Supplementary Information

N,N'-Bicarbazole Based Covalent Triazine Frameworks as High Performance

Heterogeneous Photocatalysts

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Section 1. Materials and Methods

Materials

Carbazole, *N*-Bromosuccinimide (NBS), Potassium permanganate (KMnO₄), Potassium carbonate (K₂CO₃), Tetrakis(triphenylphosphine)palladium(0) [Pd(PPh₃)₄], Copper cyanide (CuCN), [1,1'Bis(diphenylphosphino)ferrocene]dichloropalladium(II) [Pd(dppf)Cl₂], 4-Cyanophenylboronic Acid, chloroform-*d* (CDCl₃), Trifluoromethanesulfonic acid (TFMS), Dimethyl sulfoxide-*d*₆ (DMSO-*d*₆), Methyl phenyl sulfide. Rhodamine B (RhB) was purchased from Tianjin Jiangtian Chemical Company. All the solvents and reagents were obtained commercially and used without further purification.

Methods

¹H NMR and ¹³C NMR spectra in deuterated solvent were recorded on a Bruker ADVANCE III-400MHz NMR spectrometer. Chemical shifts were reported in ppm using the solvents as internal standards: ¹H: CDCl₃, 7.26 ppm, DMSO-*d*₆, 2.50 ppm; ¹³C: CDCl₃, 77.23 ppm, DMSO-*d*₆, 39.51 ppm. Coupling constants were assigned as observed. Elemental analysis (C, H, N) was analyzed on a Perkin-Elmer 240C elemental analyzer. Fourier transform infrared (FT-IR) spectra were recorded in transmission mode on a Bruker Alpha spectrometer using KBr pellets within the range 400-4000 cm⁻ ¹. Matrix-assisted laser desorption ionization time-of-flight mass (MALDI-TOF MS) spectra were performed on an Applied Biosystems BioSpectrometry model Voyager-DE-STR spectrometer in reflector or linear mode using 9-nitroanthracene ordithranol as a matrix. The thermal stabilities of the CTFs were evaluated using thermogravimetric analysis (TGA) with a differential thermal analysis instrument (TA Instruments TGA Q50-1918 analyzer) over the temperature range from 20 to 800 °C under N₂ atmosphere with a heating rate of 10 °C min⁻¹ using an empty Al₂O₃ crucible as the reference. ¹³C cross-polarization magic angle spinning (CP/MAS) spectra were recorded with a 4 mm double resonance MAS probe and at a MAS rate of 10.0 kHz with a contact time of 2 ms (ramp 100) and a pulse delay of 3 s. Surface areas were measured by nitrogen sorption at 77 K using a BELSOPR-min II analyzer with equilibration interval for 10 sec. and the samples were degassed at 150 °C for 10 h under vacuum (10⁻⁵ bar) before analysis. The pore size distribution was calculated from the adsorption branch with the nonlocal density functional theory (NLDFT). The Powder X-ray diffraction (PXRD) profiles were recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA with a Cu-target tube and a graphite monochromator. High resolution imaging of the polymer morphologies was obtained using a Hitachi S-4800 cold field emission scanning electron microscope (FE-SEM). Transmission electron microscopy (TEM) was carried out on a JEOL JEM-2100F electron microscope with a LaB6 filament operated at 200 kV. Cyclic voltammetric experiments were carried out using a CHI 660E electrochemical workstation. The cyclic voltammograms were acquired at room temperature with the scan rate of 100 mV s⁻¹. The potentials are reported versus the Fc/Fc⁺ redox couple as a standard. Electron paramagnetic resonance (EPR) was measured on a Bruker A300 spectrometer at room temperature.

The catalytic oxidations of various sulfides were carried out in 10 mL pyrex glass reactors equipped with magnetic stirring. In a typical experiment, CTF (5 mg), acetonitrile (2.5 mL) and sulfides (0.2 mmol) were charged in the reactor and the resulting mixture was stirred under an atmosphere of oxygen at 298 K. The solution was periodically analyzed by GC-MS (Shimadzu GC-QP2010SE) at appropriate intervals. The specific procedure of GC-MS was shown as follow: the initial temperature is 100 °C and keeping for 3 min, then warming up to 250 °C at a rate of 10 °C /min and keeping for another 3 min. The chromatographic column used in this method is Rtx-5MS, (solvent : acetone, solvent delay : 4 min). All products were identified by the comparison of GC retention time and mass spectra with those of the authentic samples. Selectivity = [Produced Sulfoxide]/[Consumed Sulfide] × 100%; Conversion = [Consumed Sulfide]/[Initial Sulfide] × 100%; respectively^{S6-7}.

Section 2. Synthetic Procedures



Scheme S1. Synthetic route of BC-CN.

Synthesis of 3,6-Dibromo-9H-carbazole. The synthetic method was according to the literature.^{S1} A two-neck round-bottom flask was equipped with a magnetic stirrer bar, a nitrogen gas inlet and a 250 mL addition funnel. Carbazole (10 g, 59 mmol) dissolved in toluene (20 mL) was added into the flask and cooled in an ice bath. A solution of *N*-Bromosuccinimide (22.35 g, 125 mmol) in DMF (60 mL) was added into the flask transfer through the addition funnel. After reacting for 2 h, the mixture was poured into cold water to precipitate the product, which was filtered and washed with cold methanol. The product was obtained as white crystal (16.9 g, 88%). ¹H NMR (400 MHz, CDCl₃): δ 8.13 (s, 2H), 7.52 (d, 2H, *J* = 8.6 Hz), 7.31 (d, 2H, *J* = 8.6 Hz).

Synthesis of 3, 3', 6, 6'-tetrabromo-*N*, *N***'-bicarbazole (BC-Br).** The synthetic method was referred to the literature.^{S2} To a solution of 3, 6-dibromo-carbazole (1.95 g, 6 mmol) in acetone (36 mL) was added KMnO₄ (2.14 g, 13.5 mmol) at room temperature. The reaction mixture was warmed up to 65 °C with a reflux condenser. The reaction was stirred for 6 h at 65 °C, and cooled to room temperature. After evaporation of acetone under reduced pressure, the reaction mixture was suspended in chloroform, filtered through a glass sintered funnel, and washed by chloroform. The filtrate was washed by saturated aqueous Na₂S₂O₃ solution, brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by recrystallization from chloroform/hexane to give a colorless powder (1.08 g, 66%). ¹H NMR (400 MHz, CDCl₃): δ 8.27 (s, 4H), 7.47 (d, 4H, *J* = 8.6 Hz).

Synthesis of 3, 3', 6, 6'- tetracarbonitrile-*N*, *N***'-bicarbazole (BC-CN).** The synthetic method was referred to the literature.^{S3} A mixture of BC-Br (2.58 g, 4 mmol), CuCN (9.6 g, 117 mmol), and Pd(dppf)Cl₂ (850 mg, 1.04 mmol) in *N*,*N*-dimethylformamide (100 mL) was heated at 150 °C for 36 h under N₂ atmosphere. After cooling to room temperature, ammonium hydroxide was added to the

mixture and stirred under air overnight. The crude product was collected by filtration and washed thoroughly with water, then purified by chromatography (CH₂Cl₂) to afford a white powder (1.46 g, 85%). ¹H NMR (400 MHz, CDCl₃): δ 8.12 (s, 4H), 8.07 (d, 4H, *J* = 8.3 Hz), 7.67 (d, 4H, *J* = 8.4 Hz).



Scheme S2. Synthetic route of Ph-BC-CN.

Synthesis of 4,4',4'',4'''-([N,N'-bicarbazole]-3,3',6,6'-tetrayl)tetrabenzonitrile (Ph-BC-CN).

A mixture of BC-Br (0.8 g, 1.23 mmol), 4-cyanophenylboronic acid (1.08 g, 7.38 mmol), tetrakis(triphenylphosphine)palladium [Pd(PPh₃)4] (80 mg) and K₂CO₃ (1.7 g, 12.3 mmol) in a mixed solution of 1,4-dioxane (30 mL) and H₂O (3 mL) was degassed by three freeze-pump-thaw cycles. The mixture was stirred at 100 °C for 3 days under N₂. The reaction mixture was cooled to room temperature and poured into water. The mixture was extracted with dichloromethane and washed with saturated brine, dried over with anhydrous MgSO₄, and filtered. The filtrate was rotary evaporated to dryness and the crude product was then purified by chromatography and eluting with dichloromethane to obtain pure Ph-BC-CN as a white powder (571 mg, 63%). ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.03 (s, 4H), 8.02 (dd, 16H, *J* = 8.1 Hz, 16.8 Hz), 7.84 (d, 4H, *J* = 8.9 Hz), 7.10 (d, 4H, *J* = 8.4 Hz). ¹³C NMR (100 MHz, DMSO-*d*₆, 353K): δ (ppm) 145.50, 140.63, 133.30, 133.09, 128.11, 127.11, 123.15, 121.05, 119.31, 110.36, 110.00. Elemental analysis (wt.%) calcd. For C₅₂H₂₈N₆: C 84.76, H 3.83, N 11.41; found: C 83.66, H 4.23, N 10.24. The limited solubity of compound precluded ¹³C NMR characterization. MALDI-TOF: m/z calcd. For C₅₂H₂₈N₆ [M]⁺: 736.238, found: 736.072.

Synthesis of BC-CTF S4

CHCl₃ (10 mL) and BC-CN (0.1 mmol, 43.2 mg) were charged into a dried 50 mL two neck roundbottom flask under N₂ atmosphere. The mixture was cooled to 0 °C and 0.065 mL trifluoromethanesulfonic acid was added. The mixture was stirred at 0 °C for 1 h and then the resulting solution was stirred for 15 h at room temperature. Then NH₃·H₂O was added to neutralize the reaction mixture and stirred for additional 2 h. The precipitates were collected by filtration and washed with water, methanol and acetone successively. BC-CTF was obtained as a light yellow solid (35 mg, 81%). Elemental analysis (wt.%) calcd. For $\{C_{28}H_{12}N_6\}_n$: C 77.77, H 2.80, N 19.43; found: C 74.03, H 3.84, N 18.06.

Synthesis of BC-CTF-400 S5

A mixture of BC-CN (130 mg, 0.3 mmol) and ZnCl₂ (409 mg, 3.0 mmol) were placed into a Pyrex ampoule under inert conditions. The ampoule was evacuated, sealed and heated to 400 °C for 24 h followed by cooling to room temperature. The black product was collected and stirred with water. Then the product was isolated by filtration and again stirred with 100 mL of 1 mol/L HCl for 24 h. The resulting black powder was further washed with water (3×50 mL), THF (3×30 mL), acetone (3×30 mL) and dried in vacuum. BC-CTF-400 was obtained as a blacksolid (106.7 mg, 82%). Elemental analysis (wt.%) calcd. For {C₂₈H₁₂N₆}_n: C 77.77, H 2.80, N 19.43; found: C 82.38, H 2.65, N 13.51.

Synthesis of Ph-BC-CTF

CHCl₃ (5 mL) and Ph-BC-CN (0.05 mmol, 36.8 mg) were charged into a pre-dried 50 mL two neck round-bottom flask under N₂ atmosphere. The mixture was cooled to 0 °C and 0.065 mL trifluoromethanesulfonic acid was added. The mixture was stirred at 0 °C for 1 h and then the resulting solution was stirred for 15 h at room temperature. Then NH₃·H₂O was added to neutralize the reaction mixture and stirred for another 2 h. The precipitates were collected by filtration and washed with water, methyl alcohol and acetone successively. Ph-BC-CTF was obtained as a claybank solid (29 mg, 79%). Elemental analysis (wt.%) calcd. For $\{C_{52}H_{28}N_6\}_n$: C 84.76, H 3.83, N 11.41; found: C 83.88, H 4.30, N 10.55.

Synthesis of Ph-BC-CTF-400

A mixture of Ph-BC-CN (147 mg, 0.2 mmol) and ZnCl₂ (273 mg, 2.0 mmol) were placed into a Pyrex ampoule under inert conditions. The ampoule was evacuated, sealed and heated to 400 °C for 24 h followed by cooling to room temperature. The black product was collected and stirred with water. Then the product was isolated by filtration and again stirred with 100 mL of 1 mol/L HCl for 24 h. The resulting black powder was further washed with water (3×50 mL), THF (3×30 mL), acetone (3×30 mL) and dried in vacuum. Ph-BC-CTF-400 was obtained as a black solid (113.5 mg, 77%). Elemental analysis (wt.%) calcd. For {C₅₂H₂₈N₆}_n: C 84.76, H 3.83, N 11.41; found: C 90.81, H 2.42, N 6.62.



Figure S1. ¹H NMR spectrum of 3,6-Dibromo-9H-carbazole in CDCl₃.



Figure S2. ¹H NMR spectrum of BC-Br in CDCl₃.



Figure S3. ¹H NMR spectrum of BC-CN in CDCl₃.



Figure S4. ¹H NMR spectrum of Ph-BC-CN in DMSO-*d*₆.



Figure S5. ¹³C NMR spectrum of Ph-BC-CN in DMSO- d_6 at 353K.

Entry	BC-CN (mmol)	CF3SO3H (mL)	CHCl ₃ (mL)	BET (m²/g)
1	0.1	0.065	1	556
2	0.1	0.065	2	728
3	0.1	0.065	3	835
4	0.1	0.065	5	861
5	0.1	0.065	10	934
6	0.1	0.065	20	413

Table S1. The influence of the concentration of BC-CN on the BET surface areas of BC-CTFs.

Table S2. The influence of the concentration of Ph-BC-CN on the BET surface areas of Ph-BC-CTFs.

Entry	Ph-BC-CN (mmol)	CF ₃ SO ₃ H (mL)	CHCl ₃ (mL)	BET (m²/g)
1	0.05	0.065	1	751
2	0.05	0.065	2	804
3	0.05	0.065	3	934
4	0.05	0.065	5	967
5	0.05	0.065	10	248
6	0.05	0.065	20	96

Section 3. FT-IR and BET Spectra



Figure S6. FT-IR spectra of (a) BC-CN (black), BC-CTF (red) and (b) Ph-BC-CN (black), Ph-BC-CTF (red), the CTFs obtained by TFMS.



Figure S7. FT-IR spectra of (a) BC-CTF (orange) and BC-CTF-400 (pink), (b) Ph-BC-CTF (violet) and Ph-BC-CTF-400 (olive).



Figure S8. Nitrogen adsorption (solid) and desorption (open) isotherms at 77 K of the (a) BC-CTF-400 (pink) and (c) Ph-BC-CTF-400 (olive), and pore size distribution based on NLDFT calculations of the (b) BC-CTF-400 (pink) and (d) Ph-BC-CTF-400 (olive).

Section 4. Solid State ¹³C CP/MAS NMR Spectroscopy



Figure S9. The solid-state ¹³C CP/MAS NMR spectra of (a) BC-CTF and (b) Ph-BC-CTF.

Section 5. SEM and TEM Images of CTFs



Figure S10. SEM images of (a) BC-CTF (b) Ph-BC-CTF and TEM images of (c) BC-CTF (d) Ph-BC-CTF.



Section 6. Thermogravimetric Analysis (TGA)

Figure S11. Thermogravimetric analysis of BC-CTF (orange) and Ph-BC-CTF (violet).



Section 7. PXRD Profiles

Figure S12. Powder X-ray diffraction profiles of (a) BC-CTF, (b) Ph-BC-CTF, (c) BC-CTF-400 and (d) Ph-BC-CTF-400.

Section 8. Cyclic Voltammetry



Figure S13. Cyclic voltammogram of (a) BC-CTF and (b) Ph-BC-CTF versus Fc/Fc⁺.

Table S3. Absorption maxima and energy levels of the BC-CTF and Ph-BC-	CTF
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	$\lambda_{ m abs\ (nm)}{}^{[a]}$	$E_{\rm g}~({\rm eV})^{[{\rm b}]}$	HOMO (eV) ^[c]	LUMO (eV) ^[d]
BC-CTF	379	2.95	-5.03	-2.08
Ph-BC-CTF	428	2.54	-4.91	-2.37

[a] Absorption was measured in solid state using reflectance mode; [b] Determined from the UV-vis absorption onset; [c] Measured in redistilled dichloromethane/tetra-n-butylammonium hexafluorophosphate (0.1 M) solution, using glassy carbon electrode as the working electrode, Ag/AgCl electrode as the reference electrode, platinum wire as the counter electrode with Fc/Fc⁺ as an internal standard. Estimated vs vacuum level from HOMO = $-[E^{\text{ox}}-E_{[\text{Fc/Fc}^+]}+4.8]$ eV; [d] Calculated from LUMO = HOMO + E_g .

Section 9. Catalytic Performance of BC-CTF and Ph-BC-CTF

Table S4. Photocatalytic oxidation of thioanisole under visible light using BC-CTF as photocatalyst.^[a]

	$\frac{1}{a} = \frac{BC-CT}{hv},$	$\begin{array}{c} \text{TF, } O_2 \\ \hline \text{RT.} \\ b \end{array}$	° S + (O=S=O	
Entwy	Solvent	Time (h)	Conv.	Selectiv	rity (%)
Entry	Solvent	Time (n)	(%) ^[b]	b	c
1 ^[c]	CH ₃ CN/MeOH	3	87	> 99	< 1
2 ^[d]	Toluene/MeOH	3	41	>99	< 1
3 ^[e]	THF/MeOH	3	10	>99	< 1
4	CH ₃ CN-2 mL	3	97	86	14
5	CH ₃ CN-2.5 mL	3	99	97	3
6	CH ₃ CN-2.8 mL	3	92	95	5
7	Toluene-2.5 mL	3	7	> 99	< 1

[a] Reaction conditions: 0.2 mmol substrate, 5 mg BC-CTF, Xenon lamp ($\lambda > 400$ nm) 3 h, 1 bar oxygen, RT.; [b] Conversion efficiency was determined by GC-MS; [c] 2 mL CH₃CN, 0.8 mL MeOH; [d] 2 mL Toluene, 0.8 mL MeOH; [e] 2 mL THF, 0.8 mL MeOH.

Entry	CTE	Solvent	Time (h)	Conv.	Selectivity (%)	
	CIF	Sorvent	Time (II)	(%) ^[b]	b	c
1	BC-CTF	CH ₃ CN	3	99	97	3
2	Ph-BC-CTF	CH ₃ CN	5	98	97	3

Table S5. Photocatalytic oxidation of thioanisole by different CTFs under visible light irradiation.^[a]

[a] Reaction conditions: 0.2 mmol substrate, 5 mg CTF, 2.5 mL CH₃CN, Xenon lamp ($\lambda > 400$ nm), 1 bar oxygen, RT; [b] Conversion efficiency was determined by GC-MS.

Table S6. Photocatalytic oxidation of thioanisole by the monomers under visible light irradiation.^[a]

Entry	monomer	Solvent	Time (h)	Conv. (%) ^[b]
1	BC-CN	CH ₃ CN	3	0
2	Ph-BC-CN	CH ₃ CN	5	0

[a] Reaction conditions: 0.2 mmol substrate, 5 mg monomer, 2.5 mL CH₃CN, Xenon lamp ($\lambda > 400$ nm), 1 bar oxygen, RT; [b] Conversion efficiency was determined by GC-MS.

Section 10. Typical GC-MS Spectrum of the Crude Mixture of the Photo-oxidation of Thioanisole Catalyzed by BC-CTF



Peak number	time (min)	Starting time (min)	Ending time (min)	m/z	Peak area (%)	Conv. (%) ^[a]	Selectivity (%) ^[b]
а	5.070	4.920	5.600	124.035	0.75		
b	8.849	8.615	9.560	140.030	96.07	99.25	96.80
c	9.612	9.580	11.015	156.025	3.18		

[a] Conversion = [Consumed Sulfide]/[Initial Sulfide] × 100; [b] Selectivity = [Produced Sulfoxide]/[Consumed Sulfide] × 100; respectively.

Figure S14. Typical GC-MS spectrum of the crude mixture of the photo-oxidation of thioanisole with BC-CTF as photocatalyst. Reaction time is 3 h, conversion efficiency is ~99%.





Figure S15. EPR spectra of (a) BC-CTF and (b) Ph-BC-CTF taken in dark and under light irradiation. The EPR spectra were recorded by adding 5 mg CTFs in 2.5 mL CH₃CN and irradiating for 3h. Obviously, both BC-CTF and Ph-BC-CTF showed significantly increase in EPR signals under light irradiation comparing to in the dark.

Section 12. Substrate Screening Experiments Using Ph-BC-CTF as Photocatalyst

Table S7. Screening and control experiments of the oxidative coupling of thioanisole and its derivatives using Ph-BC-CTF as photocatalyst.^[a]



[a] Reaction conditions: 0.2 mmol substrate, 5 mg CTF, 2.5 mL CH₃CN, Xenon lamp ($\lambda > 400$ nm) 5 h, 1 bar oxygen, RT; [b] Conversion determined by GC-MS.

Section 13. Photocatalytic Mechanism Investigation

Table S8. The influence of reaction conditions and scavengers on the selective oxidation of thioanisole^[a]



Entry	Catalysts	Time (h)	Oxidant	Light	Additive	Yield (%) ^[b]
1	BC-CTF	3	O ₂	+	-	99
2 ^[c]	-	3	O ₂	+	-	0
3 ^[d]	BC-CTF	3	air	+	-	53
4 ^[e]	BC-CTF	3	N_2	+	-	0
5 ^[f]	BC-CTF	3	O_2	-	-	0
6 ^[g]	BC-CTF	3	O_2	+	AO	64
7 ^[h]	BC-CTF	3	O_2	+	BQ	23
8 ^[i]	BC-CTF	3	O_2	+	NaN ₃	< 1
9 ^[j]	BC-CTF	3	O_2	+	Isopropanol	62

[a] Reaction conditions: 0.2 mmol substrate, 5 mg CTF, 2.5 mL CH₃CN, Xenon lamp ($\lambda > 400$ nm) 3 h, 1 bar oxygen, RT; [b] Conversion efficiency was determined by GC-MS; [c] Without catalyst; [d] Under air (1 bar); [e] Under N₂ (1 bar); [f] In dark; [g] Ammonium oxalate as hole scavenger; [h] Benzoquinone as superoxide scavenger; [i] NaN₃ as singlet oxygen scavenger; [j] Isopropanol as \cdot OH scavenger.



Figure S16. Light on-off experiment (the photocatalyst is BC-CTF).



Figure S17. EPR spectra of (a) TEMP ${}^{1}O_{2}$ and (b) DMPO O_{2}^{-} adducts using BC-CTF as photocatalyst in dark and under light irradiation.



Figure S18. Time-dependent EPR spectra of TEMP ${}^{1}O_{2}$ adducts using BC-CTF as photocatalyst under light irradiation for 1 h (red) and 2 h (blue).

Section 14. Optical Stabilities of BC-Based CTFs

The optical stabilities of BC-CTF and Ph-BC-CTF were examined by dispersing 5 mg CTFs in 2.5 mL CH₃CN and irradiation for 5 h under a Xenon lamp ($\lambda > 400$ nm).



Figure S19. (a) FT-IR spectra of BC-CTF before (black) and after (orange) irradiation; (b) N_2 adsorption (solid) and desorption (open) isotherms at 77 K of BC-CTF after irradiation; (c) FT-IR spectra of Ph-BC-CTF before (black) and after (violet) irradiation; (d) N_2 adsorption (solid) and desorption (open) isotherms at 77 K of Ph-BC-CTF after irradiation.

Section 15. Cyclic Stabilities of BC-Based CTFs



Figure S20. Circulatory experiments of photocatalytic oxidation of thioanisole using (a) BC-CTF and (b) Ph-BC-CTF as photocatalysts.



Figure S21. (a) FT-IR spectra of BC-CTF before (black) and after (orange) five recycling experiments; (b) N_2 adsorption (solid) and desorption (open) isotherms at 77 K of BC-CTF after five recycling experiments; (c) FT-IR spectra of Ph-BC-CTF before (black) and after (violet) five recycling experiments; (d) N_2 adsorption (solid) and desorption (open) isotherms at 77 K of Ph-BC-CTF after five recycling experiments.

Section 16. Comparison of The Surface Areas of CTFs Catalyzed by TFMS

CTF	BET (m ² /g)	Ref.
TFMT-500	421	Macromol. Rapid Commun. 2013, 34, 452
CTF-T1	19	Macromol. Rapid Commun. 2015, 36, 1799.
CTF-IP10	358	Chem. Eur. J. 2016, 22, 4931.
CTF-BT, CTF-B	90, 565	J. Mater. Chem. A 2016, 4, 7555.
PCTF-8	625	J. Mater. Chem. A 2016, 4, 13450.
CTF-1~CTF-4	200~560	Polymer 2017, 126, 283.
asy-CTF, CTF- Th and CTF-Th- Ph	52,78,62	Angew. Chem. Int. Ed. 2018, 57, 8316.
CTF-BT/Th-x	32~92	Angew. Chem., Int. Ed. 2019, 58, 8676.
CTF@TFMS	62	Chem. Eng. J. 2019, 371, 314.
P1~P6	2~1152	Adv. Mater. 2012, 24, 2357.
BC-CTF	934	This work
Ph-BC-CTF	967	This work

Table S9. BET comparison of CTFs catalyzed by TFMS.

Section 17. CO₂ Adsorption and Desorption Isotherms of The BC-Based CTFs



Figure S22. CO₂ adsorption (closed symbols) and desorption (open symbols) isotherms of the BC-CTF (orange) and Ph-BC-CTF (violet) measured up to 1 bar at 273 K.

Section 18. The Comparison of Surface Areas and CO₂ Uptakes for Some CTFs and POPs.

CTF or POP	BET (m ² /g) ^[a]	CO ₂ uptake (mg/g) ^[b]	Ref.
CTF-1~CTF-1-600	746~1553	22~35.64	<i>Energy Environ. Sci.</i> 2013 , 6, 3684.
P1~P6	2~1152	0~148.08	Adv. Mater. 2012, 24, 2357.
TCMP-0, TNCMP-2, TCMP-3, TCMP-5	494~995	53.68~115.28	Polym. Chem. 2012, 3, 928.
TPI-1~TPI-7	<10~809	29.92~107.8	Chem. Mater. 2013, 25, 970.
NOP-1~NOP-6	428~894	57.8~110.3	Polym. Chem. 2014, 5, 3424.
MCTF@300~MCTF@500	640~1510	100~130	Polym. Chem. 2013 , <i>4</i> , 2445.
fl-CTF300~fl-CTF600	15~2862	55.88~188.32	J. Mater. Chem. A 2014 , 2, 5928.
PCTF-1~PCTF-7	79~2235	81.52~143.39	J. Mater. Chem. A 2013 , 1, 14990.
cCTF400~cCTF500	744~1247	99~133	ACS Appl. Mater. Interfaces 2017 , 9, 7209.
CMP-YA, CMP-SU-1B2, CMP-SU-1B3	495~1410	91.92~93.5	Macromolecules 2017 , 50, 4993.
FCTF-1, FCTF-3	832~896	135.52~144.76	Macromol. Rapid Commun. 2016 , 37, 323.
PCTF-1, PCTF-2	784~2235	81.5~143.4	<i>Chem. Commun.</i> . 2013 , 49, 3961.
BC-CTF	934	140.1	This work
Ph-BC-CTF	967	131.7	This work

Table S10. The comparison of BET surface areas and CO₂ uptakes for some CTFs and POPs.

[a] Surface area determined by the BET method; [b] CO₂ uptake measured at 273 K and 1 bar.



Section 19. Control Experiments for Photocatalysis.

Figure S23. UV-vis spectra of RhB (25 mg/L) after different illumination time intervals in the presence of (a) no catalyst, (b) BC-CN (0.4 mg/mL) and (c) Ph-BC-CN (0.4 mg/mL) under 300 W Xenon lamp with 400 nm optical filter.

Section 20. Elemental Analysis Data and Colors of BC-Based CTFs

EA (wt%)	BC-CTF		BC-CTF-400		Ph-BC-CTF		Ph-BC-CTF-400	
	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.
С	77.77	74.03	77.77	82.38	84.76	83.88	84.76	90.81
Н	2.80	3.84	2.80	2.65	3.83	4.30	3.83	2.42
Ν	19.43	18.06	19.43	13.51	11.41	10.55	11.41	6.62
Colors of CTFs	of s							

Table S11. The elemental analysis data and colors of BC based CTFs.

Section 21. GC-MS Spectra of the Commercial Thioanisole, Sulfoxide and Sulfone.





Peak number	Retention time (min)	Starting time (min)	Ending time (min)	m/z	Peak area (%)
а	8.895	8.815	11.605	140.030	100



Peak number	Retention time (min)	Starting time (min)	Ending time (min)	m/z	Peak area (%)
а	9.711	9.650	11.755	156.025	100







Figure S25. UV–visible light absorption spectra of BC-CTF (orange), BC-CTF-400 (pink), Ph-BC-CTF (violet) and Ph-BC-CTF-400 (olive).

Section 23. Supporting References

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