Supporting Information

Photocontrolled Bromine-Iodine Transformation Reversible-Deactivation Radical Polymerization: Facile Synthesis of Star Copolymers and Unimolecular Micelles

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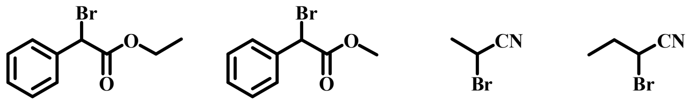
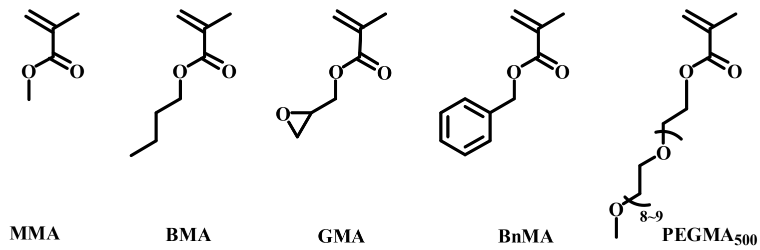


Scheme S1. The structure types of the initiator precursor which are suitable for BIT-RDRP.



Scheme S2. The chemical structures of monomers used in this work.

Table S1. [a]Polymerization of MMA.

Entry	Wavelength (nm)	t (h)	Solvent	R	[b]Conv. (%)	$M_{n,th}$ (g/mol)	[c]$M_{n,GPC}$ (g/mol)	[c]$Đ$
1	660	24	CH_2Cl_2	400/1/8/2	88.7	36800	48700	1.33
2	460	24	CH_2Cl_2	400/1/8/2	92.3	38300	55300	1.21
3	660	24	DMF	200/1/8/2	90.8	19700	29800	1.11
4	660	24	DMF	200/1/8/0	65.5	14600	20200	1.08
5	660	24	DMF	50/1/8/2	89.7	6000	9200	1.59
6	660	24	DMF	400/1/8/2	84.3	35200	51400	1.47
7	460	14	DMF	100/1/8/2	44.7	5900	8300	1.14
8	460	14	DMF	200/1/8/2	49.4	11400	21900	1.18
9	460	14	DMF	400/1/8/2	54.4	23300	37800	1.14
10	460	24	DMSO	400/1/8/2	80.8	33800	54400	1.70
11	460	24	toluene	400/1/8/2	49.1	21100	25200	1.22
12	460	24	toluene	400/1/8/4	21.5	10100	32300	1.47
13	460	14	DMF	100/1/12/2	64.0	7900	5100	1.16
14	460	14	DMF	200/1/12/2	78.5	14200	21900	1.19
15	460	14	DMF	400/1/12/2	69.3	29200	33400	1.20

[a]Polymerization conditions: R = $[MMA]_0/[THPP\text{-}4Br]_0/[NaI]_0/[TEA]_0$, V_{MMA} = 0.3 mL, $V_{Solvent}$ = 0.6 mL, under irradiation with red LED light (λ_{max} = 660 nm, 32.8 mW/cm^2) or blue LED light (λ_{max} = 460 nm, 15 mW/cm^2) at 25 ^oC. [b]Determined by gravimetry. [c]Determined by GPC using linear PMMA as the standard in THF.

Table S2. ^{a}Polymerization of $PEGMA_{500}$.

Entry	t (h)	Solvent	R	^{b}Conv. (%)	$M_{n,th}$ (g/mol)	$^{c}M_{n,GPC}$ (g/mol)	$^{c}Đ$
1	12	Methanol	20/1/12/2	45.8	6000	15800	1.31
2	8	DMF	80/1/12/2	24.8	11400	71200	1.75
3	8	DMSO	80/1/12/2	39.2	17100	80800	1.30
4	12	Anisole	80/1/12/2	21.6	10100	22700	1.16
5	12	Acetone	80/1/12/2	52.5	22500	59300	1.55
6	12	Dioxane	80/1/12/2	27.4	12400	33000	1.27
7	12	Ethanol	20/1/12/2	88.7	10300	12200	1.31
8	12	Ethanol	40/1/12/2	72.4	15900	17300	1.24
9	12	Ethanol	80/1/12/2	75.6	31700	34100	1.27

^{a}Polymerization conditions: R = $[PEGMA]_0/[THPP\text{-}4Br]_0/[NaI]_0/[TEA]_0$, V_{PEGMA} = 0.3 mL, $V_{Solvent}$ = 0.6 mL, under irradiation with blue LED light (λ_{max} = 460 nm, 15 mW/cm^2) at 25 ^{o}C. ^{b}Determined by gravimetry. ^{c}Determined by GPC using linear PMMA as the standard in THF.

Table S3 ^{a}Polymerization of $PEGMA_{500}$ by using linear PMMA as the macroinitiator.

Entry	t (h)	$M_{n,PMMA}$ (g/mol)	R	$^{b}M_{n,GPC}$ (g/mol)	$^{c}M_{n,NMR}$ (g/mol)	$^{b}Đ$	^{d}BR
1	72	11500	400/1/3/0.5	40400	43300	1.23	$PMMA_{112}$-*b*-$PPEGMA_{64}$
2	72	15000	400/1/3/0.5	30500	32800	1.29	$PMMA_{147}$-*b*-$PPEGMA_{36}$
3	72	18000	400/1/3/0.5	42400	44100	1.32	$PMMA_{177}$-*b*-$PPEGMA_{52}$

^{a}Polymerization conditions: R = $[PEGMA]_0/[PMMA]_0/[NaI]_0/[TEA]_0$, $V_{PEGMA_{500}}$ = 0.5 mL, $V_{C_2H_5OH}$ = 1.0 mL, under irradiation with blue LED light (λ_{max} = 460 nm, 15 mW/cm^2) at 25 ^{o}C. ^{b}Determined by GPC using linear PMMA as the standard in THF. ^{c}Calculated by ^{1}H NMR results. ^{d}Block ratio of amphiphilic linear block copolymers calculated from ^{1}H NMR results.

Table S4 Estimation of the hydrodynamic radius of UIM.

Entry	BR	^{a}Rc (nm)	^{b}Ro (nm)	$^{c}R_S$ (nm)
1	THPP-4PMMA$_{93}$-*b*-4PPEGMA$_{66}$	1.3	8.3	7.0
2	THPP-4PMMA$_{115}$-*b*-4PPEGMA$_{63}$	1.4	9.1	7.7
3	THPP-4PMMA$_{167}$-*b*-4PPEGMA$_{62}$	1.4	10.6	9.2
4	THPP-4PMMA$_{105}$-*b*-4PPEGMA$_{52}$	1.4	8.6	7.2
8	THPP-4PMMA$_{131}$-*b*-4PPEGMA$_{66}$	1.4	9.6	8.2
10	THPP-4PMMA$_{158}$-*b*-4PPEGMA$_{50}$	1.4	10.2	8.8
11	THPP-4PMMA$_{158}$-*b*-4PPEGMA$_{71}$	1.4	10.4	9.0
13	THPP-4PMMA$_{171}$-*b*-4PPEGMA$_{56}$	1.4	10.6	9.2
14	THPP-4PMMA$_{171}$-*b*-4PPEGMA$_{66}$	1.4	10.7	9.3

[a]The hydrodynamic radius of the core, $R_C = N_B^{0.065}$. [b]The hydrodynamic radius of the overall micelle, $R_O = N_B^{0.408} N_A^{0.065}$. [c]The hydrodynamic radius of the shell, $R_S = R_O - R_C$. N_B and N_A are respectively the polymerization degree of the hydrophobic and hydrophilic segments of the star block copolymer.

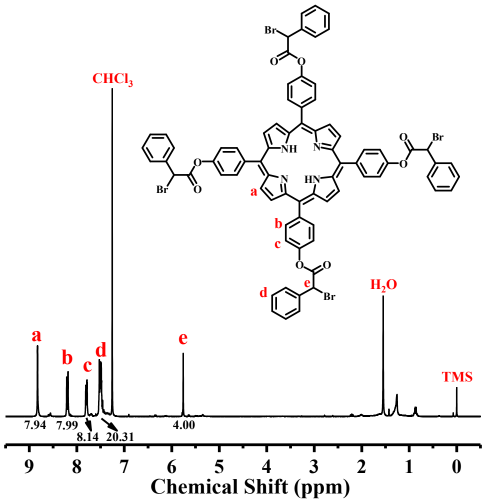


Figure S1. ^{1}H NMR spectrum of THPP-4Br in $CDCl_3$.

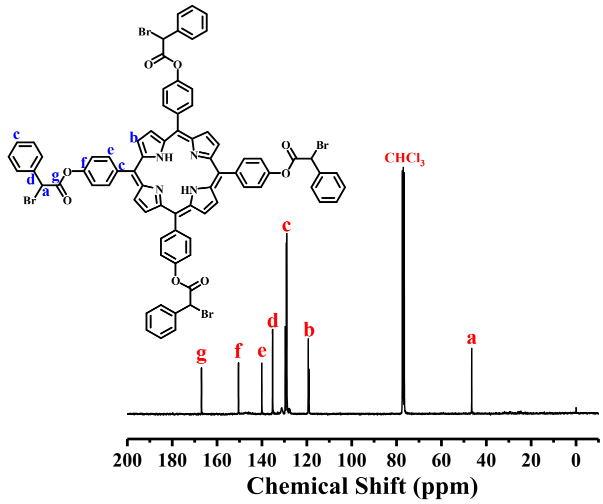


Figure S2. ^{13}C NMR spectrum of THPP-4Br in $CDCl_3$.

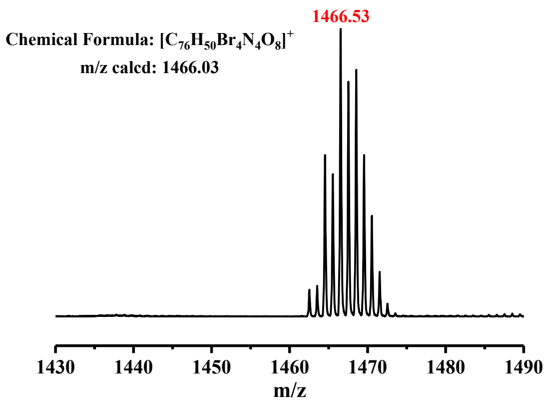


Figure S3. MALDI-TOF MS spectrum of THPP-4Br in $CHCl_3$.

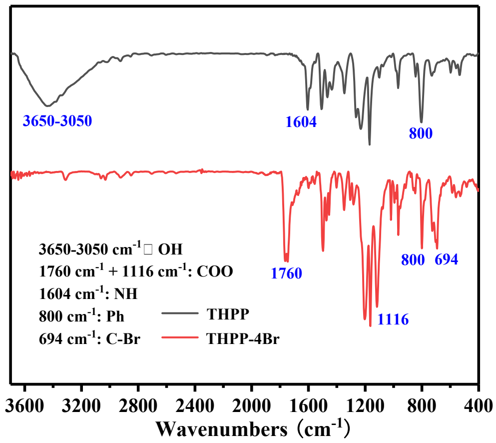


Figure S4. FT-IR spectra of THPP and THPP-4Br.

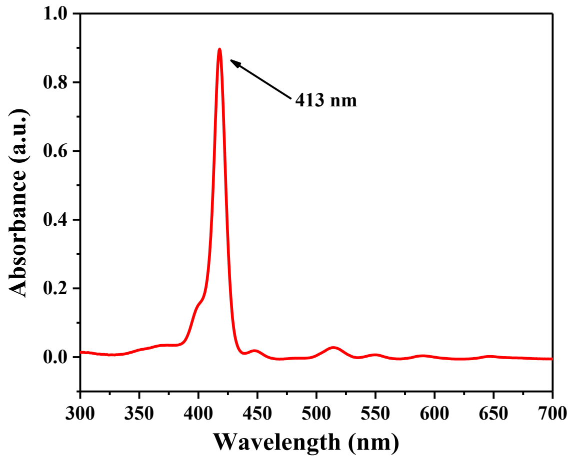


Figure S5. UV-vis absorption spectrum of THPP-4Br.

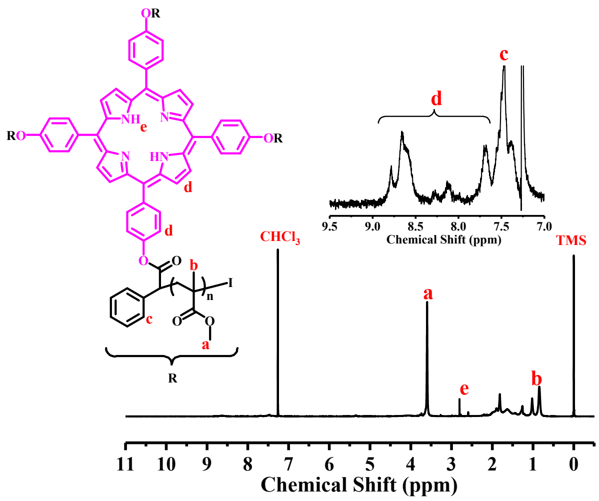


Figure S6. [1]H NMR spectrum of THPP-4PMMA ($M_{n,GPC}$ = 14600 g/mol, $Đ$ = 1.22) in $CDCl_3$.

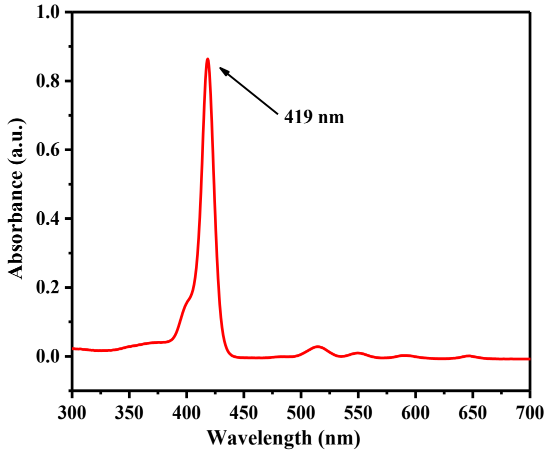


Figure S7. UV-vis absorption spectrum of THPP-4PMMA ($M_{n,NMR}$ = 14600 g/mol, $Đ$ = 1.22).

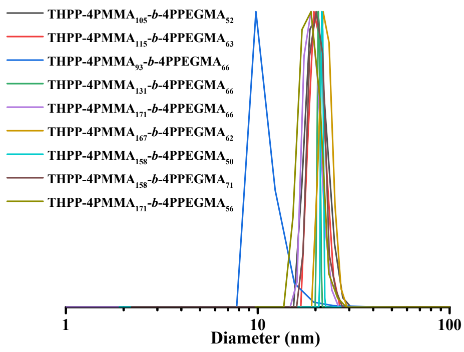


Figure S8. Size distributions from DLS of star copolymer THPP-4PMMA-*b*-4PPEGMA micelles.

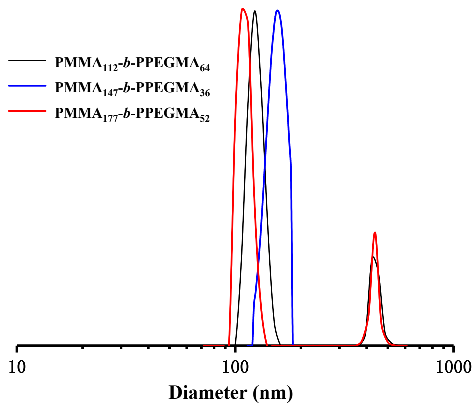


Figure S9. Size distributions from DLS of amphiphilic linear block copolymer PMMA-*b*-PPEGMA micelles.

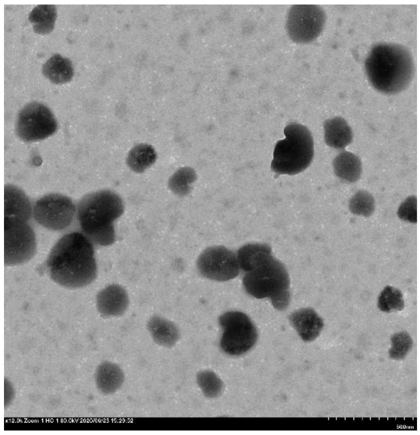


Figure S10. TEM image of the amphiphilic linear block copolymer PMMA-*b*-PPEGMA micelles. Sample: $PMMA_{112}$-*b*-$PPEGMA_{64}$, $M_{n,GPC}$ = 40400 g/mol, $M_{n,NMR}$ = 43300 g/mol, $Đ$ = 1.23.

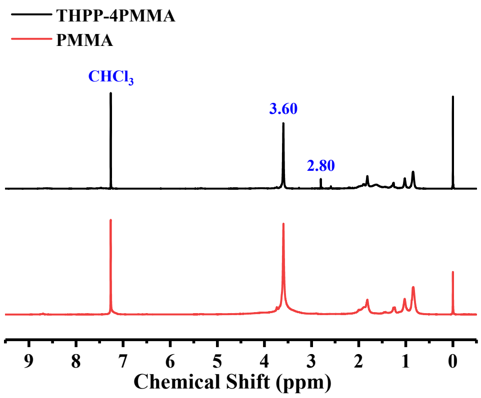


Figure S11. ^{1}H NMR spectra of THPP-4PMMA ($M_{n,GPC}$ = 14600 g/mol, $Đ$ = 1.22) and linear PMMA ($M_{n,GPC}$ = 4100 g/mol, $Đ$ = 1.09) in $CDCl_3$.

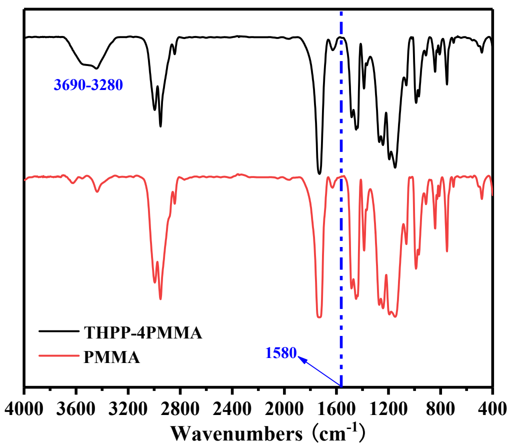


Figure S12. FT-IR Spectra of THPP-4PMMA ($M_{n,GPC}$ = 14600 g/mol, $Đ$ = 1.22) and linear PMMA ($M_{n,GPC}$ = 4100 g/mol, $Đ$ = 1.09).

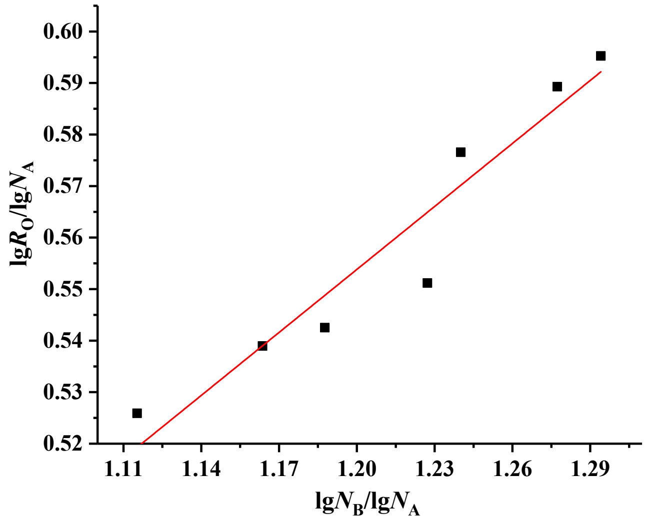


Figure S13. $\lg R_O/\lg N_A$ as a function of $\lg N_B/\lg N_A$.