

**Direct synthesis of covalent triazine-based frameworks (CTFs)  
through aromatic nucleophilic substitution reactions**

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## Table of Contents

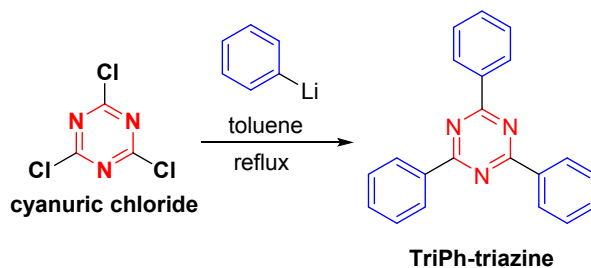
General	S4
Synthesis of 2,4,6-triphenyl-1,3,5-triazine ( <b>M1</b> )	S5
Fig. S1. HR-ESI-MS spectrum of <b>M1</b>	S5
Fig. S2. <sup>1</sup> H NMR of <b>M1</b>	S6
Synthesis of 1,4-bis(4,6-dichloro-1,3,5-triazine-2-yl)benzene ( <b>M2</b> )	S7
Fig. S3. HR-ESI-MS spectrum of <b>M2</b>	S7
Fig. S4. <sup>1</sup> H NMR of <b>M2</b>	S8
Synthesis of <b>CTF-1</b>	S9
Synthesis of <b>CTF-2</b>	S9
Fig. S5. The ideal network structures of <b>CTF-1</b> or <b>CTF-2</b>	S9
XPS of <b>CTF-1</b> and <b>CTF-2</b>	S10
Table S1. Peaks of <b>CTF-1</b> in XPS survey spectrum	S10
Fig. S6. C1s scan and N1s scan of <b>CTF-1</b>	S10
Table S2. Peaks of <b>CTF-2</b> in XPS survey spectrum	S11
Fig. S7. C1s scan and N1s scan of <b>CTF-2</b>	S11
Porosity of <b>CTF-1</b> and <b>CTF-2</b>	S12
Fig. S8. Nitrogen sorption isotherm of <b>CTF-1</b> and <b>CTF-2</b> .	S12
Table S3. Porosity data of <b>CTF-1</b> and <b>CTF-2</b> .	S12
Band gap values calculated by DFT method	S13
Fig. S9. Band gap values of the <b>CTFs</b> calculated by DFT method.	S17
Fig. S10. Ultraviolet-visible diffuse reflectance spectroscopy of the <b>CTFs</b>	S17
Fig.S11. Images of <b>CTF-1</b> (left) and <b>CTF-2</b> (right) on water	S18
Fig. S12. FTIR of <b>CTF-2</b> (blue) and cyanuric chloride (black)	S18
<b>Charge Distribution Calculation</b>	S19
Fig. S13. Structure formula of <b>M3</b> used in place of <b>CTF-1</b> : the charge distribution of blue dotted rectangle was exhibited at <b>Fig. S15</b> , <b>Fig. S16</b> and <b>Table S4</b>	S19
Fig. S14. Structure formula of <b>M4</b> used in place of <b>CTF-2</b> ; the charge distribution of blue dotted rectangle was exhibited at <b>Fig. S17</b> , <b>Fig. S18</b> and <b>Table S5</b>	S19
Fig. S15. The local charge distribution of <b>M3</b>	S20
Fig. S16. The local serial number of <b>M3</b>	S20
Table S4. The atom charge value of <b>M3</b>	S20
Fig. S17. The local charge distribution of <b>M4</b>	S21
Fig. S18. The local serial number of <b>M4</b>	S21
Table S5. The atom charge value of <b>M4</b>	S21
Fig. S19. FE-SEM and FE-TEM of both <b>CTFs</b> .	S22

Table S6. The quantum yields of up-conversion fluorescence of CTF-1 and CTF-2 excited at 800nm	S22
<b>Reference</b>	<b>S22</b>

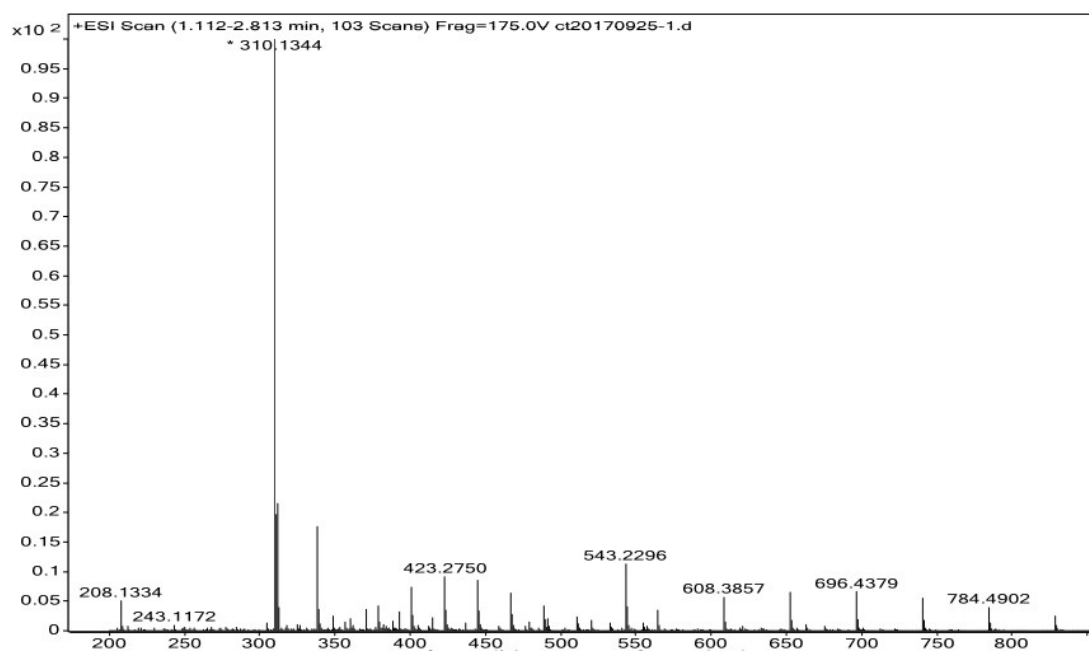
## General

Unless otherwise noted, reagents and solvents were purchased from commercial sources and were used as received. Toluene and 1,4-dioxane were dried with activated molecular( 4A molecular sieves, 3-5 mm, pellets, activated under 400 °C in an oven for 4 h). <sup>1</sup>H-NMR spectra were recorded on a Bruker Avance III HD 500 NMR spectrometer or on a 400 MHz. The Fourier-transformed infrared (FT-IR) spectra were obtained on a PerkinElmer Spectrum Two FT-IR spectrometer with Attenuated Total Reflection (ATR) technique. Ultraviolet-visible Diffuse Reflectance Spectra (UV-Vis DRS) were collected on a UV-2700 using absorption value of BaSO<sub>4</sub> as baseline. TGA were carried on a SDT Q600 thermogravimetric analyzer, and the samples were heated to 1000 °C with a rate of 10 °C/min under a nitrogen atmosphere. The FE-SEM were conducted on a Hitachi S-4800 field emission scanning electron microscope. The FE-TEM were conducted on a JEOL JEM-2100F. The PXRD were obtained on a Bruker AXS D8 ADVANCE X-ray diffractometer with a Cu K $\alpha$  ( $\lambda$  = 1.5418 Å) radiation source operated at 40 kV and 40 mA. Surface area, nitrogen adsorption isotherms (77K) and pore size distributions were measured on a JW-BK122W, the sample were degassed at 80 °C for 6h under reduced pressure before analysis. <sup>13</sup>C cross polarization magic angle spinning nuclear magnetic resonance (<sup>13</sup>C CP/MAS NMR) spectra were recorded on a 700 MHz Bruker Avance NEO spectrometer. Mass spectra (ESI analysis) were recorded on an Esquire 6000 spectrometer (LC/MS). The photoemission spectra were recorded on a optical path system equipped with a femtosecond laser (Coherent ChameleonVision, 80 MHz) and a spectrometer (Horiba-IH530), and the background (silicon oxide, crystal orientation: 100, thickness of oxide layer: 200 nm, electrical resistivity < 0.0015 $\Omega$ ·cm) purchased from a commercial source. The powder was dispersed in dichloromethane (DCM) before coated on the background, then the DCM was evaporated in a cupboard provided with a draught. The photocatalytic experiments were performed under visible light irradiation (>420 nm) with a Xe 500W lamp(Perfectlight). The temperature of the system was maintained at 25 °C by the flow cooling water. In the experiments, 50 mg of photocatalyst powder was dispersed in 100 mL aqueous solution contained 10 mL triethanolamine (TEOA) as a photogenerated hole scavenger. 1.5 mg (3 wt%) of Pt was added as cocatalyst by in-situ photodeposition method using H<sub>2</sub>PtCl<sub>6</sub>. The mixture was bubbled with argon (carrier gas) from the bottom of the reactor to remove air thoroughly. The power density of the irradiation is ~130 mW/cm<sup>2</sup> as measured by an irradiance meter. The hydrogen evolution was analyzed by gas chromatography (SHIMADZU, GC-2014) equipped with a thermal conductive detector(TCD).

## Synthesis of 2,4,6-triphenyl-1,3,5-triazine (**M1**)



To dry toluene (20 mL) in a three-necked flask was added a solution of phenyllithium in ethyl ether (15 mL, 1.0 M, 15.0 mmol) under nitrogen, and the resulting solution was then refluxed under nitrogen. After a solution of 2,4,6-trichloro-1,3,5-triazine (cyanuric chloride) (940.8 mg, 98%, 5.0 mmol) in dry dioxane (10 mL) was added slowly, the reaction mixture was continually refluxed for 22 h, and then cooled to room temperature, quenched by adding a saturated  $\text{NH}_4\text{Cl}$  aqueous solution (100 mL), and extracted with EtOAc ( $3 \times 50$  mL). The combined extras were washed with dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated. The residual crude was subjected to chromatography to afford **M1** (1.35 g, 87%).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  7.71 (m, 6H), 7.55 (m, 6H), 7.45 (m, 3H). HRMS (m/z) calcd. for  $\text{C}_{21}\text{H}_{16}\text{N}_3$   $[\text{M}+\text{H}]^+$  310.1339; found 310.1344.



**Fig. S1.** HR-ESI-MS spectrum of 2,4,6-triphenyl-1,3,5-triazine (**M1**).

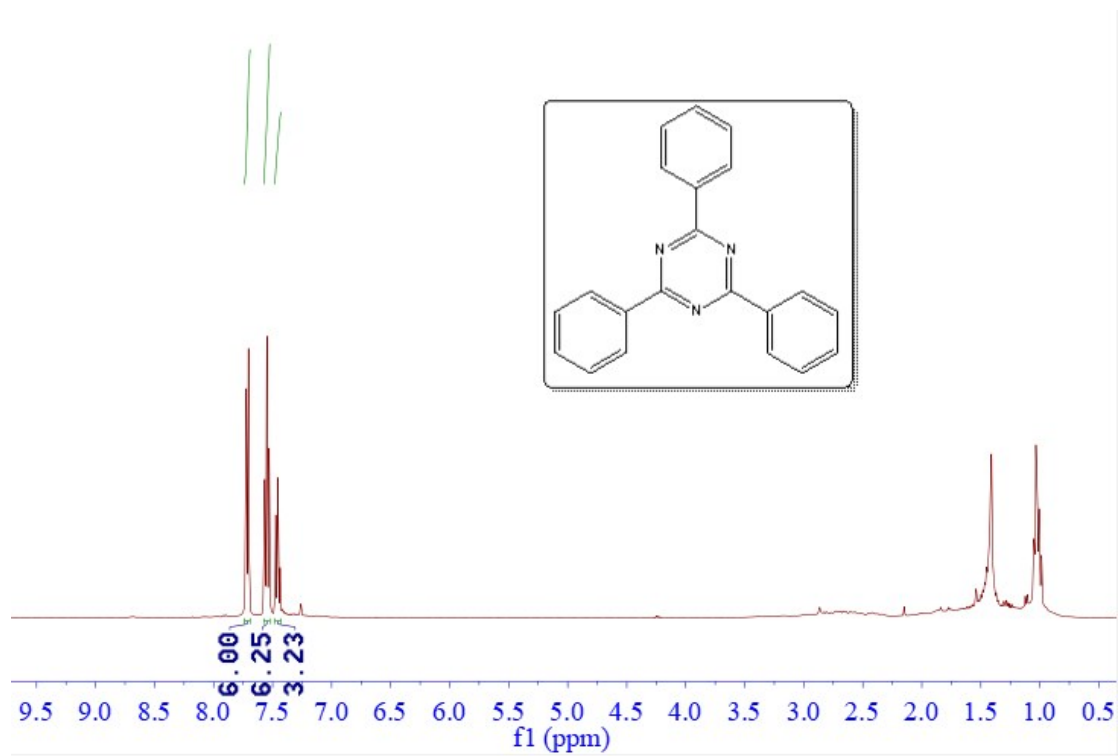
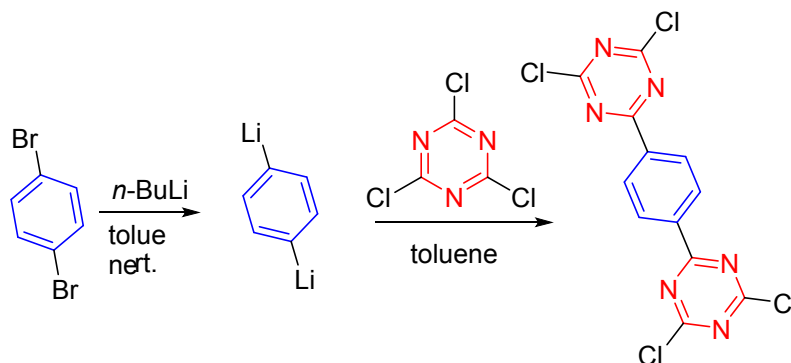


Fig. S2. <sup>1</sup>H NMR of M1

### Synthesis of 1,4-bis(4,6-dichloro-1,3,5-triazine-2-yl)benzene (M2)



To dry toluene (30 mL) in a three-necked flask was added 1,4-dibromobenzene (241 mg, 98%, 1 mmol), and a solution of *n*-butyllithium in *n*-hexane (0.8 mL, 2.5 M, 2 mmol) was added slowly at room temperature under nitrogen. The reaction mixture was cooled to -10 °C. After a solution of 2,4,6-trichloro-1,3,5-triazine (3.76 g, 98%, 20 mmol) in dry 1,4-dioxane (20 mL) was added slowly, the reaction mixture was continually stirred for 1 h at -10 °C, then quenched by adding H<sub>2</sub>O (100 mL), and extracted with EtOAc (3 × 30 mL). The combined extracts were washed with dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The residual crude was subjected to chromatography to afford low-melting 1,4-bis(4,6-dichloro-1,3,5-triazine-2-yl)benzene (32 mg, 9%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), δ 7.36 (s, 4H). HRMS (m/z) calc. for C<sub>12</sub>H<sub>4</sub>N<sub>6</sub>Cl<sub>4</sub> [M]<sup>+</sup> 371.9246; found 371.1016.

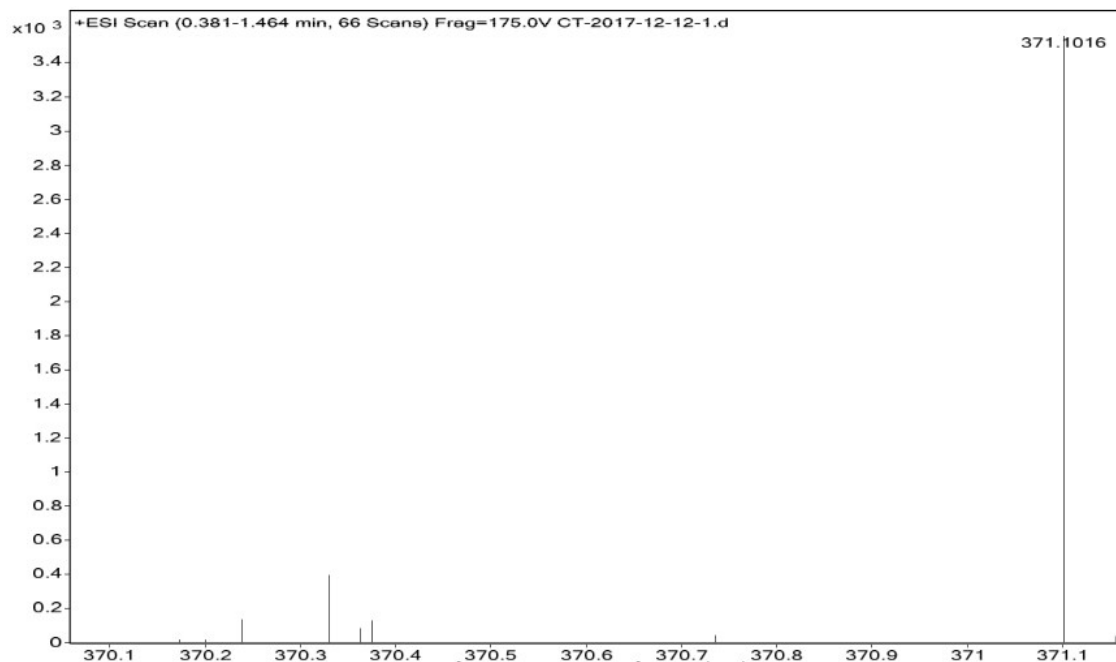
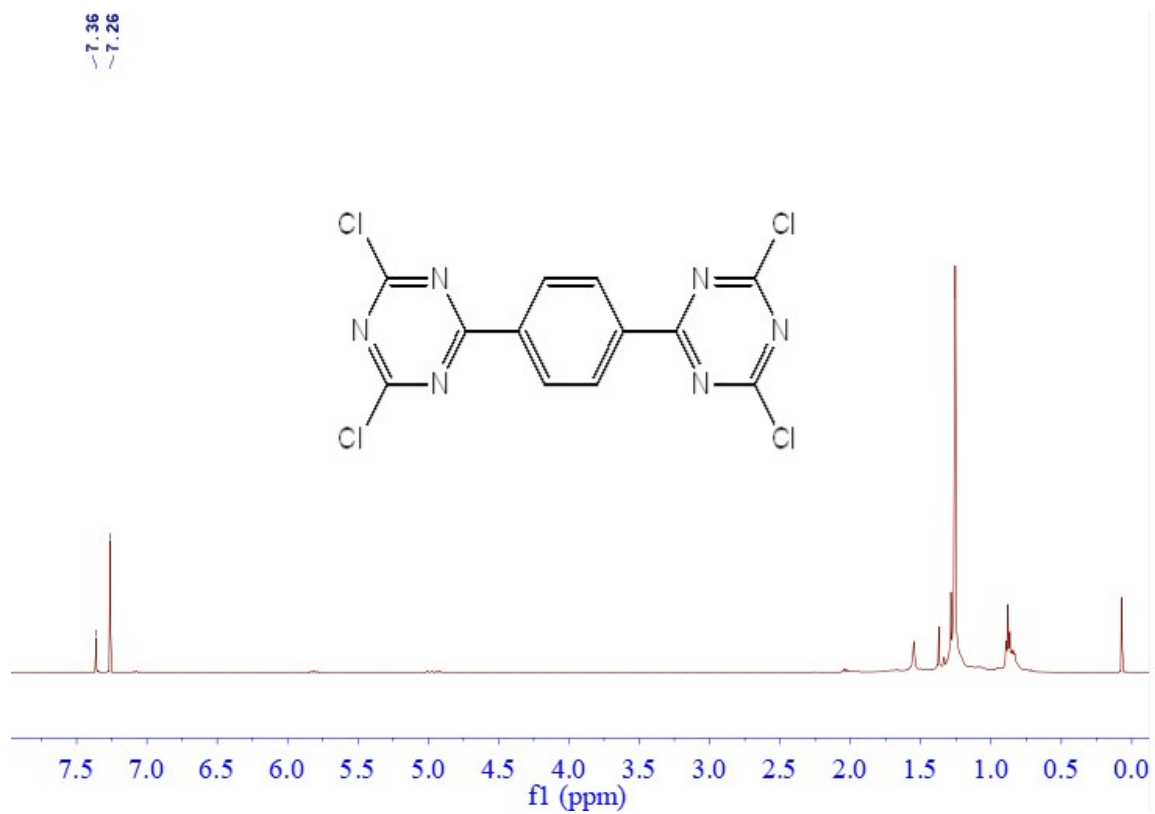


Fig. S3. HR-ESI-MS spectrum of M2.



**Fig. S4.** <sup>1</sup>H NMR of M2.



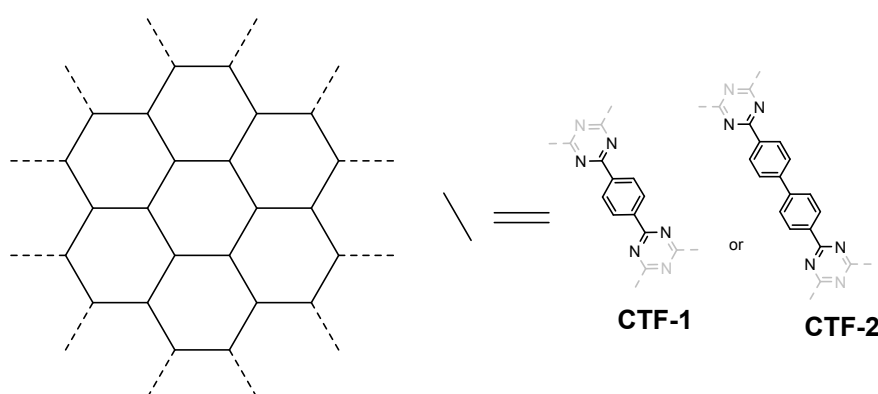
## Synthesis of CTF-1

To solution of 1, 4-diiodobenzene (2.69 g, 98%, 8.0 mmol) in dry toluene (50 mL) in a three-necked flask was added a solution of *n*-butyllithium in *n*-hexane (7.0 mL, 2.5 M, 17.5 mmol) under nitrogen (Caution: the standard operating procedure of *n*-BuLi should be strictly followed for operators' safety), and the resulting mixture was stirred as room temperature for 30 min, and then heated till refluxing. After a solution of 2,4,6-trichloro-1,3,5-triazine (940 mg, 98%, 5 mmol) in dry toluene (15 mL) was added dropwise, the reaction mixture was refluxed for 22 hours, cooled to room temperature, and quenched by adding H<sub>2</sub>O (10 mL). The precipitate formed were harvested by filtration, followed by water scrubbing. The crude product was washed with toluene (3 × 30 mL), dioxane (3 × 30 mL), ethyl acetate(5 × 100 mL), methanol (5 × 100 mL) and water (5 × 200 mL), and dried under reduced pressure (110 °C, 6 h) to afford **CTF-1** (904 mg, 88.2 %).

**NOTICE:** Model molecules (such as TriPh-triazine) and monomers are soluble in common organic solvents, and the as-synthesized products were washed by toluene, 1,4-dioxane, ethyl acetate, methanol and water to remove oligomers, leaving behind the polymers.

## Synthesis of CTF-2

CTF-2 was prepared by following a procedure similar to the above one with using 4,4'-diiodobiphenyl (3.31 g, 98%, 8.0 mmol) in yield of 96%.

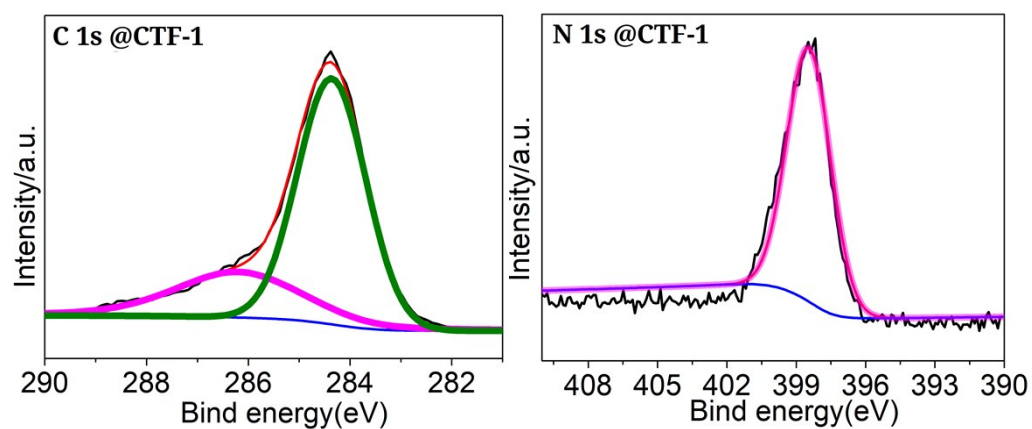


**Fig. S5.** The ideal network structures of **CTF-1** or **CTF-2**.

## XPS of CTF-1 or CTF-2

**Table S1.** Peaks of CTF-1 in XPS survey spectrum.

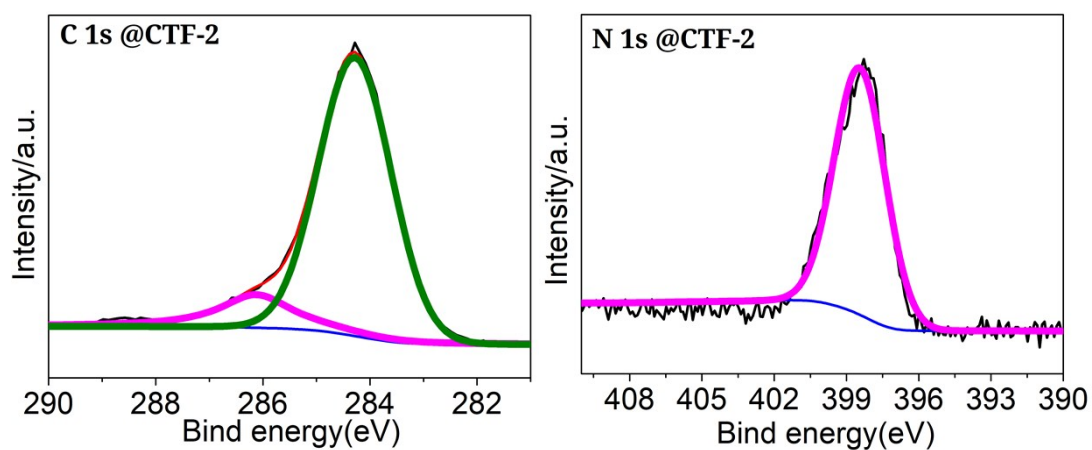
CTF-1	Start BE	Peak BE	End BE	Height CPS	FWHM (eV)	Area (P) (eV)	Area (N) TPP-2M	Atomic %	Peak Type
Cl2p	204.58	197.88	194.28	197.15	2.31	875.44	0	0.44	Standard
N1s	402.88	398.45	394.58	5721.47	2.25	14468.37	0.11	12.69	Standard
C1s	291.08	284.37	281.38	28958.81	1.65	61037.64	0.77	86.58	Standard
I3d	636.08	620.52	615.38	1479.14	1.62	7486.19	0	0.28	Standard



**Fig. S6.** C1s scan (left) and N1s (right) scan of CTF-1: the ratio of carbon (286.2 eV, triazine): carbon (284.3 eV, phenyl) = 1 : 2.55.

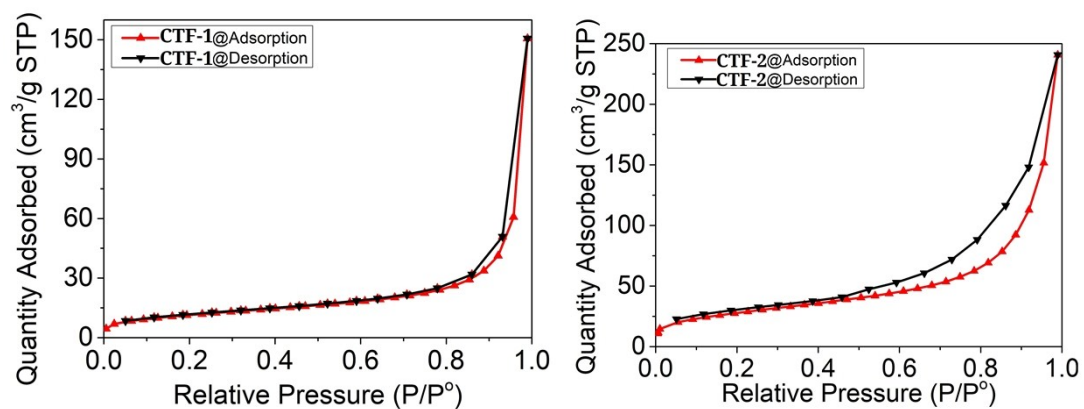
**Table S2.** Peaks of CTF-2 in XPS survey spectrum.

CTF-2	Start BE	Peak BE	End BE	Height CPS	FWHM (eV)	Area (P) CPS. (eV)	Area (N) TPP-2M	Atomic %	Peak Type
Cl2p	205.18	197.22	193.98	161.39	0.33	664.7	0	0.24	Standard
N1s	403.58	398.29	394.68	4645.04	2.69	13046.28	0.1	8.04	Standard
C1s	290.38	284.27	281.28	47129.3	1.62	91717.69	1.16	91.44	Standard
I3d	636.18	620.45	613.48	1729.42	1.85	10429.53	0	0.28	Standard



**Fig. S7.** C1s scan (left) and N1s scan (right) of CTF-2: the ratio of carbon (286.2 eV, triazine) : carbon (284.3 eV, phenyl) = 1 : 5.71.

## Porosity of CTF-1 or CTF-2



**Fig. S8.** Nitrogen sorption isotherm of **CTF-1** (left) and **CTF-2** (right).

**Table S3.** Porosity data of the **CTFs**

Sample	BET surface area (m <sup>2</sup> /g)	Langmuir surface area (m <sup>2</sup> /g)	Pore diameter* (nm)	Pore Volume** (cm <sup>3</sup> /g)
<b>CTF-1</b>	41.03	185.64	23.93	0.231
<b>CTF-2</b>	99.40	451.16	15.61	0.368

\* : BJH adsorption average pore width (4V/A).

\*\* : BJH adsorption cumulative pore volume.

## Band gap values calculated by DFT method

DMol3 package (Materials Studio 8.0) was used to optimized the geometric configurations and calculated band gap values of the CTFs.

DFT calculations under the local density approximation (LDA) and using the PWC functional in the Dmol3 code after geometry optimization.

Electronic parameters are listed below:

Spin polarization: restricted

Basis set: DNP

Functional: PWC

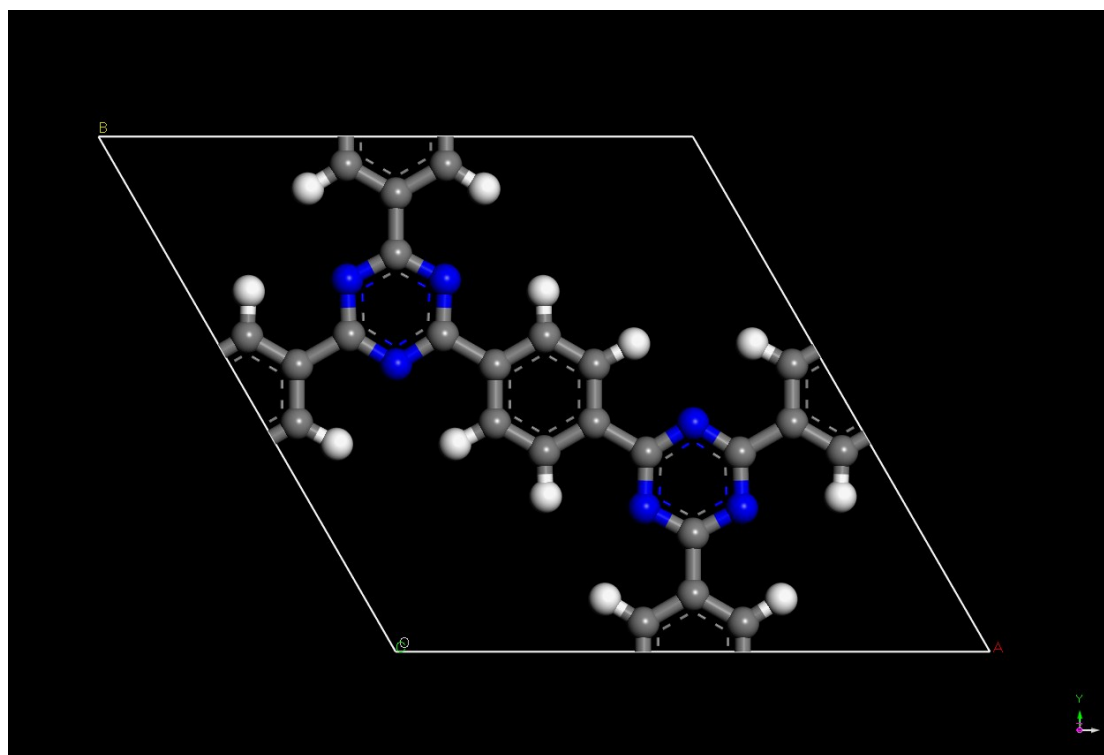
SCF density convergence: 1.0E-6

SCF charge mixing 2.0E-1

Global orbital Cutoff: 3.7 Å

k-point set: fine (1x1x1)

CTF-1, Orientation standard: A along X, B in XY plane.



\$coordinates

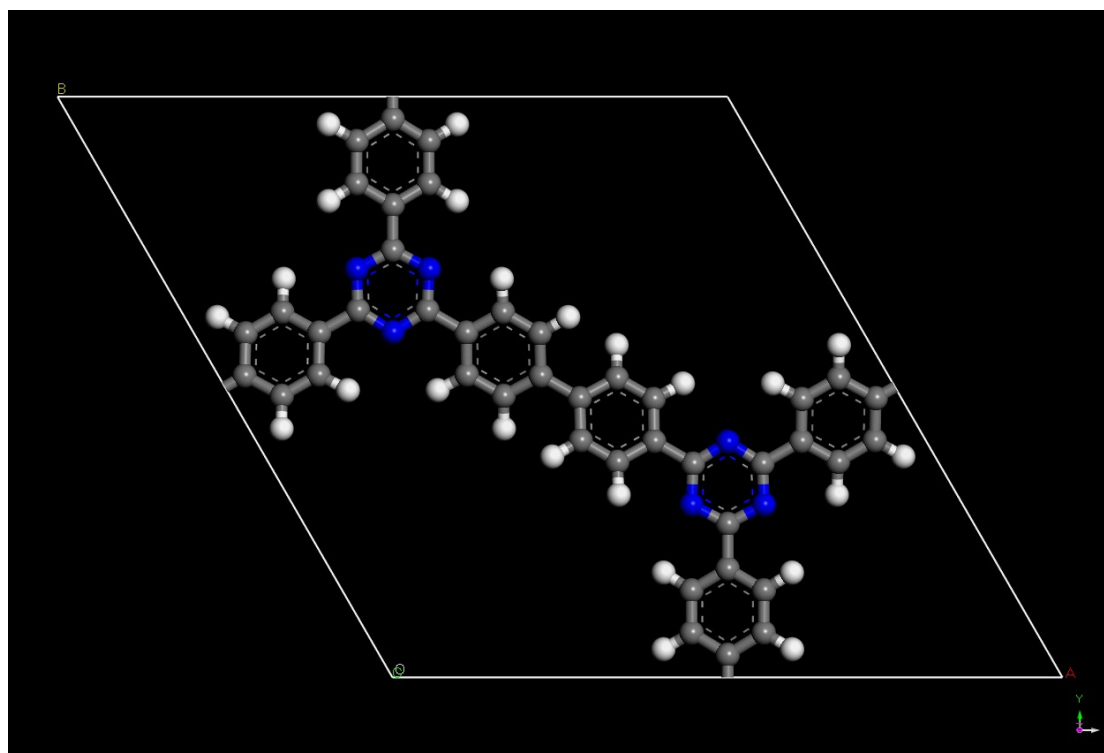
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C	13.59280001707889	2.61769419908662	0.00000000000000
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H	6.73859606049384	16.46159274476451	0.00000000000000
C	-4.52851821297668	10.44796094420172	0.00000000000000
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C	15.87314133256322	1.30216865718436	0.00000000000000
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N	0.00000000000000	13.11724036170455	0.00000000000000
N	2.23293663612923	16.98480006614827	0.00000000000000
N	15.82573665320812	6.55862018085228	0.00000000000000
N	13.59280001707889	10.42617988529600	0.00000000000000
N	11.35986338094966	6.55862018085228	0.00000000000000

\$end

DFT energy gap: 0.099155 Ha 2.698 eV  
valence band edge: -0.248788 Ha -6.770 eV  
conduction band edge: -0.149633 Ha -4.072 eV

CTF-2, Orientation standard: A along X, B in XY plane.



\$coordinates

C	27.36833350231642	13.23186756930539	-0.45303817531668
C	29.61856741582871	14.54278683574784	-0.47641271176223
H	27.29137307739859	11.19997646542643	-0.82199868989521
H	31.37215306362547	13.54762248956621	-0.93012806476662
C	16.03213130280931	17.08573828856199	-0.45303817531668
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C	22.72070659812321	13.11780607011733	0.00000000000000
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C	-9.09931137760175	18.51915659441319	0.00000000000000
C	-2.13299084307430	22.54116363017045	0.00000000000000
C	4.51933733386691	21.16340584105895	0.00000000000000
C	9.09931137760175	18.51915659441319	0.00000000000000
C	2.13299084307430	22.54116363017045	0.00000000000000
C	0.00000000000000	28.99112771845768	0.00000000000000
C	0.00000000000000	34.27962621174918	0.00000000000000
C	0.00000000000000	26.23561214023467	0.00000000000000
N	20.58771575504892	14.45958994234148	0.00000000000000



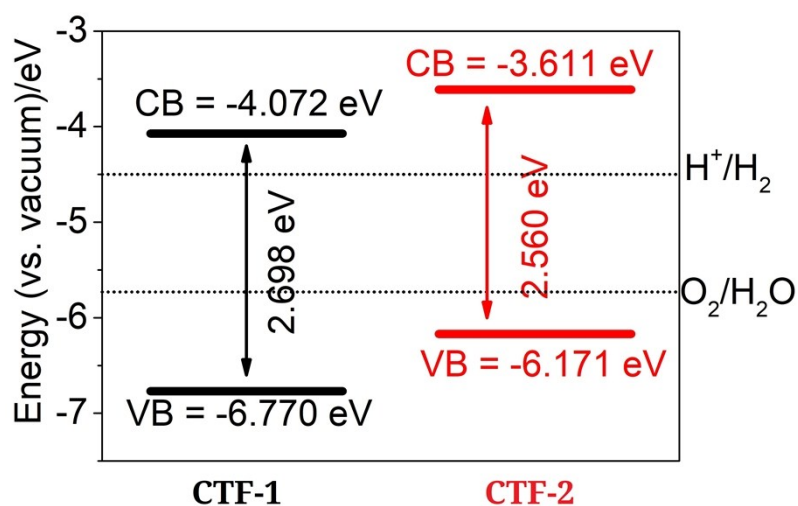
N	18.35920141253369	10.59968987802828	0.00000000000000
N	22.81623009756413	10.59968987802828	0.00000000000000
N	0.00000000000000	21.19937975605657	0.00000000000000
N	2.22851434251522	25.05927982225949	0.00000000000000
N	-2.22851434251522	25.05927982225949	0.00000000000000

\$end

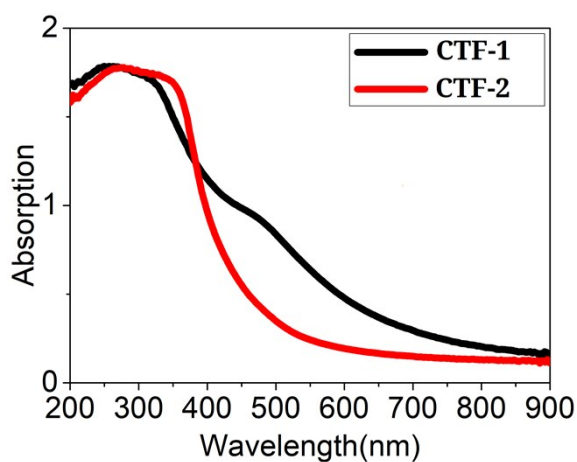
DFT energy gap: 0.094089 Ha 2.560 eV

valence band edge: -0.226790 Ha -6.171 eV

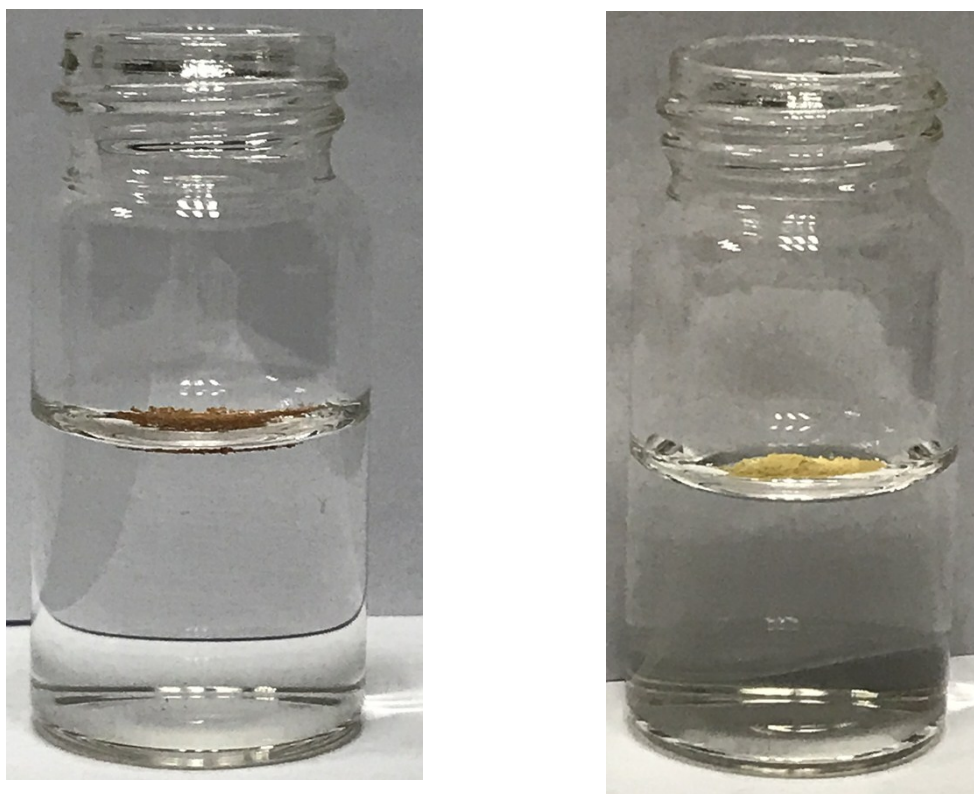
conduction band edge: -0.132700 Ha -3.611 eV



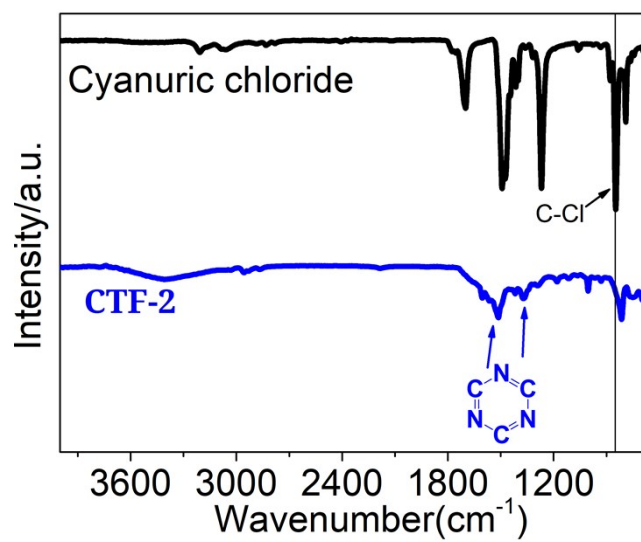
**Fig. S9.** Band gap values of the CTFs calculated by DFT method.



**Fig. S10.** Ultraviolet-visible diffuse reflectance spectroscopy of the CTFs.



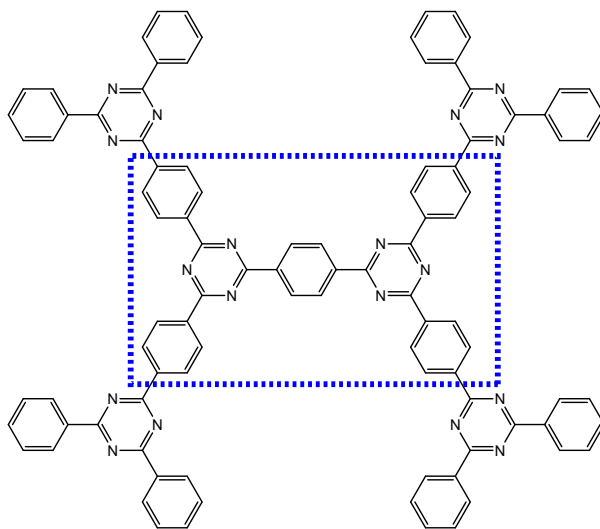
**Fig. S11.** Images of CTF-1 (left) and CTF-2 (right) on water.



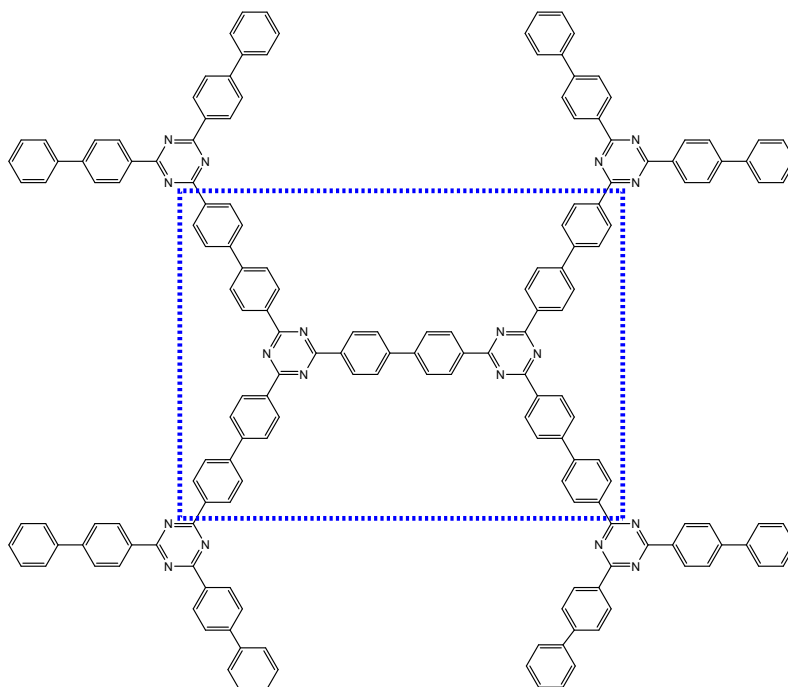
**Fig. S12.** FTIR of CTF-2 (blue) and cyanuric chloride (black).

## Charge Distribution Calculation

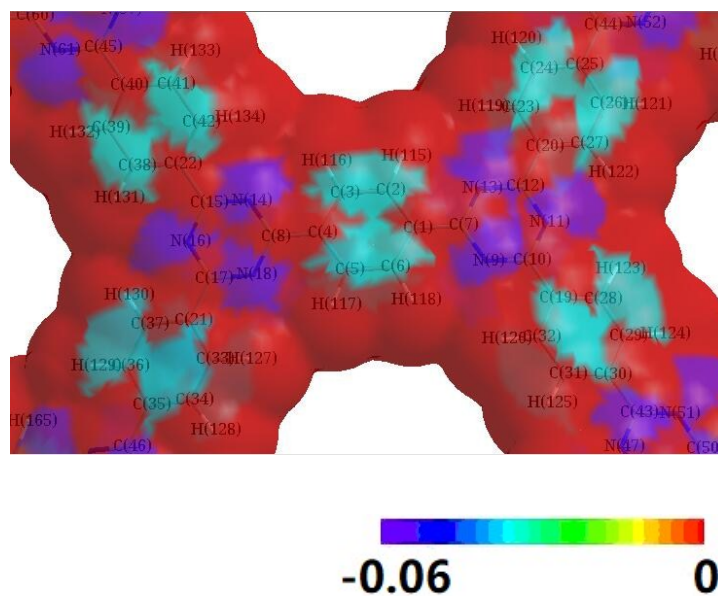
The force field<sup>[1]</sup> (MM2) was used to minimize the energy of the **M3** and **M4** to get their optimized configurations, subsequently, the charges was calculated by Extended Hückel method, and exhibited on the solvent accessible surface of each molecular.



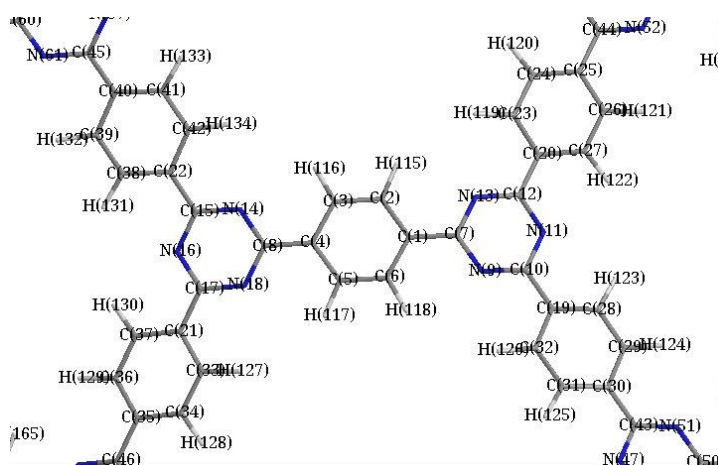
**Fig. S13.** Structure formula of **M3** used in place of **CTF-1**; the charge distribution of blue dotted rectangle was exhibited at **Fig. S15**, **Fig. S16** and **Table S4**.



**Fig. S14.** Structure formula of **M4** used in place of **CTF-2**; the charge distribution of blue dotted rectangle was exhibited at **Fig. S17**, **Fig. S18** and **Table S5**.



**Fig. S15.** The local charge distribution of M3.



**Fig. S16.** The local serial number of M3.

**Table S4.** The atom charge value of M3.

Atom	Charge (Hückel)	Atom	Charge (Hückel)	Atom	Charge (Hückel)
C (1)	0.028544	<b>C (7)</b>	<b>0.319123</b>	N (13)	-0.31195
<b>C (2)</b>	<b>-0.03554</b>	<b>C (8)</b>	<b>0.318347</b>	N (14)	-0.30825
<b>C (3)</b>	<b>-0.03581</b>	N (9)	-0.3133	C (15)	0.318086
C (4)	0.029601	C (10)	0.31931	N (16)	-0.31114
C (5)	-0.03624	N (11)	-0.31382	C (17)	0.319247

C (6)	-0.03547	C (12)	0.318508	N (18)	-0.31424
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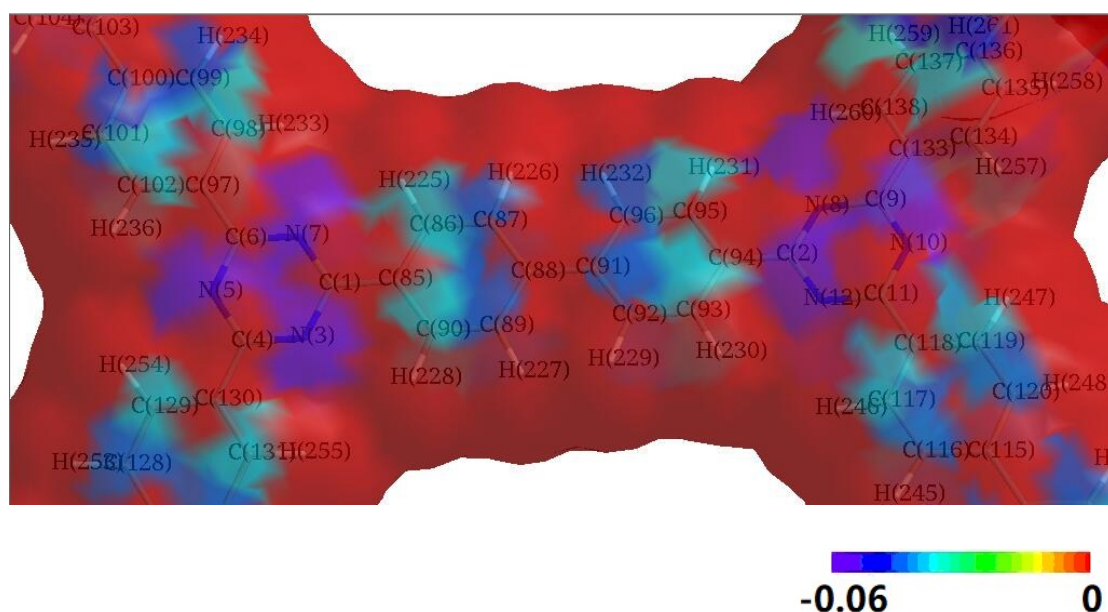


Fig. S17. The local charge distribution of M4.

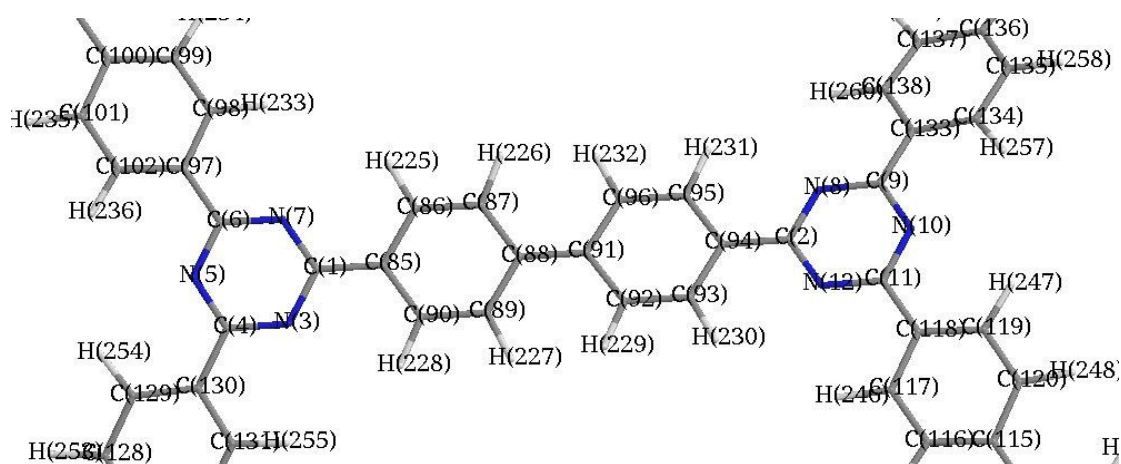
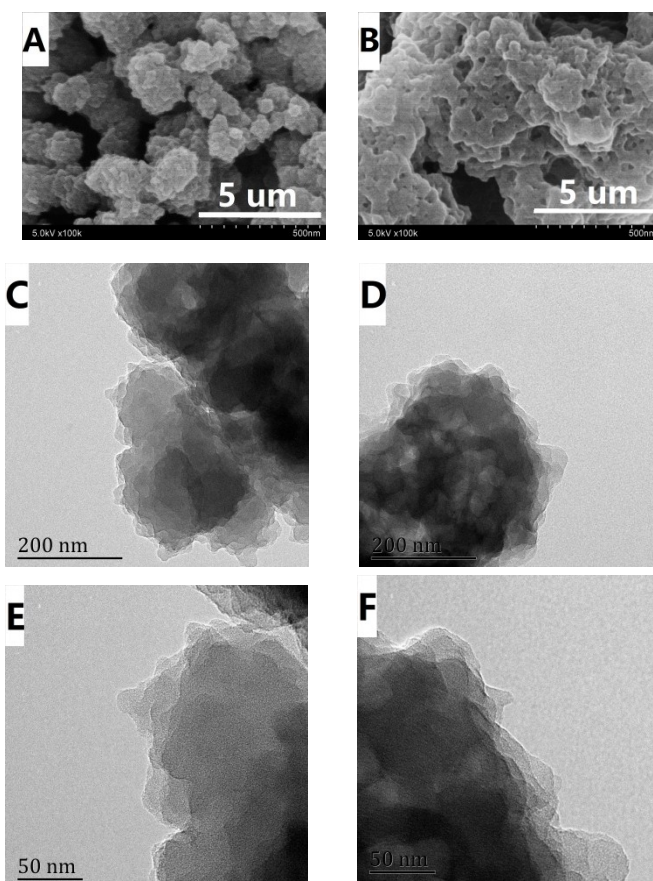


Fig. S18. The local serial number of M4.

Table S5. The atom charge value of M4.

Atom	Charge (Hückel)	Atom	Charge (Hückel)	Atom	Charge (Hückel)
C (1)	0.318113	C (9)	0.321438	<b>C (89)</b>	<b>-0.0417269</b>
C (2)	0.318052	N (10)	-0.31493	C (90)	-0.036259
N (3)	-0.313728	C (11)	0.317622	C (91)	0.0516172
C (4)	0.318269	N (12)	-0.312059	<b>C (92)</b>	<b>-0.0415724</b>

N (5)	-0.31534	C (85)	0.0233751	C (93)	-0.036578
C (6)	0.31941	C (86)	-0.0365876	C (94)	0.0234154
N (7)	-0.317918	<b>C (87)</b>	<b>-0.0417059</b>	C (95)	-0.0364851
N (8)	-0.319842	C (88)	0.0518759	<b>C (96)</b>	<b>-0.0417057</b>



**Fig. S19.** FE-SEM of CTF-1(A), CTF-2 (B); FE-TEM of CTF-1 (C, E) and CTF-2 (D, F).

**Table S6.** The quantum yields of up-conversion fluorescence of CTF-1 and CTF-2 excited at 800nm

	Cursor1-2: 788.77- 809.34(nm)	Cursor3-4: 416.53 - 764.48(nm)	Quantum Yield	Abs	Peak Wavelength	Peak Count	Peak FWHM
CTF-1	170108693	4222	<b>0.000299</b>	0.077	799.06	49783.14	4.00
CTF-2	183772752	25933	<b>0.057082</b>	0.002	799.06	53819.17	4.00

## Reference



[1] Lan, Z. A.; Fang, Y. X.; Zhang, Y. F. and Wang, X. C. *Angew. Chem. Int. Ed.*, **2018**, 57,470-474.

[2] N. L. Allinger, *J. Am. Chem. Soc.*, **1977**, 99 (25), 8127 – 8134.