

Supporting Information for

**Structural Engineering of Graphitic Carbon Nitrides for Enhanced Metal-free
PET-RAFT Polymerizations in Heterogeneous and Homogeneous Systems**

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Supporting Figures

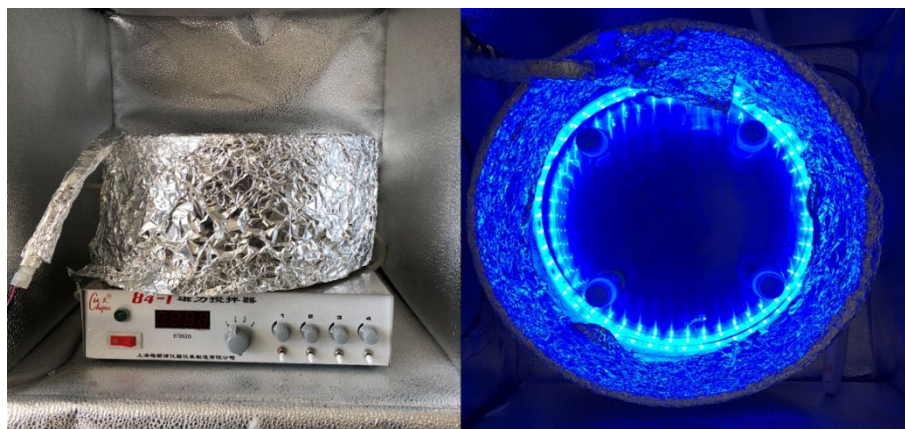


Figure S1. Photographs of the setup for PET-RAFT polymerization

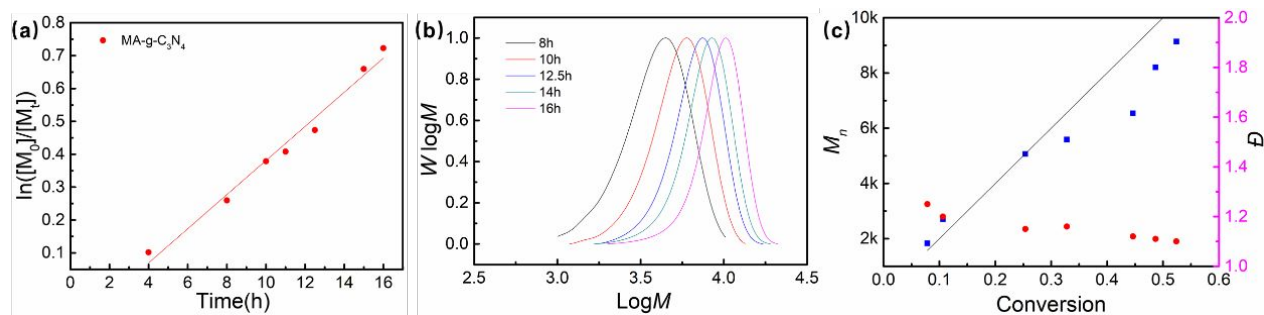


Figure S2. Kinetic study of MA-g-C₃N₄ catalyzed PET-RAFT polymerization of MMA using CPADB as the chain transfer agent under blue LED irradiation ($\lambda_{\text{max}}=465$ nm, 3 mW/cm²). The molar ratio of [MMA]/[CPADB]=200: 1 in 1 mL DMSO: (a) $\ln([M]_0/[M]_t)$ versus irradiation time and the fitted kinetic curve; (b) GPC profiles of PMMA synthesized in the kinetic study; (c) Number average molecular weight (M_n) and dispersity (D) of PMMA obtained in the kinetic study.

Supporting Tables

Table S1. Kinetic study on PET-RAFT polymerization of MMA catalyzed by TCA-g-C₃N₄ under 3 mW/cm² blue LED irradiation.

Entry	g-C ₃ N ₄	[MMA]:[CPADB]	m _{g-C₃N₄}	Time (h)	α (%)	$M_{n,theo}$	$M_{n,GPC}$	\bar{D}
1	TCA	200:1	5	4	15	3,000	2,200	1.35
2	TCA	200:1	5	6	20	4,100	4,000	1.21
3	TCA	200:1	5	8	23	4,700	5,400	1.17
4	TCA	200:1	5	10	32	6,400	6,900	1.13
5	TCA	200:1	5	11	36	7,200	7,500	1.12
6	TCA	200:1	5	12.5	43	8,600	8,400	1.11
7	TCA	200:1	5	14	49	9,900	9,300	1.11
8	TCA	200:1	5	15	55	11,000	10,100	1.10
9	TCA	200:1	5	16	60	12,000	10,800	1.10

Table S2. Kinetic study on PET-RAFT polymerization of MMA catalyzed by MA-g-C₃N₄ under 3 mW/cm² blue LED irradiation.

Entry	g-C ₃ N ₄	[MMA]:[CPADB]	m _{g-C₃N₄}	Time (h)	α (%)	$M_{n,theo}$	$M_{n,GPC}$	\bar{D}
1	MA	200:1	5	6	12	2,400	2,700	1.20
2	MA	200:1	5	8	22	4,600	3,600	1.21
3	MA	200:1	5	10	31	6,300	5,000	1.15
4	MA	200:1	5	11	33	6,700	5,600	1.16
5	MA	200:1	5	12.5	37	7,500	6,500	1.12
6	MA	200:1	5	14	49	9,800	7,500	1.14
7	MA	200:1	5	16	51	10,000	9,100	1.10