

Supporting Information

Polytriazine Porous Networks for Effective Iodine Capture

Chenchen Feng,^a Guangjuan Xu,^a Wei Xie,^a Shuran Zhang,^a Chan Yao,^{*a} and Yanhong Xu^{*a,b}

^aKey Laboratory of Preparation and Applications of Environmental Friendly Materials, Key Laboratory of Functional Materials Physics and Chemistry of the Ministry of Education (Jilin Normal University), Ministry of Education, Changchun, 130103, China. Email: xuyh198@163.com

^bSchool of Chemistry and Environmental Engineering, the Collaborative Innovation Center of Optical Materials and Chemistry, Changchun University of Science and Technology, Changchun, 130022, China.

Contents

Section A. Materials and methods

Section B. Synthetic procedures

Section C. FT-IR spectra

Section D. The elemental analysis

Section E. The solid-state ¹³C NMR spectra

Section F. Powder X-ray diffraction patterns

Section G. The UV spectra

Section H. TEM images

Section I. TGA curves

Section J. Pore size distribution curves

Section K. Iodine capture analyses

Section L. XPS spectrum

Section M. Iodine release photos

Section N. Reusability of the CMPs

Section O. CO₂ adsorption isotherms

Section P. References

Section A. Materials and methods

N^2,N^4,N^6 -Tris(4-bromophenyl)-1,3,5-triazine-2,4,6-triamine (TBTT) was purchased from Shanghai YuKang company. 2,4,6-Triaminotriazine was purchased from Shanghai Macklin biochemical company. 4,4''-Diamino-*p*-terphenyl, benzidine and *p*-Phenylenediamine were purchased from Aladdin. Bis(dibenzylideneacetone)palladium (0) was purchased from Energy Chemical. Sodium tert-butoxide and 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl were purchased from san bang chemical. All solvents used were purchased from Aladdin.

Fourier transform Infrared (FT-IR) spectra were recorded on a Perkin-elmer model FT-IR-frontier infrared spectrometer. For all FT-IR tests, a small amount of sample can be directly mixed with potassium bromide and ground into a powder, and then compressed, and the pressed product can be directly tested. The UV-visible analyzer was used for JASCO V-770ST. For the UV test, the blank sample test is first carried out with the solid barium sulfate powder as the background, and then the holder with solid samples of CMPs was mounted onto the window of the integration sphere. Solid-state ^{13}C CP/MAS NMR measurements was recorded using a Bruker AVANCE III 400 WB spectrometer at a MAS rate of 5 kHz and a CP contact time of 2 ms. X-ray photoelectron spectra (XPS) were recorded on an ESCALAB250Xi electron spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA). Field-emission scanning electron microscopy (FE-SEM) images were performed on a JEOL model JSM-6700 operating at an accelerating voltage of 5.0 kV. High-resolution transmission electron microscopy (HR-TEM) images were obtained on a JEOL model JEM-3200 microscopy. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku model RINT Ultima III diffractometer by depositing powder on glass substrate, from $2\theta = 1.5^\circ$ up to 60° with 0.02° increment. TGA analysis data were carried out using a Q5000IR analyser (TA Instruments) with an automated vertical overhead thermobalance. Before measurement, the samples were heated for 12 h at a rate of 5°C min^{-1} under a nitrogen atmosphere.

Nitrogen sorption isotherms were measured at 77 K with ASIQ (iQ-2) volumetric adsorption analyzer. Carbon dioxide sorption isotherms were measured at 318 K and 70 bar with a iSorbHP2 analyzer, respectively. Before measurement, the samples were also degassed in vacuum at 120°C more than 10 h.

Section B. Synthetic procedures

Synthesis of TBTT-CMP@1

Firstly, *N*²,*N*⁴,*N*⁶-Tris(4-bromophenyl)-1,3,5-triazine-2,4,6-triamine (TBTT) (44.4 mg, 0.075 mmol), *p*-phenylenediamine (12.2 mg, 0.113 mmol), 2-dicyclohexylphosphine-2,4,6-triisopropylbiphenyl (21.5 mg, 0.046 mmol), bis(dibenzylideneacetone)palladium (17.3 mg, 0.03 mmol), and sodium tert-butoxide (192.2 mg, 2 mmol) were added to the two-necked bottle in turn. Next, the 4 mL of anhydrous toluene and 2 mL of anhydrous *n*-butanol were separately added into a 50 mL two-necked flask, then the flask was exchanged 3 cycles under vacuum/N₂. After evacuating three times, it was filled with nitrogen gas, and then the reaction was heated to 120 °C for 48 h. After completion of the reaction, the obtained product was cooled to room temperature, and washed with water, methanol and chloroform for three times, respectively, to give TBTT-CMP@1 as black powder (71% yield).

Synthesis of TBTT-CMP@2-3

Similar method was used for the preparation of TBTT-CMP@1, when the monomer *p*-phenylenediamine was changed to benzidine (20.82 mg, 0.113 mmol) finally obtained TBTT-CMP@2 as black powder (73% yield). When the monomer *p*-phenylenediamine was changed to 4,4'-diaminoterphenyl (29.41 mg, 0.113 mmol) to give TBTT-CMP@3 as black powder (75% yield).

Section C. FT-IR spectra

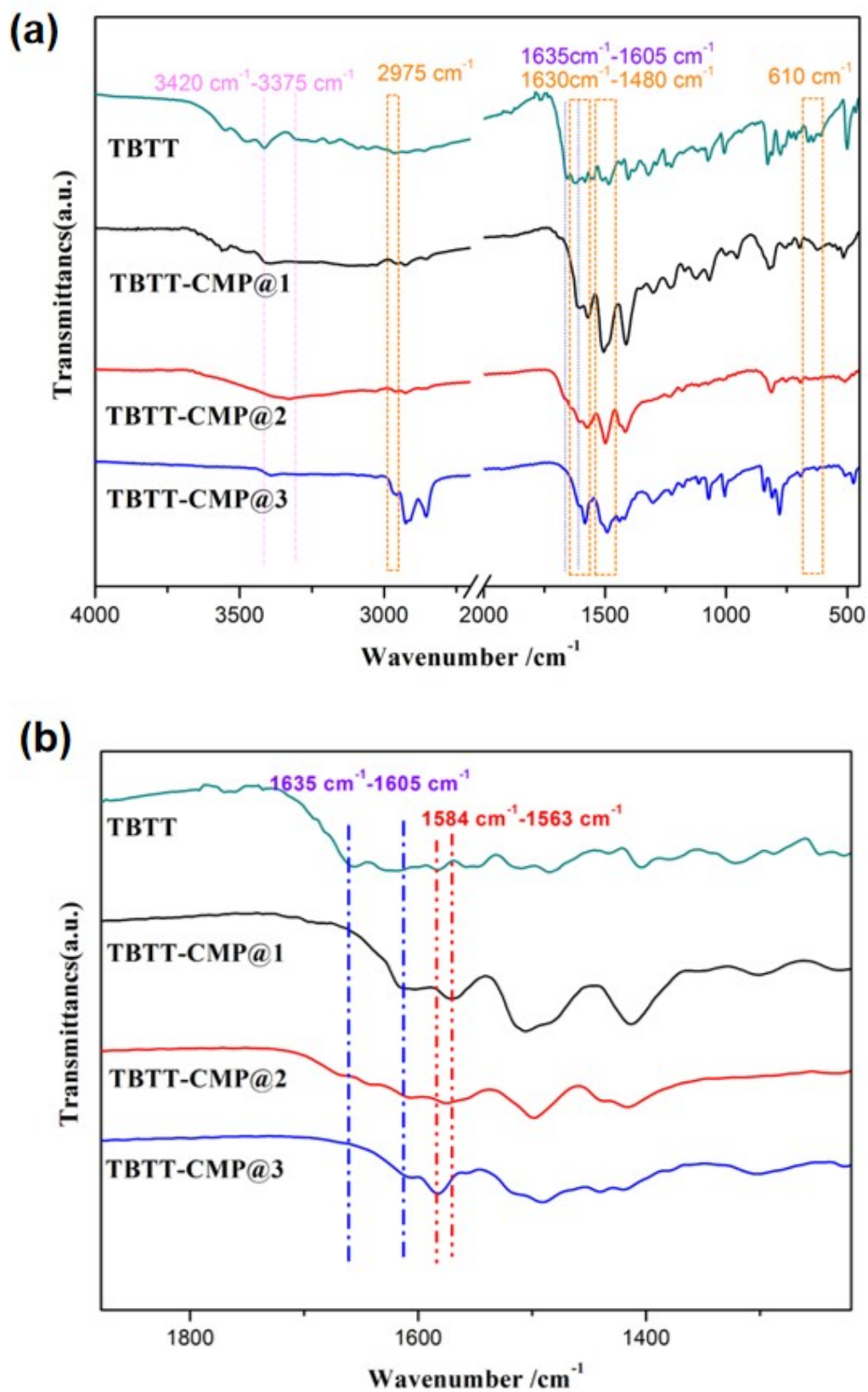


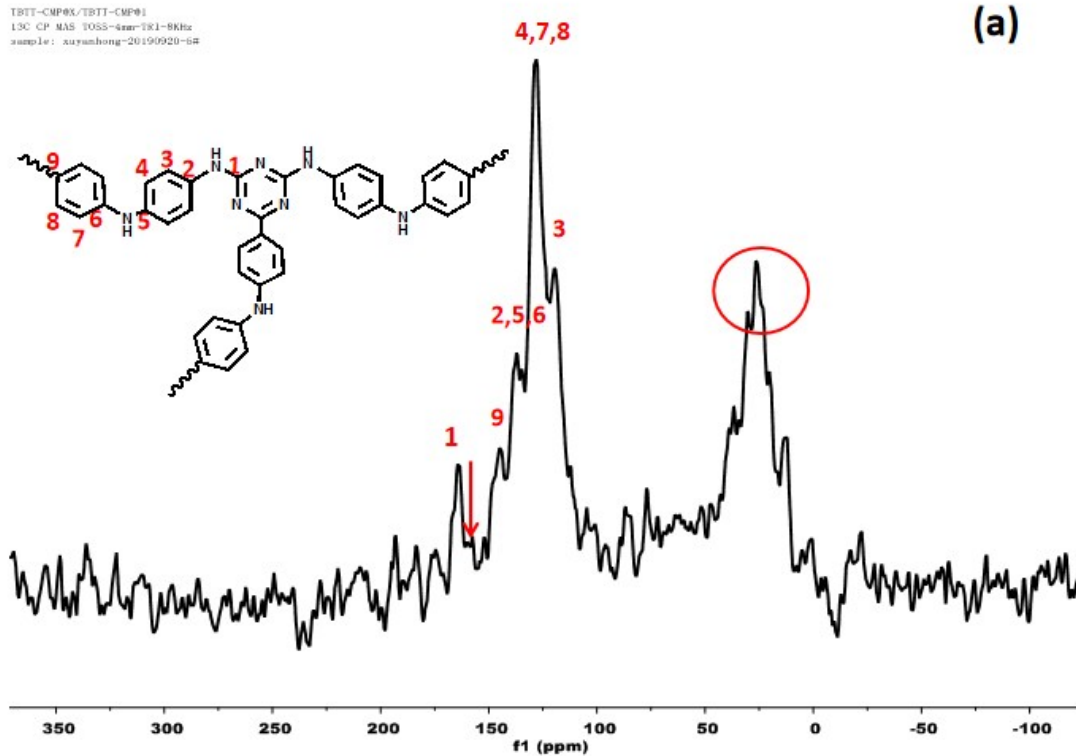
Fig. S1 (a) FT-IR spectra of monomer TBTT (green), TBTT-CMP@1 (black), TBTT-CMP@2 (red), and TBTT-CMP@3 (blue). (b) FT-IR spectra of TBTT (green), TBTT-CMP@1 (black), TBTT-CMP@2 (red), and TBTT-CMP@3 (blue) in 1850-1240 cm⁻¹.

Section D. The elemental analysis**Table S1.** Elemental analysis data of TBTT-CMP@1, TBTT-CMP@2, and TBTT-CMP@3

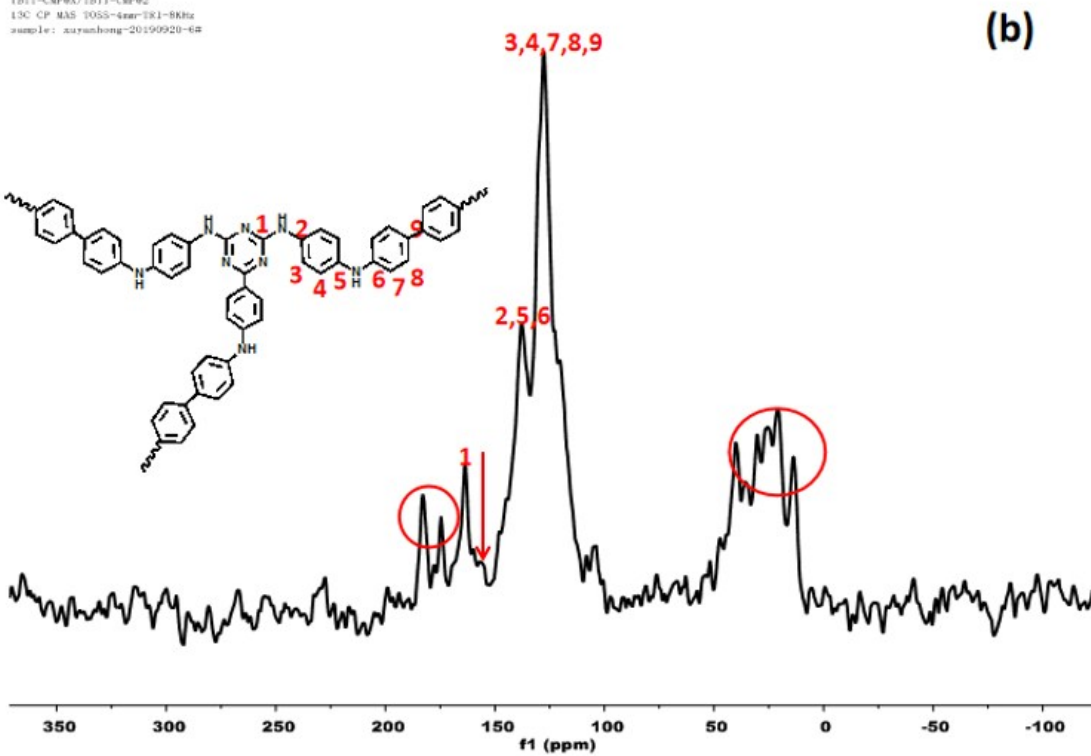
wt%		C	H	N
TBTT-CMP@1	Anal. calcd.	70.57	5.92	23.51
	Found	72.36	5.28	21.98
TBTT-CMP@2	Anal. calcd.	76.41	5.77	17.82
	Found	78.97	5.11	15.72
TBTT-CMP@3	Anal. calcd.	79.97	5.68	14.35
	Found	81.67	5.04	13.09

Section E. The solid-state ^{13}C NMR spectra

TBTT-CMP8X/TBTT-CMP9I
13C CP MAS TOSS-4arr-1K1-8KHz
sample: xuyanhong-20190920-6R



TBTT-CMP8X/TBTT-CMP9I
13C CP MAS TOSS-4arr-1K1-8KHz
sample: xuyanhong-20190920-6R



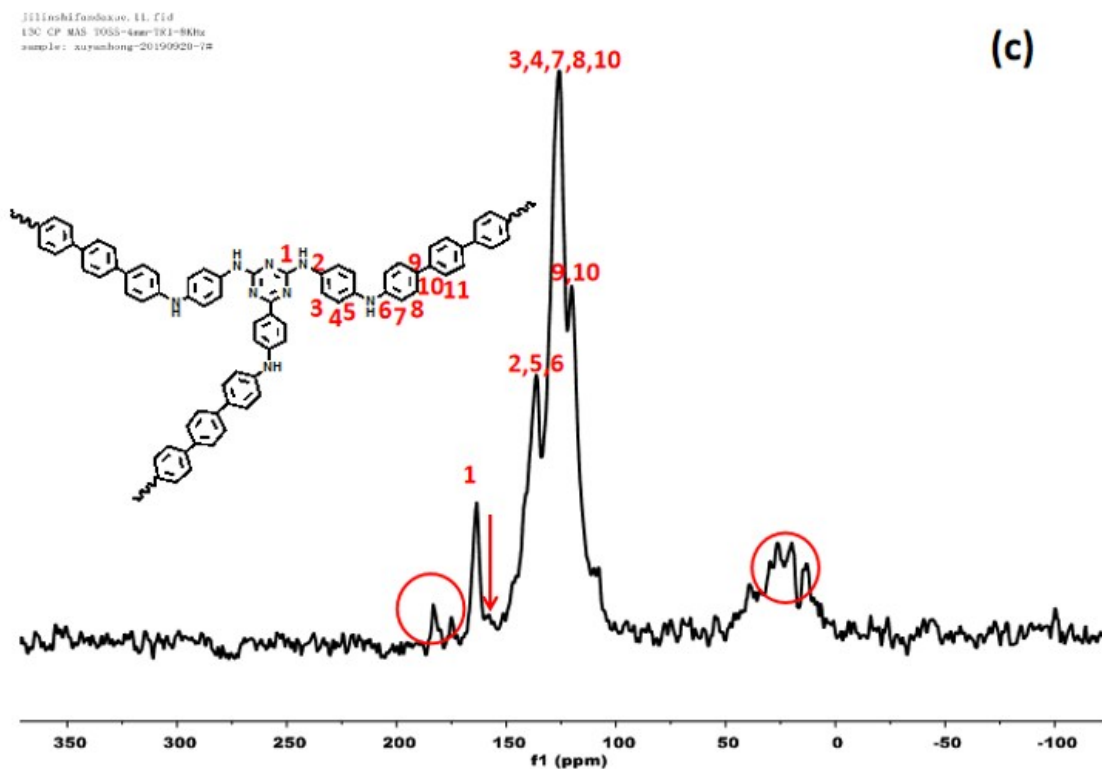


Fig. S2 The solid-state ^{13}C CP-MAS NMR of (a) TBTT-CMP@1, (b) TBTT-CMP@2, and (c) TBTT-CMP@3. The peaks at 157.3 marked by the red arrow are the characteristic peaks of the C=N.

Section F. Powder X-ray diffraction patterns

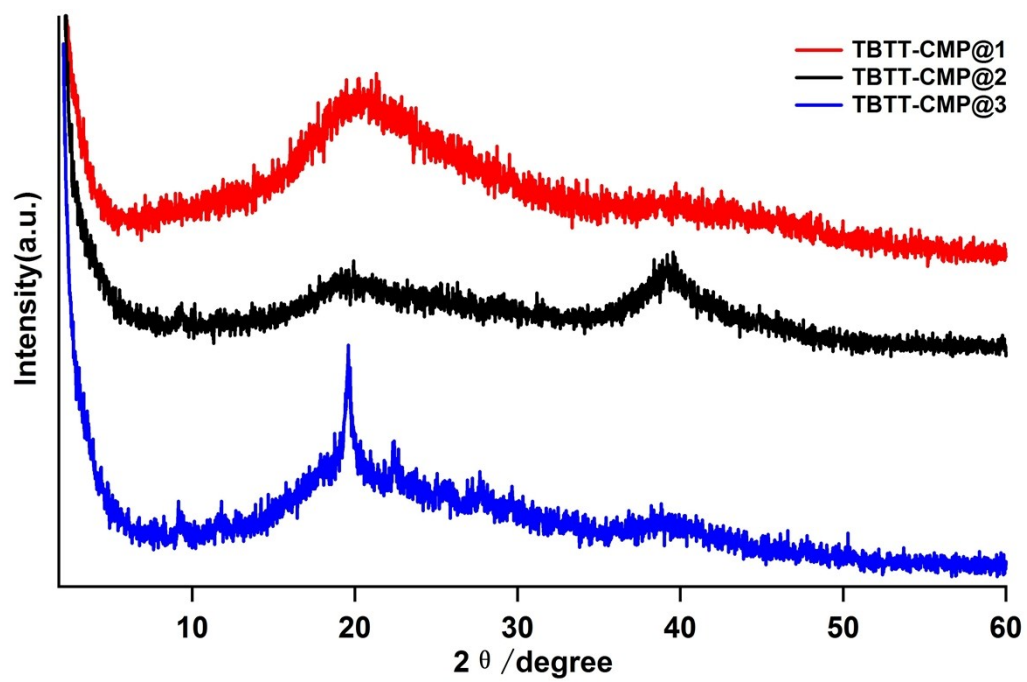


Fig. S3 Powder X-ray diffraction profiles of TBTT-CMP@1, TBTT-CMP@2 and TBTT-CMP@3.

Section G. The Solid-UV spectra

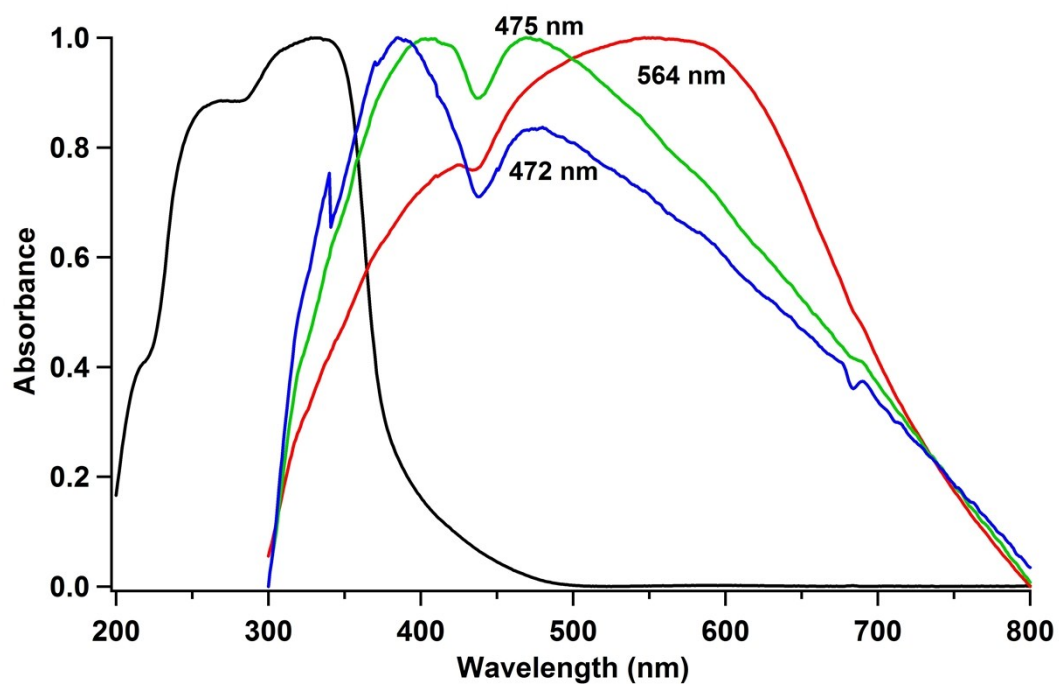


Fig. S4 The normalized solid state UV/Vis spectra of TBTT (black), TBTT-CMP@1 (blue), TBTT-CMP@2 (green) and TBTT-CMP@3 (red), respectively.

Section H. TEM images

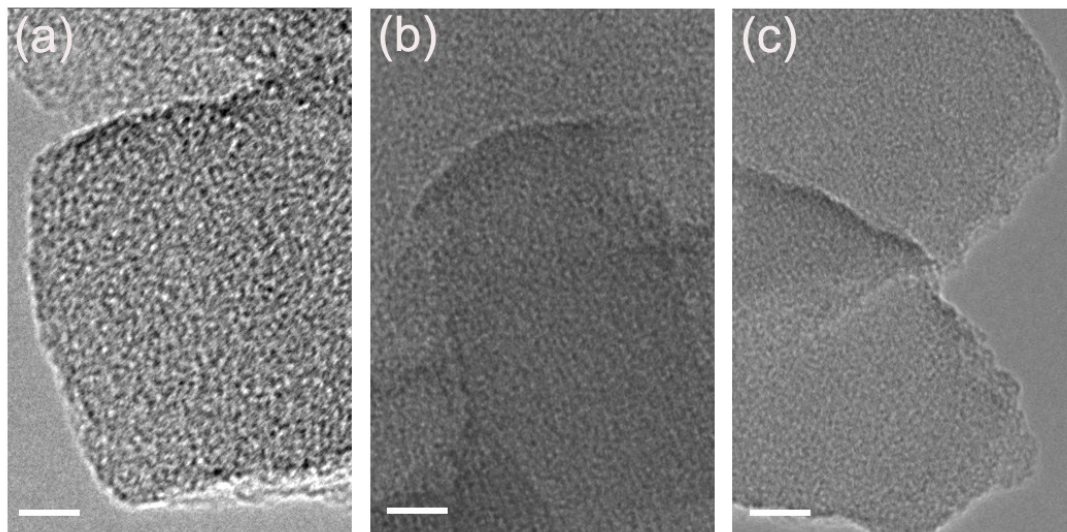


Fig. S5 TEM images of TBTT-CMP@1, TBTT-CMP@2 and TBTT-CMP@3 (10 nm width).

Section I. TGA curves

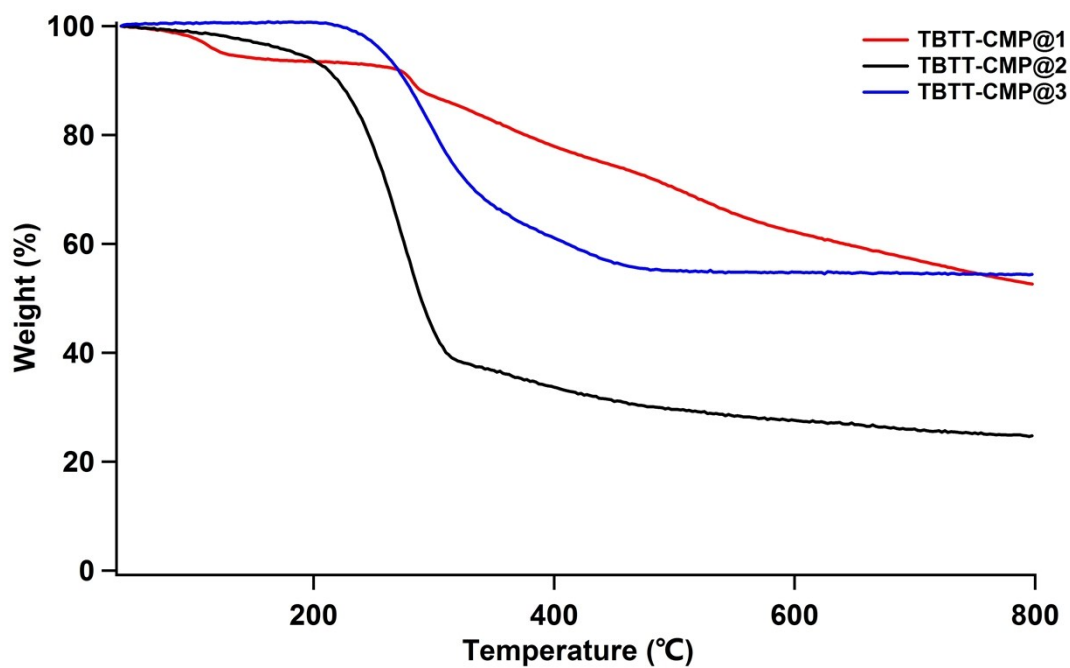


Fig. S6 TGA curves of TBTT-CMP@1 (red), TBTT-CMP@2 (black) and TBTT-CMP@3 (blue).

Table S2. Summary of iodine capacity of porous materials.

Polymers	S_{BET} (m² g⁻¹)	V_{total} (cm³ g⁻¹)	Iodine Uptake (wt.%)	References
TBTT-CMP@1	58.84	0.45	442	This work
TBTT-CMP@2	64.23	0.38	357	
TBTT-CMP@3	14.98	0.29	352	
TTPPA	512.39	0.2997	490	S1
TTDAB	1.643	0.004	313	
Tm-MTDAB	2.778	0.007	304	
TPT-BD	109	0.3	543	S2
TPT-DHBD₂₅	188	0.32	465	
TPT-DHBD₅₀	124	0.19	430	
TPT-DHBD₇₅	157	0.19	412	
TPT-DHBD	297	0.54	403	
SIOC-COF-7	618	0.41	481	S3
TTBT	222.25	0.1271	443	S4
Azo-Trip	520	0.47	238	S5
BDP-CPP-1	635	0.78	283	S6
BDP-CPP-2	235	0.18	223	

Section J. Pore size distribution curves

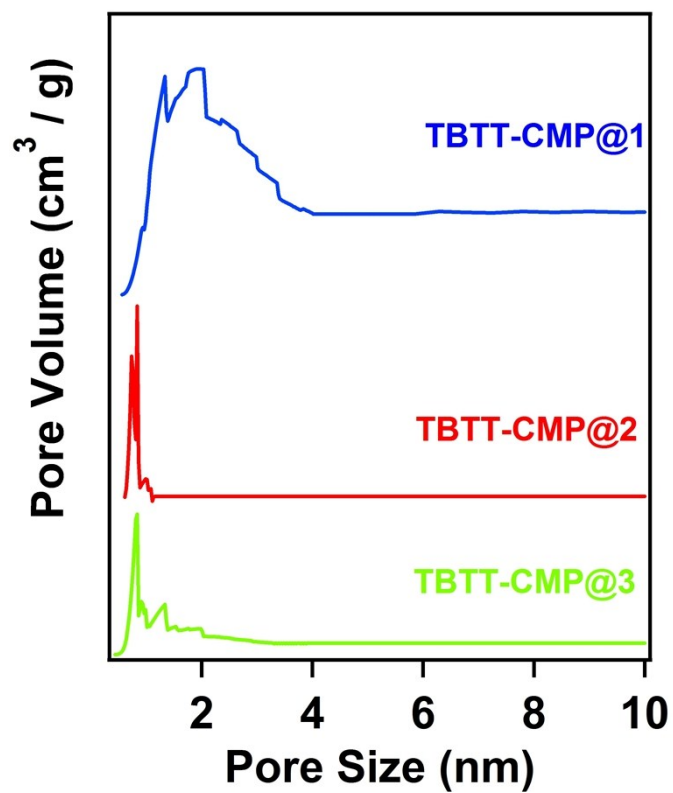
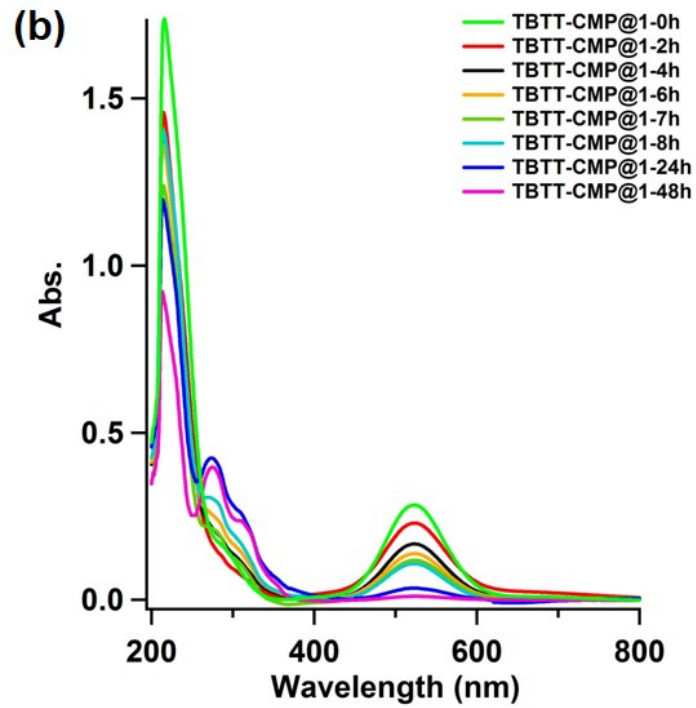
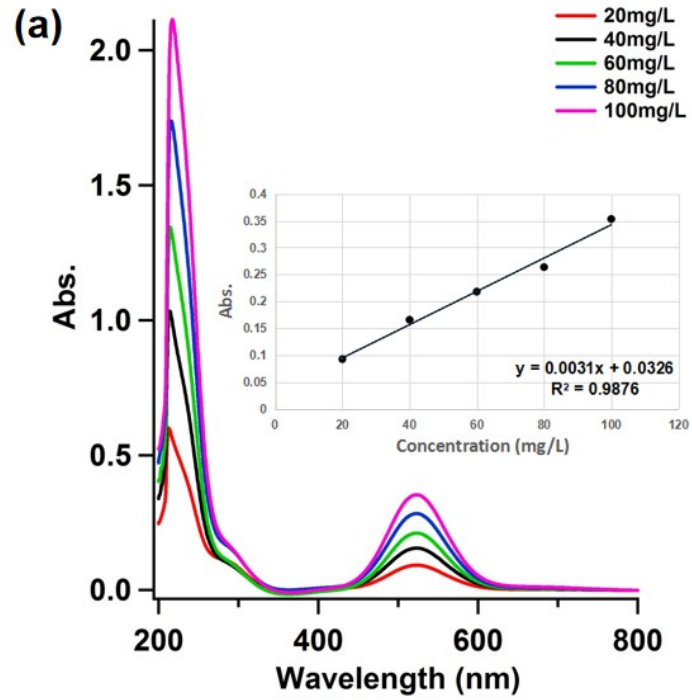


Fig. S7 Pore size distribution curves for the TBTT-CMPs networks.

Section K. Iodine capture analyses



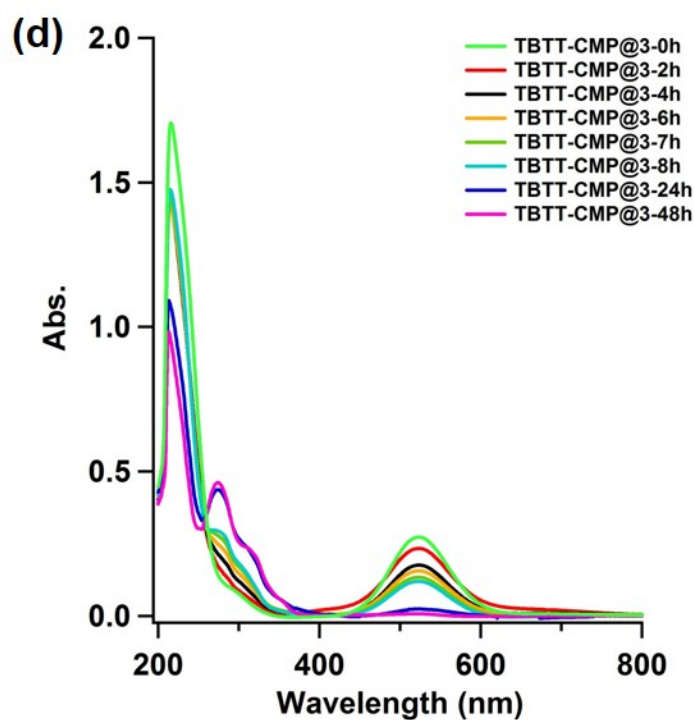
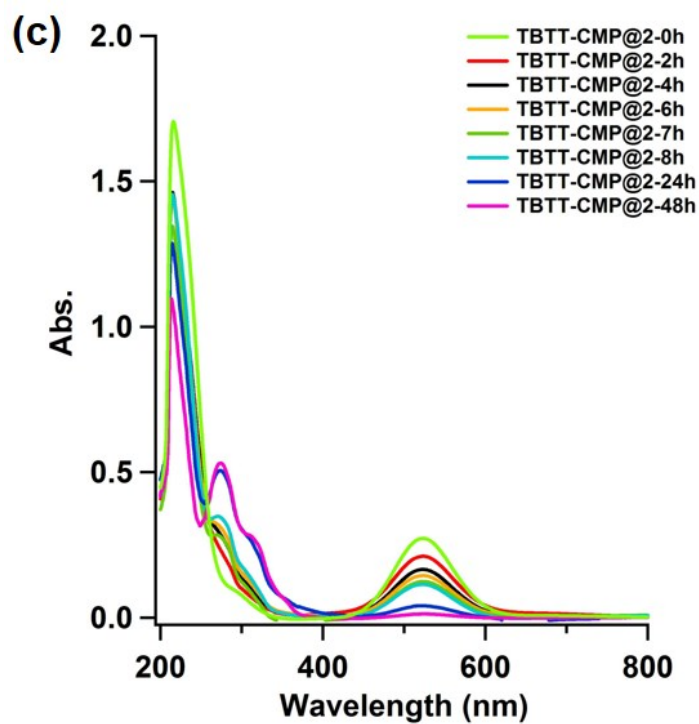


Fig. S8 (a) The standard curve of iodine in cyclohexane solution (Inset is the fitting curve of Abs value vs concentration of iodine in cyclohexane solution, the value of R^2 indicated that the curve with the relatively good linearity satisfies Lambert-Beer Law. The iodine adsorption capacity of TBTT-CMPs was calculated according to the standard curve); (b-d) the UV/Vis spectra upon immersion of 30 mg TBTT-CMPs in cyclohexane solution of I_2 (6 mg/mL). All experiments were performed at ambient temperature and pressure.

Sorption Kinetic Studies:**The linear form of the pseudo-first-order kinetic model:**

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t$$

Where Q_t and Q_e are the mass percent of iodine adsorbed at time t and equilibrium (%), k_1 is the pseudo-first-order rate constant of adsorption process (h^{-1}).

The linear form of the pseudo-second-order kinetic model:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}$$

Where Q_t and Q_e are the mass percent of iodine adsorbed at time t and equilibrium (%), k_2 is the pseudo-second-order rate constant of adsorption process ($(\% \text{ h})^{-1}$).

Table S3. Parameters of the different isotherm models extracted from the pseudo-first-order model and the pseudo-second-order model for TBTT-CMP@1, TBTT-CMP@2 and TBTT-CMP@3.

Adsorbent	Pseudo-first-order			Pseudo-second-order		
	k_1 (1/h)	Q_e (%)	R^2	k_2 (1/h)	Q_e (%)	R^2
TBTT-CMP@1	0.1278	98.58434	0.9908	0.00114	118.09719	0.98148
TBTT-CMP@2	0.12808	96.90864	0.98756	0.0012	115.25231	0.99756
TBTT-CMP@3	0.10672	101.82767	0.99341	0.000843	125.08153	0.97802

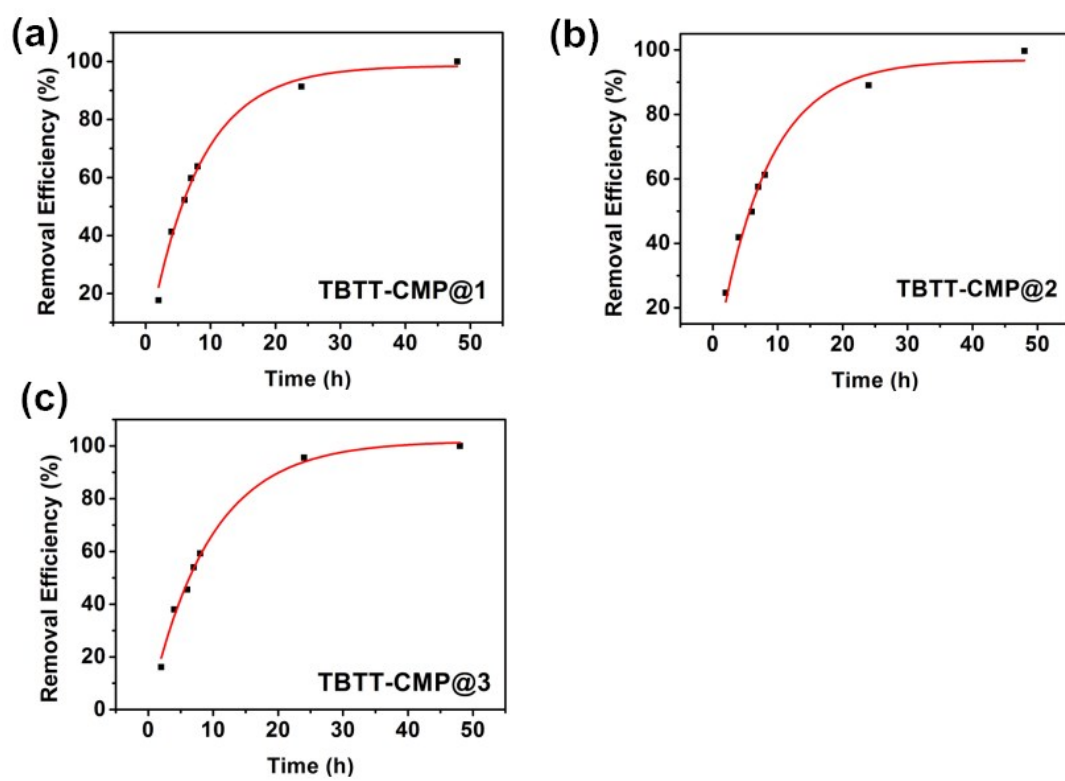


Fig. S9 The iodine adsorption kinetic was analyzed by the pseudo-first-order model.

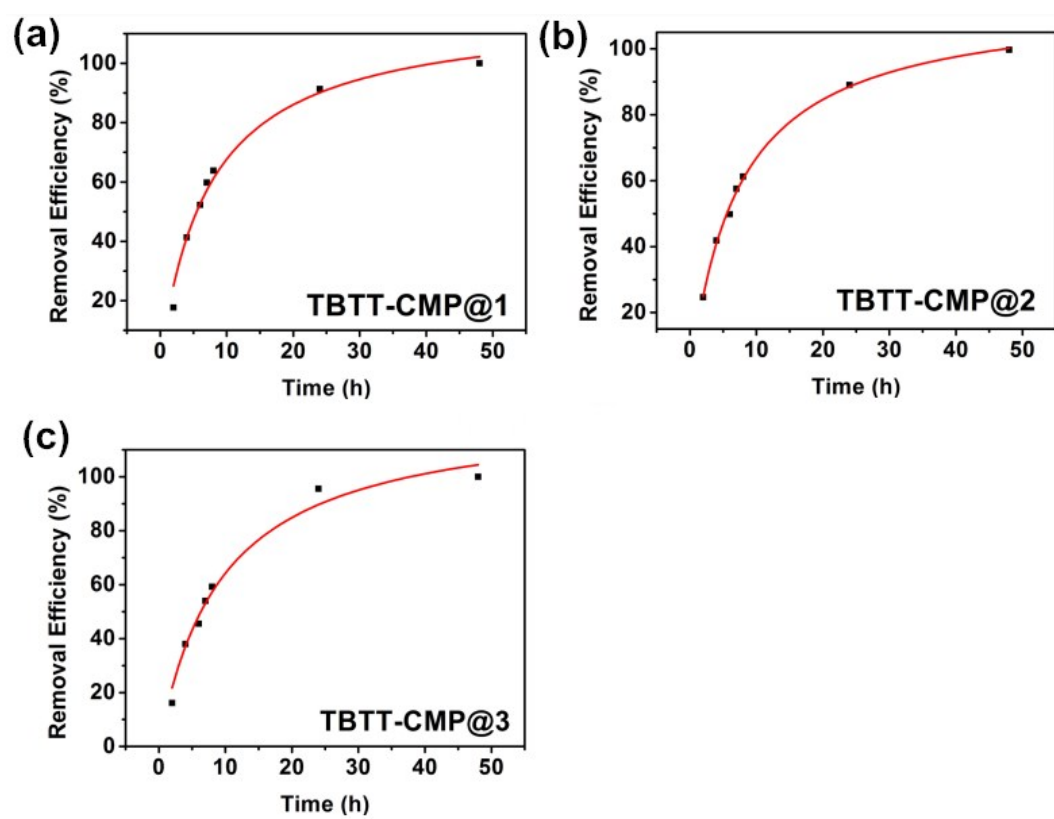


Fig. S10 The iodine adsorption kinetic was analyzed by the pseudo-second-order model.

Section L. XPS spectra

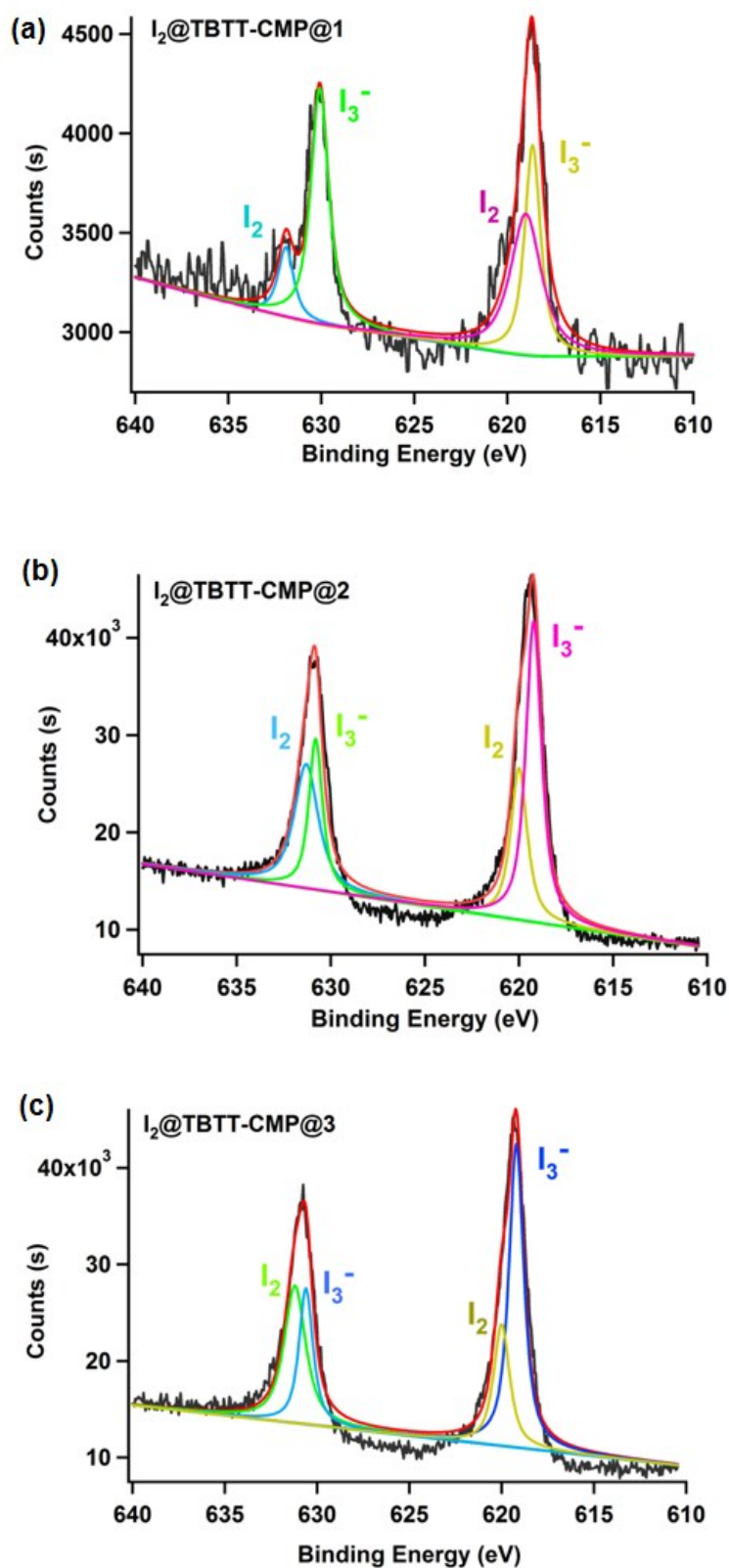


Fig. S11 Deconvoluted XPS spectra for I3d3 and I5d5 in the (a) $I_2@TBTT-CMP@1$, (b) $I_2@TBTT-CMP@2$ and (c) $I_2@TBTT-CMP@3$, respectively.

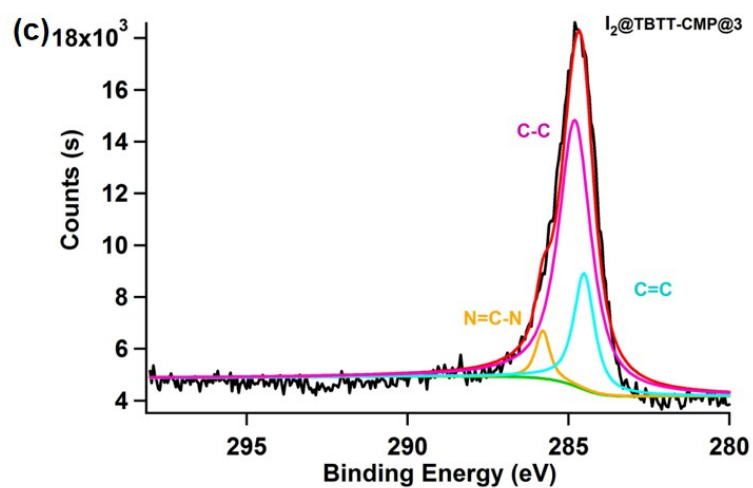
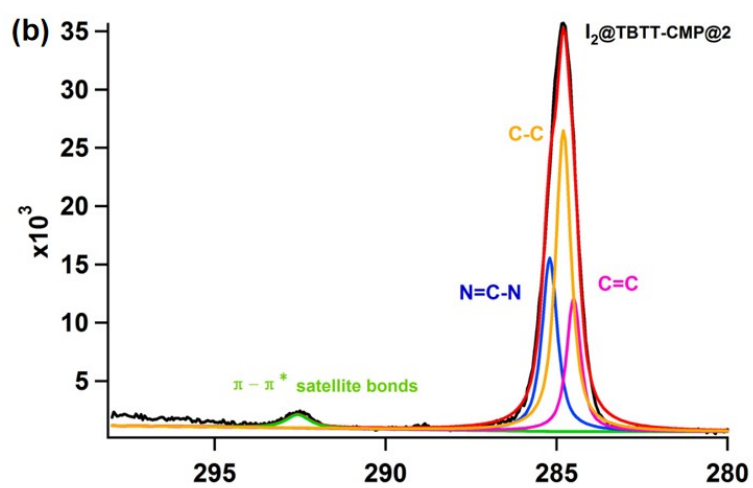
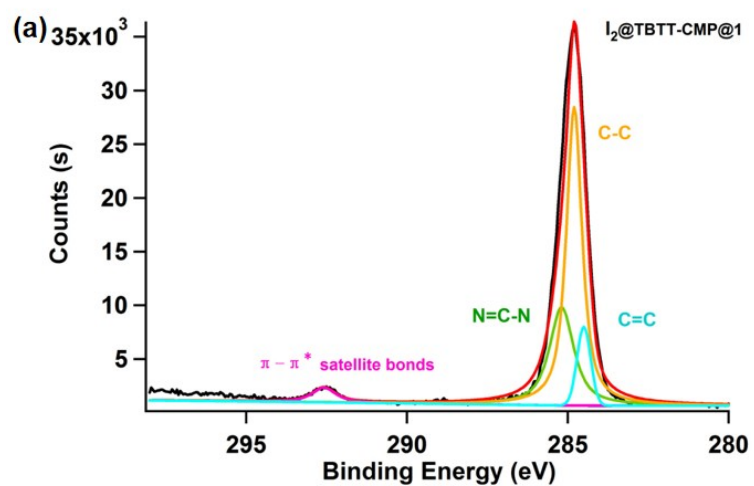


Fig. S12 Deconvoluted C 1s spectra of (a) $I_2@TBTT-CMP@1$, (b) $I_2@TBTT-CMP@2$ and (c) $I_2@TBTT-CMP@3$, respectively.

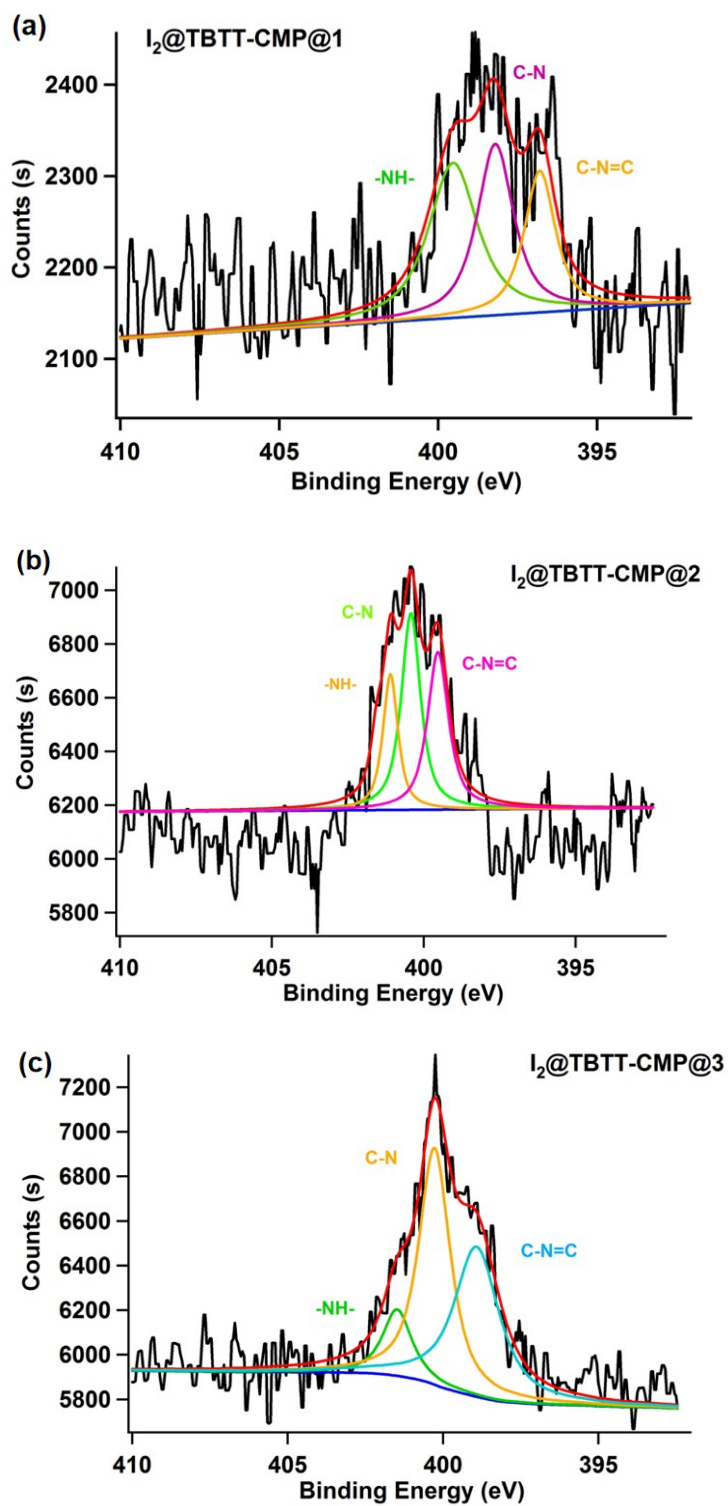
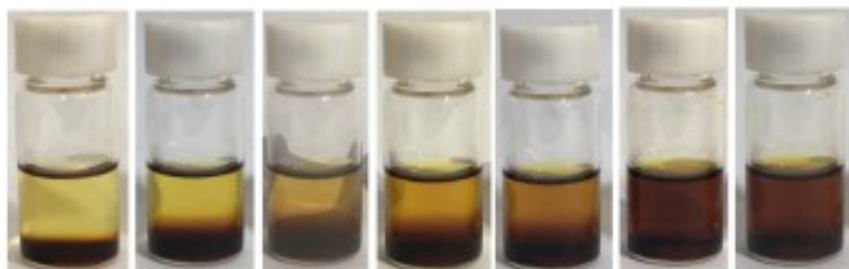


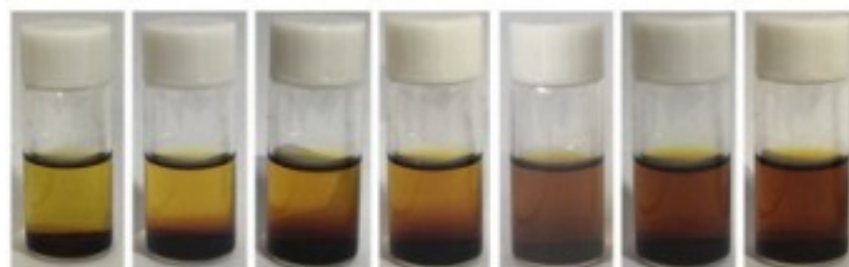
Fig. S13 Deconvoluted N 1s spectra of (a) I₂@TBTT-CMP@1, (b) I₂@TBTT-CMP@2 and (c) I₂@TBTT-CMP@3, respectively.

Section M. Iodine release photos

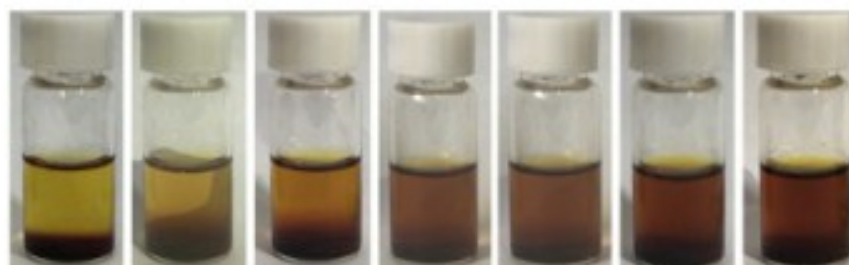
$I_2@TBTT-CMP@1$



$I_2@TBTT-CMP@2$



$I_2@TBTT-CMP@3$



0h 2h 4h 8h 12h 24h 48h

Fig. S14 Photographs showing progress of the iodine release from $I_2@TBTT-CMP@1$, $I_2@TBTT-CMP@2$ and $I_2@TBTT-CMP@3$, respectively, when the containing iodine polymer networks were immersed in ethanol.

Section N. Reusability of the CMPs

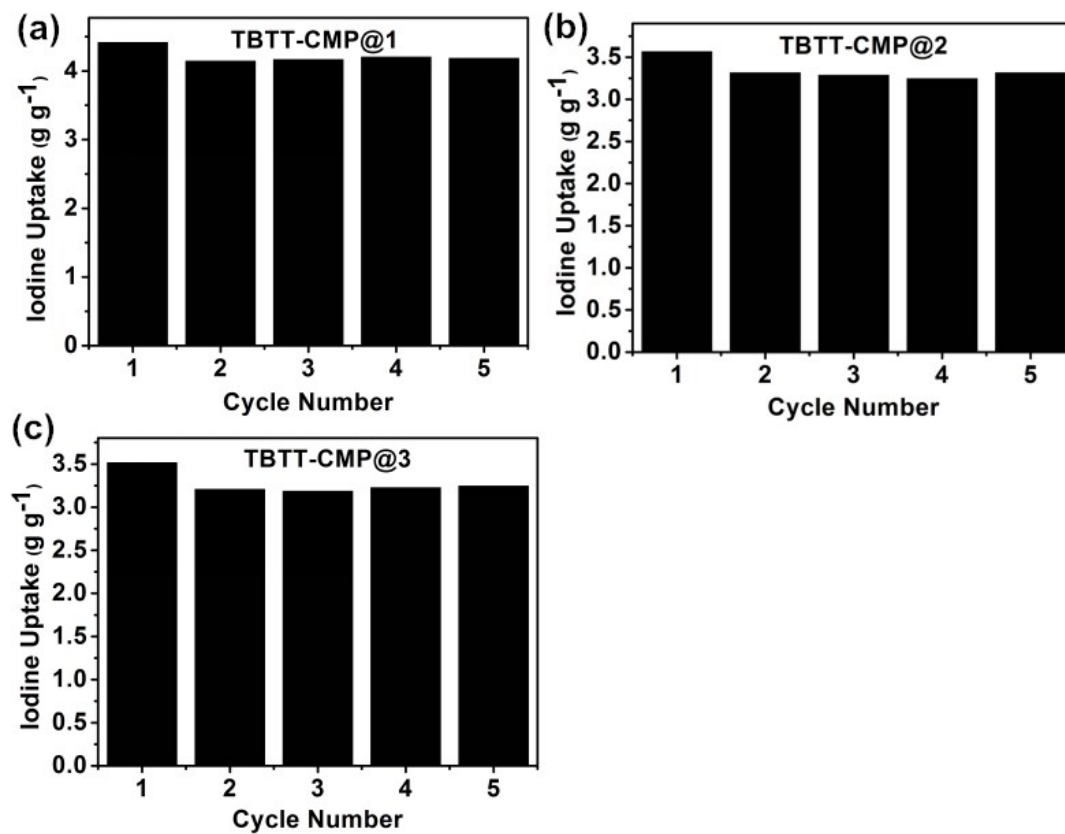


Fig. S15 Reusabilities of the TBTT-CMP@1-3 polymers for iodine adsorption by vapor sublimation.

Section O. CO₂ adsorption isotherms

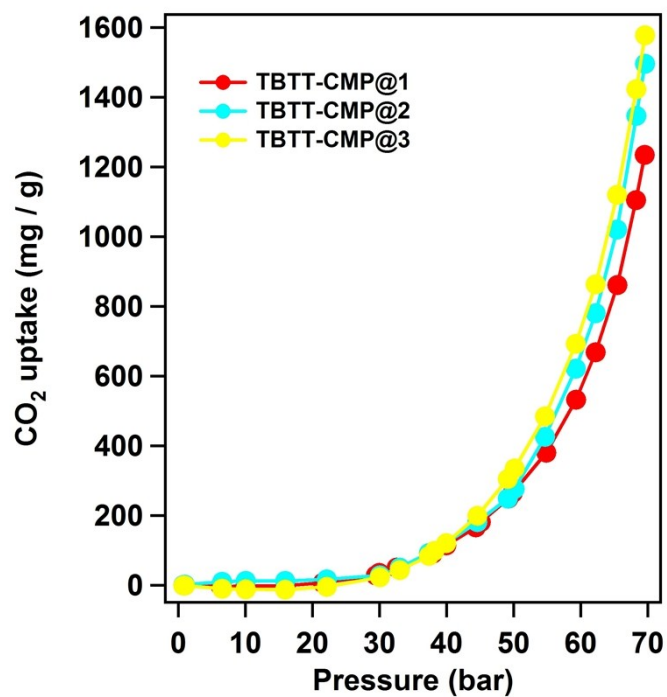


Fig. S16 CO₂ adsorption isotherms of TBTT-CMP@1-3 collected at 318 K at 70 bar.

Section P. References

- S1. T. M. Geng, S. N. Ye, Z. M. Zhu and W. Y. Zhang, *J. Mater. Chem. A* 2018, 6, 2808.
- S2. X. H. Guo, Y. Tian, M. C. Zhang, Y. Li, R. Wen, X. Li, L. J. Ma, C. Q. Xia and S. J. Li, *Chem. Mater.* 2018, 30, 2299.
- S3. Z. J. Yin, S. Q. Xu, T. G. Zhan, Q. Y. Qi, Z. Q. Wu and X. Zhao, *Chem. Commun.* 2017, 53, 7266.
- S4. T. M. Geng, Z. M. Zhu, W. Y. Zhan and Y. Wang, *J. Mater. Chem. A* 2017, 5, 7612.
- S5. Q. Q. Dang, X. M. Wang, Y. F. Zhang and X. M. Zhang, *Poly. Chem.* 2016, 7, 643.
- S6. Y. L. Zhu, Y. J. Ji, D. G. Wang, Y. Zhang, H. Tang, X. R. Jia, M. Song, G. P. Yu and G. C. Kuang, *J. Mater. Chem. A* 2017, 5, 6622