Electronic Supplementary Material (ESI) for Polymer Chemistry.

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_2 uptake

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Experimental section

Chemicals

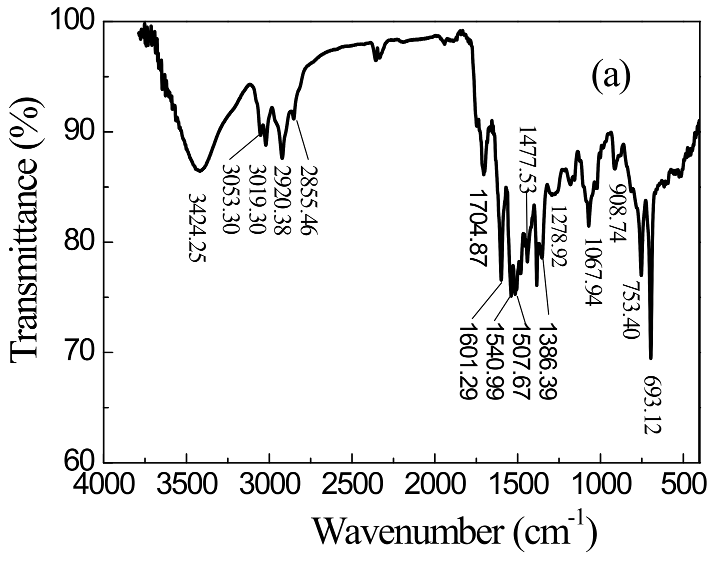
2,3,4,5-Tetraphenylthiophene (98%) was purchased from J&K China Chemical Ltd. Co. (Shanghai) and used as received. 2,4,6-trichloro-1,3,5-triazine (TCT) and anhydrous aluminium chloride, methane-sulfonic acid were purchased from Aladdin reagent Co., Ltd. (Shanghai) and used as received. Unless otherwise 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}C cross polarization magic angle spinning (^{13}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 2θ range 5–60^{o} 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^{o} min^{-1}. Thermogravimetric analysis (TGA) were carried out using a Mettler ATA409PC thermogravimetric analysis instrument in a flowing N_2 atmosphere with a heating rate of 10^{o} C min^{-1} from r.t. to 800 ^{o}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 ^{o}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_{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_{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^{-1} NaOH solution, 0.2 mol L^{-1} H_2SO_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 $(C_{34}H_{16}N_6S_1)n$: 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. s s^{13}C NMR (δ ppm) : 171.16, 137.77, 127.38. FT-IR (cm^{-1}): 1704.87, 1601.29, 1540.99, 1519.35, 1386.3.



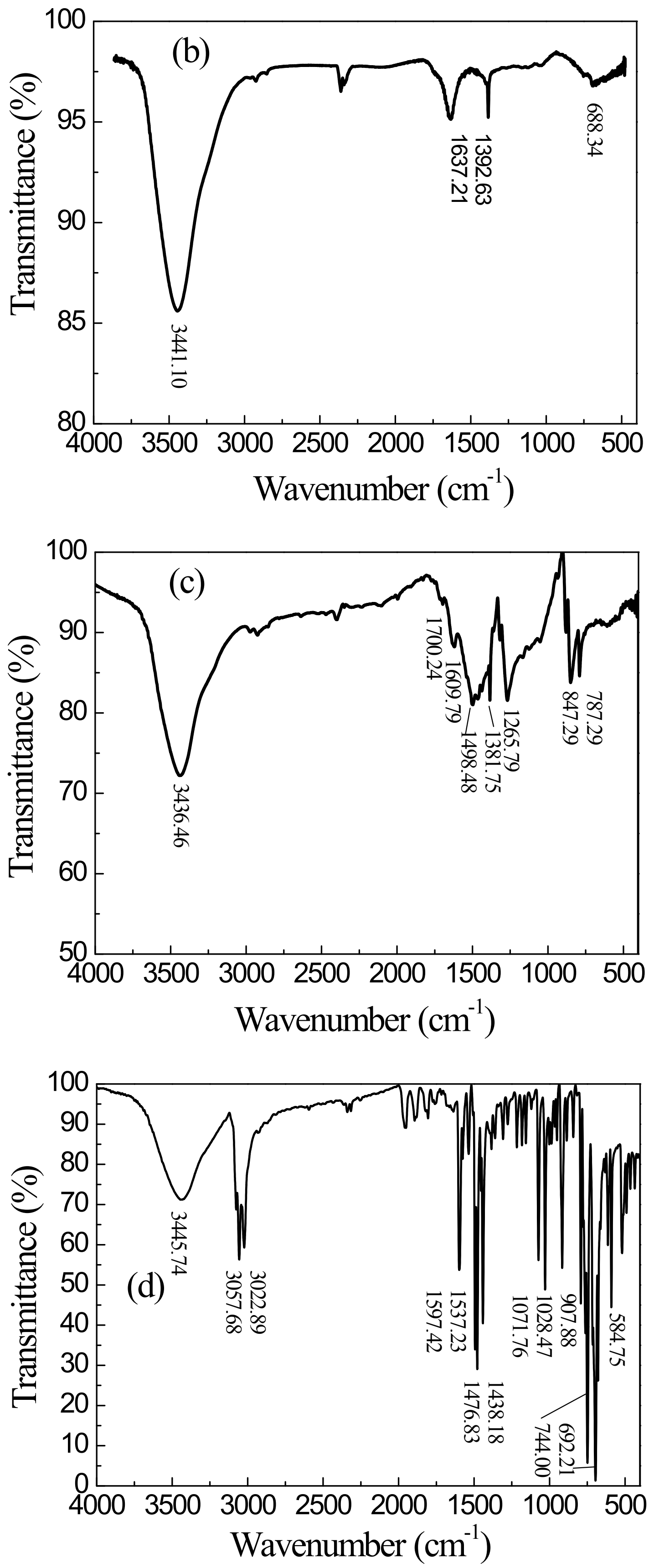


Fig. S1. FT-IR spectra of the (a) TTPT, (b) I_2@TPTT, (c) TCT, and (d) TPT.

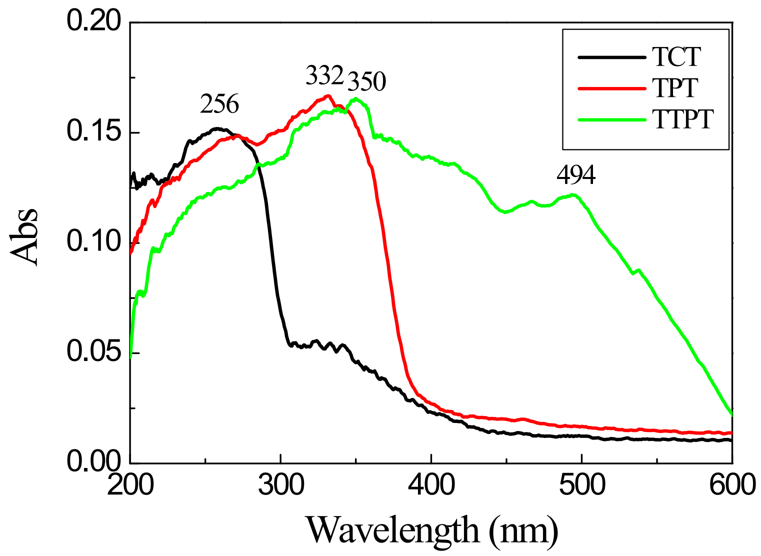


Fig. S2. Solid-State UV-VIS spectra of TTPT, TCT and TPT.

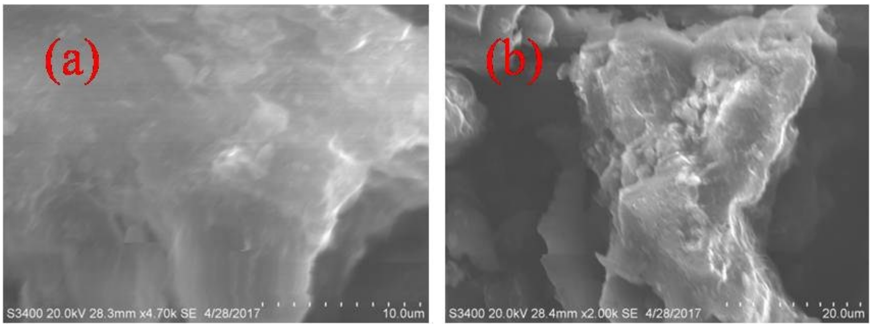


Fig. S3. SEM pictures of TTPT. Scale: (a) 10.0 μm, (b) 20.0 μm.

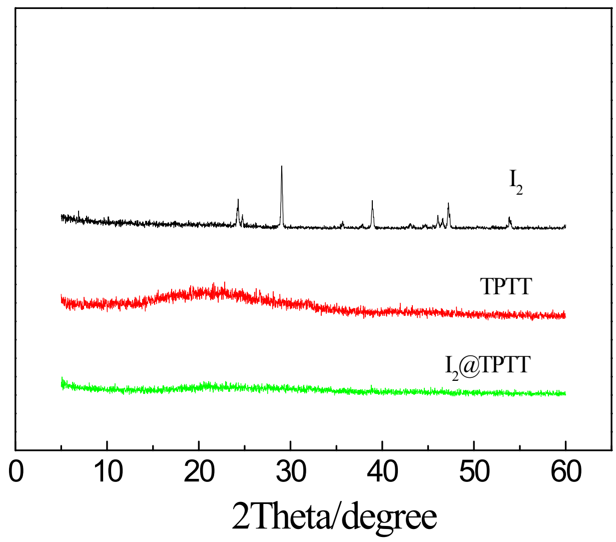


Fig. S4. X-ray powder diffraction patterns of I_2, TTPT and I_2@TTPT.

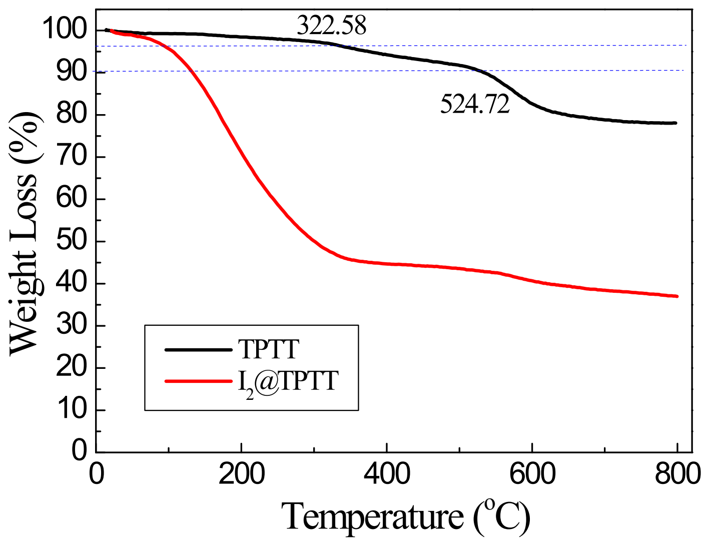


Fig. S5. TGA curves for TTPT and I_2@TTPT with a heating rate of 10 °C·min^{-1} in N_2.

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

Polymer	S_{BET} [a] ($m^2\ g^{-1}$)	S_{LAN} [a] ($m^2\ g^{-1}$)	V_{Total} [b] ($cm^3\ g^{-1}$)	V_{micro} [c] ($cm^3\ g^{-1}$)	V_{micro}/ V_{total}	S_{micro} ($m^2\ g^{-1}$)	$S_{external}$ ($m^2\ g^{-1}$)	Pore Diameter Dv(d) (nm)
TTPT	315.5	361.0	0.232	0.127	0.5474	231.99	129.03	1.428

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.

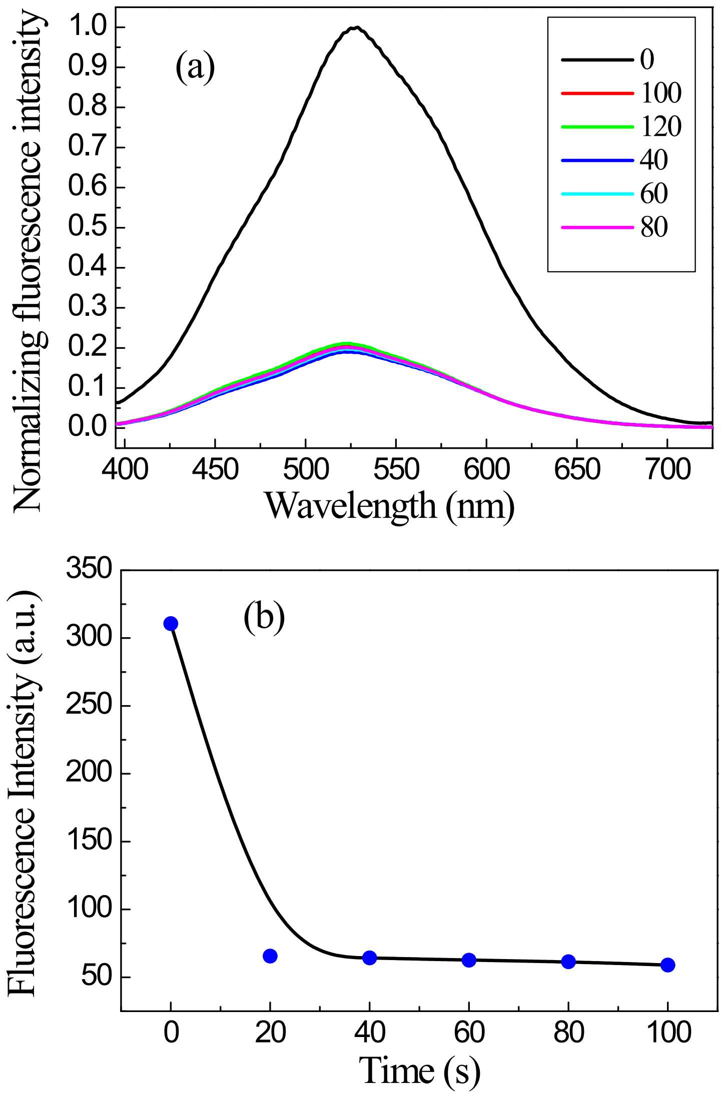
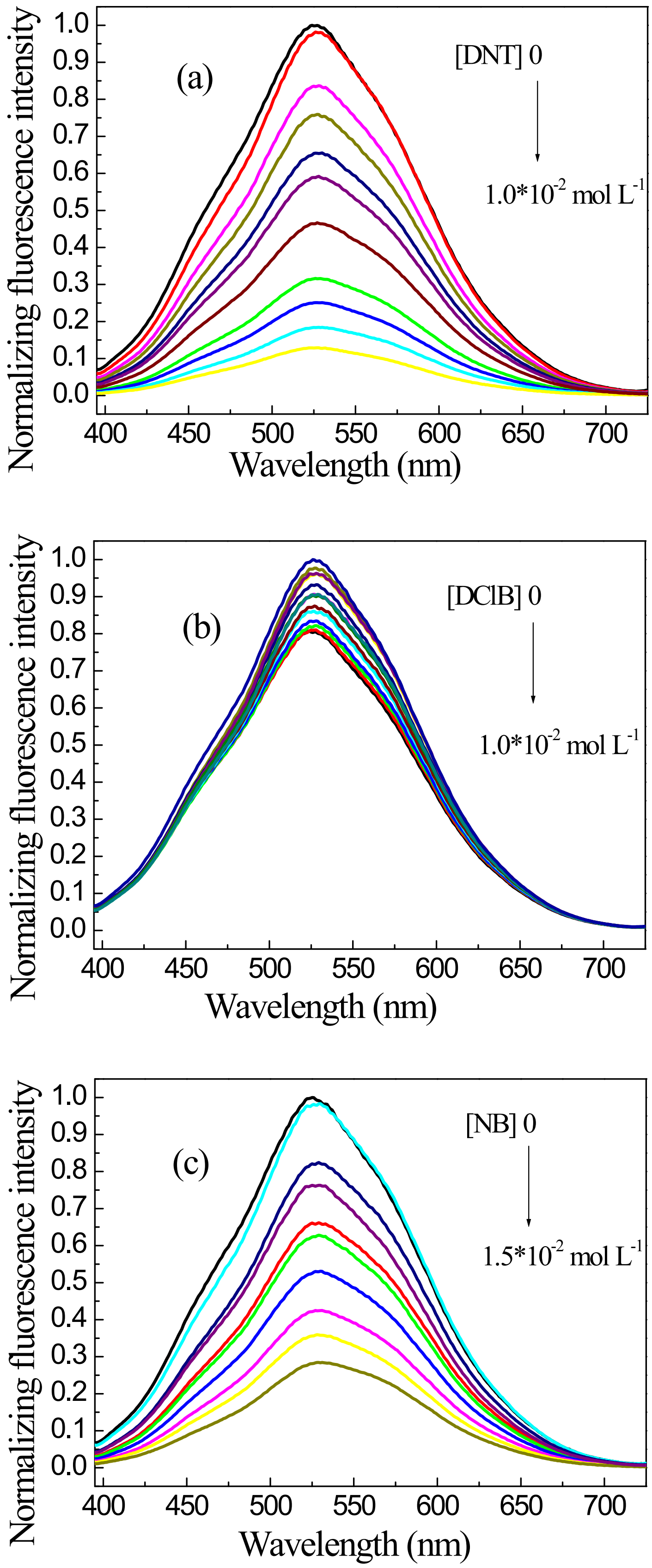


Fig. S6. (a) Fluorescence spectral changes of TTPT dispersed in THF upon addition of o-NP (5.0×10^{-5} mol L^{-1}). (b) The curve of (b) is the evolution of maximum fluorescence intensity as a function of time. The excitation wavelength was 370 nm.


(a)
[DNT] 0
1.0*10-2 mol L-1
Normalizing fluorescence intensity
Wavelength (nm)
(b)
[DClB] 0
1.0*10-2 mol L-1
Normalizing fluorescence intensity
Wavelength (nm)
(c)
[NB] 0
1.5*10-2 mol L-1
Normalizing fluorescence intensity
Wavelength (nm)

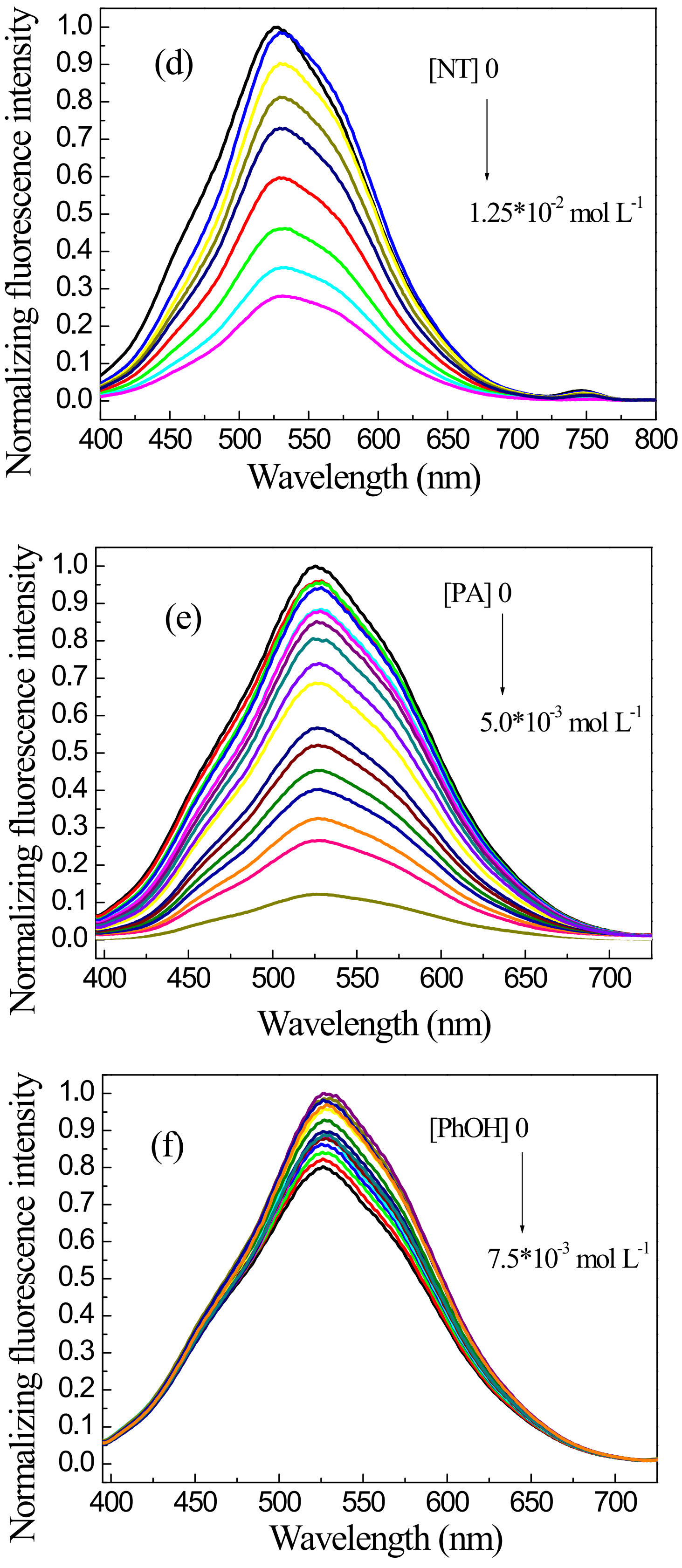


Fig. S7. Fluorescence spectra of the TTPT measured in dispersions of THF (1.0 mg mL^{-1}, excited at 370 nm). (a) DNT, (b) DClB, (c) NB, (d) NT, (e) PA, and (f) PhOH.

Table S2 The equation of I_0/I of TTPT to the concentrations of NACs for suspension in THF exciting at 370 nm.

The equation	Regression coefficient (R)	The concentration range of NACs (mol L^{-1})
$I_0/I=0.9873+9.74\times10^2[PA]$	0.9974	0 to 1.25×10^{-3}
$I_0/I=0.97231+6.20\times10^3[o\text{-}NP]$	0.9969	0 to 2.5×10^{-4}
$I_0/I=0.89042+1.39\times10^2[NT]$	0.9977	1.0×10^{-3} to 3.5×10^{-3}
$I_0/I=0.85168+3.37\times10^2[DNT]$	0.9972	5.0×10^{-4} to 4.5×10^{-3}
$I_0/I=0.90466+1.16\times10^2[NB]$	0.9892	1.0×10^{-3} to 6.0×10^{-3}

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

	TTPT	o-NP	PA	DNT	NB	NT
LUMO(eV)	-2.40916	-2.71069	-3.89792	-2.97687	-2.4855	-2.31762
HOMO(eV)	-5.90153	-6.79646	-8.23738	-8.11308	-7.13665	-7.36362

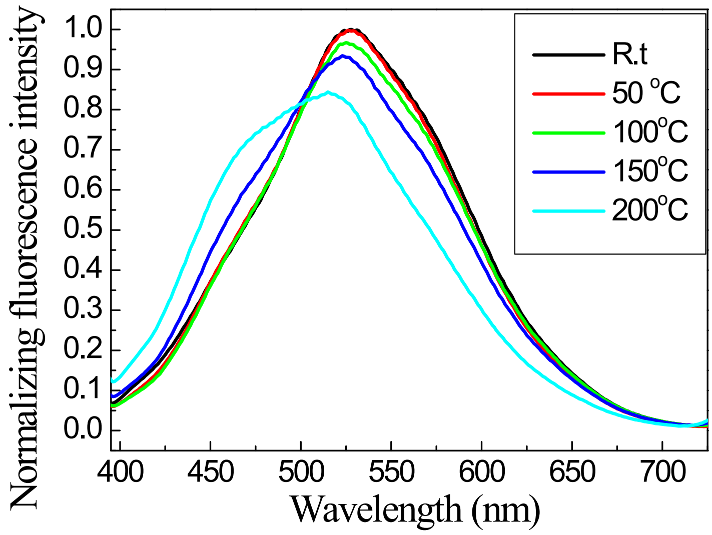


Fig. S8. Fluorescent spectra of the TTPT before and after annealing at different temperatures for 30 min in air. (1.0 mg mL^{-1} in THF, λex=370 nm.)

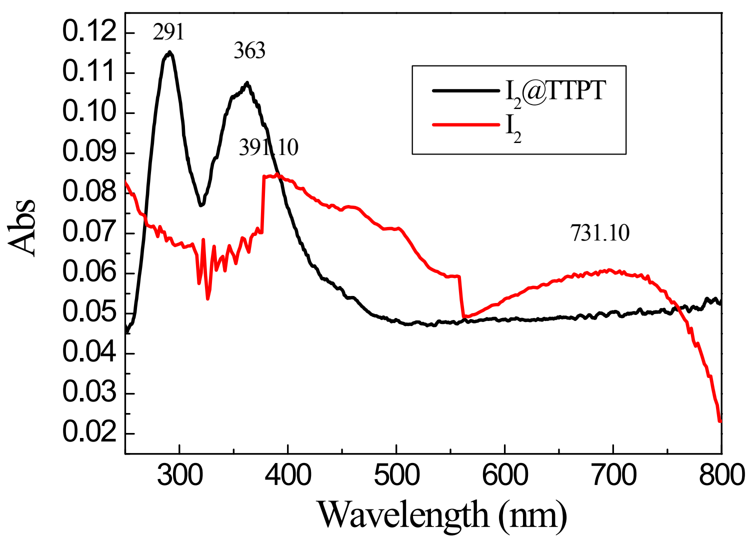


Fig. S9 UV−vis spectra of I_2@TTPT and I_2.

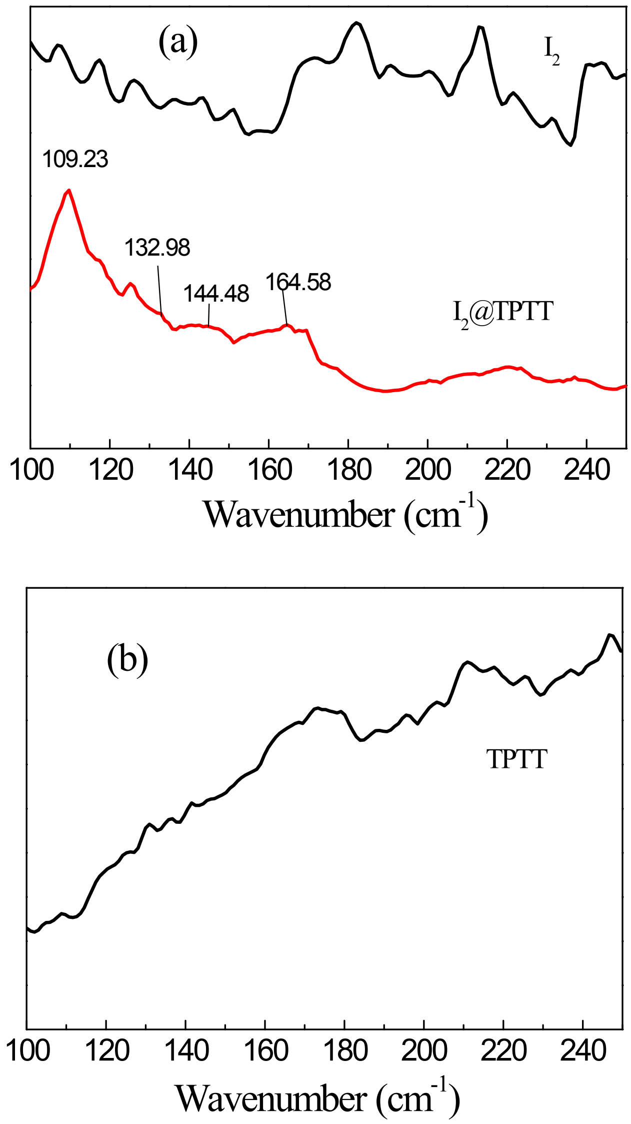
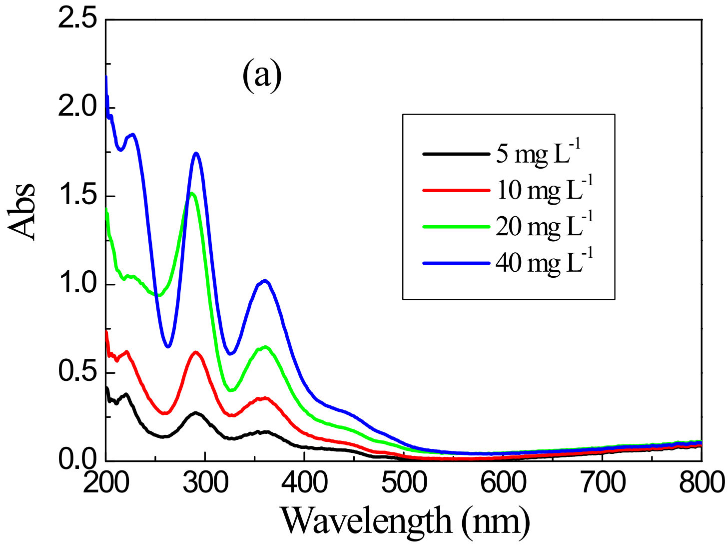


Fig. S10 Raman spectrums of (a) I_2, iodine-loaded TTPT (I_2@TTPT) and (b) TTPT.



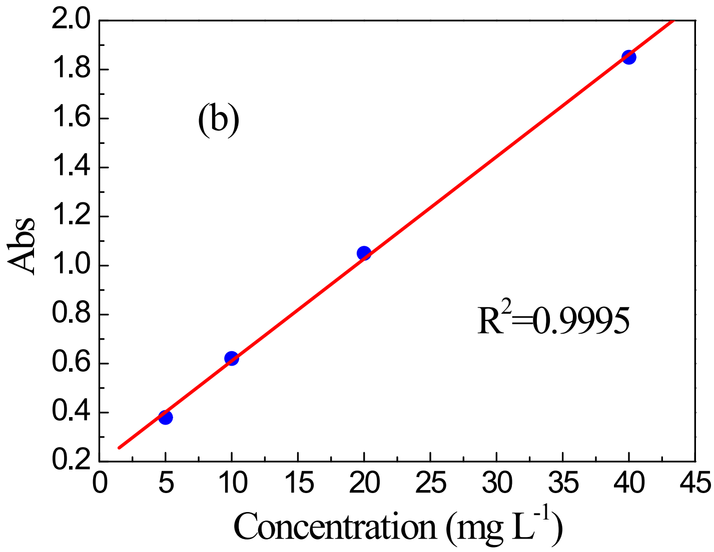


Fig. S11 (a) Calibration plot of standard iodine by UV-Vis spectra in ethanol solution. (b) The fitting of Abs value vs concentration of I_2 with the relatively good linearity satisfies Lambert-Beer Law.

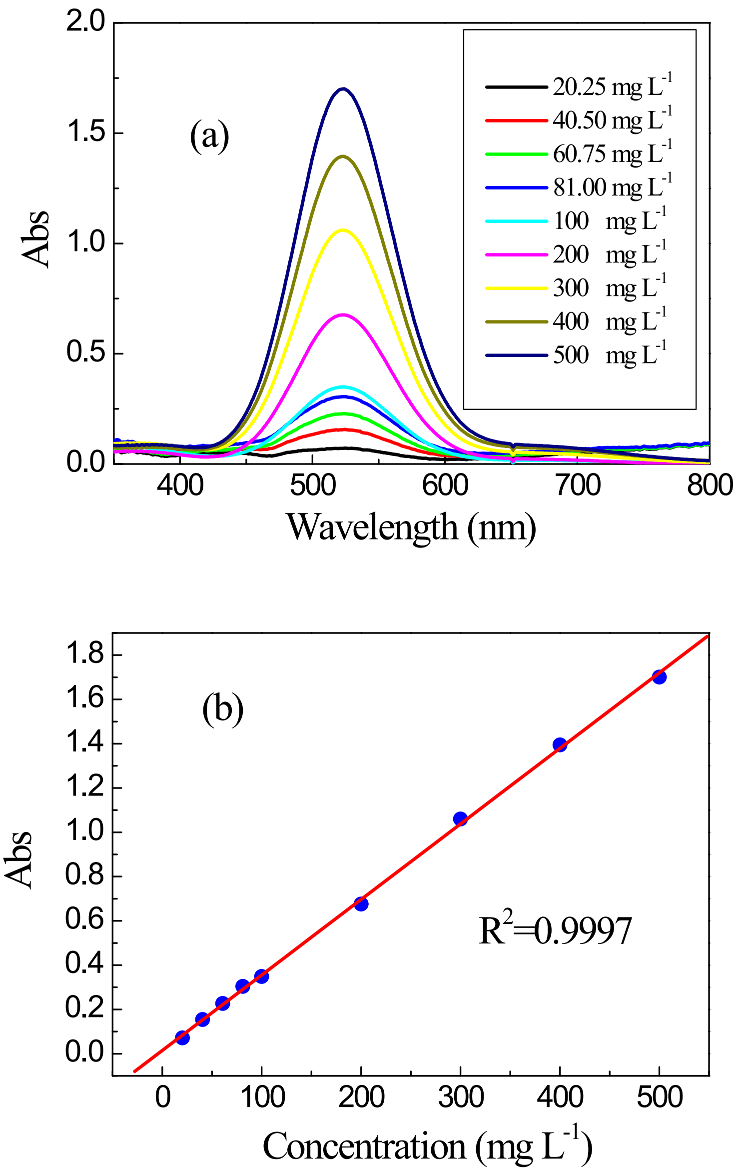


Fig. S12 (a) Calibration plot of standard iodine by UV-Vis spectra in cyclohexane solution solution. (b) The fitting of Abs value vs concentration of I_2 with the relatively good linearity satisfies Lambert-Beer Law.