume, could be evaluated from the obtained adsorption–desorption isotherms. Before each measurement, the samples were degassed for 12 h at 150 °C under vacuum. 50–100 mg polymer was used for each gas sorption test. For all adsorption–desorption measurements, the gases used were of ultra-high purity grade. The specific surface area (\(S_{\text{BET}}\)) was calculated according to the Dubinin–Radushkevich models over the relative pressure \((P/P_0)\) range from 0.01 to 0.05. The pore size distribution was derived from the adsorption branches using the non-local density functional theory (NLDFT) approach. The total pore volume (\(V_{\text{total}}\)) was estimated from the sorption curves at a relative pressure \(P/P_0\) of 0.996. Scanning electron microscopy (SEM) was recorded using a JEOL-3400LV microscope with at accelerating voltage of 10 kV. Before measurement, the sample was sputter coated with gold. UV–vis absorption of sample solutions in THF were measured in a 1 cm quartz cell using a PerkinElmer Lambda 950 UV–vis spectrophotometer. Fluorescence spectra were conducted on RF-5301PC Spectrophotometer (Shimadzu), and the sample was ultrasonically dispersed in THF. Raman spectra were measured on DXR Raman spectrometer.
Synthesis of TTPT by Friedel–Crafts Polymerization

A typical procedure for the polymerization is as follows: To a solution of 2,3,4,5-Tetraphenylthiophene (1.457 g, 3.75 mmol) in dichloromethane (50 mL), 2,4,6-trichloro-1,3,5-triazine (0.9221 g, 5.0 mmol) and anhydrous aluminum chloride (2.400 g, 18.0 mmol) were added. After reflux for 24 h, the reaction mixture was then cooled to room temperature. The product was isolated by filtration, washed with methanol, 0.2 mol L\textsuperscript{-1} NaOH solution, 0.2 mol L\textsuperscript{-1} H\textsubscript{2}SO\textsubscript{4}, water, acetone, and chloroform to remove any impurities. Further purification was done by soxhlet extraction with methanol. Finally, the product was dried at 323 K overnight to give a brown red powder (54.41 % yield). Anal. Calcd for (C\textsubscript{34}H\textsubscript{16}N\textsubscript{6}S\textsubscript{1})\textsubscript{n}: C 75.540, H 2.983, N 15.546, S 5.931. Found: C 76.18, H 3.484, N 13.470, S 5.929. \textsuperscript{13}C NMR (\delta ppm) : 171.16, 137.77, 127.38. FT-IR (cm\textsuperscript{-1}): 1704.87, 1601.29, 1540.99, 1519.35, 1386.3.
Fig. S1. FT-IR spectra of the (a) TTPT, (b) I$_2$@TPTT, (c) TCT, and (d) TPT.
Fig. S2. Solid-State UV-VIS spectra of TTPT, TCT and TPT.

Fig. S3. SEM pictures of TTPT. Scale: (a) 10.0 μm, (b) 20.0 μm.

Fig. S4. X-ray powder diffraction patterns of I₂, TTPT and I₂@TTPT.
Fig. S5. TGA curves for TTPT and I$_2$@TTPT with a heating rate of 10 °C·min$^{-1}$ in N$_2$.

Table S1. BET surface area, total pore volume, micropore volume for TTPT

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$S_{\text{BET}}$ $^a$ (m$^2$ g$^{-1}$)</th>
<th>$S_{\text{LAN}}$ $^a$ (m$^2$ g$^{-1}$)</th>
<th>$V_{\text{Total}}$ $^b$ (cm$^3$ g$^{-1}$)</th>
<th>$V_{\text{micro}}$ $^c$ (cm$^3$ g$^{-1}$)</th>
<th>$V_{\text{micro}}/V_{\text{total}}$</th>
<th>$S_{\text{micro}}$ (m$^2$ g$^{-1}$)</th>
<th>$S_{\text{external}}$ (m$^2$ g$^{-1}$)</th>
<th>Pore Diameter Dv(d) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TTPT</td>
<td>315.5</td>
<td>361.0</td>
<td>0.232</td>
<td>0.127</td>
<td>0.5474</td>
<td>231.99</td>
<td>129.03</td>
<td>1.428</td>
</tr>
</tbody>
</table>

a) Calculated using adsorption branches over the pressure range 0.05~0.25 P/P$_0$ of N$_2$ isotherm at 77 K.

b) Determined from the N$_2$ isotherms at P/P$_0$=0.996.

c) Determined from the t-plot method based on the Halsey thickness equation.
Fig. S6. (a) Fluorescence spectral changes of TTPT dispersed in THF upon addition of o-NP \((5.0 \times 10^{-5} \text{ mol L}^{-1})\). (b) The curve of (b) is the evolution of maximum fluorescence intensity as a function of time. The excitation wavelength was 370 nm.
Fig. S7. Fluorescence spectra of the TTPT measured in dispersions of THF (1.0 mg mL$^{-1}$, excited at 370 nm). (a) DNT, (b) DCIB, (c) NB, (d) NT, (e) PA, and (f) PhOH.
Table S2 The equation of $I_0/I$ of TTPT to the concentrations of NACs for suspension in THF exciting at 370 nm.

<table>
<thead>
<tr>
<th>The equation</th>
<th>Regression coefficient (R)</th>
<th>The concentration range of NACs (mol L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_0/I=0.9873+9.74\times10^2[PA]$</td>
<td>0.9974</td>
<td>0 to $1.25\times10^{-3}$</td>
</tr>
<tr>
<td>$I_0/I=0.97231+6.20\times10^3[o-NP]$</td>
<td>0.9969</td>
<td>0 to $2.5\times10^{-4}$</td>
</tr>
<tr>
<td>$I_0/I=0.89042+1.39\times10^2[NT]$</td>
<td>0.9977</td>
<td>$1.0\times10^{-3}$ to $3.5\times10^{-3}$</td>
</tr>
<tr>
<td>$I_0/I=0.85168+3.37\times10^2[DNT]$</td>
<td>0.9972</td>
<td>$5.0\times10^{-4}$ to $4.5\times10^{-3}$</td>
</tr>
<tr>
<td>$I_0/I=0.90466+1.16\times10^2[NB]$</td>
<td>0.9892</td>
<td>$1.0\times10^{-3}$ to $6.0\times10^{-3}$</td>
</tr>
</tbody>
</table>

Table S3. HOMO-LUMO energy levels of the TTPT and NACs simulated by DFT calculations at the B3LYP 6-31G** level.

<table>
<thead>
<tr>
<th></th>
<th>TTPT</th>
<th>o-NP</th>
<th>PA</th>
<th>DNT</th>
<th>NB</th>
<th>NT</th>
</tr>
</thead>
<tbody>
<tr>
<td>LUMO(eV)</td>
<td>-2.40916</td>
<td>-2.71069</td>
<td>-3.89792</td>
<td>-2.97687</td>
<td>-2.4855</td>
<td>-2.31762</td>
</tr>
<tr>
<td>HOMO(eV)</td>
<td>-5.90153</td>
<td>-6.79646</td>
<td>-8.23738</td>
<td>-8.11308</td>
<td>-7.13665</td>
<td>-7.36362</td>
</tr>
</tbody>
</table>
Fig. S8. Fluorescent spectra of the TTPT before and after annealing at different temperatures for 30 min in air. (1.0 mg mL$^{-1}$ in THF, $\lambda_{ex}$=370 nm.)

Fig. S9 UV–vis spectra of I$_2$@TTPT and I$_2$. 
Fig. S10 Raman spectrums of (a) I$_2$, iodine-loaded TTPT (I$_2$@TTPT) and (b) TTPT.
Fig. S11 (a) Calibration plot of standard iodine by UV-Vis spectra in ethanol solution.

(b) The fitting of Abs value vs concentration of $I_2$ with the relatively good linearity satisfies Lambert-Beer Law.
Fig. S12 (a) Calibration plot of standard iodine by UV-Vis spectra in cyclohexane solution. (b) The fitting of Abs value vs concentration of I$_2$ with the relatively good linearity satisfies Lambert-Beer Law.