Supporting Information

Functional group boosting triazine ring-opening for low-temperature synthesis of heptazine-based graphitic carbon nitride

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EXPERIMENTAL SECTION

Materials and Methods.

Melamine (99%, NH_2-DT), 2,4-diamino-6-phenyl-1,3,5-triazine (98%, Ph-DT), 6-methyl-1,3,5-triazine-2,4-diamine (98%, CH_3-DT), and 2-chloro-4,6-diamino-1,3,5-triazine (95%, Cl-DT) were purchased from Macklin Inc. and used as received without further purification. Each precursor (1 g) was heated in a tube furnace under a nitrogen atmosphere at a ramp rate of 2.3 °C min^{-1} to the designated temperature and maintained for 1 h, followed by natural cooling to room temperature. Specifically, NH_2-DT was heated to 500 °C (labeled as NH_2-DT-500) and 550 °C (NH_2-DT-550), Ph-DT to 370 °C (Ph-DT-370) and 420 °C (Ph-DT-420), CH_3-DT to 300 °C CH_3-DT-300) and 350 °C (CH_3-DT-350), and Cl-DT to 300 °C (Cl-DT-300) and 350 °C (Cl-DT-350).

Characterizations.

The morphologies of the samples were observed using a SEM (Regulus 8100, Hitachi, Japan) and TEM (JEM-F200, JEOL, Japan). XRD measurements were performed using a D-MAX 2500/PC diffractometer (Rigaku, Japan) with Cu-Kα radiation (λ = 1.54059 Å). FT-IR spectra were recorded on a Nicolet iS20 spectrometer (Thermo Fisher Scientific, USA) in the range of 4000-400 cm^{-1}. Solid-state ^{13}C cross-polarization/magic angle spinning (CP/MAS) NMR spectra were acquired on a 400 MHz spectrometer (Bruker, Germany). XPS profiles were measured using an AXIS SUPRA spectrometer (Shimadzu, Japan) with a monochromatic Al Kα X-ray source. LC-MS measurements were conducted on an Acquity UPLC H-Class coupled with a Xevo G2-XS QTof mass spectrometer (Waters, USA).

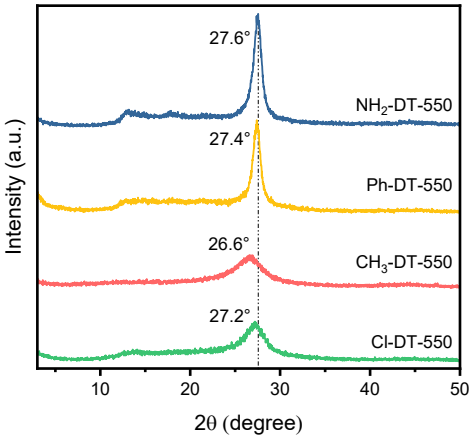

Fig. S1 XRD patterns for the thermal polymerization products of four precursors at 550°C.

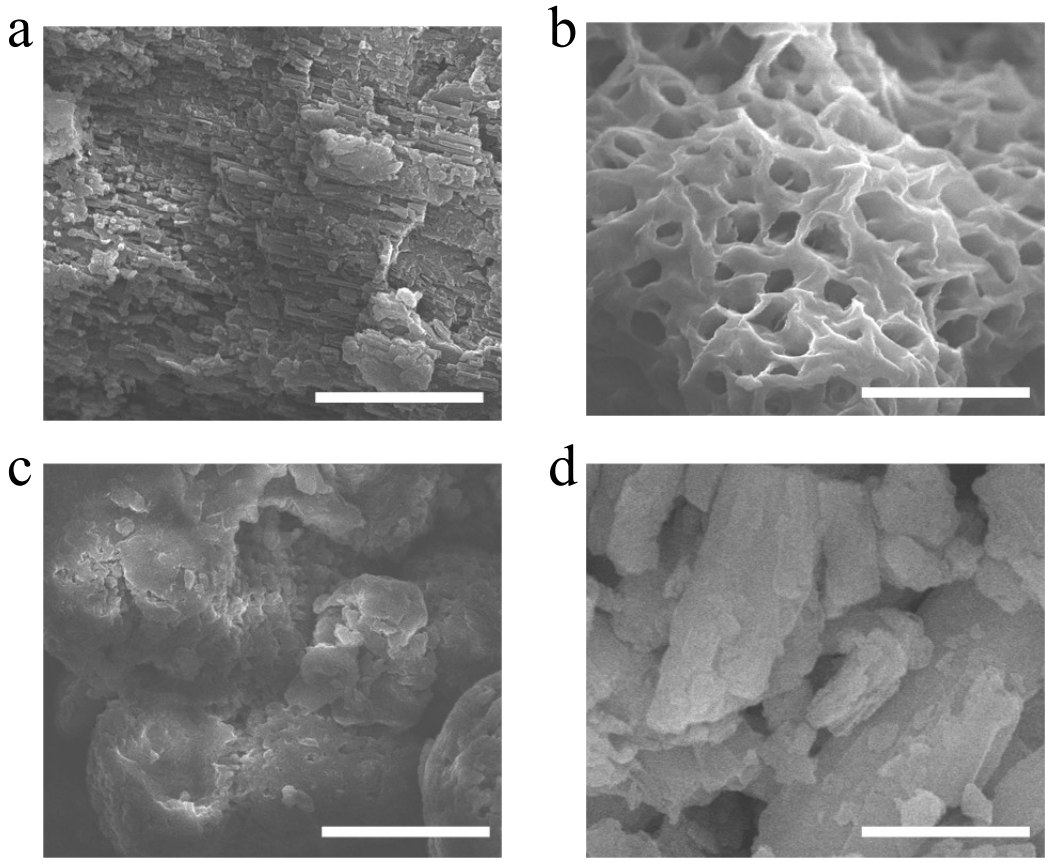

Fig. S2 SEM images of samples (a) NH_2-DT-550, (b) Ph-DT-420, (c) CH_3-DT-350, and (d) Cl-DT-300. The scale bars are 2 μm.

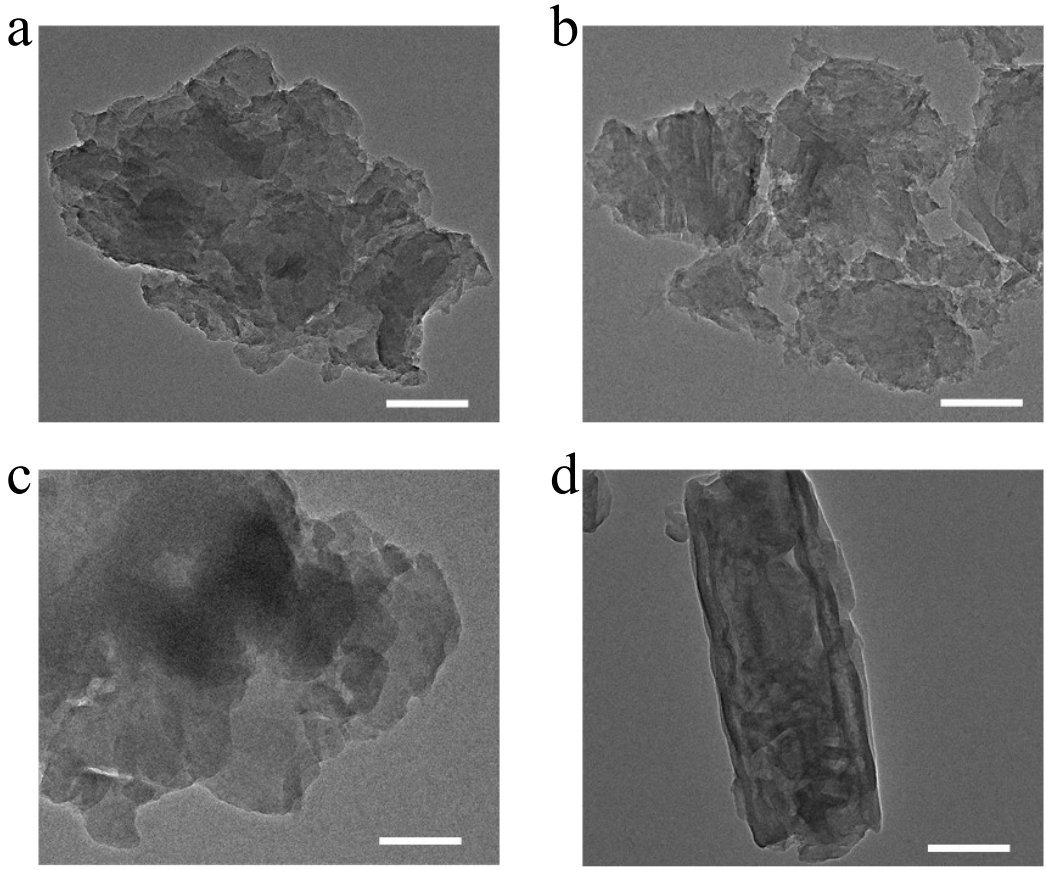

Fig. S3 TEM images of samples (a) NH_2-DT-550, (b) Ph-DT-420, (c) CH_3-DT-350, and (d) Cl-DT-300. The scale bars are 200 nm.

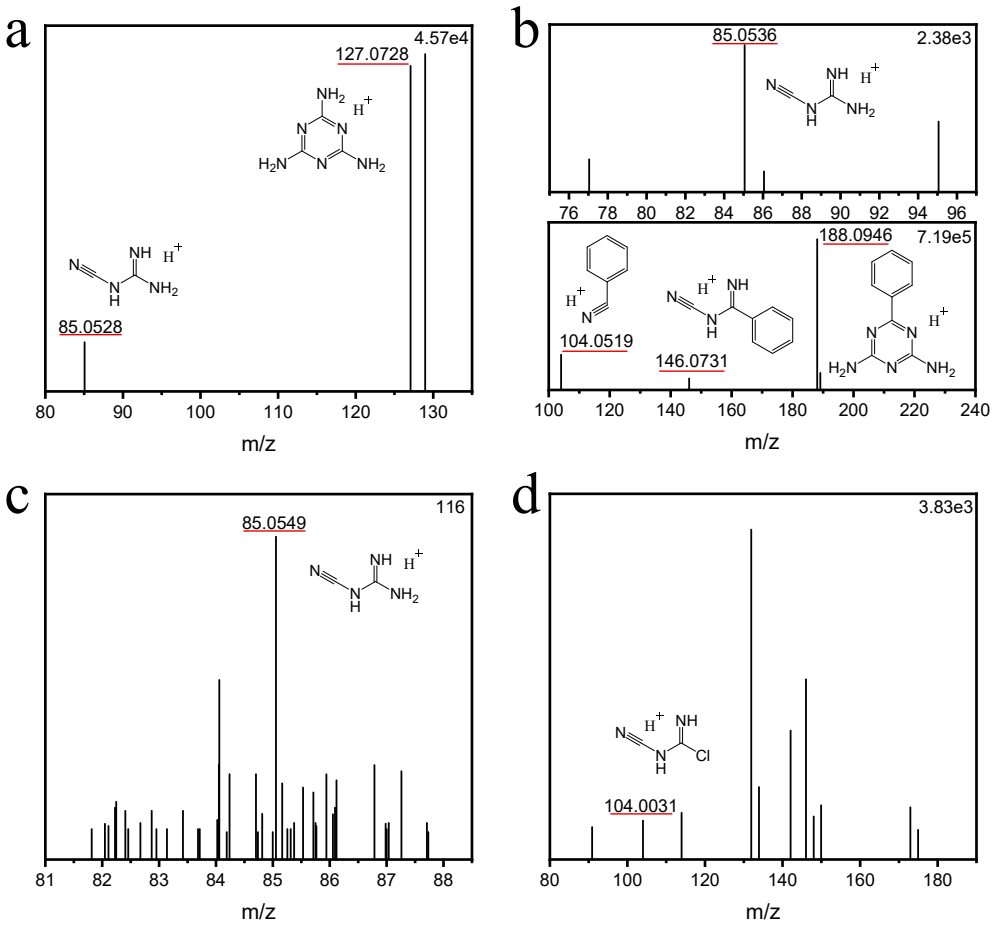

Fig. S4 LC-MS spectra of exhaust gas during synthesizing the samples (a) NH_2-DT-550. (b) Ph-DT-420. (c) CH_3-DT-350. (d) Cl-DT-300. Insets are the molecular structures of volatile constituent.

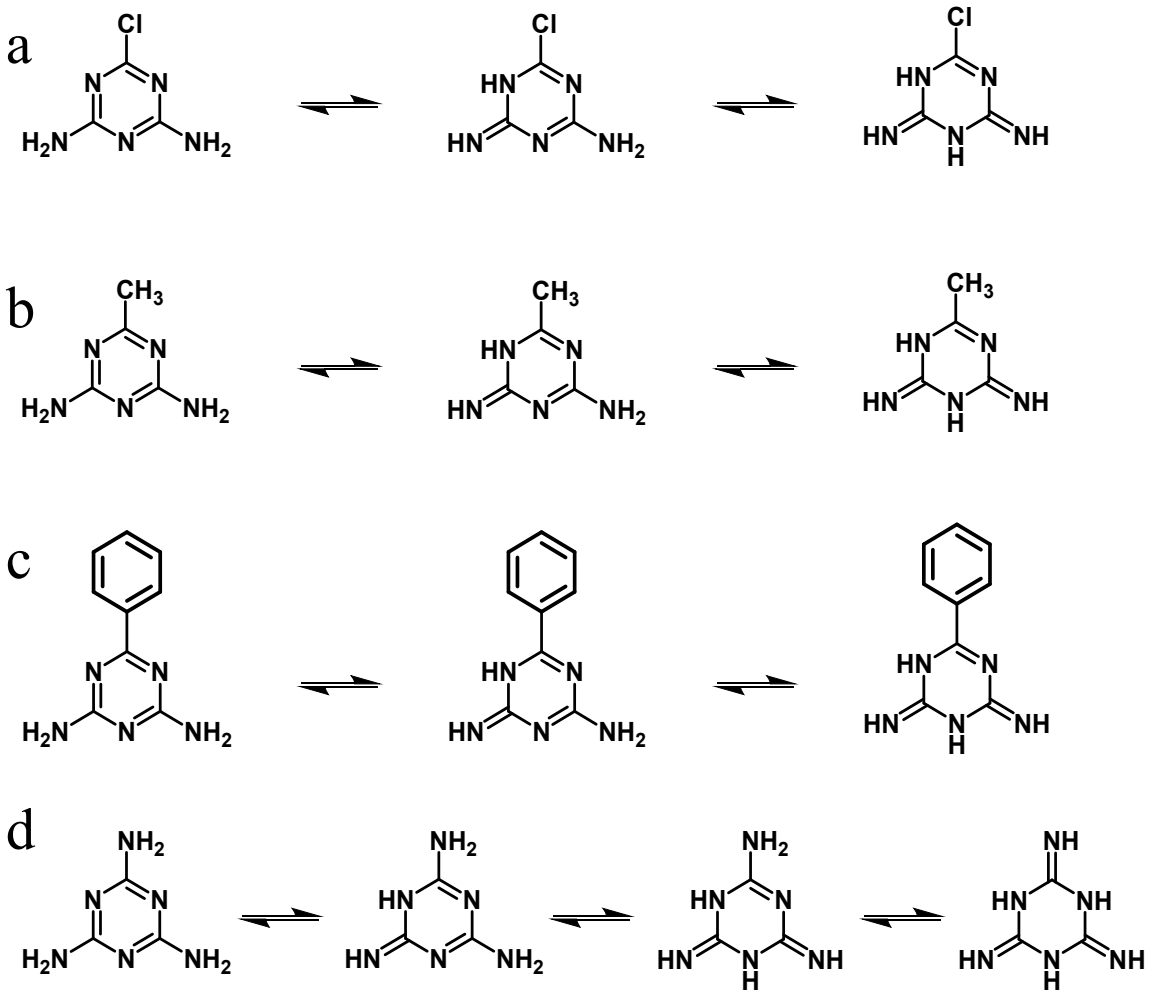

Fig. S5 Tautomeric forms of four precursor molecules (a) NH_2-DT, (b) Ph-DT, (c) CH_3-DT, (d) Cl-DT.

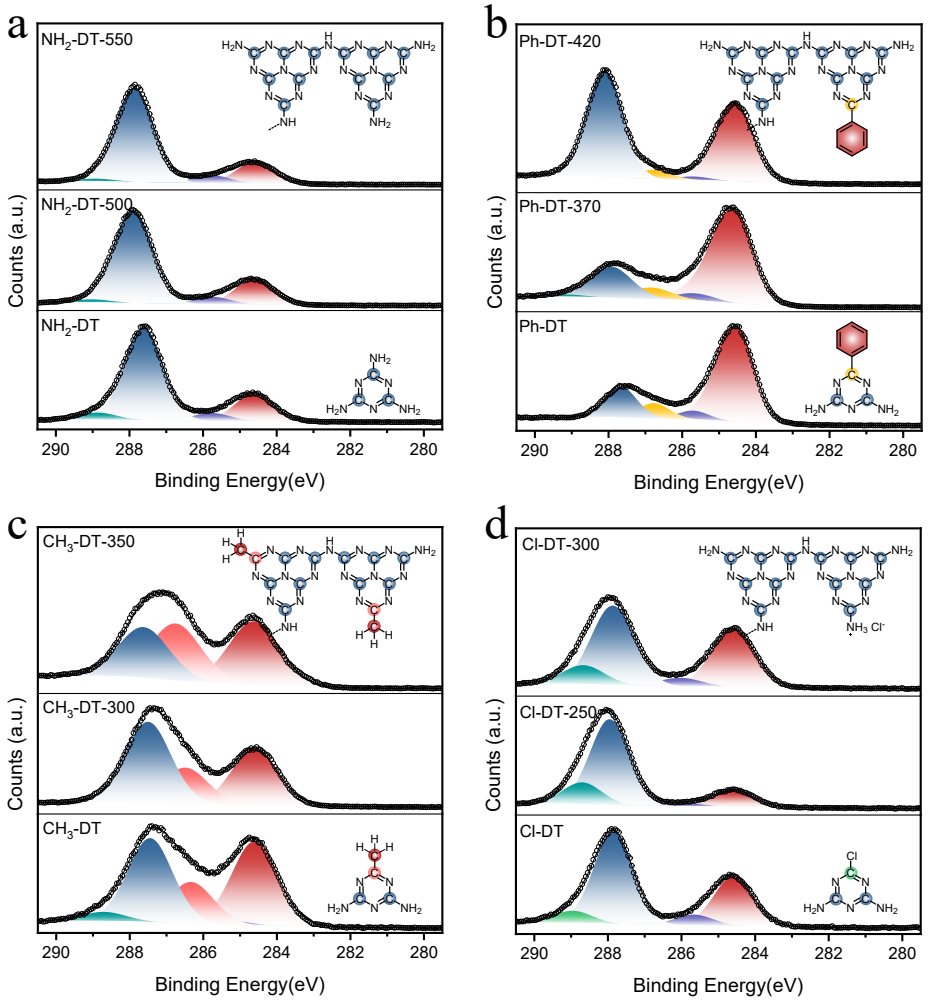

Fig. S6 XPS spectra of C 1s for the precursors and their thermal polymerization products at different temperatures, (a) NH_2-DT, (b) Ph-DT, (c) CH_3-DT, (d) Cl-DT. The main structural unit of the material is inserted in each panel.

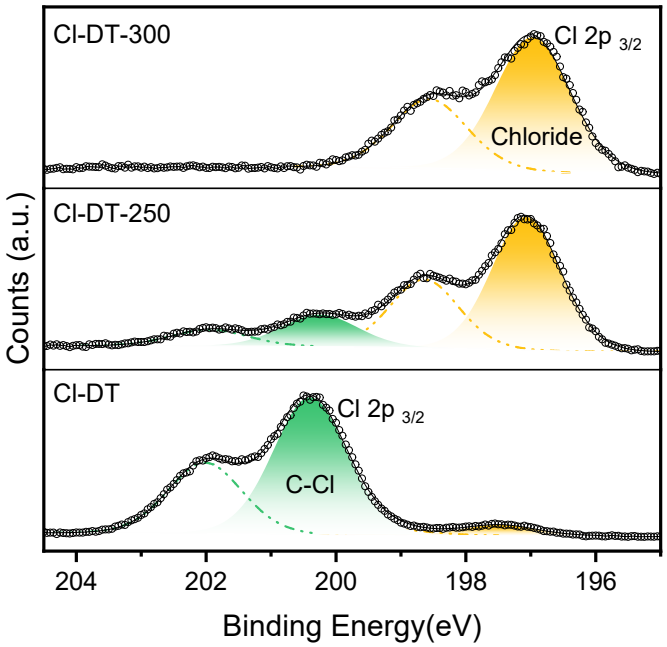

Fig. S7 XPS spectra of Cl 2p for Cl-DT-300, Cl-DT-250 and Cl-DT.

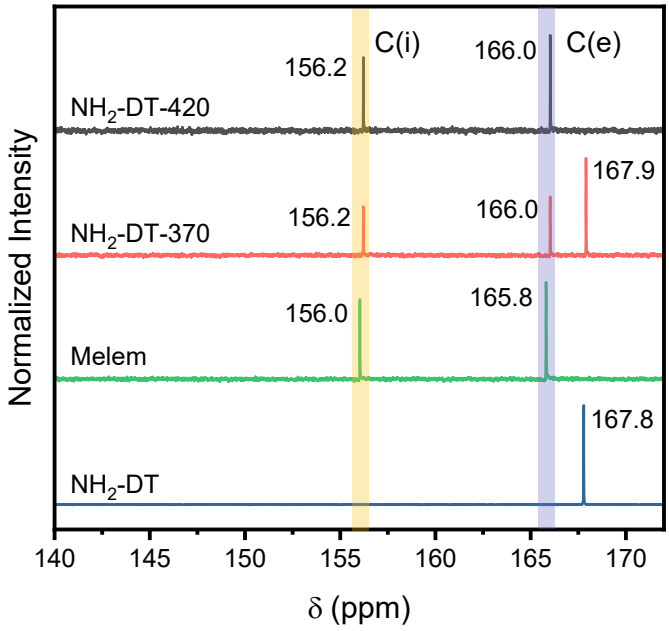

Fig. S8 Solution-state ^{13}C NMR spectra of NH_2-DT, melem, NH_2-DT-370 and NH_2-DT-420 in DMSO-d_6.

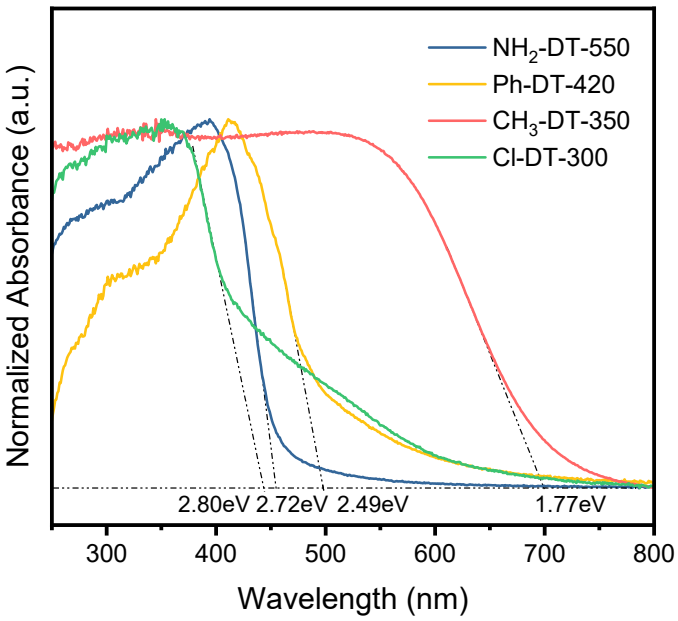

Fig. S9 UV-Visible absorption spectra of four g-CN samples.

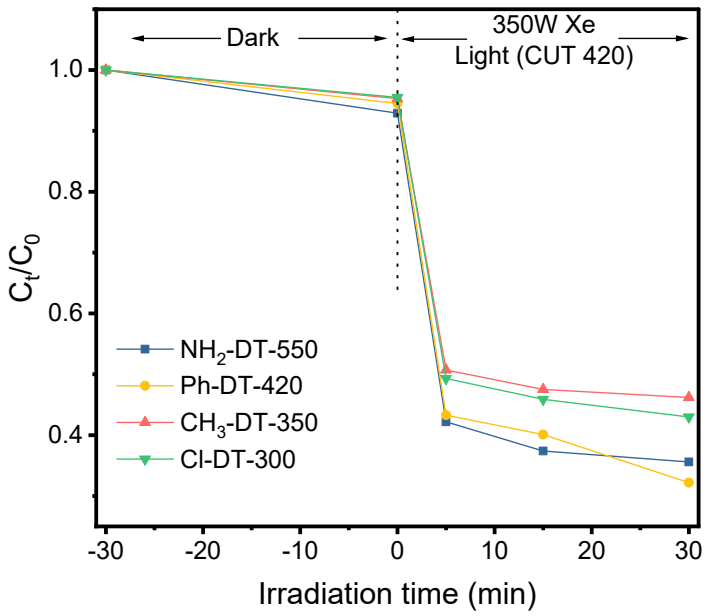

Fig. S10 Photocatalytic degradation efficiency of tetracycline by four g-CN samples.

Tab. S1 Binding energy, FWHM, and atomic percentage of fitted peaks in the N 1s spectrum for NH_2-DT, NH_2-DT-500, and NH_2-DT-550.

		N_R-$(C)_3$	Tautomers NH-$(C)_2$	NH-$(C)_2$	NH_2-C	N_R-$(C)_2$
NH_2-DT	Peak BE (eV)		400.3		399.2	398.3
	FWHM (eV)		1.3		1.3	1.3
	Atomic (%)		3.7		43.7	52.6
NH_2-DT-500	Peak BE (eV)	400.9		399.9	399.0	398.3
	FWHM (eV)	1.2		1.2	1.2	1.2
	Atomic (%)	8.8		10.5	22.2	58.8
NH_2-DT-550	Peak BE (eV)	400.8		399.9	399.1	398.3
	FWHM (eV)	1.2		1.2	1.2	1.2
	Atomic (%)	9.4		10.7	12.8	67.1

Tab. S2 Binding energy, FWHM, and atomic percentage of fitted peaks in the N 1s spectrum for Ph-DT, Ph-DT-370, and Ph-DT-420.

		N_R-$(C)_3$	NH-$(C)_2$	Tautomers NH-$(C)_2$	NH_2-C	N_R-$(C)_2$
Ph-DT	Peak BE (eV)			400.0	399.2	398.3
	FWHM (eV)			1.3	1.3	1.3
	Atomic (%)			6.9	36.0	57.1
Ph-DT-370	Peak BE (eV)	401.3	400.3		399.4	398.5
	FWHM (eV)	1.3	1.3		1.3	1.3
	Atomic (%)	5.5	17.1		31.3	46.1
Ph -DT-420	Peak BE (eV)	401.1	400.1		399.3	398.6
	FWHM (eV)	1.2	1.2		1.2	1.2
	Atomic (%)	8.3	9.0		13.8	69.0

Tab. S3 Binding energy, FWHM, and atomic percentage of fitted peaks in the N 1s spectrum for CH_3-DT, CH_3-DT-300, and CH_3-DT-350.

□	□	N_R-$(C)_3$	Tautomers NH-$(C)_2$	NH-$(C)_2$	NH_2-C	N_R-$(C)_2$
CH_3-DT	Peak BE (eV)		400.1		399.1	398.2
	FWHM (eV)		1.42		1.4	1.4
	Atomic (%)		5.9		40.3	53.8
CH_3-DT-300	Peak BE (eV)			399.9	399.0	398.2
	FWHM (eV)			1.4	1.4	1.4
	Atomic (%)			7.7	32.7	59.5
CH_3-DT-350	Peak BE (eV)	400.4		399.6	398.7	398.1
	FWHM (eV)	1.3		1.3	1.3	1.3
	Atomic (%)	7.9		21.2	29.5	41.5

Tab. S4 Binding energy, FWHM, and atomic percentage of fitted peaks in the N 1s spectrum for Cl-DT, Cl-DT-250, and Cl-DT-300.

		N_R-$(C)_3$	Tautomers NH-$(C)_2$	NH-$(C)_2$	NH_2-C	N_R-$(C)_2$
Cl-DT	Peak BE (eV)		400.7		399.5	398.7
	FWHM (eV)		1.4		1.4	1.4
	Atomic (%)		4.5		31.4	64.1
Cl-DT-250	Peak BE (eV)	400.9		400.2	399.3	398.5
	FWHM (eV)	1.3		1.3	1.3	1.3
	Atomic (%)	7.5		15.1	27.1	50.3
Cl-DT-300	Peak BE (eV)	400.8		400.0	399.0	398.3
	FWHM (eV)	1.4		1.4	1.4	1.4
	Atomic (%)	9.1		17.3	32.5	41.2

Tab. S5 Binding energy, FWHM, and atomic percentage of fitted peaks in the C 1s spectrum for NH_2-DT, NH_2-DT-500, and NH_2-DT-550.

□	□	C=O	C_R	C-O	C-C
NH_2-DT	Peak BE (eV)	288.9	287.6	285.8	284.6
	FWHM (eV)	1.3	1.3	1.3	1.3
	Atomic (%)	5.4	67.6	6.1	20.9
NH_2-DT-500	Peak BE (eV)	289.0	287.9	285.8	284.6
	FWHM (eV)	1.3	1.3	1.3	1.3
	Atomic (%)	2.8	70.9	6.4	19.9
NH_2-DT-550	Peak BE (eV)	289.0	287.9	285.8	284.6
	FWHM (eV)	1.3	1.3	1.3	1.3
	Atomic (%)	2.2	73.5	6.6	17.6

Tab. S6 Binding energy, FWHM, and atomic percentage of fitted peaks in the C 1s spectrum for Ph-DT, Ph-DT-370, and Ph-DT-420.

□	□	C=O	C_R-N	C_R-Ph	C-O	C-C/C=C
Ph-DT	Peak BE (eV)		287.7	286.8	285.7	284.5
	FWHM (eV)		1.1	1.1	1.1	1.1
	Atomic (%)		20.9	10.1	5.7	63.3
Ph-DT-370	Peak BE (eV)	289.2	287.9	286.9	285.7	284.6
	FWHM (eV)	1.4	1.4	1.4	1.4	1.2
	Atomic (%)	2.0	20.3	7.8	4.6	65.4
Ph-DT-420	Peak BE (eV)		288.1	286.8	285.7	284.6
	FWHM (eV)		1.2	1.2	1.2	1.3
	Atomic (%)		51.5	4.6	2.1	41.8

Tab. S7 Binding energy, FWHM, and atomic percentage of fitted peaks in the C 1s spectrum for CH_3-DT, CH_3-DT-300, and CH_3-DT-350.

□	□	C=O	C_R-N	C_R-CH_3	C-O	C-C/C-H
CH_3-DT	Peak BE (eV)	288.7	287.5	286.3	285.3	284.6
	FWHM (eV)	1.5	1.5	1.5	1.5	1.5
	Atomic (%)	4.2	37.1	18.6	2.3	37.9
CH_3-DT-300	Peak BE (eV)		287.5	286.5		284.6
	FWHM (eV)		1.5	1.5		1.5
	Atomic (%)		46.5	20.9		32.6
CH_3-DT-350	Peak BE (eV)		287.6	286.8		284.6
	FWHM (eV)		1.7	1.7		1.7
	Atomic (%)		29.5	33.2		37.3

Tab. S8 Binding energy, FWHM, and atomic percentage of fitted peaks in the C 1s spectrum for Cl-DT, Cl-DT-250, and Cl-DT-300.

		C_R-Cl /C=O	C_R-N	C-O	C-C
Cl-DT	Peak BE (eV)	289.0	287.9	285.7	284.6
	FWHM (eV)	1.3	1.3	1.3	1.3
	Atomic (%)	7.3	55.9	6.7	30.2
Cl-DT-250	Peak BE (eV)	288.7	288.0	285.9	284.6
	FWHM (eV)	1.3	1.3	1.3	1.3
	Atomic (%)	17.3	66.7	2.7	13.3
Cl -DT-300	Peak BE (eV)	288.7	287.9	286.0	284.6
	FWHM (eV)	1.4	1.4	1.4	1.4
	Atomic (%)	11.5	48.1	5.3	35.1

Tab. S9 Binding energy, FWHM, and atomic percentage of fitted peaks in the Cl 2p spectrum for Cl-DT, Cl-DT-250, and Cl-DT-300.

□	□	C-Cl		Chloride	
		$2p_{3/2}$	$2p_{1/2}$	$2p_{3/2}$	$2p_{1/2}$
Cl-DT	Peak BE (eV)	200.4	202.0	197.5	199.0
	FWHM (eV)	1.4	1.4	1.4	1.4
	Atomic (%)	92.6		7.4	
Cl-DT-250	Peak BE (eV)	200.3	202.0	197.1	198.6
	FWHM (eV)				
	Atomic (%)	21.3		78.7	
Cl-DT-300	Peak BE (eV)			197.0	198.6
	FWHM (eV)			1.4	1.4
	Atomic (%)			100	