

Supporting Information

Screening RAFT agents and photocatalysts to mediate PET-RAFT polymerization using a high throughput approach

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Table S1. Enthalpy values of RAFT stability (ΔH_{stab}), the fragmentation efficiency (ΔH_{frag}), and the radical stabilization energy (RSE \bullet) of the leaving R group radicals (kJ/mol) for the various RAFT agents.

RAFT Agent	ΔH_{stab} (kJ mol ⁻¹)	ΔH_{frag} (kJ mol ⁻¹)	RSE of R \bullet (kJ mol ⁻¹)
R1	59.4	-4.4	41.3
R2	59.4	-4.4	59.0
R3	59.4	-4.4	54.9
R4	86.8	-44.3	41.3
R5	41.3	21.0	59.0
R6	47.9	-5.5	31.9
R7	45.0	-3.2	59.0
R8	90.6	-32.7	59.0
R9	90.6	-32.7	31.9
R10	90.6	-32.7	31.9

Note: The values of ΔH_{stab} , ΔH_{frag} , and RSE of R \bullet (kJ/mol) for RAFT agents were collected from the literature.^{1, 2}

The ΔH_{stab} and ΔH_{frag} of R1 are 59.4 kJ/mol and -4.4 kJ/mol, with respect to S(CH₂)₂CH₃ group.

RSE of R \bullet for the R group (CH(CH₃)COOH) of R1 = 41.3 kJ/mol.

The ΔH_{stab} and ΔH_{frag} of R2 are 59.4 kJ/mol and -4.4 kJ/mol, with respect to S(CH₂)₁₁CH₃ group.

RSE of R \bullet for the R group (C(CH₃)(CN)(CH₂)₂COOH) of R2 \approx 59.0 kJ/mol, based on C(CH₃)₂CN.

The ΔH_{stab} and ΔH_{frag} of R3 are 59.4 kJ/mol and -4.4 kJ/mol, with respect to S(CH₂)₁₁CH₃ group.

The RSE of R \bullet for the R group C(CH₃)₂COOH of R3 \approx 54.9 kJ/mol, based on C(CH₃)₂COOCH₃.

The ΔH_{stab} and ΔH_{frag} of R4 are 86.8 kJ/mol and -44.3 kJ/mol, with respect to OCH₂CH₃ group.

The RSE of R \bullet for the R group CH(CH₃)COOCH₃ of R4 = 41.3 kJ/mol.

The ΔH_{stab} and ΔH_{frag} of R5 are 41.3 kJ/mol and 21.0 kJ/mol, with respect to C₆H₅ (phenyl) group.

The RSE of R \bullet for the R group C(CH₃)(CN)(CH₂)₂COOH of R5 \approx 59.0 kJ/mol.

The ΔH_{stab} and ΔH_{frag} of R6 are 50.0 kJ/mol and -3.0 kJ/mol, with respect to 3,5-dimethyl-pyrazole group.

The RSE of R• for the R group CH₂CN of R6 = 31.9 kJ/mol.

The ΔH_{stab} and ΔH_{frag} of R7 are 45.0 kJ/mol and -10.0 kJ/mol, with respect to 4-chloro-3,5-dimethyl-pyrazole group.

The RSE of R• for the R group (C(CH₃)(CN)CH₂CH₃) of R7 \approx 59.0 kJ/mol, based on C(CH₃)₂CN.

The ΔH_{stab} and ΔH_{frag} of R8 are 90.6 kJ/mol and -32.7 kJ/mol, with respect to methyl-*N*-(pyridin-4-yl) group.

The RSE of R• for the R group (C(CH₃)(CN)CH₂CH₃) of R8 \approx 59.0 kJ/mol, based on C(CH₃)₂CN.

The ΔH_{stab} and ΔH_{frag} of R9 are 90.6 kJ/mol and -32.7 kJ/mol, with respect to methyl-*N*-(pyridin-4-yl) group.

The RSE of R• for the R group CH₂CN of R9 = 31.9 kJ/mol.

The ΔH_{stab} and ΔH_{frag} of R10 are 90.6 kJ/mol and -32.7 kJ/mol, with respect to methyl-*N*-(phenyl) group.

The RSE of R• for the R group CH₂CN of R10 = 31.9 kJ/mol.

Table S2. PET-RAFT polymerization of **DMA** mediated with **ZnTPP (C1)** as photocatalyst conducted directly in 96-well plates.

RAFT	α^a (%)	$M_{n,th}^b$ (g/mol)	$M_{n,GPC}^c$ (g/mol)	M_w/M_n^c
R1	96	9 800	9 700	1.18
R2	94	9 700	11 900	1.09
R3	91	9 400	9 300	1.19
R4	86	8 800	9 200	1.42
R5	-	-	-	-
R6	94	9 600	10 800	1.16
R7	90	9 200	9 400	1.15
R8	28	3 100	10 100	1.65
R8*	67	6 900	8 100	1.33
R9	83	8 500	11 500	1.55
R9*	93	9 500	12 100	1.28
R10	12	1 400	14 900	1.68

Notes: Polymerizations were conducted under green LED light ($\lambda_{max} = 530$ nm, 5.5 mW/cm²) irradiated for 4 h, targeted at ($[Monomer]:[RAFT]:[Catalyst] = 100:1:0.015$ and $[Monomer]_0 = 1.0$ M); ^aMonomer conversion (α) was determined by ¹H NMR spectroscopy using DMF as an internal standard; ^bTheoretical molecular weights ($M_{n,th}$) were calculated using the following equation: $M_{n,th} = [M]/[RAFT] \times \alpha \times MW_{monomer} + MW_{RAFT}$; ^cexperimental molecular weights ($M_{n,GPC}$) and polymer dispersities (M_w/M_n) were determined by GPC using PMMA standards for calibration.

Table S3. PET-RAFT polymerization of **DMA** mediated with **Cl-ZnTPP (C2)** as photocatalyst conducted directly in 96-well plates.

RAFT	α^a (%)	$M_{n,th}^b$ (g/mol)	$M_{n,GPC}^c$ (g/mol)	M_w/M_n^c
R1	96	9 800	9 400	1.16
R2	95	9 900	11 400	1.15
R3	82	8 500	8 900	1.17
R4	71	7 400	8 100	1.46
R5	-	-	-	-
R6	93	9 500	9 600	1.16
R7	89	9 200	12 300	1.17
R8	26	2 900	9 900	1.70
R8*	78	8 000	10 000	1.11
R9	82	8 400	11 500	1.41
R9*	94	9 600	13 000	1.11
R10	18	2 100	15 700	1.58

Notes: Polymerizations were conducted under green LED light ($\lambda_{max} = 530$ nm, 5.5 mW/cm²) irradiated for 4 h, targeted at ($[Monomer]:[RAFT]:[Catalyst] = 100:1:0.015$ and $[Monomer]_0 = 1.0$ M); ^aMonomer conversion (α) was determined by ¹H NMR spectroscopy using DMF as an internal standard; ^bTheoretical molecular weights ($M_{n,th}$) were calculated using the following equation: $M_{n,th} = [M]/[RAFT] \times \alpha \times MW_{monomer} + MW_{RAFT}$; ^cexperimental molecular weights ($M_{n,GPC}$) and polymer dispersities (M_w/M_n) were determined by GPC using PMMA standards for calibration.

Table S4. PET-RAFT polymerization of **DMA** mediated with **F-ZnTPP (C3)** as photocatalyst conducted directly in 96-well plates.

RAFT	α^a (%)	$M_{n,th}^b$ (g/mol)	$M_{n,GPC}^c$ (g/mol)	M_w/M_n^c
R1	53	5 500	6 000	1.09
R2	78	8 200	8 400	1.19
R3	63	6 600	6 700	1.18
R4	54	5 600	6 300	1.50
R5	-	-	-	-
R6	71	7 300	9 000	1.13
R7	93	9 500	18 600	1.34
R8	48	5 000	8 800	1.68
R8*	87	8 900	11 600	1.23
R9	86	8 800	13 600	1.49
R9*	98	10 000	13 100	1.10
R10	22	2 400	16 700	1.65

Notes: Polymerizations were conducted under green LED light ($\lambda_{max} = 530$ nm, 5.5 mW/cm²) irradiated for 4 h, targeted at ($[Monomer]:[RAFT]:[Catalyst] = 100:1:0.015$ and $[Monomer]_0 = 1.0$ M); ^aMonomer conversion (α) was determined by ¹H NMR spectroscopy using DMF as an internal standard; ^bTheoretical molecular weights ($M_{n,th}$) were calculated using the following equation: $M_{n,th} = [M]/[RAFT] \times \alpha \times MW_{monomer} + MW_{RAFT}$; ^cexperimental molecular weights ($M_{n,GPC}$) and polymer dispersities (M_w/M_n) were determined by GPC using PMMA standards for calibration.

Table S5. PET-RAFT polymerization of **DMA** mediated with **Zn-TCPP (C4)** as photocatalyst conducted directly in 96-well plates.

RAFT	α^a (%)	$M_{n,th}^b$ (g/mol)	$M_{n,GPC}^c$ (g/mol)	M_w/M_n^c
R1	98	10 000	10 400	1.07
R2	93	9 700	9 400	1.17
R3	92	9 500	10 500	1.07
R4	51	5 300	6 300	1.46
R5	-	-	-	-
R6	63	6 500	6 700	1.09
R7	51	5 300	4 900	1.16
R8	21	2 300	4 400	1.41
R8*	86	8 800	14 100	1.19
R9	89	9 100	9 400	1.44
R9*	95	9 700	16 200	1.14
R10	16	1 800	16 100	2.17

Notes: Polymerizations were conducted under green LED light ($\lambda_{max} = 530 \text{ nm}$, 5.5 mW/cm^2) irradiated for 4 h, targeted at ($[\text{Monomer}]:[\text{RAFT}]:[\text{Catalyst}] = 100:1:0.015$ and $[\text{Monomer}]_0 = 1.0 \text{ M}$); ^aMonomer conversion (α) was determined by ¹H NMR spectroscopy using DMF as an internal standard; ^bTheoretical molecular weights ($M_{n,th}$) were calculated using the following equation: $M_{n,th} = [M]/[RAFT] \times \alpha \times MW_{monomer} + MW_{RAFT}$; ^cexperimental molecular weights ($M_{n,GPC}$) and polymer dispersities (M_w/M_n) were determined by GPC using PMMA standards for calibration.

Table S6. PET-RAFT polymerization of **BzA** mediated with **ZnTPP (C1)** as photocatalyst conducted directly in 96-well plates.

RAFT	α^a (%)	$M_{n,th}^b$ (g/mol)	$M_{n,GPC}^c$ (g/mol)	M_w/M_n^c
R1	95	15 700	11 300	1.14
R2	91	15 200	12 600	1.08
R3	88	14 700	10 200	1.16
R4	47	7 900	15 600	1.65
R5	-	-	-	-
R6	86	14 200	11 200	1.26
R7	59	9 900	7 600	1.13
R8	24	4 100	11 300	1.73
R8*	72	11 900	11 100	1.34
R9	16	2 800	33 400	2.27
R9*	81	13 400	28 900	1.54
R10	9	1 700	59 900	2.61

Notes: Polymerizations were conducted under green LED light ($\lambda_{max} = 530 \text{ nm}$, 5.5 mW/cm^2) irradiated for 4 h, targeted at ($[\text{Monomer}]:[\text{RAFT}]:[\text{Catalyst}] = 100:1:0.015$ and $[\text{Monomer}]_0 = 1.0 \text{ M}$); ^aMonomer conversion (α) was determined by ¹H NMR spectroscopy using DMF as an internal standard; ^bTheoretical molecular weights ($M_{n,th}$) were calculated using the following equation: $M_{n,th} = [M]/[RAFT] \times \alpha \times MW_{monomer} + MW_{RAFT}$; ^cexperimental molecular weights ($M_{n,GPC}$) and polymer dispersities (M_w/M_n) were determined by GPC using PMMA standards for calibration.

Table S7. PET-RAFT polymerization of **BzA** mediated with **Cl-ZnTPP (C2)** as photocatalyst conducted directly in 96-well plates.

RAFT	α^a (%)	$M_{n,th}^b$ (g/mol)	$M_{n,GPC}^c$ (g/mol)	M_w/M_n^c
R1	92	15 200	10 800	1.13
R2	86	14 300	11 800	1.13
R3	92	15 300	10 600	1.11
R4	39	6 600	14 700	1.58
R5	-	-	-	-
R6	85	14 100	11 100	1.24
R7	77	12 800	9 700	1.08
R8	19	3 300	3 900	1.40
R8*	63	10 500	10 900	1.33
R9	13	2 400	30 900	2.42
R9*	82	13 500	24 400	1.46
R10	17	4 700	84 400	1.84

Notes: Polymerizations were conducted under green LED light ($\lambda_{max} = 530$ nm, 5.5 mW/cm²) irradiated for 4 h, targeted at ($[Monomer]:[RAFT]:[Catalyst] = 100:1:0.015$ and $[Monomer]_0 = 1.0$ M); ^aMonomer conversion (α) was determined by ¹H NMR spectroscopy using DMF as an internal standard; ^bTheoretical molecular weights ($M_{n,th}$) were calculated using the following equation: $M_{n,th} = [M]/[RAFT] \times \alpha \times MW_{monomer} + MW_{RAFT}$; ^cexperimental molecular weights ($M_{n,GPC}$) and polymer dispersities (M_w/M_n) were determined by GPC using PMMA standards for calibration.

Table S8. PET-RAFT polymerization of **BzA** mediated with **F-ZnTPP (C3)** as photocatalyst conducted directly in 96-well plates.

RAFT	α^a (%)	$M_{n,th}^b$ (g/mol)	$M_{n,GPC}^c$ (g/mol)	M_w/M_n^c
R1	27	4 600	4 500	1.20
R2	58	9 600	9 200	1.15
R3	50	8 300	7 400	1.13
R4	49	8 200	15 900	1.51
R5	-	-	-	-
R6	56	9 300	11 400	1.30
R7	86	14 200	13 700	1.11
R8	15	2 700	3 700	1.84
R8*	85	14 000	15 000	1.19
R9	16	2 800	32 400	2.28
R9*	89	14 700	24 600	1.46
R10	12	2 200	77 300	2.10

Notes: Polymerizations were conducted under green LED light ($\lambda_{max} = 530 \text{ nm}$, 5.5 mW/cm^2) irradiated for 4 h, targeted at ($[\text{Monomer}]:[\text{RAFT}]:[\text{Catalyst}] = 100:1:0.015$ and $[\text{Monomer}]_0 = 1.0 \text{ M}$); ^aMonomer conversion (α) was determined by ¹H NMR spectroscopy using DMF as an internal standard; ^bTheoretical molecular weights ($M_{n,th}$) were calculated using the following equation: $M_{n,th} = [M]/[RAFT] \times \alpha \times MW_{monomer} + MW_{RAFT}$; ^cexperimental molecular weights ($M_{n,GPC}$) and polymer dispersities (M_w/M_n) were determined by GPC using PMMA standards for calibration.

Table S9. PET-RAFT polymerization of **BzA** mediated with **Zn-TCPP (C4)** as photocatalyst conducted directly in 96-well plates.

RAFT	α^a (%)	$M_{n,th}^b$ (g/mol)	$M_{n,GPC}^c$ (g/mol)	M_w/M_n^c
R1	85	14 000	11 000	1.11
R2	88	14 500	11 900	1.10
R3	87	14 300	11 100	1.09
R4	43	7 200	14 600	1.68
R5	-	-	-	-
R6	88	14 500	13 500	1.11
R7	72	11 900	10 900	1.29
R8	32	5 400	5 500	1.52
R8*	78	12 900	15 600	1.18
R9	11	2 000	29 200	2.43
R9*	84	13 900	22 400	1.39
R10	17	3 000	128 800	1.87

Notes: Polymerizations were conducted under green LED light ($\lambda_{max} = 530$ nm, 5.5 mW/cm²) irradiated for 4 h, targeted at ($[Monomer]:[RAFT]:[Catalyst] = 100:1:0.015$ and $[Monomer]_0 = 1.0$ M); ^aMonomer conversion (α) was determined by ¹H NMR spectroscopy using DMF as an internal standard; ^bTheoretical molecular weights ($M_{n,th}$) were calculated using the following equation: $M_{n,th} = [M]/[RAFT] \times \alpha \times MW_{monomer} + MW_{RAFT}$; ^cexperimental molecular weights ($M_{n,GPC}$) and polymer dispersities (M_w/M_n) were determined by GPC using PMMA standards for calibration.

Table S10. PET-RAFT polymerization of **BzMA** mediated with **ZnTPP (C1)** as photocatalyst conducted directly in 96-well plates.

RAFT	α^a (%)	$M_{n,th}^b$ (g/mol)	$M_{n,GPC}^c$ (g/mol)	M_w/M_n^c
R1	66	11 900	15 400	1.79
R2	71	12 800	12 600	1.26
R3	62	11 200	14 100	1.75
R4	14	2 700	211 900	2.27
R5	25	4 600	5 200	1.21
R6	31	5 700	49 600	1.97
R7	49	8 900	17 500	1.66
R8	18	3 400	11 600	1.49
R8*	65	11 700	17 200	1.33
R9	5	1 200	107 800	1.73
R9*	41	7 500	25 600	1.48
R10	6	1 300	182 100	2.10

Notes: Polymerizations were conducted under green LED light ($\lambda_{max} = 530 \text{ nm}$, 5.5 mW/cm^2) irradiated for 4 h, targeted at ($[\text{Monomer}]:[\text{RAFT}]:[\text{Catalyst}] = 100:1:0.015$ and $[\text{Monomer}]_0 = 1.0 \text{ M}$); ^aMonomer conversion (α) was determined by ¹H NMR spectroscopy using DMF as an internal standard; ^bTheoretical molecular weights ($M_{n,th}$) were calculated using the following equation: $M_{n,th} = [M]/[RAFT] \times \alpha \times MW_{monomer} + MW_{RAFT}$; ^cexperimental molecular weights ($M_{n,GPC}$) and polymer dispersities (M_w/M_n) were determined by GPC using PMMA standards for calibration.

Table S11. PET-RAFT polymerization of **BzMA** mediated with **Cl-ZnTPP (C2)** as photocatalyst conducted directly in 96-well plates.

RAFT	α^a (%)	$M_{n,th}^b$ (g/mol)	$M_{n,GPC}^c$ (g/mol)	M_w/M_n^c
R1	56	10 100	21 900	1.70
R2	67	12 200	11 900	1.31
R3	55	9 900	41 700	1.64
R4	19	3 600	296 900	1.72
R5	23	4 300	4 900	1.22
R6	24	4 500	232 800	1.82
R7	47	8 500	19 600	1.44
R8	13	2 500	9 400	1.47
R8*	61	11 000	27 800	1.54
R9	8	1 600	28 400	2.29
R9*	44	8 000	65 200	1.76
R10	7	1 500	54 200	2.66

Notes: Polymerizations were conducted under green LED light ($\lambda_{max} = 530 \text{ nm}$, 5.5 mW/cm^2) irradiated for 4 h, targeted at ($[\text{Monomer}]:[\text{RAFT}]:[\text{Catalyst}] = 100:1:0.015$ and $[\text{Monomer}]_0 = 1.0 \text{ M}$); ^aMonomer conversion (α) was determined by ¹H NMR spectroscopy using DMF as an internal standard; ^bTheoretical molecular weights ($M_{n,th}$) were calculated using the following equation: $M_{n,th} = [M]/[RAFT] \times \alpha \times MW_{monomer} + MW_{RAFT}$; ^cexperimental molecular weights ($M_{n,GPC}$) and polymer dispersities (M_w/M_n) were determined by GPC using PMMA standards for calibration.

Table S12. PET-RAFT polymerization of **BzMA** mediated with **F-ZnTPP (C3)** as photocatalyst conducted directly in 96-well plates.

RAFT	α^a (%)	$M_{n,th}^b$ (g/mol)	$M_{n,GPC}^c$ (g/mol)	M_w/M_n^c
R1	13	2500	57100	3.28
R2	59	10600	11200	1.82
R3	31	5700	24000	1.83
R4	11	2200	50100	2.43
R5	43	7800	9200	1.36
R6	32	8000	31900	2.03
R7	52	9400	15700	1.71
R8	6	1300	23900	2.76
R8*	67	12100	18300	1.42
R9	5	1100	62400	1.92
R9*	61	11000	55000	1.83
R10	8	1600	66800	2.95

Notes: Polymerizations were conducted under green LED light ($\lambda_{max} = 530 \text{ nm}$, 5.5 mW/cm^2) irradiated for 4 h, targeted at ($[\text{Monomer}]:[\text{RAFT}]:[\text{Catalyst}] = 100:1:0.015$ and $[\text{Monomer}]_0 = 1.0 \text{ M}$); ^aMonomer conversion (α) was determined by ¹H NMR spectroscopy using DMF as an internal standard; ^bTheoretical molecular weights ($M_{n,th}$) were calculated using the following equation: $M_{n,th} = [M]/[RAFT] \times \alpha \times MW_{monomer} + MW_{RAFT}$; ^cexperimental molecular weights ($M_{n,GPC}$) and polymer dispersities (M_w/M_n) were determined by GPC using PMMA standards for calibration.

Table S13. PET-RAFT polymerization of **BzMA** mediated with **Zn-TCPP (C4)** as photocatalyst conducted directly in 96-well plates.

RAFT	α^a (%)	$M_{n,th}^b$ (g/mol)	$M_{n,GPC}^c$ (g/mol)	M_w/M_n^c
R1	33	6 100	40 100	2.31
R2	55	10 100	9 000	1.29
R3	38	7 000	26 600	1.93
R4	18	3 400	198 100	2.28
R5	17	3 200	3 600	1.20
R6	21	3 900	104 600	2.22
R7	42	7 600	15 800	1.63
R8	8	1 600	81 300	2.57
R8*	72	13 000	22 100	1.40
R9	4	900	136 600	2.13
R9*	49	8 900	27 600	1.87
R10	9	1 800	233 700	2.08

Notes: Polymerizations were conducted under green LED light ($\lambda_{max} = 530 \text{ nm}$, 5.5 mW/cm^2) irradiated for 4 h, targeted at ($[\text{Monomer}]:[\text{RAFT}]:[\text{Catalyst}] = 100:1:0.015$ and $[\text{Monomer}]_0 = 1.0 \text{ M}$); ^aMonomer conversion (α) was determined by ¹H NMR spectroscopy using DMF as an internal standard; ^bTheoretical molecular weights ($M_{n,th}$) were calculated using the following equation: $M_{n,th} = [M]/[RAFT] \times \alpha \times MW_{monomer} + MW_{RAFT}$; ^cexperimental molecular weights ($M_{n,GPC}$) and polymer dispersities (M_w/M_n) were determined by GPC using PMMA standards for calibration.

Table S14. PET-RAFT polymerization of **HPMA** mediated with **ZnTPP (C1)** as photocatalyst conducted directly in 96-well plates.

RAFT	α^a (%)	$M_{n,th}^b$ (g/mol)	$M_{n,GPC}^c$ (g/mol)	M_w/M_n^c
R1	65	9 500	21 400	1.81
R2	75	11 100	24 200	1.28
R3	74	10 900	24 400	1.41
R4	37	5 500	112 400	1.70
R5	21	3 200	11 700	1.11
R6	56	8 200	96 700	1.85
R7	69	10 100	27 100	1.12
R8	22	3 300	12 200	1.36
R8*	68	9 900	25 600	1.15
R9	35	5 200	13 200	1.46
R9*	62	9 100	75 800	1.56
R10	29	4 400	140 600	1.65

Notes: Polymerizations were conducted under green LED light ($\lambda_{max} = 530$ nm, 5.5 mW/cm²) irradiated for 24 h, targeted at ($[Monomer]:[RAFT]:[Catalyst] = 100:1:0.015$ and $[Monomer]_0 = 1.0$ M); ^aMonomer conversion (α) was determined by ¹H NMR spectroscopy using DMF as an internal standard; ^bTheoretical molecular weights ($M_{n,th}$) were calculated using the following equation: $M_{n,th} = [M]/[RAFT] \times \alpha \times MW_{monomer} + MW_{RAFT}$; ^cexperimental molecular weights ($M_{n,GPC}$) and polymer dispersities (M_w/M_n) were determined by GPC using PMMA standards for calibration.

Table S15. PET-RAFT polymerization of **HPMA** mediated with **Cl-ZnTPP (C2)** as photocatalyst conducted directly in 96-well plates.

RAFT	α^a (%)	$M_{n,th}^b$ (g/mol)	$M_{n,GPC}^c$ (g/mol)	M_w/M_n^c
R1	62	9 100	36 600	1.93
R2	70	10 400	20 600	1.56
R3	73	10 900	22 300	1.41
R4	33	5 000	127 600	1.54
R5	15	2 400	7 200	1.10
R6	67	9 800	79 900	1.70
R7	75	11 000	29 600	1.14
R8	20	3 100	11 500	1.29
R8*	67	9 800	24 600	1.14
R9	33	4 900	14 300	1.43
R9*	60	8 800	87 700	1.54
R10	27	4 100	168 200	1.56

Notes: Polymerizations were conducted under green LED light ($\lambda_{max} = 530 \text{ nm}$, 5.5 mW/cm^2) irradiated for 24 h, targeted at ($[\text{Monomer}]:[\text{RAFT}]:[\text{Catalyst}] = 100:1:0.015$ and $[\text{Monomer}]_0 = 1.0 \text{ M}$); ^aMonomer conversion (α) was determined by ¹H NMR spectroscopy using DMF as an internal standard; ^bTheoretical molecular weights ($M_{n,th}$) were calculated using the following equation: $M_{n,th} = [M]/[RAFT] \times \alpha \times MW_{monomer} + MW_{RAFT}$; ^cexperimental molecular weights ($M_{n,GPC}$) and polymer dispersities (M_w/M_n) were determined by GPC using PMMA standards for calibration.

Table S16. PET-RAFT polymerization of **HPMA** mediated with **F-ZnTPP (C3)** as photocatalyst conducted directly in 96-well plates.

RAFT	α^a (%)	$M_{n,th}^b$ (g/mol)	$M_{n,GPC}^c$ (g/mol)	M_w/M_n^c
R1	31	4 700	16 900	1.57
R2	51	7 700	20 700	1.45
R3	54	8 200	18 000	1.36
R4	23	3 500	22 900	1.70
R5	19	3 000	9 400	1.08
R6	76	11 100	26 800	1.64
R7	57	8 400	28 300	1.44
R8	24	3 700	11 000	1.36
R8*	80	11 700	33 900	1.44
R9	19	3 000	13 100	1.51
R9*	72	10 500	27 800	1.42
R10	18	2 800	29 300	1.88

Notes: Polymerizations were conducted under green LED light ($\lambda_{max} = 530$ nm, 5.5 mW/cm²) irradiated for 24 h, targeted at ($[Monomer]:[RAFT]:[Catalyst] = 100:1:0.015$ and $[Monomer]_0 = 1.0$ M); ^aMonomer conversion (α) was determined by ¹H NMR spectroscopy using DMF as an internal standard; ^bTheoretical molecular weights ($M_{n,th}$) were calculated using the following equation: $M_{n,th} = [M]/[RAFT] \times \alpha \times MW_{monomer} + MW_{RAFT}$; ^cexperimental molecular weights ($M_{n,GPC}$) and polymer dispersities (M_w/M_n) were determined by GPC using PMMA standards for calibration.

Table S17. PET-RAFT polymerization of **HPMA** mediated with **Zn-TCPP (C4)** as photocatalyst conducted directly in 96-well plates.

RAFT	α^a (%)	$M_{n,th}^b$ (g/mol)	$M_{n,GPC}^c$ (g/mol)	M_w/M_n^c
R1	42	6 300	25 700	1.97
R2	51	7 700	18 900	1.63
R3	46	7 000	16 600	1.46
R4	18	2 800	18 900	1.54
R5	22	3 400	11 600	1.12
R6	74	10 800	28 700	1.68
R7	81	11 800	36 700	1.45
R8	19	3 000	11 100	1.36
R8*	69	10 100	25 900	1.15
R9	31	4 700	13 700	1.40
R9*	65	9 500	49 600	1.53
R10	15	2 400	23 900	1.48

Notes: Polymerizations were conducted under green LED light ($\lambda_{max} = 530$ nm, 5.5 mW/cm²) irradiated for 24 h, targeted at ($[Monomer]:[RAFT]:[Catalyst] = 100:1:0.015$ and $[Monomer]_0 = 1.0$ M); ^aMonomer conversion (α) was determined by ¹H NMR spectroscopy using DMF as an internal standard; ^bTheoretical molecular weights ($M_{n,th}$) were calculated using the following equation: $M_{n,th} = [M]/[RAFT] \times \alpha \times MW_{monomer} + MW_{RAFT}$; ^cexperimental molecular weights ($M_{n,GPC}$) and polymer dispersities (M_w/M_n) were determined by GPC using PMMA standards for calibration.

Table S18. PET-RAFT polymerization of **BzMA** mediated with **ZnTPP (C1)** as photocatalyst conducted in glass cuvettes in the absence and presence of oxygen.

RAFT	α^a (%)	$M_{n,th}^b$ (g/mol)	$M_{n,GPC}^c$ (g/mol)	M_w/M_n^c
R2 ^d	72	13 100	12 800	1.25
R2 ^e	77	14 000	13 500	1.16

Notes: Polymerizations were conducted under green LED light ($\lambda_{max} = 530 \text{ nm}$, 5.5 mW/cm^2) targeted at ($[\text{Monomer}]:[\text{RAFT}]:[\text{Catalyst}] = 100:1:0.015$ and $[\text{Monomer}]_0 = 1.0 \text{ M}$); ^aMonomer conversion (α) was determined by ¹H NMR spectroscopy using DMF as an internal standard; ^bTheoretical molecular weights ($M_{n,th}$) were calculated using the following equation: $M_{n,th} = [M]/[RAFT] \times \alpha \times MW_{monomer} + MW_{RAFT}$; ^cexperimental molecular weights ($M_{n,GPC}$) and polymer dispersities (M_w/M_n) were determined by GPC using PMMA standards for calibration, ^dpresence of oxygen (Oxygenated system) and ^eabsence of oxygen (deoxygenated system).

Table S19. Polymerization kinetics of **BTPA (R1)** mediated by PET-RAFT polymerization of **DMA** conducted directly in 96-well plates using four different catalysts.

Catalyst	α^a (%)	$M_{n,th}^b$ (g/mol)	$M_{n,GPC}^c$ (g/mol)	M_w/M_n^c	Time (min)
C1	27	2 900	2 600	1.12	15
C1	52	5 400	5 900	1.08	30
C1	71	7 300	8 000	1.08	60
C1	91	9 300	9 900	1.06	120
C2	17	1 900	1 700	1.11	15
C2	42	4 400	4 400	1.07	30
C2	62	6 400	6 700	1.08	60
C2	84	8 600	10 100	1.06	120
C3	-	-	-	-	15
C3	-	-	-	-	30
C3	7	900	1 800	1.14	60
C3	19	2 100	2 300	1.17	120
C4	11	1 300	1 200	1.04	15
C4	38	4 000	3 400	1.09	30
C4	55	5 700	6 100	1.07	60
C4	78	8 100	11 000	1.10	120

Notes: Polymerizations were conducted under green LED light ($\lambda_{max} = 530 \text{ nm}$, 5.5 mW/cm^2) targeted at ($[Monomer]:[RAFT]:[Catalyst] = 100:1:0.015$ and $[Monomer]_0 = 1.0 \text{ M}$); ^aMonomer conversion (α) was determined by ¹H NMR spectroscopy using DMF as an internal standard; ^bTheoretical molecular weights ($M_{n,th}$) were calculated using the following equation: $M_{n,th} = [M]/[RAFT] \times \alpha \times MW_{monomer} + MW_{RAFT}$; ^cexperimental molecular weights ($M_{n,GPC}$) and polymer dispersities (M_w/M_n) were determined by GPC using PMMA standards for calibration.

Table S20. Polymerization kinetics of **DTC1 (R6)** mediated by PET-RAFT polymerization of **DMA** conducted directly in 96-well plates using four different catalysts.

Catalyst	α^a (%)	$M_{n,th}^b$ (g/mol)	$M_{n,GPC}^c$ (g/mol)	M_w/M_n^c	Time (min)
C1	21	2 300	2 100	1.15	15
C1	39	4 100	4 600	1.13	30
C1	63	6 500	6 700	1.08	60
C1	87	8 900	10 800	1.06	120
C2	16	1 800	1 800	1.11	15
C2	30	3 200	3 500	1.12	30
C2	49	5 100	6 700	1.09	60
C2	72	7 400	9 700	1.08	120
C3	8	1 000	1 700	1.13	15
C3	18	2 000	2 900	1.19	30
C3	37	3 900	4 900	1.14	60
C3	60	6 200	7 900	1.15	120
C4	5	700	-	-	15
C4	10	1 200	-	-	30
C4	15	1 700	2 200	1.12	60
C4	29	3 100	3 800	1.14	120

Notes: Polymerizations were conducted under green LED light ($\lambda_{max} = 530 \text{ nm}$, 5.5 mW/cm^2) targeted at ($[\text{Monomer}]:[\text{RAFT}]:[\text{Catalyst}] = 100:1:0.015$ and $[\text{Monomer}]_0 = 1.0 \text{ M}$); ^aMonomer conversion (α) was determined by ¹H NMR spectroscopy using DMF as an internal standard; ^bTheoretical molecular weights ($M_{n,th}$) were calculated using the following equation: $M_{n,th} = [M]/[RAFT] \times \alpha \times MW_{monomer} + MW_{RAFT}$; ^cexperimental molecular weights ($M_{n,GPC}$) and polymer dispersities (M_w/M_n) were determined by GPC using PMMA standards for calibration.

Table S21. Polymerization kinetics of **DTC2 (R7)** mediated by PET-RAFT polymerization of **DMA** conducted directly in 96-well plates using four different catalysts.

Catalyst	α^a (%)	$M_{n,th}^b$ (g/mol)	$M_{n,GPC}^c$ (g/mol)	M_w/M_n^c	Time (min)
C1	8	1 000	-	-	15
C1	10	1 200	-	-	30
C1	42	4 500	6 100	1.10	60
C1	74	7 600	10 200	1.06	120
C2	4	700	-	-	15
C2	8	1 100	-	-	30
C2	36	3 900	6 800	1.12	60
C2	63	6 500	9 400	1.11	120
C3	19	2 100	7 000	1.11	15
C3	41	4 300	12 600	1.22	30
C3	67	6 900	16 900	1.25	60
C3	85	8 700	18 100	1.36	120
C4	2	500	-	-	15
C4	5	800	-	-	30
C4	9	1 200	-	-	60
C4	17	2 000	1 900	1.10	120

Notes: Polymerizations were conducted under green LED light ($\lambda_{max} = 530 \text{ nm}$, 5.5 mW/cm^2) targeted at ($[\text{Monomer}]:[\text{RAFT}]:[\text{Catalyst}] = 100:1:0.015$ and $[\text{Monomer}]_0 = 1.0 \text{ M}$); ^aMonomer conversion (α) was determined by ¹H NMR spectroscopy using DMF as an internal standard; ^bTheoretical molecular weights ($M_{n,th}$) were calculated using the following equation: $M_{n,th} = [M]/[RAFT] \times \alpha \times MW_{monomer} + MW_{RAFT}$; ^cexperimental molecular weights ($M_{n,GPC}$) and polymer dispersities (M_w/M_n) were determined by GPC using PMMA standards for calibration.

Table S22. Apparent propagation rate (min^{-1}) measured for PET-RAFT polymerization of **DMA** mediated by ZnTPP (**C1**), Cl-ZnTPP (**C2**), F-ZnTPP (**C3**) and Zn-TCPP (**C4**) under green LED light ($\lambda_{\text{max}} = 530 \text{ nm}$, 5.5 mW/cm^2) targeted at ($[\text{Monomer}]:[\text{RAFT}]:[\text{Catalyst}] = 100:1:0.015$ and $[\text{Monomer}]_0 = 1.0 \text{ M}$) with reaction time of 2 h.

		$K_p^{\text{app}} (\text{min}^{-1})$
C1	R1	1.94×10^{-2}
	R6	1.71×10^{-2}
	R7	1.26×10^{-2}
C2	R1	1.52×10^{-2}
	R6	1.04×10^{-2}
	R7	0.95×10^{-2}
C3	R1	0.21×10^{-2}
	R6	0.80×10^{-2}
	R7	1.59×10^{-2}
C4	R1	1.27×10^{-2}
	R6	0.27×10^{-2}
	R7	0.16×10^{-2}

Table S23. PET-RAFT polymerization of **DMA** mediated with **FTPP** (non-metalated) as photocatalyst conducted directly in 96-well plates.

RAFT	α^a (%)	$M_{n,th}^b$ (g/mol)	$M_{n,GPC}^c$ (g/mol)	M_w/M_n^c
R1	13	1 600	1 300	1.10
R2	21	2 500	2 100	1.14
R3	35	3 900	3 200	1.13
R4	24	2 600	4 900	1.48
R5	-	-	-	-
R6	18	2 100	1 500	1.12
R7	17	2 000	1 500	1.11
R8	4	700	-	-
R9	28	3 000	7700	1.69
R10	6	900	-	-

Notes: Polymerizations were conducted under green LED light ($\lambda_{max} = 530$ nm, 5.5 mW/cm²) targeted at ([Monomer]:[RAFT]:[Catalyst] = 100:1:0.015 and [Monomer]₀ = 1.0 M); ^aMonomer conversion (α) was determined by ¹H NMR spectroscopy using DMF as an internal standard; ^bTheoretical molecular weights ($M_{n,th}$) were calculated using the following equation: $M_{n,th} = [M]/[RAFT] \times \alpha \times MW_{monomer} + MW_{RAFT}$; ^cexperimental molecular weights ($M_{n,GPC}$) and polymer dispersities (M_w/M_n) were determined by GPC using PMMA standards for calibration.

Table S24. PET-RAFT polymerization of **DMA** mediated with **TCPP** (non-metalated) as photocatalyst conducted directly in 96-well plates.

RAFT	α^a (%)	$M_{n,th}^b$ (g/mol)	$M_{n,GPC}^c$ (g/mol)	M_w/M_n^c
R1	35	3 700	3 000	1.13
R2	30	3 300	3 100	1.12
R3	56	6 000	5 700	1.08
R4	43	4 600	5 400	1.43
R5	-	-	-	-
R6	31	3 400	3 500	1.18
R7	54	5600	5900	1.15
R8	12	1 500	-	-
R9	34	3 600	9 400	1.62
R10	9	1 200	-	-

Notes: Polymerizations were conducted under green LED light ($\lambda_{max} = 530$ nm, 5.5 mW/cm²) targeted at ([Monomer]:[RAFT]:[Catalyst] = 100:1:0.015 and [Monomer]₀ = 1.0 M); ^aMonomer conversion (α) was determined by ¹H NMR spectroscopy using DMF as an internal standard; ^bTheoretical molecular weights ($M_{n,th}$) were calculated using the following equation: $M_{n,th} = [M]/[RAFT] \times \alpha \times MW_{monomer} + MW_{RAFT}$; ^cexperimental molecular weights ($M_{n,GPC}$) and polymer dispersities (M_w/M_n) were determined by GPC using PMMA standards for calibration.

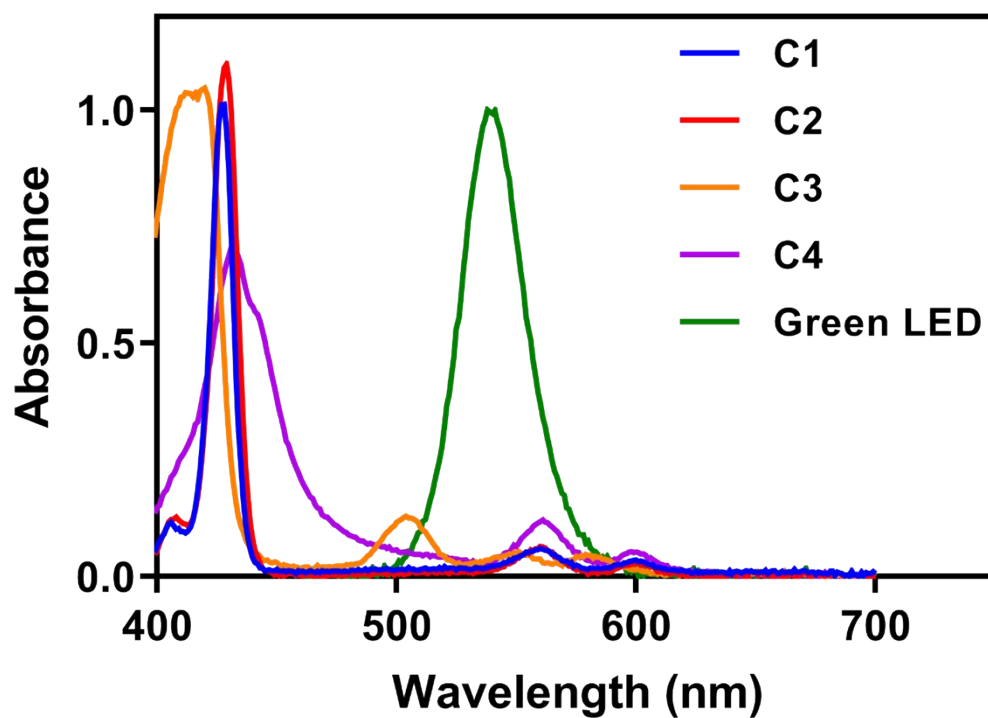


Figure S1. The Q-band absorption spectrum of C1 (ZnTPP), C2 (Cl-ZnTPP), C3 (F-ZnTPP) and C4 (ZnTCPP) recorded in DMSO and green LED emission ($\lambda = 530$ nm).



Figure S2. Digital image of the HT-PET RAFT wellplate polymerization setup.

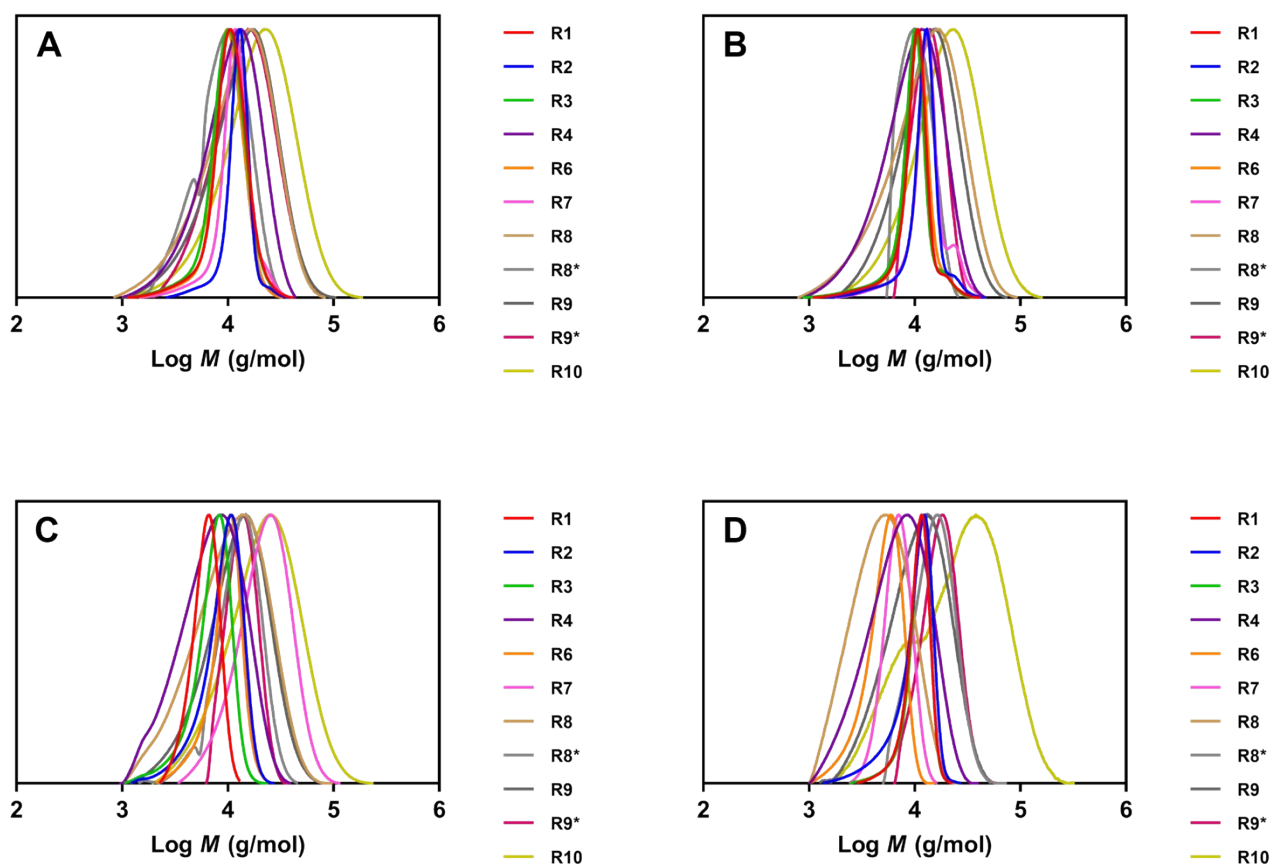


Figure S3. Molecular weight distributions for *N,N*-dimethylacrylamide (DMA) polymers prepared using PET-RAFT polymerization conducted in 96-well plates. Polymerizations were conducted for 4 hours under green LED light ($\lambda_{\text{max}} = 530 \text{ nm}$, 5.5 mW/cm^2) targeted at ($[\text{Monomer}]:[\text{RAFT}]:[\text{Catalyst}] = 100:1:0.015$ and $[\text{Monomer}]_0 = 1.0 \text{ M}$), catalyzed by different photocatalyst where (A) ZnTPP (C1), (B) Cl-ZnTPP (C2), (C) F-ZnTPP (C3), and (D) Zn-TCPP (C4).

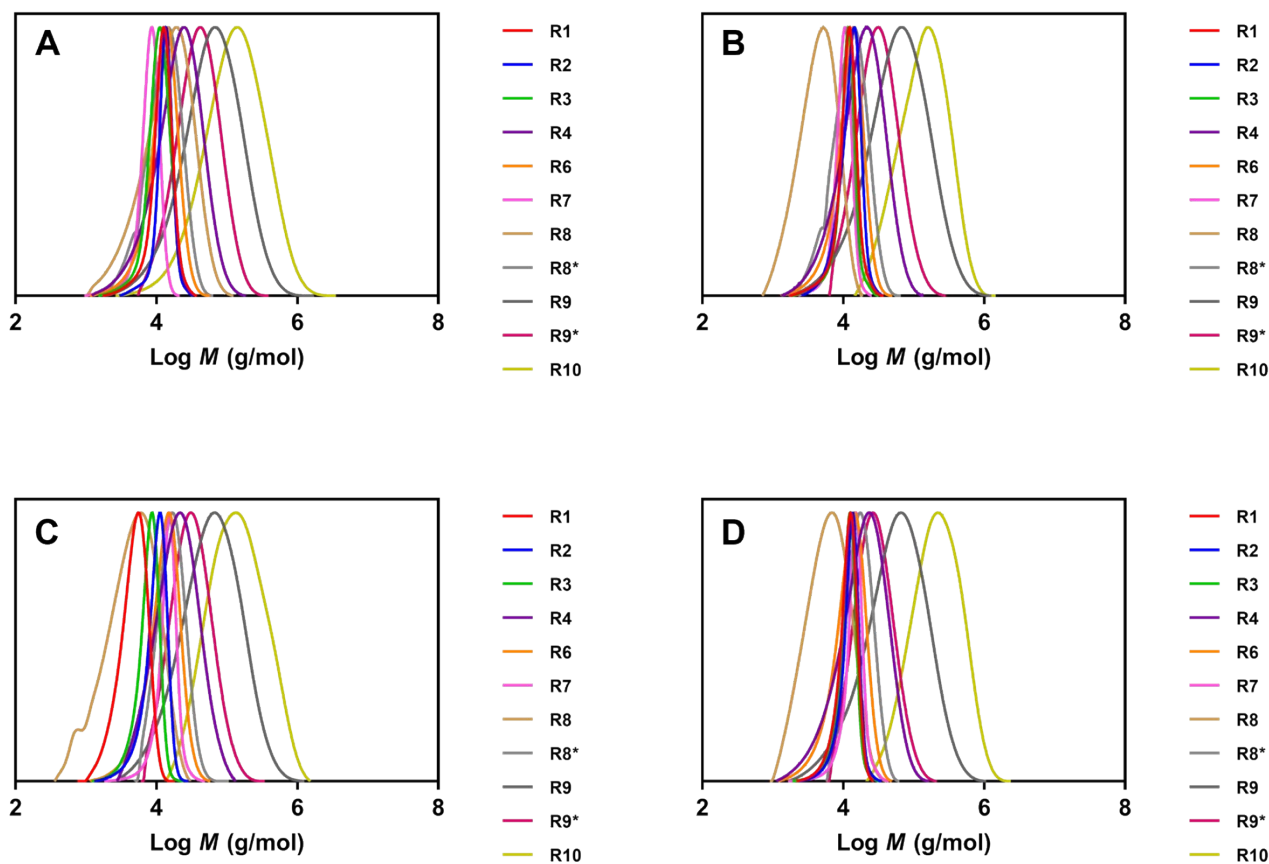


Figure S4. Molecular weight distributions for benzyl acrylate (BzA) polymers prepared using PET-RAFT polymerization conducted in 96-well plates. Polymerizations were conducted for 4 hours under green LED light ($\lambda_{\text{max}} = 530 \text{ nm}$, 5.5 mW/cm^2) targeted at ($[\text{Monomer}]:[\text{RAFT}]:[\text{Catalyst}] = 100:1:0.015$ and $[\text{Monomer}]_0 = 1.0 \text{ M}$), catalyzed by different catalyst where (A) ZnTPP (C1), (B) Cl-ZnTPP (C2), (C) F-ZnTPP (C3), and (D) Zn-TCPP (C4).

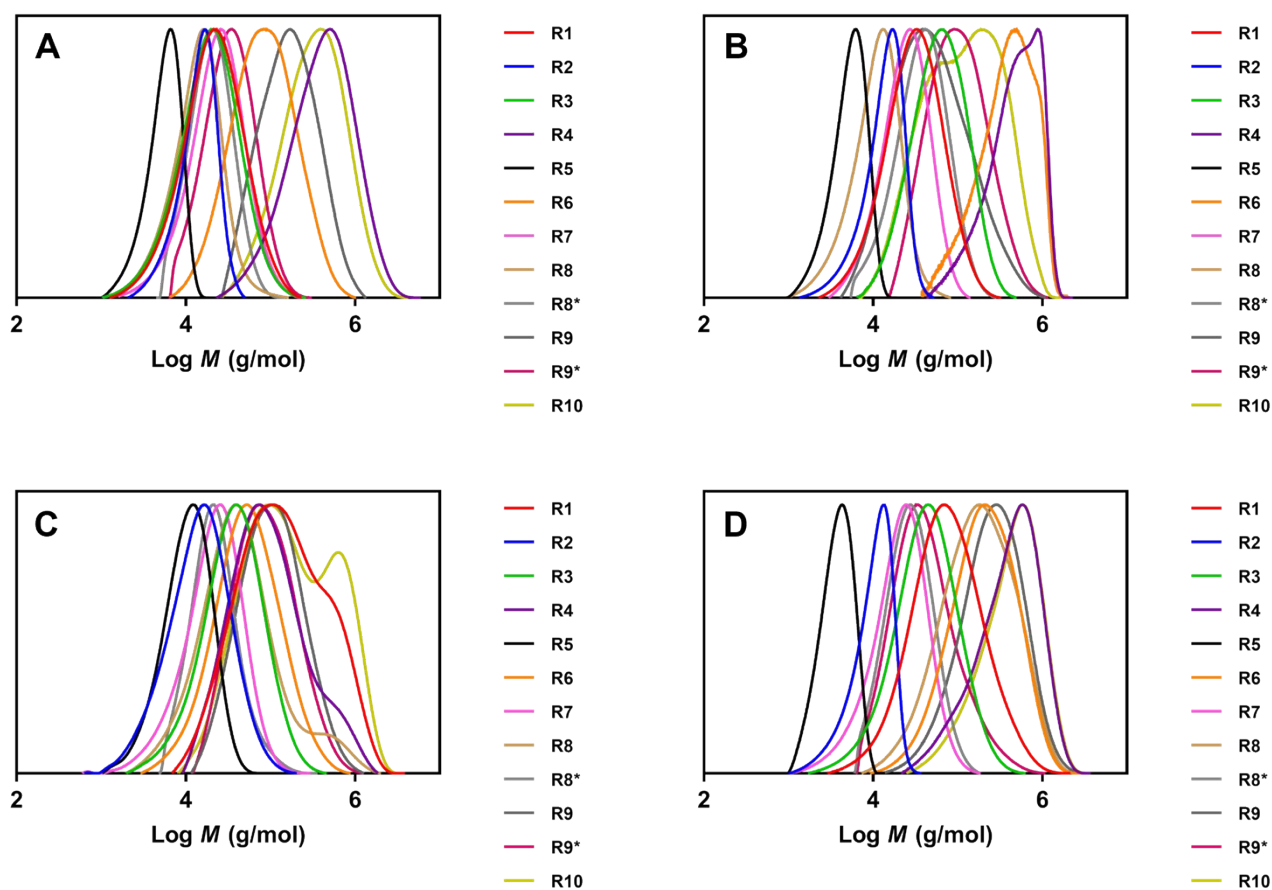


Figure S5. Molecular weight distributions for benzyl methacrylate (BzMA) polymers prepared using PET-RAFT polymerization conducted in 96-well plates. Polymerizations were conducted for 4 hours under green LED light ($\lambda_{\text{max}} = 530 \text{ nm}$, 5.5 mW/cm^2) targeted at ($[\text{Monomer}]:[\text{RAFT}]:[\text{Catalyst}] = 100:1:0.015$ and $[\text{Monomer}]_0 = 1.0 \text{ M}$), catalyzed by different catalyst where (A) ZnTPP, (B) Cl-ZnTPP, (C) F-ZnTPP, and (D) Zn-TCPP.

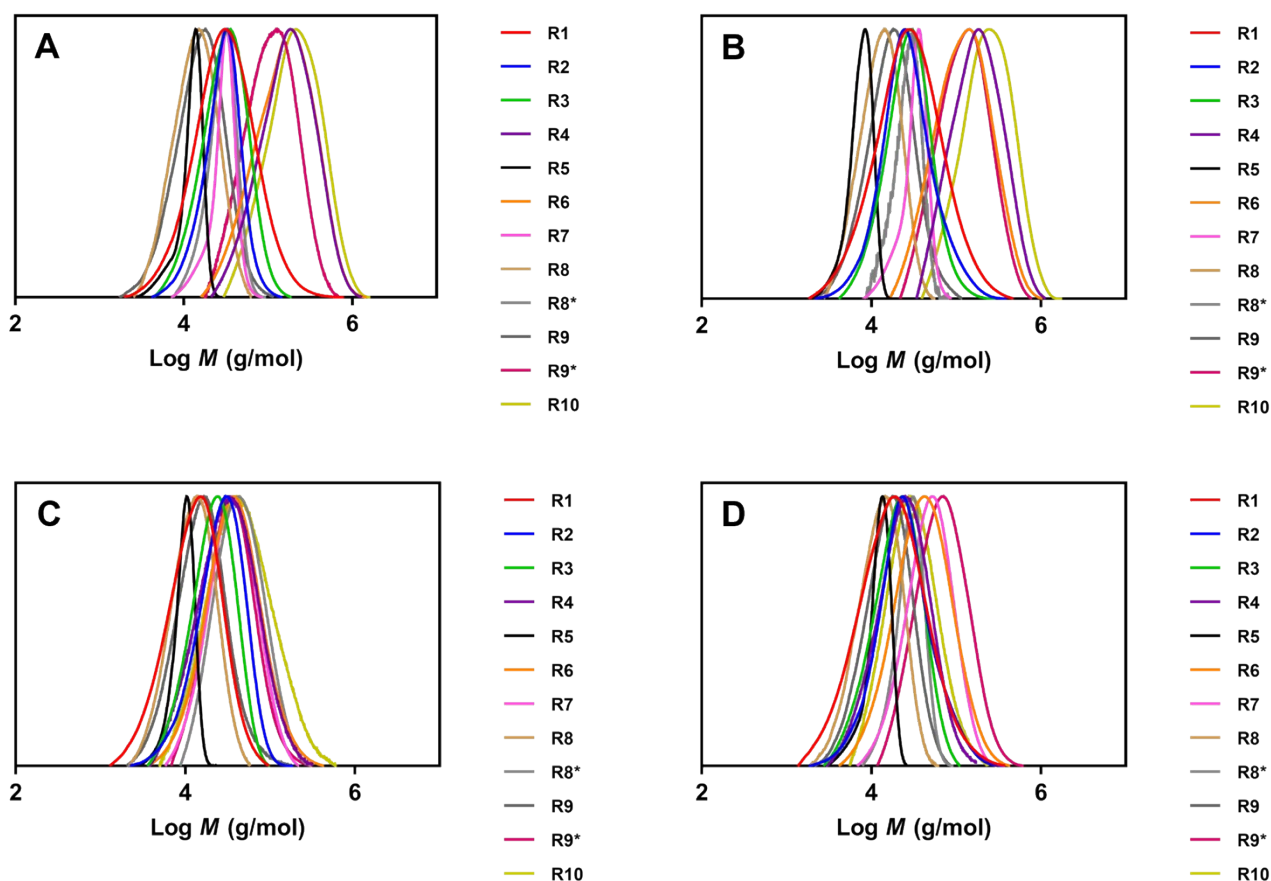


Figure S6. Molecular weight distributions for 2-hydroxypropyl methacrylamide (HPMA) polymers prepared using PET-RAFT polymerization conducted in 96-well plates. Polymerizations were conducted for 24 hours under green LED light ($\lambda_{\text{max}} = 530 \text{ nm}$, 5.5 mW/cm^2) targeted at ($[\text{Monomer}]:[\text{RAFT}]:[\text{Catalyst}] = 100:1:0.015$ and $[\text{Monomer}]_0 = 1.0 \text{ M}$), catalyzed by different catalyst where (A) ZnTPP, (B) Cl-ZnTPP, (C) F-ZnTPP, and (D) Zn-TCPP.

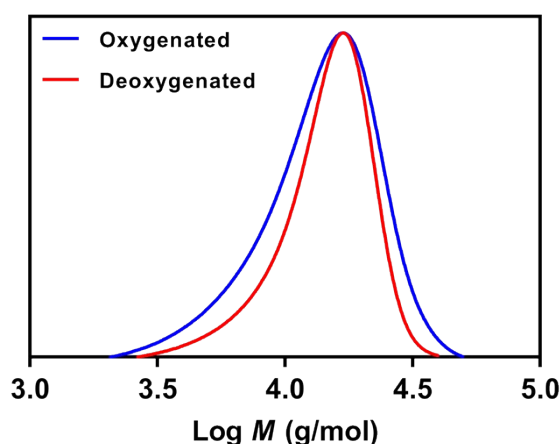


Figure S7. Molecular weight distributions for benzyl methacrylate (BzMA) polymers prepared using PET-RAFT polymerization conducted in glass cuvettes. Polymerizations were conducted for 4 hours under green LED light ($\lambda_{\text{max}} = 530 \text{ nm}$, 5.5 mW/cm^2) targeted at ($[\text{Monomer}]:[\text{RAFT}]:[\text{Catalyst}] = 100:1:0.015$ and $[\text{Monomer}]_0 = 1.0 \text{ M}$).

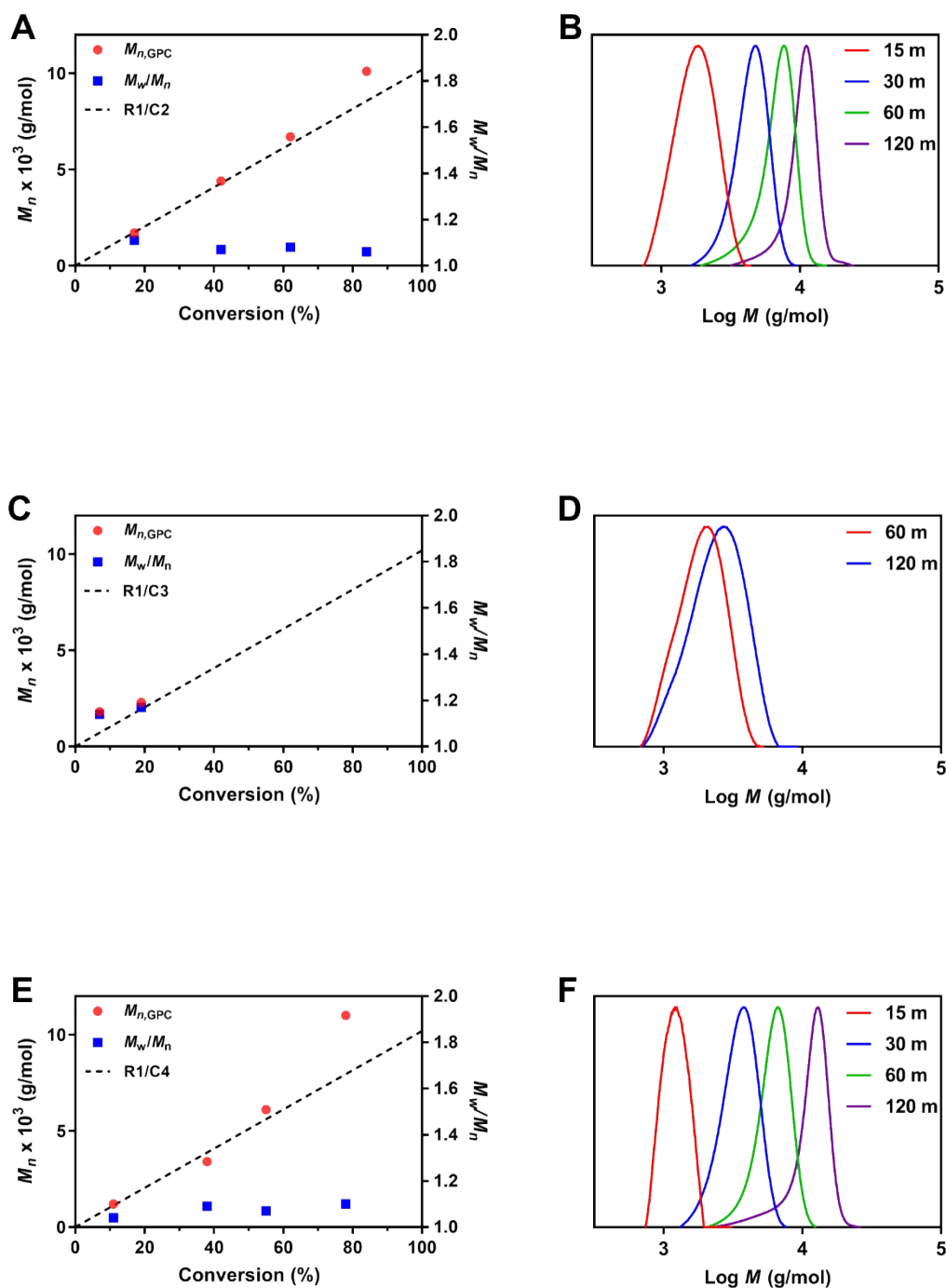


Figure S8. PET-RAFT polymerization of DMA conducted in 96-well plates irradiated under green LED light ($\lambda_{\max} = 530$ nm, 5.5 mW/cm²) targeted at ([DMA]:[BTPA]:[Catalyst] = 100:1:0.015 and [DMA]₀ = 1.0 M) using three different RAFT agents. Evolution of the GPC derived molecular weight and dispersity with monomer conversion conducted with **BTPA** RAFT agent using (A) C2, (C) C3, (E) C4 catalysts. The respective molecular weight distributions at various time points for the corresponding M_n versus conversion graph using different catalysts (B) C2, (D) C3, (F) C4.

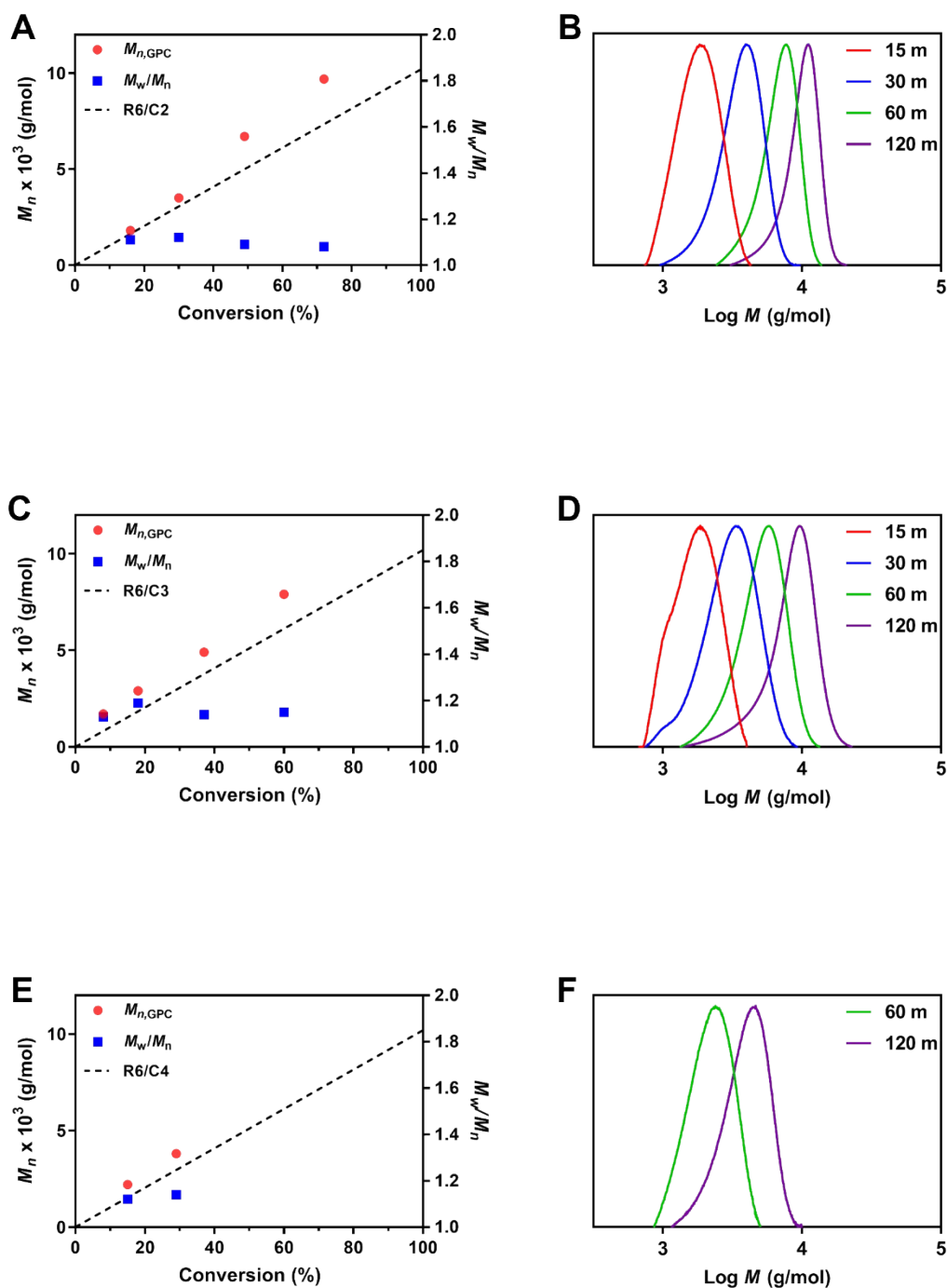


Figure S9. PET-RAFT polymerization of DMA conducted in 96-well plates irradiated under green LED light ($\lambda_{\max} = 530$ nm, 5.5 mW/cm²) targeted at ([DMA]:[DTC1]:[Catalyst] = 100:1:0.015 and [DMA]₀ = 1.0 M) using three different RAFT agents. Evolution of the GPC derived molecular weight and dispersity with monomer conversion conducted with **DTC1** RAFT agent using (A) C2, (C) C3, (E) C4 catalysts. The respective molecular weight distributions at various time points for the corresponding M_n versus conversion graph using different catalysts (B) C2, (D) C3, (F) C4.

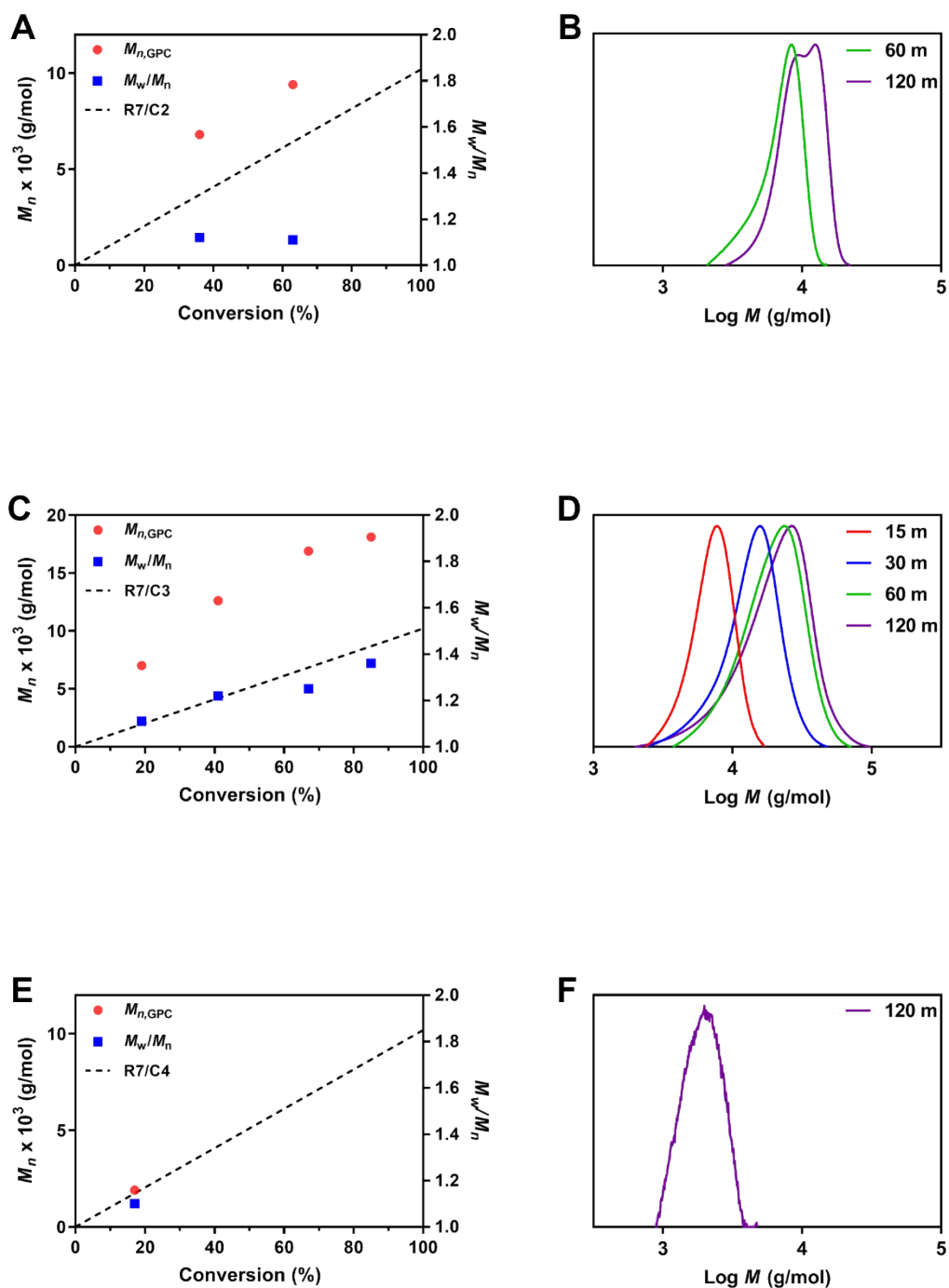


Figure S10. PET-RAFT polymerization of DMA conducted in 96-well plates irradiated under green LED light ($\lambda_{\text{max}} = 530 \text{ nm}$, 5.5 mW/cm^2) targeted at $([\text{DMA}]:[\text{DTC2}]:[\text{Catalyst}] = 100:1:0.015$ and $[\text{DMA}]_0 = 1.0 \text{ M}$) using three different catalysts. Evolution of the GPC derived molecular weight and dispersity with monomer conversion conducted with **DTC2** RAFT agent using (A) C2, (C) C3, (E) C4 catalysts. The respective molecular weight distributions at various time points for the corresponding M_n versus conversion graph using different catalysts (B) C2, (D) C3, (F) C4.

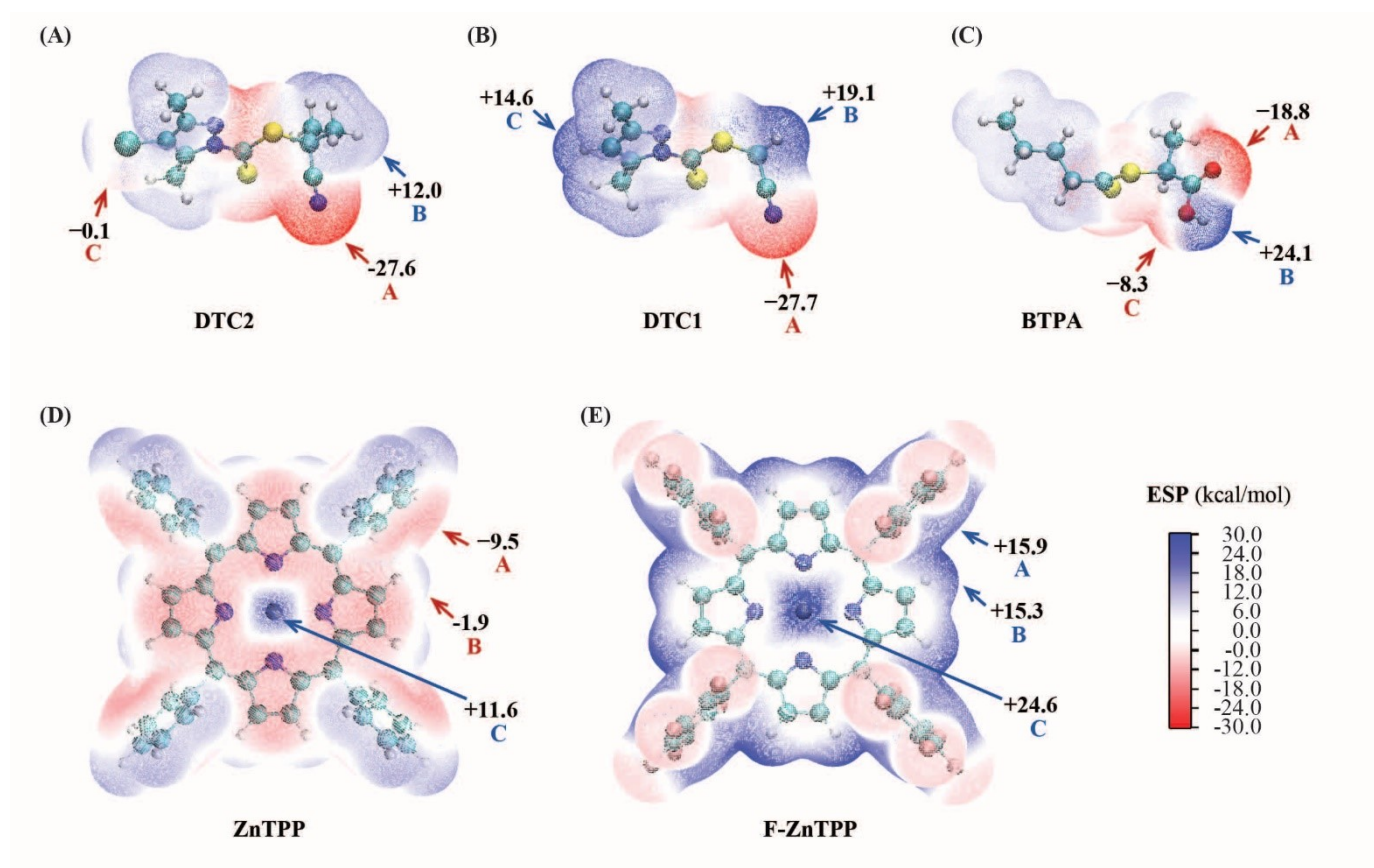


Figure S11. Electrostatic potential (ESP) surfaces for (A) R7 (DTC2), (B) R6 (DTC1), (C) R1 (BTPA), (D) C1 (ZnTPP) and (E) C3 (F-ZnTPP) respectively, calculated at the B3LYP-GD3BJ/def2-SVP level of theory with SMD-water solvation model.

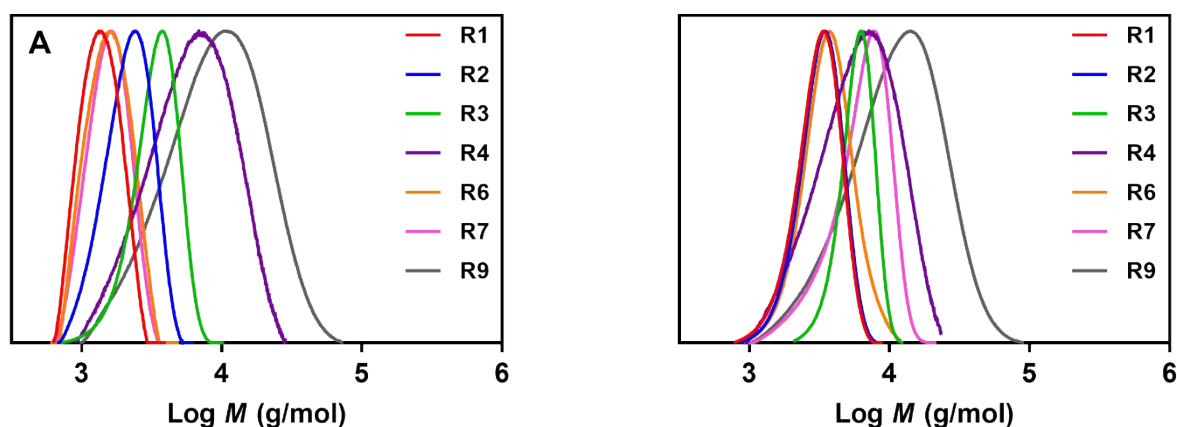


Figure S12. Molecular weight distributions for *N,N*-dimethylacrylamide (DMA) polymers prepared using PET-RAFT polymerization conducted in 96-well plates. Polymerizations were conducted for 4 hours under green LED light ($\lambda_{\text{max}} = 530 \text{ nm}$, 5.5 mW/cm^2) targeted at ($[\text{Monomer}]:[\text{RAFT}]:[\text{Catalyst}] = 100:1:0.015$ and $[\text{Monomer}]_0 = 1.0 \text{ M}$), catalyzed by non-metalated catalyst (A) FTPP, (B) TCPP.

Additional discussion on the interactions between C3 and RAFT agents

A peculiar result was observed for C3 (F-ZnTPP) and DTC2 (R7). Among all the ten RAFT agents, DTC2 (R7) exhibited the fastest polymerization kinetics in the presence of C3, almost twice the k_p^{app} of the DTC1 (R6) system and eight times the k_p^{app} of the BTPA (R1) system. The slow polymerization kinetics observed with BTPA mediated by C3 was ascribed to the highly electron withdrawing of fluorine substituents present on C3, which reduces the lowest triplet excited state (T_1) state of C3. The low T_1 state is unable to effectively activate BTPA (R1) and therefore the polymerization.³

To understand the unusual superiority of C3 over other photocatalysts to activate R7, we performed electrostatic potential (ESP) analysis for C1 (ZnTPP) and C3 (F-ZnTPP) to visualize the distribution of electrostatic potentials on their molecular surfaces. Molecular electrostatic potential maps illustrate information about the charge distribution of a molecule or electron distribution (**SI, Figure S7**). A region of higher-than-average electrostatic potential energy indicates the absence of negative charges, which means that there are fewer electrons in this region. In contrast, a negative electrostatic potential energy indicates rich electron domains. The presence of 20 highly electron-withdrawing -F atoms on the phenyl rings of F-ZnTPP (**SI, Figure S7E**) renders the middles of the four phenyl rings (site **A**) and the peripheral H atoms (site **B**) of porphyrin highly positively charged (ca. 15-16 kcal/mol). This is in stark contrast to those in ZnTPP (**SI, Figure S7D**) – the middles of the phenyl rings (site **A**) and peripheral H (site **B**) of porphyrin are negatively charged (electron rich). Meanwhile, we noted that DTC2 (R7) (**SI, Figure S7A**) has a strongly negative -CN group (site **A**, -27.6 kcal/mol). The presence of this negative charge on site **A** of DTC2 can interact with the positive sites **A** and **B** of F-ZnTPP. In addition, the electron-withdrawing effect of the -CN group is enhanced by its interaction with F-ZnTPP which affects the electron density of C-S bond, weakening the C-S bond in DTC2. Moreover, F-ZnTPP also exhibits a more positively charged Zn centre (site **C**, 24.6 kcal/mol) compared to ZnTPP with a much less positive Zn centre (site **C**, 11.6 kcal/mol). The negative dithioester-imidazole plane can also form π - π conjugation with one of the pentafluorophenyl groups.

To test this hypothesis, we optimized the geometry of the T_1 state of F-ZnTPP/DTC2 exciplex. The equilibrium geometry of the exciplex corresponds to the geometry proposed (see **Figure 5A**, middle), i.e., site **C** (Cl atom) of DTC2 binding with site **C** of F-ZnTPP, dithioester-imidazole plane stacked with the porphyrin plane and site **A** of DTC2 exhibiting electrostatic affinity with site A/B of F-ZnTPP. Subsequently, we performed climbing-image nudged elastic band (CI-NEB)⁴⁻⁶ calculations to optimize the reaction path for the activation of DTC2 via T_1 state F-ZnTPP. As shown in **Figure 5A**, the starting point of this reaction path has a C-S bond length of 1.88 Å whereas the ending point bears a C-S bond length of 3.25 Å, in which DTC2 cleaved to a dimethylcyano-carbon radical and a dithioester leaving group. Encouragingly, this reaction path exhibited an energy barrier of 13.8 kcal/mol, which is deemed sufficiently low for efficient activation of PET-RAFT polymerization.⁷

Secondly, we performed NEB calculations to optimize a reaction path for activation of DTC1 (R6) by F-ZnTPP (**Figure 5B**). Consistent with the experimental observation (lower k_p^{app} than F-ZnTPP/DTC2), the F-ZnTPP/DTC1 system bears a higher energy barrier of 25.9 kcal/mol. We attributed this difference of energy of DTC1 to DTC2 in two aspects: (i) DTC1 does not have a -Cl group capable to interact with Zn which does not decrease the C-S dissociation bond energy; (ii) the carbon radical generated by DTC1 is a cyano-carbon radical which is less stable than that of DTC2.

As for BTPA (R1), we found its equilibrium geometry possessed a negative region (site **A**, -18.8 kcal/mol) located in the carbonyl group but less negative than -CN of DTC2 and DTC1. However, unlike the strong interaction of -CN groups in DTC2 and DTC1, the interaction of the carbonyl acid group is reduced due to the adjacent methyl group due to steric hindrance, which reduces the interactions with **A** and **B** sites of F-ZnTPP. However, by rotation of the carbonyl group, we were still able to locate a low-energy configuration where the carbonyl group can interact with site **A** and **B** in F-ZnTPP. A reaction path was found for the F-ZnTPP/BTPA (**Figure 5C**) system as well which displayed a higher energy barrier of 28.0 kcal/mol than the other two systems, partly because of this weak interaction. This high energy barrier calculated by NEB is consistent with the experimental observation that the F-ZnTPP/BTPA system displayed the lowest k_p^{app} .

Supporting Information - References

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