Supplementary Material (ESI) for Chemical Communications

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Developing a Polymeric Semiconductor Photocatalyst with Visible Light Response

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Electronic Supplementary Information

I. Experimental details

I. Preparation of carbon nitride polymer (CNP) and g-C_3N_4:

CNP was prepared by the following way: 10 g melamine powder was put into an alumina crucible with a cover, and then this system was heated to 400℃, 450℃ and 520 ℃ in a muffle furnace, respectively. Heating rate was 7℃/min and the temperature maintained for 4 h.

g-C_3N_4 was prepared by two step heat treatment: (1) heating 10g melamine in an alumina crucible with a cover at 500℃ for 2 h, (2) deaminating at 520 for 2h.

II. Preparation of PMDA-coupled CNP (PMCNP):

2g 1,2,4,5-benzene tetracarboxylic dianhydride (PMDA) firstly dissolved in 40 ml acetone at 40℃ under stirring conditions, following by addition of 1g the prepared CNP sample into the PMDA-acetone solution. After acetone volatilized completely at 40℃, the PMDA-CNP mixture was put into alumina crucible, which was heated in muffle furnace to 350 ℃ with a heating rate of 7℃/min. The temperature maintained for 4 h.

The product was washed by acetone for removing the un-reacted PMDA.

III. Characterization of CNP and PMCNP samples

The samples were characterized by X-ray diffraction (XRD) for phase identification on the Rigaku RINT2000 diffractometer. UV-vis diffuse reflection spectra were measured using a UV-vis spectrophotometer (Varian CARY 100, USA) and converted from reflection to absorbance by the Kubelka-Munk method. The C/N ratios for all samples were determined by elemental analysis on the elemental analyzer (vario EL II, Elementar, Germany). The experimental error in weighing was (0.001mg). All solid-state NMR experiments were performed on a Bruker Aduvance III 400WB spectrometer equipped with a 9.4T magnet. The ^{13}C and ^{1}H NMR data were recorded using a Bruker 4-mm CP-MAS probe with zirconia rotors spinning at 14 kHz with Larmor frequencies of 100.62 and 400.13MHz. For 1H NMR, the

relaxation delay was 10-60s, the 90 pulse width was 4us, and a three-pulse sequence pulse program was applied to suppress deading and background signal. The chemical shift was referenced to trimethylsilane(TMS). For ^{13}C CP-MAS NMR experience, the relaxation delay was 10~60s, the contact time was 5ms, a ramp-contact and TMMP15 decoupling pulse program was used. The chemical shift was referenced to adamantane.

Photocatalytic activity of PMDA, CNP400, CNP450, CNP520, PMCNP400, PMCNP450, PMCNP520, PMCNP450/N_2, PMCNP450/CH_3OH, g-C_3N_4 and N-TiO_2 were evaluated by photodegrading methyl orange (MO) in a Pyrex reactor. 0.2 g sample was dispersed in MO aqueous solution (100mL, 20mg/L). The light irradiation system contains a 300WXe lamp with a filter (420 nm) for visible light and a water filter to eliminate the temperature effect.

II. Computational Details

All calculations are performed with Gaussian 03 program.

B3LYP/6-31g method was used to optimize CNP and PMCNP models. HOMO and LUMO orbitals of CNP and PMCNP models were constructed with Gview program based the B3LYP/6-31g-optimized results.

HF/6-31g method was used to optimize CNP and PMCNP models for acquiring HOMO and LUMO orbital energies.

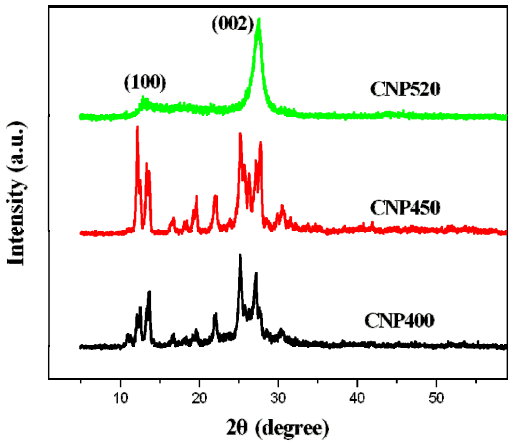


Fig. S1 XRD patterns of CNP400, CNP450 and CNP520 samples

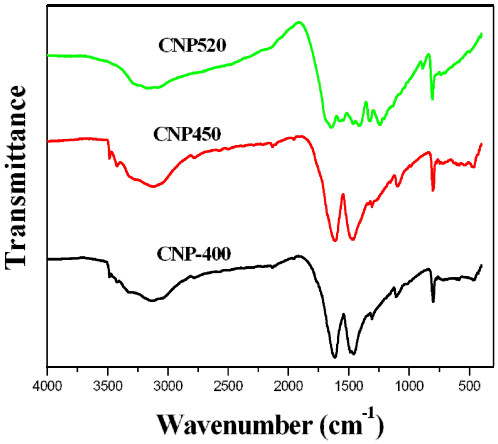


Fig. S2 Fourier transform infrared (FT-IR) spectra of CNP400, CNP450 and CNP520 samples

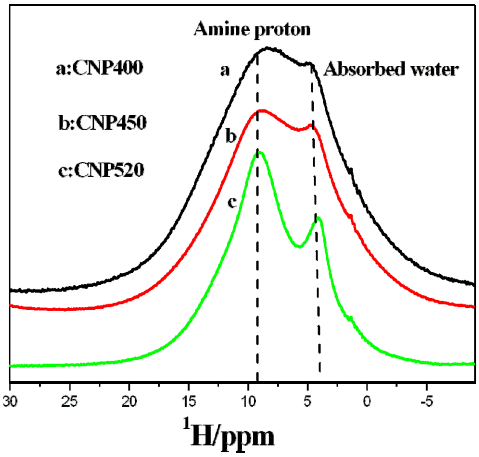


Fig.S3 ^{1}H NMR spectrum of CNP400, CNP450 and CNP520 samples

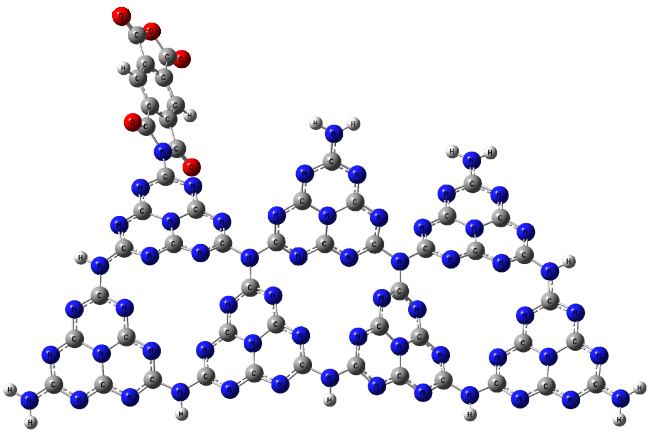


Fig.S4 The optimized geometries of PMCNP model

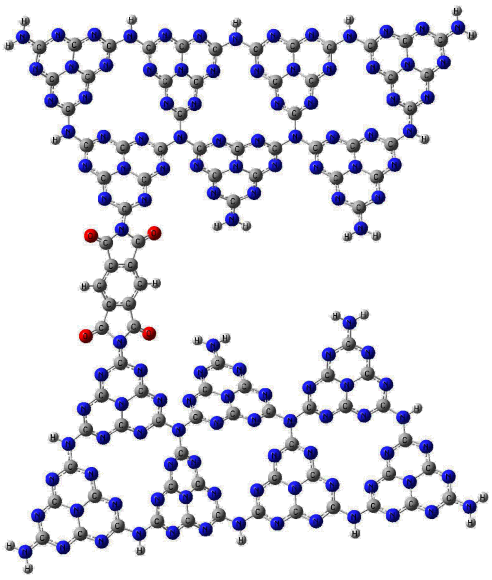


Fig.S5 The possible structure of PMCNP, in which PMDA group acts as bridge to connect two CNP together.

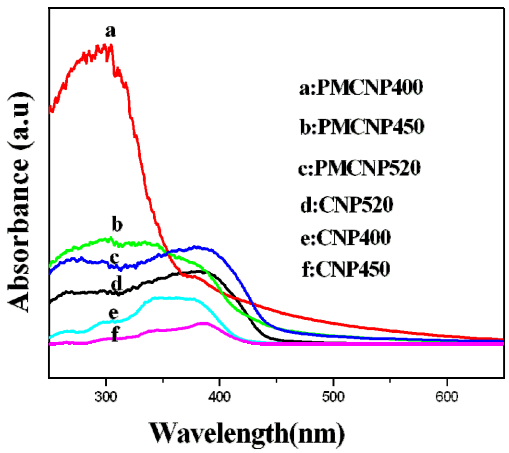


Fig. S6 Uv-vis absorption spectra for CNP400, CNP450, CNP520, PMCNP400, PMCNP450 and PMCNP520 samples.

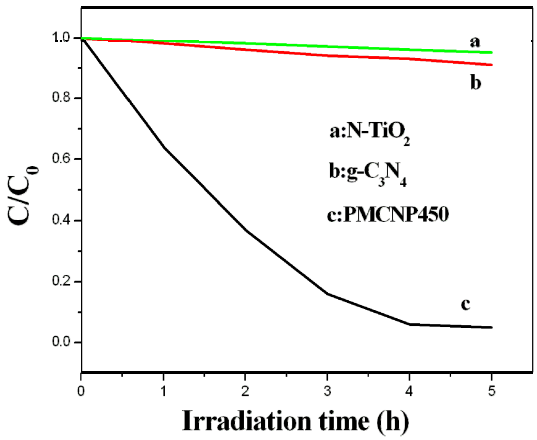


Fig. S7 Photodegradation of methyl orange (20mg/L) by N-TiO_2, g-C_3N_4 and PMCNP450 samples under visible light (λ>420nm) irradiation.

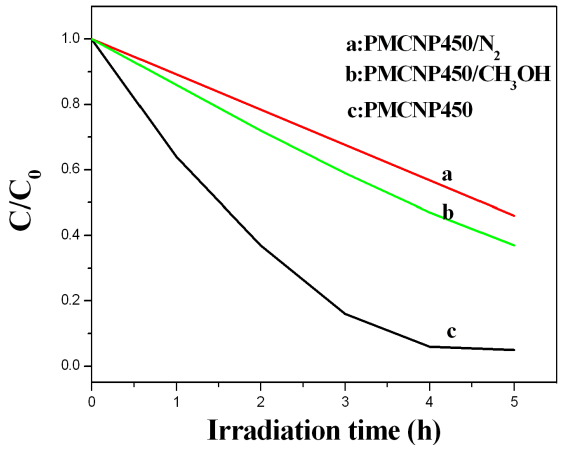
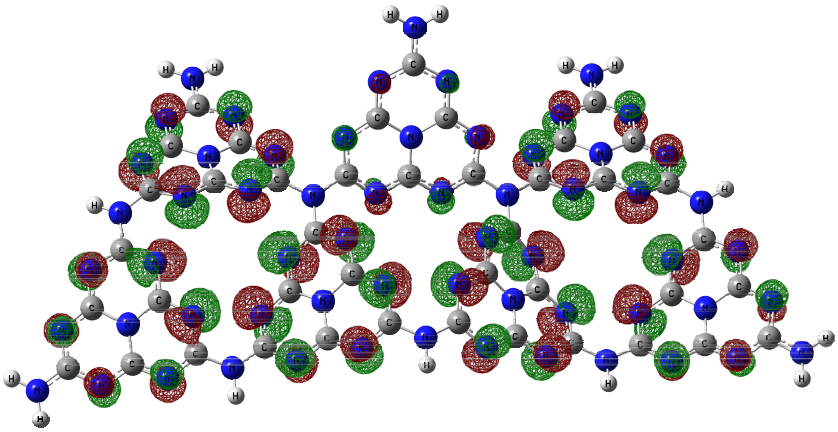
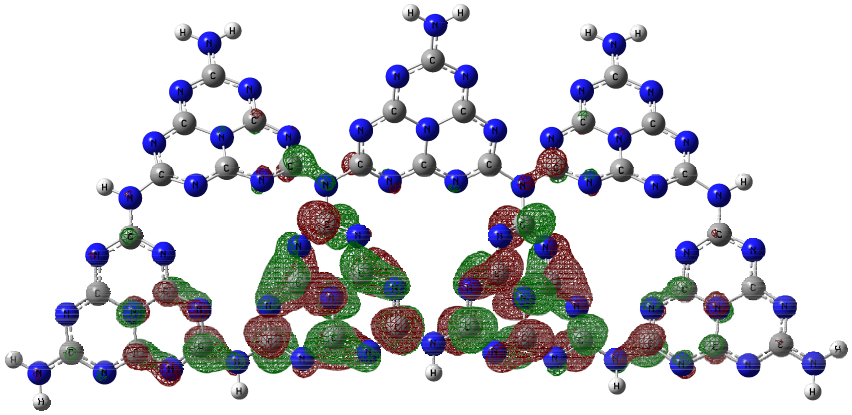


Fig. S8 Photodegradation of methyl orange (20mg/L) by PMCNP450/N_2, PMCNP450/CH_3OH and PMCNP450 samples under visible light (λ>420nm) irradiation.



HOMO



LUMO

Fig.S9 HOMO and LUMO orbitals of the optimized CNP model

Table S.1 Elemental analysis results of CNP400, CNP450 and CNP520 samples.

Sample	C	H	N	C/N
CNP400	32.29%	3.38%	57.70%	0.65
CNP450	33.03%	2.87%	56.54%	0.68
CNP520	34.8%	2.25%	55.40%	0.73

Table S.2 Elemental analysis results of PMCNP400, PMCNP450 and PMCNP520 samples.

Sample	C	H	N	C/N
PMCNP400	46.77%	2.25%	23.44%	2.34
PMCNP450	45.40%	2.43%	29.13%	1.82
PMCNP520	36.00%	2.13%	54.86%	0.77