Supplementary Information

For

Metal-Free Photoinduced Electron Transfer - Atom Transfer Radical Polymerization (PET-ATRP) via a Visible Light Organic Photocatalyst†

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Table S1. Effects of light source type on metal-free ATRP of MMA.[a]

Entry	Light source	$[M]_0/[EBPA]_0/[FL]_0/[Et_3N]_0$	Time (h)	Conv. (%)	$M_{n,th}$ (g/mol)	$M_{n,GPC}$ (g/mol)	M_w/M_n	I^*(EBPA) (%)
1	Blue LED	200/0/0.3/9	12	NA	-	-	-	-
2	Blue LED	200/1/0/0	12	NA	-	-	-	-
3	—	200/1/0.3/9 [b]	12	NA	-	-	-	-
4	Blue LED	200/0/0.3/0	12	2.6	-	62100	1.92	-
5	Blue LED	200/1/0.2/6	32	87.4	17740	32700	1.49	54.3
6	Blue LED	400/1/0.3/9	20	90.5	36490	40000	1.60	91.2
7	Blue LED	400/1/0.4/12	24	85.2	34360	37500	1.64	91.6
8	Purple LED	200/1/0.2/6	4	48.1	9870	45500	1.48	21.7
9	Green LED	200/1/0.2/6	4	62.8	12820	47300	1.47	27.1
10	Green LED	200/1/0.4/12	4	54.8	11220	46300	1.52	24.2
11	Green LED	400/1/0.4/12	4	55.5	22470	43700	1.46	51.4
12	Green LED	400/1/0.8/24	4	45.2	18340	45500	1.54	40.3
14	Yellow LED	200/1/0.2/6	22	18.6	3970	179000	1.57	2.2
15	Incandescent lamp	200/1/0.2/6	0.5	15.6	3370	29100	1.34	11.6
16	Incandescent lamp	200/1/0.2/6	1.5	42.3	8710	29900	1.40	29.1
S1[c]	Blue LED	100/1/0.1	22	80.6	8310	28500	1.66	29.2

S2[c]	Blue LED	100/1/0.2	22	79.9	8240	20400	1.78	40.4

[a] Polymerization conditions: V_{MMA} = 1.0 mL, V_{DMSO} = 2.0 mL; samples were irradiated by LED light at rt.
[b] Polymerization performed in the dark. Theoretical number-average molecular weight $M_{n,th} = M_{EBPA} + [MMA]_0/[EBPA]_0 \times$ conversion $\times M_{MMA}$. Initiator efficiency (I^*) = theoretical number average molecular weight $M_{n,th}$ /experimentally measured $M_{n,GPC} \times 100$.
[c] Polymerization conditions: V_{MMA} = 1.0 mL, V_{DMA} = 2.0 mL; 10-phenylphenothiazine (PTH) was used as the photocatalyst; samples were irradiated by blue LED light at rt.

Table S2. Effects of acid and alkaline on the metal-free ATRP of MMA at $[MMA]_0$: $[EBPA]_0$ = 200 : 1.

Entry	$[FL]_0$ / $[TEA]_0$	$[FL]_0$ / $[Acetic\ Acid]_0$	Time (h)	Conv. (%)	$M_{n,th}$ (g/mol)	$M_{n,GPC}$ (g/mol)	M_w/M_n	I^*(EBPA) (%)
1	0.1/1	0.1/0	1.5	27.2	5690	26700	1.43	21.3
2	0.1/2	0.1/0	1.5	29.5	6150	24400	1.41	25.2
3	0.1/3	0.1/0	1.5	31.0	6450	24500	1.41	26.3
4	0.1/4	0.1/0	1.5	27.1	5670	22200	1.45	25.5
5	0.1/1	0.1/0	2	39.5	8150	27700	1.50	29.4
6	0.1/2	0.1/0	2	41.6	8570	26500	1.48	32.3
7	0.1/3	0.1/0	2	41.1	8470	25400	1.44	33.3
8	0.1/4	0.1/0	2	42.9	8830	24300	1.51	36.3
9	0.1/0	0.1/0	2	6.4	1520	58500	2.54	2.6
10	0.1/0	0.1/1	4	23.0	4850	57600	1.86	8.4
11	0.1/0	0.1/2	4	17.5	3750	55000	2.04	6.8
12	0.1/0	0.1/3	4	14.5	3150	56100	2.50	5.6
13	0.1/0	0.1/4	4	16.9	3630	61400	2.17	5.9

Polymerization conditions: $[MMA]_0$:$[EBPA]_0$:$[FL]_0$:[TEA or Acetic Acid]$_0$ = 200:1:0.1:x, V_{MMA} = 1.0 mL, V_{DMSO} = 2.0 mL; samples were irradiated by a blue LED at rt.

Table S3. Effects of initiator type on metal-free ATRP of MMA.

Entry	Initiator	Time (h)	Conv. (%)	$M_{n,th}$ (g/mol)	$M_{n,GPC}$ (g/mol)	M_w/M_n	I^*(EBPA) (%)
1	P-TsCl	12	49.4	10130	79200	1.73	12.8
2	EBiB	12	46.2	9490	57000	1.56	16.6
3	BPN	12	83.7	17000	36200	1.54	47.0
4	MBP	12	74.9	15200	66200	1.56	23.0
5	MCP	12	15.7	3390	51700	1.61	6.6
6	BPAN	12	20.2	4290	37700	3.49	11.4
7	EBPA	12	64.5	13160	30700	1.46	42.9
8	PEBr	12	35.8	7410	83100	1.67	8.9

Polymerization conditions: $[MMA]_0$:$[EBPA]_0$:$[FL]_0$:$[Et_3N]_0$ = 200:1:0.2:6, V_{MMA} = 1.0 mL, V_{DMSO} = 2.0 mL; samples were irradiated by a blue LED at rt.

Table S4. Effects of conventional solvents and monomers on metal-free ATRP of MMA.

Entry	Solvent	$[M]_0/[EBPA]_0/[FL]_0/[Et_3N]_0$	Time (h)	Conv. (%)	$M_{n,th}$ (g/mol)	$M_{n,GPC}$ (g/mol)	M_w/M_n	I^*(EBPA) (%)
1	DMSO	100:1:0.1:3	3	57.3	5980	28400	1.52	21.1
2	DMSO	100:1:0.4:12	4	20.3	2280	13800	1.53	16.5
3	DMSO	200:1:0.2:6	3	48.7	9990	27200	1.44	36.7
4	Acetone	100:1:0.1:3	3	16.1	1860	17200	1.45	10.8
5	Acetone	200:1:0.2:6	15	14.9	3230	19600	1.41	16.5
6	Anisole	100:1:0.1:3	3	26.3	2880	21900	1.42	13.2
7	Anisole	200:1:0.2:6	15	10.1	2270	20700	1.26	11.0
8	DMA	100:1:0.1:3	3	50.0	5250	22300	1.44	23.5
9	DMA	200:1:0.2:6	15	31.0	6450	18500	1.43	34.9
10	DMF	100:1:0.1:3	3	38.1	4060	20300	1.46	20.0
11	DMF	200:1:0.2:6	15	16.6	3570	19200	1.27	18.6

Polymerization conditions: V_{MMA} = 1.0 mL, $V_{Solvent}$ = 2.0 mL; samples were irradiated by LED light at rt.

Table S5. Effect of the solvent volume on metal-free ATRP of MMA at $[MMA]_0/[EBPA]_0/[FL]_0/[Et_3N]_0$ = 200/1/0.3/9.

Entry	$[M]_0/[EBPA]_0/[FL]_0/[Et_3N]_0$	Solvent (ml)	Time (h)	Conv. (%)	$M_{n,th}$ (g/mol)	$M_{n,GPC}$ (g/mol)	M_w/M_n	I^*(EBPA) (%)
1	200/1/0.3/9	1	1	34.4	7130	25100	1.39	28.4
2	200/1/0.3/9	1	8	68.6	14000	23500	1.51	59.6
3	200/1/0.3/9	2	3	20.0	4250	18800	1.27	22.6
4	200/1/0.3/9	2	7	38.9	8030	20800	1.44	38.6
5	200/1/0.3/9	2	35	77.2	15700	27300	1.66	57.5
6	200/1/0.3/9	4	2	24.8	5210	22600	1.29	23.1
7	200/1/0.3/9	4	9	54.5	11160	26600	1.41	42.0
8	200/1/0.3/9	4	21	70.1	14280	26900	1.44	53.1

Polymerization conditions: $[MMA]_0:[EBPA]_0:[FL]_0:[Et_3N]_0$ = 200:1:0.3:9, V_{MMA} = 1.0 mL;samples were irr adiated by LED light at rt.

Table S6. Effect of the solvent volume on metal-free ATRP of MMA at $[MMA]_0$:$[EBPA]_0$ = 400:1.

Entry	$[M]_0/[EBPA]_0/[FL]_0/[Et_3N]_0$	Solvent (ml)	Time (h)	Conv. (%)	$M_{n,th}$ (g/mol)	$M_{n,GPC}$ (g/mol)	M_w/M_n	I^*(EBPA) (%)
1	400/1/0.2/6	2	2	44.9	18220	37100	1.61	49.1
2	400/1/0.2/6	2	12	86.3	34800	46500	1.62	74.8
3	400/1/0.4/12	1	1	21.5	8850	21700	1.31	40.8
4	400/1/0.4/12	1	8	46.8	19000	21700	1.72	87.6
5	400/1/0.4/12	2	1	20.9	8610	25400	1.39	33.9
6	400/1/0.4/12	2	3	40.8	16580	28600	1.56	58.0
7	400/1/0.4/12	2	24	85.2	32830	37500	1.64	87.5
8	400/1/0.4/12	4	2	31.4	12820	33600	1.58	38.2
9	400/1/0.4/12	4	9	63.2	25550	36100	1.51	70.8
10	400/1/0.8/24	4	13	24.0	9850	32600	1.47	30.2
11	400/1/0.8/24	4	38	58.6	23710	34500	1.51	68.7
12	400/1/1.2/36	4	18	20.6	8490	35100	1.39	24.2
13	400/1/1.2/36	4	42	53.9	21830	37800	1.54	57.8

Polymerization conditions: V_{MMA} = 1.0 mL; samples were irradiated by LED light at rt.

Table S7. Effects of the molar ratio of $[MMA]_0$:$[EBPA]_0$ on metal-free ATRP of MMA.

Entry	$[M]_0/[EBPA]_0/[FL]_0/[Et_3N]_0$	Time (h)	Conv. (%)	$M_{n,th}$ (g/mol)	$M_{n,GPC}$ (g/mol)	M_w/M_n	I^*(EBPA) (%)
1	500/1/1.0/30	10	15.8	8150	32000	1.42	25.5
2	500/1/1.0/30	30	57.8	29200	37700	1.53	77.5
3	600/1/1.2/36	10	10.5	6550	32000	1.38	20.5
4	600/1/1.2/36	30	51.6	31240	38200	1.56	81.8
5	800/1/1.6/48	10	9.1	7530	32000	1.33	23.5
6	800/1/1.6/48	30	39.2	31640	36700	1.53	86.2

Polymerization conditions: V_{MMA} = 1.0 mL, V_{DMSO} = 2.0 mL; samples were irradiated by LED light at rt.

Table S8. Effects of the content of fluorescein (FL) on metal-free ATRP of MMA at $[MMA]_0/[EBPA]_0 = 100/1$.

Entry	Monomer	$[M]_0/[EBPA]_0/[FL]_0/[Et_3N]_0$	Time (h)	Conv. (%)	$M_{n,th}$ (g/mol)	$M_{n,GPC}$ (g/mol)	M_w/M_n
1	MMA	100/1/0.1/3	0.5	17.4	1990	24400	1.41
2	MMA	100/1/0.1/3	3	57.3	5980	28400	1.52
3	MMA	100/1/0.1/3	6	79.94	8250	31900	1.53
4	MMA	100/1/0.2/6	3	39.2	4170	19500	1.32
5	MMA	100/1/0.2/6	12	61.6	6410	20300	1.47
6	St	200:1:0.2:6	2	3.9	1060	6200	1.35
7	St	200:1:0.2:6	6	10.1	2350	8000	1.56
8	PEGMA	50:1:0.2:6	16	78.2[a]	19790	18900	1.53
9	AN	100:1:0.2:6	7	25.2	1580	12200	1.79
10	tBA	200:1:0.2:6	10	72.1[b]	20750	49300	1.57
11	GMA	200:1:0.2:6	10	67.3	19380	12100	1.90
12	BnMA	200:1:0.2:6	10	72.8	25900	23100	1.89

[a] Calculated by ^{1}H NMR analysis. [b] Purified by the precipitation in methanol-water (2/1, v/v).

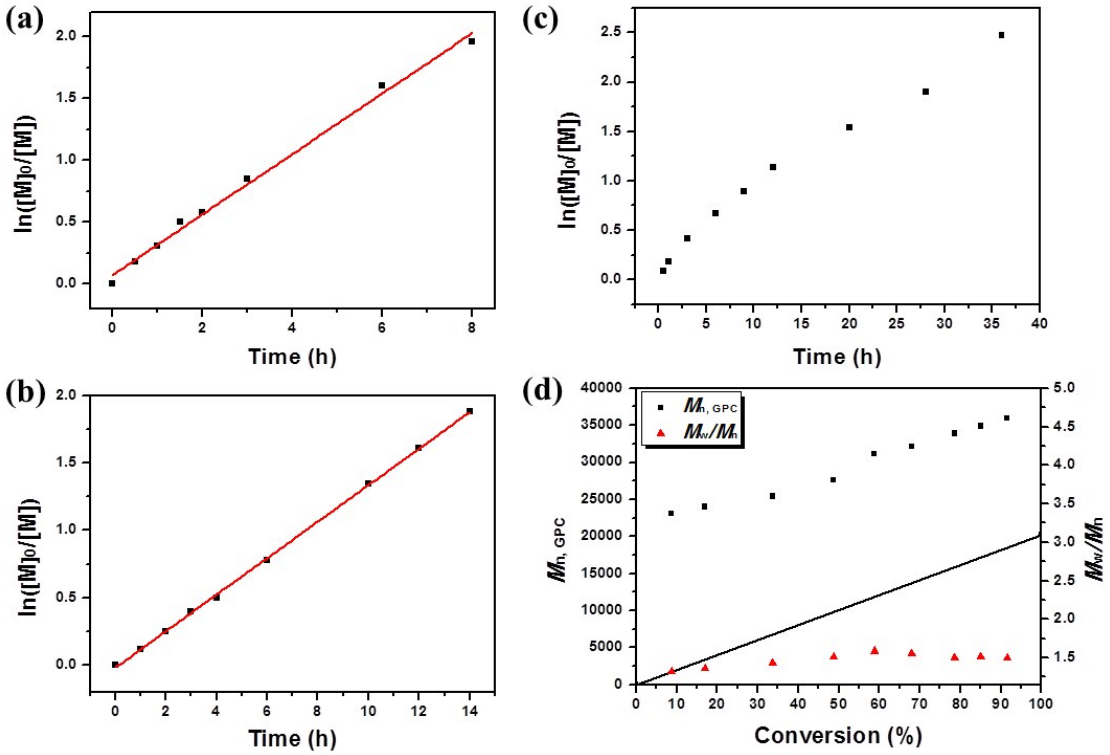

Fig. S1 ln([M]$_0$/[M]) as a function of time for metal-free ATRP of MMA. Polymerization conditions: (a) [MMA]$_0$:[EBPA]$_0$:[FL]$_0$:[TEA]$_0$ = 100:1:0.1:3, V_{MMA} = 1.0 mL, V_{DMSO} = 2.0 mL; (b) [MMA]$_0$:[EBPA]$_0$:[FL]$_0$:[Et_3N]$_0$ = 100:1:0.1:3, V_{MMA} = 1.0 mL, V_{DMF} = 2.0 mL;samples were irradiated by a blue LED at rt. ln([M]$_0$/[M]) as a function of time (c) and number-average molecular weight ($M_{n,GPC}$) and molecular weight distribution (M_w/M_n) *versus* conversion (d) for metal-free ATRP of MMA. Polymerization conditions: [MMA]$_0$:[EBPA]$_0$:[FL]$_0$:[TEA]$_0$ = 200:1:0.25:7.5, V_{MMA} = 1.0 mL, V_{DMSO} = 2.0 mL; samples were irradiated by a blue LED at rt.

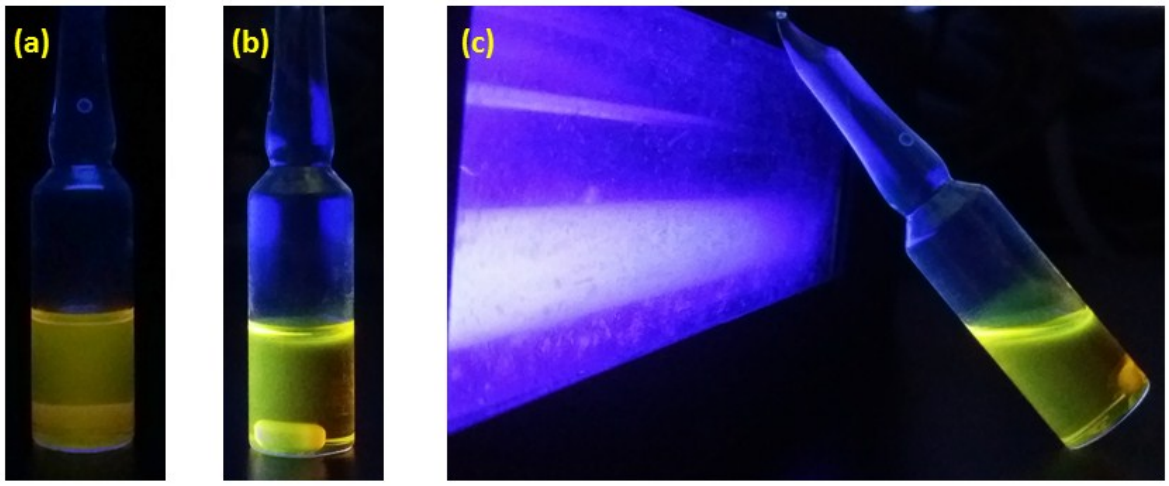

Fig. S2 Photographs of reaction system before (a) and after (b, c) polymerization relating to entry 3 in Table S8 on excitation at 365 nm using a UV lamp.

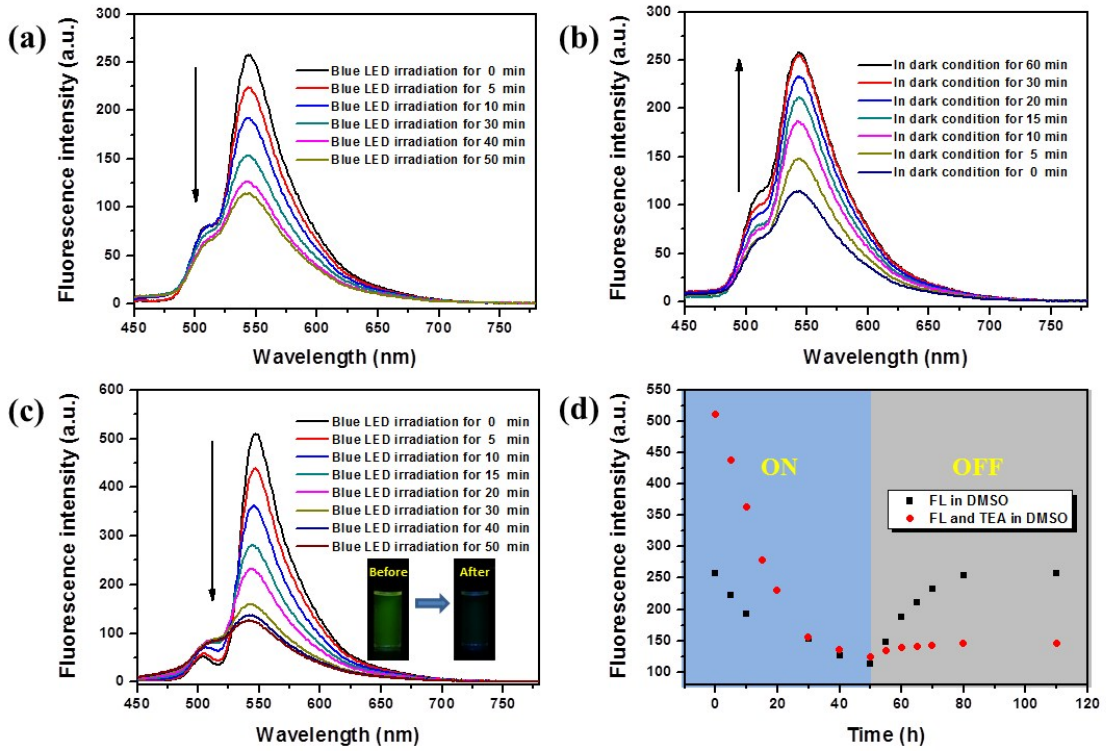

Fig. S3 (a) Fluorescence spectra of FL in DMSO (0.1 mM) under varying time of blue LED irradiation; (b) fluorescence spectra of FL in DMSO (0.1 mM) changed to dark environment for varying time after 50 min of blue LED irradiation; (c) fluorescence quenching studies of a solution of FL (0.1 mM) and TEA (30 equiv.) in DMSO under varying time of blue LED irradiation. The inset shows the fluorescence changes of FL (0.1 mM) before and after blue LED irradiation for 50 min on excitation at 365 nm using a UV lamp; (d) time depended fluorescence intensity at 542 nm (FL in DMSO) and 546 nm (FL and TEA in DMSO) processed with "on-off" blue LED irradiation.

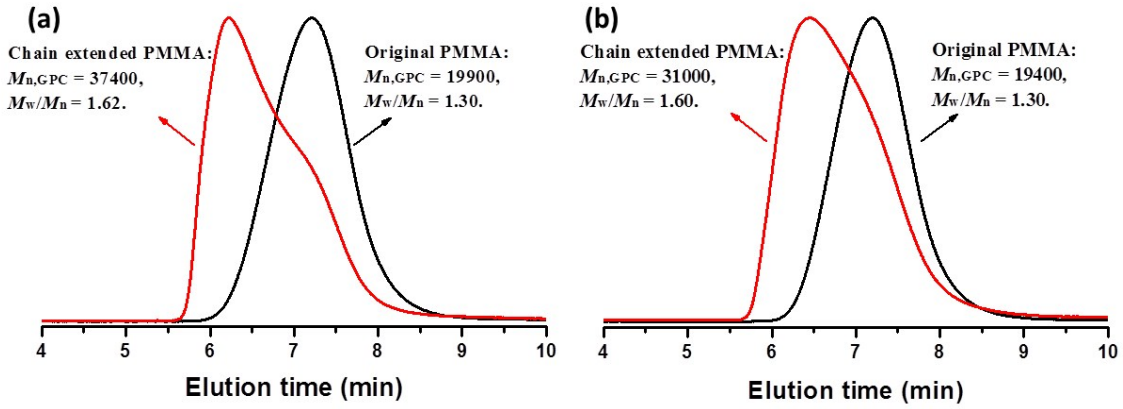

Fig. S4 (a) GPC traces of PMMA before and after chain extension using PMMA prepared by metal-free ATRP of MMA as the macroinitiator ($M_{n,GPC}$ = 19900 g mol^{-1}, M_w/M_n = 1.30). (b) GPC traces of PMMA before and after chain extension using PMMA prepared by metal-free ATRP of MMA as the macroinitiator ($M_{n,GPC}$ = 19400 g mol^{-1}, M_w/M_n = 1.30).