Construction of Superior Visible-Light-Driven Photocatalyst Based on "C_3N_4 Active Centre-Photoeletron Shift Platform-Electron Withdrawing Unit" Triadic Structure Covalent Organic Framework

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Experimental Section.

Materials.

1,3,5-Triformylphloroglucinol, melamine, phenol, 1,4-dioxane, mesitylene, *tert*-butanol, and *p*-benzoquinone were purchased from J&K Chemical Co. Ltd. (Beijing, China). Acetic acid (≥99.5%), acetone, tetrahydrofuran (THF), ethylenediaminetetraacetic acid disodium salt (EDTA-2Na), and methyl orange (MO) were obtained from Sinopharm Chemistry Reagent Co. Ltd. (Beijing, China). All chemicals were used as received without any further purification. Ultrapure water was prepared by using Milli-Q SP reagent water system (Millipore, Bedford, MA, USA).

Synthesis of Bulk g-C_3N_4.

Pure bulk g-C_3N_4 was synthesized according to the previous literature[1]. Typically, 5 g of melamine power was calcined at 520 ℃ for 4 h with the rate of 5 ℃ min^{-1} in a muffle furnace.

Synthesis of TpMA.

1,3,5-Triformylphloroglucinol (0.5 mmol, 0.105 mg) and melamine (0.5 mmol, 0.063 mg) were dissolved in a ternary solvent mixture of mesitylene/1,4-dioxane/3 M acetic acid (5/5/1 by vol.; 11.0 mL). The reaction mixture was sonicated for 15 minutes, bubbled with N_2 for another 15 minutes, and then heated at 120 ℃ for 3 days. After the mixture had cool down to room temperature, the precipitate was isolated by centrifugation while being washed with acetone, THF, and hot water. The obtained powder was dried under vacuum at 120 ℃ for 10 h.

Characterization.

Hitachi S-5500 field-emission scanning electron microscope (FE-SEM, Tokyo, Japan) and Hitachi H-7500 transmission electron microscope (TEM, Tokyo, Japan) were applied to characterize the morphology of the synthesized photocatalyst. X-ray diffraction analyses (XRD, PANalytical X′Pert diffractometer, Almelo, Netherlands) were performed on a monochromatized X-ray beam with nickel-filtered Cu Kα radiation with 0.4 ° min^{-1} scan rate. Fourier transform-infrared (FT-IR) spectra were recorded on a Nicolet Thermo NEXUS 670 Infrared Fourier Transform Spectrometer (Waltham, MA). Surface analysis by X-ray photoelectron spectroscopy (XPS) was carried out using a Thermo Fisher ESCALAB 250Xi equipment (Waltham, MA), and the X-ray source was Al Kα radiation (1486.6 eV, monochromatic). Elemental analysis was conducted on an EA3000 analyzer (EUROVECTOR). Solid-state nuclear magnetic resonance (NMR) spectroscopy was obtained on a Bruker AVANCE III 400 MHz spectrometer. Thermogravimetric analysis (TGA) was run on a TGA Q5000 IR thermogravimetric analyzer (TA Instruments, New Castle, U.S.A.) with the heating rate of 10 ℃ min^{-1} under N_2 atmosphere. Nitrogen sorption isotherm was measured at 77 K using a Quadrasorb SI equipped with surface area and pore size analyzer (Quantachrome Instruments, Boynton Beach, FL). The diffuse reflectance spectra (DRS) were collected with a Hitachi U-3900 UV–vis spectrophotometer ($BaSO_4$ as a reflectance standard). The photoluminescence (PL) measurements were recorded on a F-7000 fluorescence spectrophotometer (Hitachi, Tokyo, Japan). Photocurrent response and electrochemical impedance spectroscopy (EIS) were measured with a CHI660E electrochemical analyzer (Chenhua, Shanghai, China) in a standard three-electrode system, using a platinum foil as the counter electrode and Ag/AgCl (saturated KCl) as the reference electrode. Sodium sulfate (0.1 mol L^{-1}) served as the electrolyte solution. The working electrodes were prepared as follow: 5 mg of photocatalyst powder was dispersed in 0.5 mL of DMF, which was dip-coated on the surface of indium tin oxide (ITO) glass substrate. Subsequently, 5 % Nafion was dripped onto the sample film and dried at 100 °C. Visible-light irradiation was provided by a CEL-HXF300F3 300 W xenon lamp (CEAULIGHT) with a 420 nm cut-off filter. The EIS frequency ranged from 10 m to 100 kHz with an AC voltage magnitude of 10 mV.

Photocatalytic Activity Measurements.

The photocatalytic activity of TpMA was evaluated by degradation of MO or phenol under visible light irradiation. In a typical photocatalytic test, 30 mg of the as-prepared photocatalyst was dispersed into 50 mL organic substance solution with a concentration of 10 mg L^{-1}. The suspension containing TpMA with model pollutant was magnetically stirred in dark for 1 h to reach an adsorption-desorption equilibrium before illumination. Then it was exposed to a 300 W xenon lamp with an optical cutoff filter ($\lambda \geq 420$ nm). At the given intervals, 3 mL of aliquot was extracted and centrifuged to remove the photocatalyst. After that, the resulting supernatant was analyzed by monitoring the maximal absorption (462 nm for MO and 270 nm for phenol) in a UV–vis light spectrophotometer. After completion of the photodegadation of MO, the recovered TpMA photocatalyst was thoroughly washed by deionized water, and then dried at 60 ℃ overnight, finally reutilized in the next run. The mineralization of MO under different irradiation times was studied by a total organic carbon (TOC) analyzer (SHIMADZU). For comparison, photocatalytic decomposition of MO or phenol on g-C_3N_4 was carried out under the same experimental condition.

Reference

1 J. Zhou, M. Zhang and Y. Zhu, *Phys. Chem. Chem. Phys.* 2015, **17**, 3647-3652

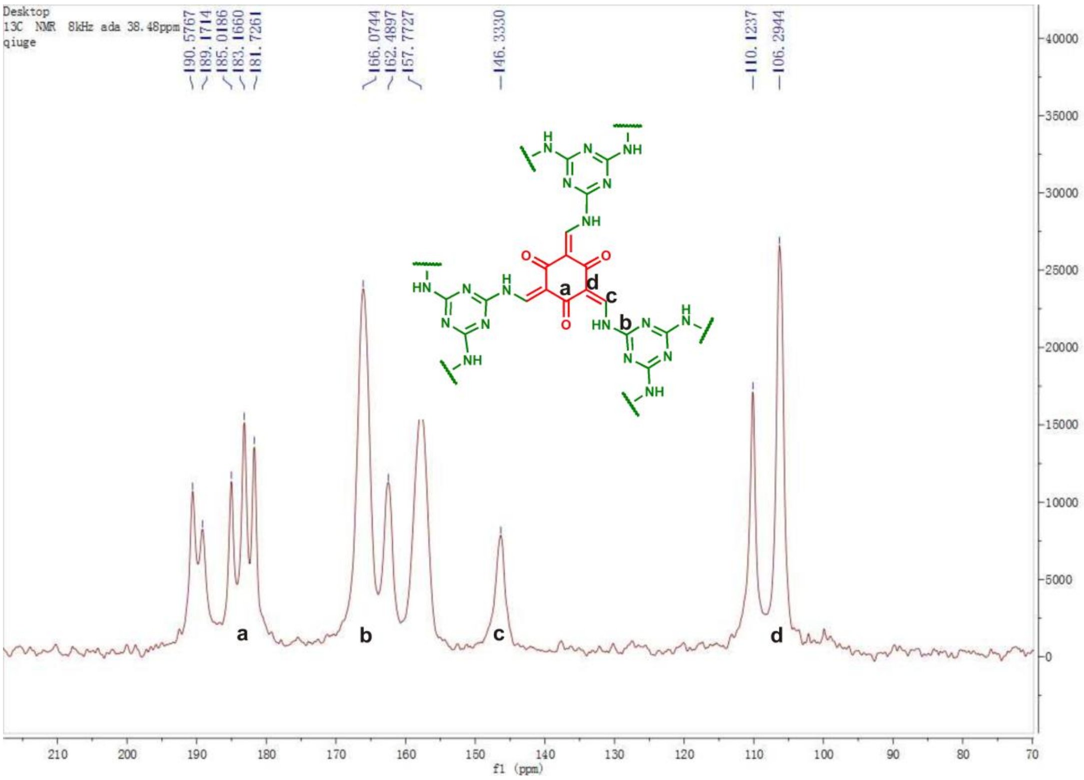

Figure S1. Solid-state ^{13}C cross-polarization magic-angle spinning (CP-MAS) NMR spectrum of TpMA.

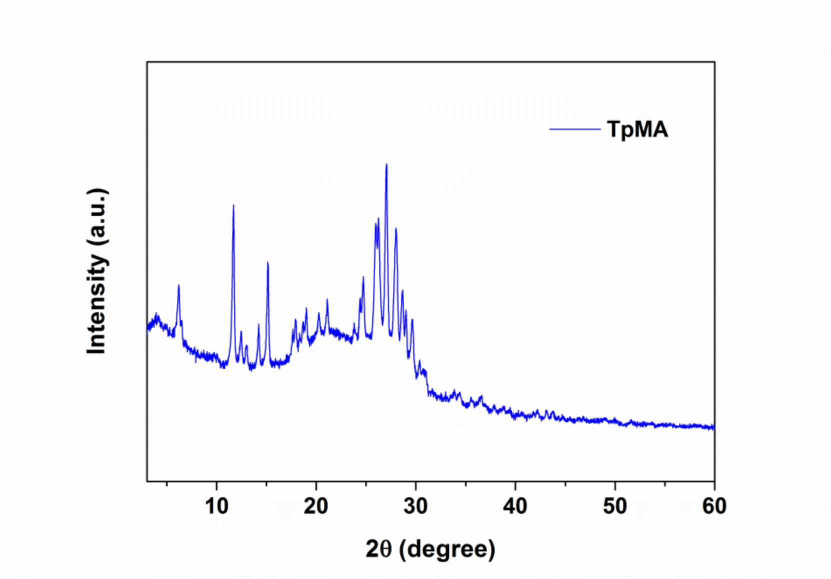

Figure S2. XRD patterns of TpMA.

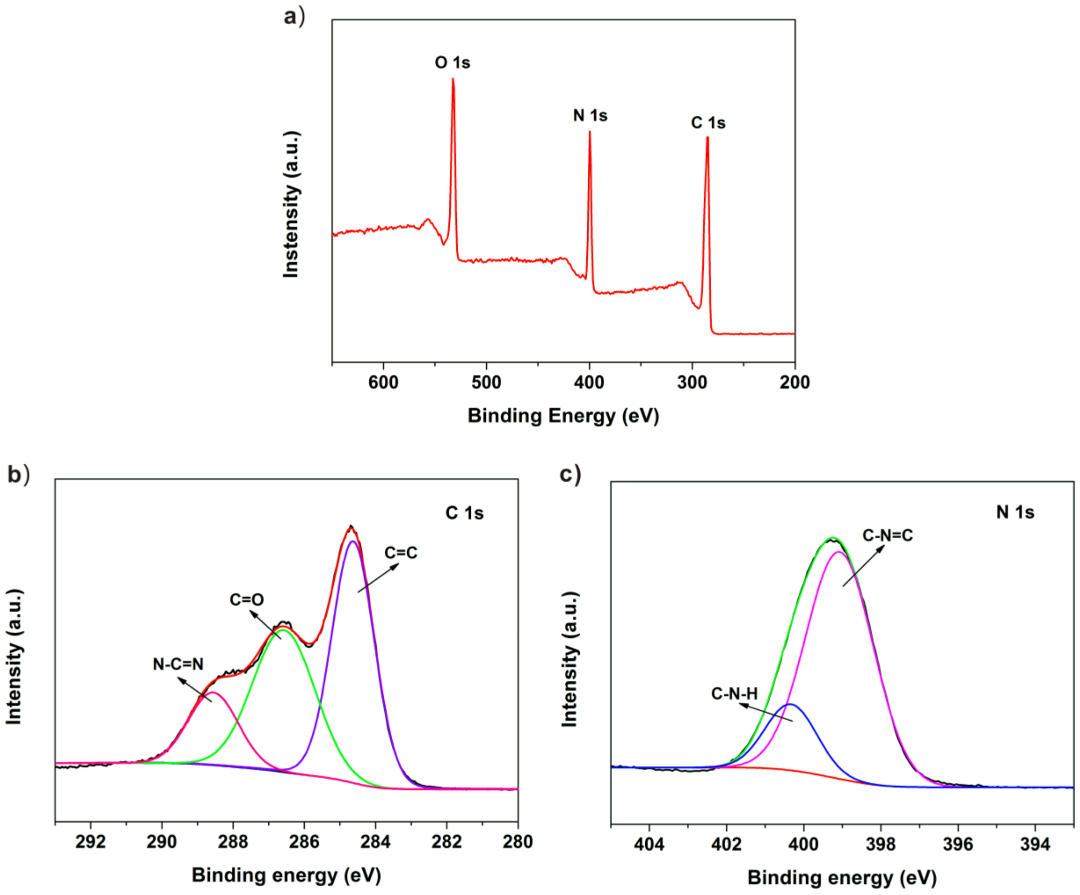

Figure S3. XPS survey spectrum of TpMA (a), high-resolution spectra of C 1s (b) and N 1s (c) for TpMA.

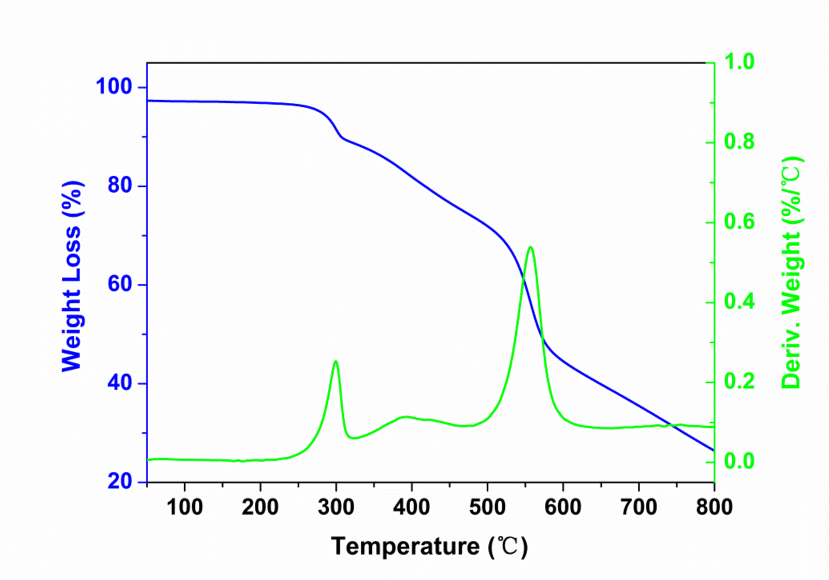

Figure S4. Thermogravimetric analysis (TGA) profile of TpMA.

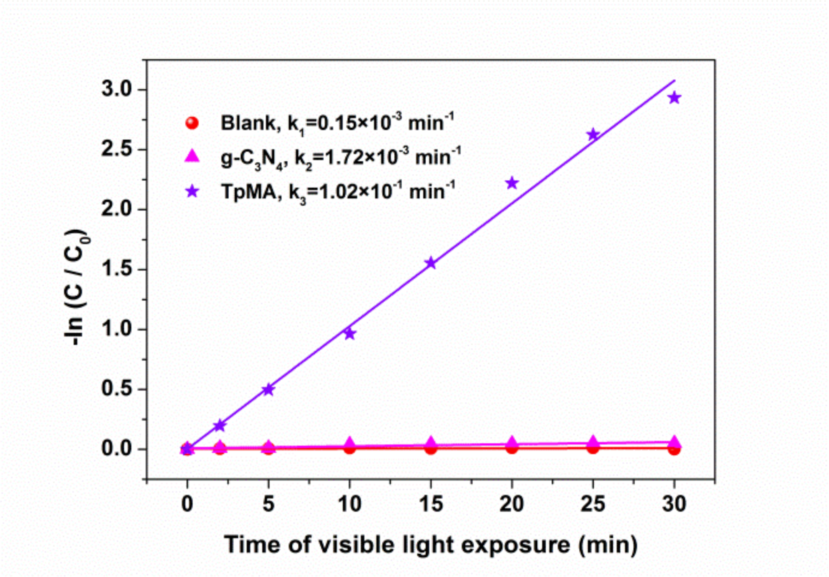

Figure S5. Kinetics linear simulation curves of MO photodegradation over different photocatalysts and the inset is the value of the rate constant *k*.

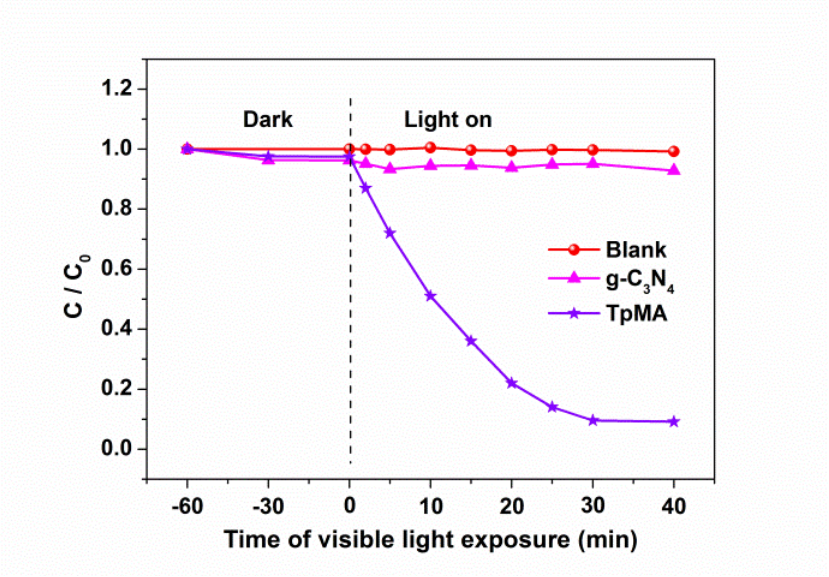

Figure S6. Photocatalytic degradation of phenol (10 mg L^{-1}) over g-C_3N_4 and TpMA under visible light irradiation.

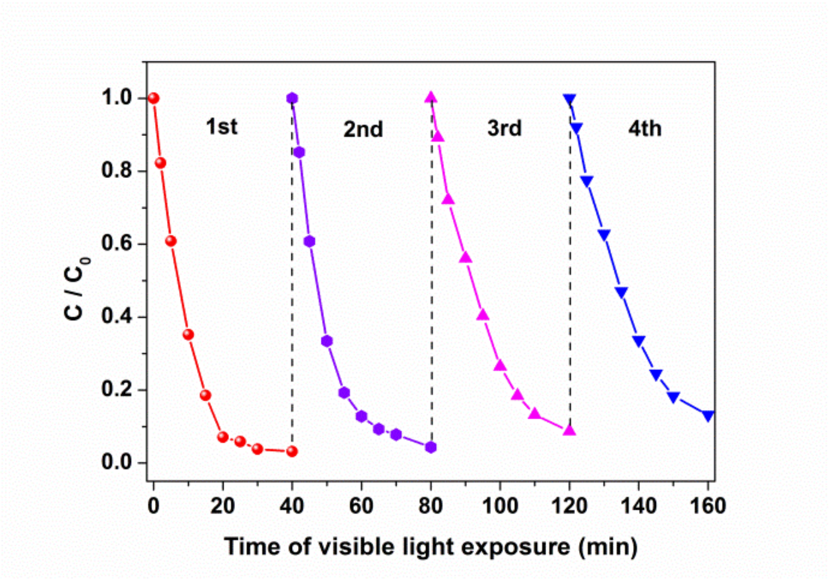

Figure S7. Recycling runs of TpMA for the photodegradation of MO (10 mg L^{-1}) under visible light irradiation.

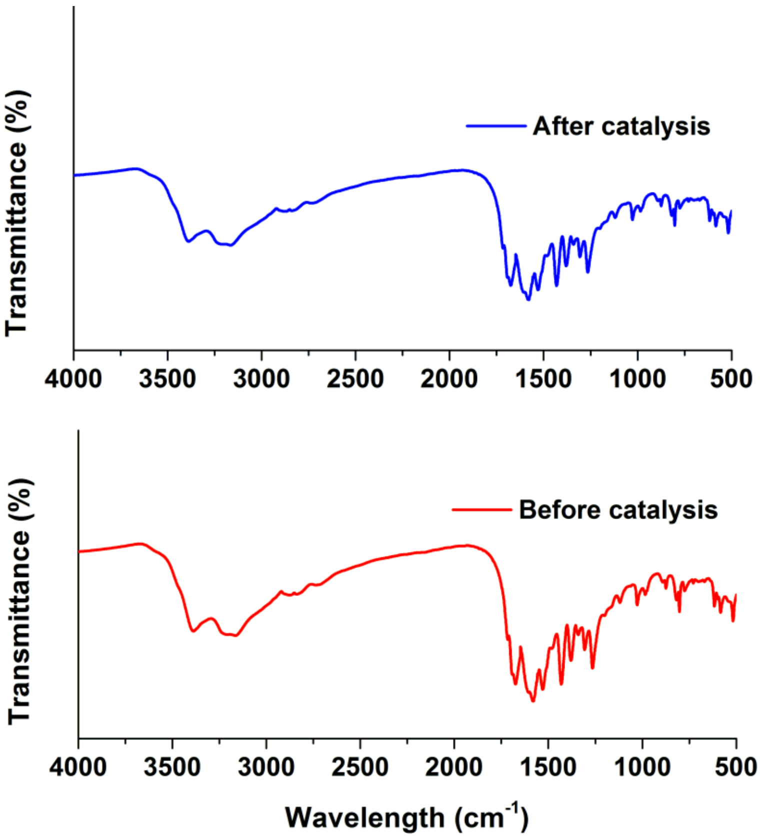

Figure S8. FT-IR spectra of TpMA before and after MO photodegradation.

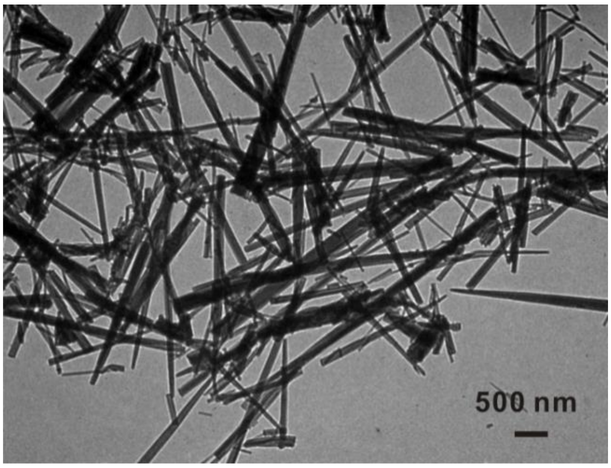

Figure S9. TEM image of TpMA after MO degradation.