Electronic Supplementary Information for:

**Covalent triazine framework as an efficient catalyst for photo degradation of methylene blue under visible light illumination**

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**Experimental details:**

**Chemicals.** 1,4-Dicyanobenzene and ZnCl\textsubscript{2} were purchased from J&K Scientific Ltd. (Beijing) and used without further purification. Na\textsubscript{2}SO\textsubscript{4}, Methylene Blue was obtained from Sinopharm Chemical Reagent Co., Ltd. and used as received.

**Preparation of CTF-A and CTF-C.** CTF-A was prepared according to a reported method\textsuperscript{1}. Typically, 3 mmol (384.4 mg) of 1,4-dicyanobenzene was mixed with 6 mmol (817.8 mg) anhydrous ZnCl\textsubscript{2} in a glove box. Then, the mixture were put into a glass ampoule (volume \textit{ca}. 20 mL, body length 18 cm, neck length 9 cm) and sealed under vacuum. The sealed tube was then placed into a muffle furnace and heated to 400 °C. 1,4-dicyanobenzne sealed into the tube became polymerization at 400 °C in ZnCl\textsubscript{2} melts and all of the monomers were nearly transformed into CTF-A after 60 h of reaction. Then the glass tube was allowed to cool to room temperature and was cracked. Immediately, the as-obtained black solid was ground into fine powder and...
dispersed into 20 mL of HCl solution (6 mol/L) to dissolve ZnCl₂. After 24 h of treatment, the as-obtained CTF-A powder was filtrated and washed by distilled water thoroughly, and then dried in air in a 110 °C oven for 12 h. CTF-C was also prepared as the same as CTF-A except for the mole ratio of 1,4-dicyanobenzene and anhydrous ZnCl₂. For CTF-C preparing, 3 mmol (384.4 mg) of 1,4-dicyanobenzene and 3 mmol (408.9 mg) anhydrous ZnCl₂ were mixed together in a glove box, sealed in a 20 mL glass ampoule, and kept at 400 °C for 60 h.

**Photocatalytic degradation experiments.** For the photo catalytic ability test of CTF-A and CTF-C, 1 mg of CTF-A or CTF-C was dispersed into 10 mL of methylene blue solution (100 mg/L) in a 50 mL beaker and stirred vigorously. Then, the as-prepared reaction mixture was allowed to illumination by a 300 W Xe lamp (PLS-SXE300/UV, Beijing Perfectlight Technology Co., Ltd.) with a UV cut filter (λ≥420 nm) for methylene blue degradation. The distance between the reaction mixture and the light exit position was kept 10 cm and the current was located at 15 A in all of the photo degradation experiments for the uniformity of light intensity. Certain amount of reaction mixture was collected for quantitatively analysis at different time intervals. After 2 h of degradation, the reaction was stopped and the as-obtained reaction mixture was measured by a UV-Vis spectrometer immediately to confirm the residual methylene blue concentration. In the photo catalytic ability test of ZnCl₂, 0.1 mg of ZnCl₂ was dissolved into 10 mL of MB solution (100 mg/L) and proceeded as the above mentioned.

**Mott-Schottky test.** For Mott-Schottky (M-S) plot test, 10 mg of CTF-A or CTF-C powder were mixed with 0.1 mg of PTFE (1%, used as the binder) in an agate mortar. The mixture was then ground thoroughly and pressed into a flake in 1 mm thickness and was fixed on an ITO electrode with carbon paste. Then, the as-prepared electrodes were insulated using enamel to ensure that only the CTF-A or CTF-C flakes with certain areas (6 mm × 7 mm) were exposed and were electricity conductive. Afterwards, the three electrodes system (working electrode: CTF-A or CTF-C flake,
counter electrode: Pt wire, reference electrode: SCE electrode) was used to measuring the M-S plots in 0.1 M Na\(_2\)SO\(_4\) electrolyte (pH = 7) on a CHI 660D electrochemical workstation. All of the potentials in M-S plots were relative to SCE and were converted into versus NHE for easily comparison with other literature in our work.

I-V plots test of CTFs. For the I-V plots test of CTF-A and CTF-C, certain amount of CTF-A or CTF-C powder was put into a cubic sample cell (7 mm × 2 mm × 1 mm) and pressed into bulks under 0.5 MPa pressure. In the height direction of the sample cell, two conductive walls (Cu foils) were reserved for easily electrical measurement. I-V plots of bulk CTF-A and CTF-C were measured from the two conductive walls using a CHI 660D electrochemical workstation.

Cyclic voltammetry test. In cyclic voltammetry measurement, the concentrations of methylene blue were kept at 100 mg/L in 0.1 M Na\(_2\)SO\(_4\) (pH=7) electrolyte. The three electrodes system (working electrode: bare glass carbon electrode, counter electrode: Pt wire, reference electrode: SCE electrode) was still employed. The potential window was maintained in -1 V~1 V vs. SCE and the scan rate was kept at 20 mV/s. The potentials in all of the CV plots were also converted into new values versus NHE. The blank experiments without any pollutants in 0.1 M Na\(_2\)SO\(_4\) were also carried out to confirm the origination of the oxidation-reduction peaks.

Characterization. The as-prepared CTF-A and CTF-C were characterized by Fourier Transform Infrared spectroscopy (FTIR, BRUKER, TENSOR-27), X-ray photoelectron spectroscopy (XPS, VGESCALAB 220i-XL), X-ray diffraction (XRD, BRUKER D/max-2500), Solid-state \(^{13}\)C NMR spectra (BRUKER Avance III Spectrometer, 100 MHz), Combustion elemental analysis (Vario EL III Elementar Analyser Systeme), N\(_2\) adsorption-desorption spectroscopy (MICROMERITICS, ASAP 2020M), and UV-Vis spectrophotometer (Hitachi, U-3010) equipped with an integrating sphere. All of the electronic measurements were carried out on a CHI 660D (Shanghai Chenhua Instruments Co., Ltd.) electrochemical workstation.
Scheme S1. Synthesis of CTF-A and CTF-C. CTF-A was synthesized using 1,4-dicyanobenzene (DCB) and ZnCl₂ mixture with a mole ratio of 1:2, while CTF-C was prepared via 1,4-dicyanobenzene (DCB) and ZnCl₂ mixture with a mole ratio of 1:1. The trimerization of the cyano group builds a big molecular network of the benzene and triazine ring.

Table S1. Elemental analysis of CTF-A and CTF-C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Found (%)</th>
<th>Calculated (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>N</td>
</tr>
<tr>
<td>CTF-A</td>
<td>69.23</td>
<td>12.02</td>
</tr>
<tr>
<td>CTF-C</td>
<td>64.41</td>
<td>15.18</td>
</tr>
</tbody>
</table>

Figure S1. FTIR of CTF-A, CTF-C, and 1,4-dicyanobenzene. For CTF-A and CTF-C, the absorption bands at 2230 cm⁻¹ disappeared after polymerization compared to 1,4-dicyanobenzene and this indicated the successful trimerization of the monomer. In
the FTIR spectrum of CTF-C, the bands of triazine ring were very strong and located at 1510 cm\(^{-1}\), 1350 cm\(^{-1}\), and 810 cm\(^{-1}\), respectively. For CTF-A, the bands at 1050-1270 cm\(^{-1}\) was according to the strong absorption of C-N stretch and the bands at 1690-1560 cm\(^{-1}\) came from the open-chain imino group due to the ring fragmentation \(^1\).

**Figure S2.** XPS results of CTF-A and CTF-C. The present of N 1s, C 1s, and O 1s peaks confirmed the as-obtained CTF-A and CTF-C were consist of N, C, and O elements, which came from 1,4-dicyanobenzene. And also, the peaks of Cl 2p located at 199 eV and Zn 2p located at 1022 eV originate from the residual ZnCl\(_2\) (Zn atom content: 1.08%).

**Figure S3.** XRD patterns of CTF-A and CTF-C. Two obvious diffraction peaks located at 2\(\theta\) = 7.1° and 25.5° were clearly seen in the XRD pattern of CTF-C, which indicated the crystalline property of the CTF-C. In contrast, only a weak and broaden XRD peak was obtained from CTF-A, which proved the amorphous structure of
CTF-A.

**Figure S4.** Solid-state $^{13}$C NMR spectra of CTF-A and CTF-C. Compared to CTF-C, the signal located at 170 ppm $^2$ (peak 1) nearly disappeared in $^{13}$C NMR spectra of CTF-A, which indicated that most of the triazine rings have been broken in CTF-A.

**Figure S5.** N$_2$ adsorption-desorption isothermal curve of CTF-A at 77 K. BET analysis gave a specific surface area of 1475 m$^2$/g for CTF-A.
Figure S6. N$_2$ adsorption-desorption isothermal curve of CTF-C at 77 K. BET analysis gave a specific surface area of 1104 m$^2$/g for CTF-C.

Figure S7. (a) The UV-Vis spectra of MB solutions photodegraded by visible light ($\lambda$>420 nm) for 10 min, 20 min, 40 min, 60 min, 90 min, and 120 min in the present of pure ZnCl$_2$; (b) the corresponding photodegradation rate of MB solutions. The photodegradation process is first-order as the plot of ln(C/C$_0$) vs. time is linear, and the rate constant is about 2.2×10$^{-4}$ s$^{-1}$ which is similar to the result of MB photodegradation rate with no catalyst. Thus, ZnCl$_2$ has no photocatalytic ability for MB degradation.

Reference