Supporting information

From 0-Dimension to 1-Dimensions: Au Nanocrystals as Versatile Plasmonic Photocatalyst for Broadband Light Induced RAFT Polymerization

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Preparation of Au NCs

Preparation of Au NSs.[S1] The seed solution consisted of trisodium citrate (5×10^{-4} M, 10 mL) and $HAuCl_4 \cdot 3H_2O$ (5×10^{-4} M, 10 mL). Next, 0.6 mL of ice-cold, freshly prepared 0.1 M $NaBH_4$ solution was added to the solution while stirring. The seed solution was kept at 25 °C and used within 2−3 h. For the growth solution, $HAuCl_4 \cdot 3H_2O$ (5×10^{-4} M, 45 mL) was mixed with CTAB (0.16 M, 45 mL). Ascorbic acid (0.1 M, 0.5 mL) was added to the growth solution. Next, 7 mL of seed solution was added while stirring. The particles prepared here were denoted as NS-A and also used as seeds for preparing NS-B 30 min after preparation. Au NSs were purified by centrifugation at 13000 rpm. NS-B was prepared by the same method.

Preparation of Au NRs.[S2] The seed solution consisted of CTAB (0.2 M, 10 mL) and $HAuCl_4 \cdot 3H_2O$ (5×10^{-4} M, 10 mL). Then, $NaBH_4$ (0.01 M, 0.46 mL) in 0.01 M NaOH was added to the solution while stirring. The seed solution was kept at 25 °C and used within 2−3 h. For the growth solution, $HAuCl_4 \cdot 3H_2O$ (1×10^{-3} M, 100 mL) was mixed

with CTAB (0.2 M, 100 mL). Next, a certain amount of 0.01 M AgNO$_3$ solution (1, 2, 3, 5 and 8 mL, respectively) were added to the growth solution. After vigorous mixing, hydroquinone (0.1 M, 10 mL) was added sequentially into each sample under stirring. Finally, the seed solution (3.2 mL) was added into the growth solution, mixed thoroughly, and allowed to age overnight at 27 °C. Au NRs were purified by centrifugation at 13000 rpm. The Au NRs were denoted as NR-A, NR-B, NR-C, NR-D and NR-E, respectively.

Table S1 Summary of different Au NCs

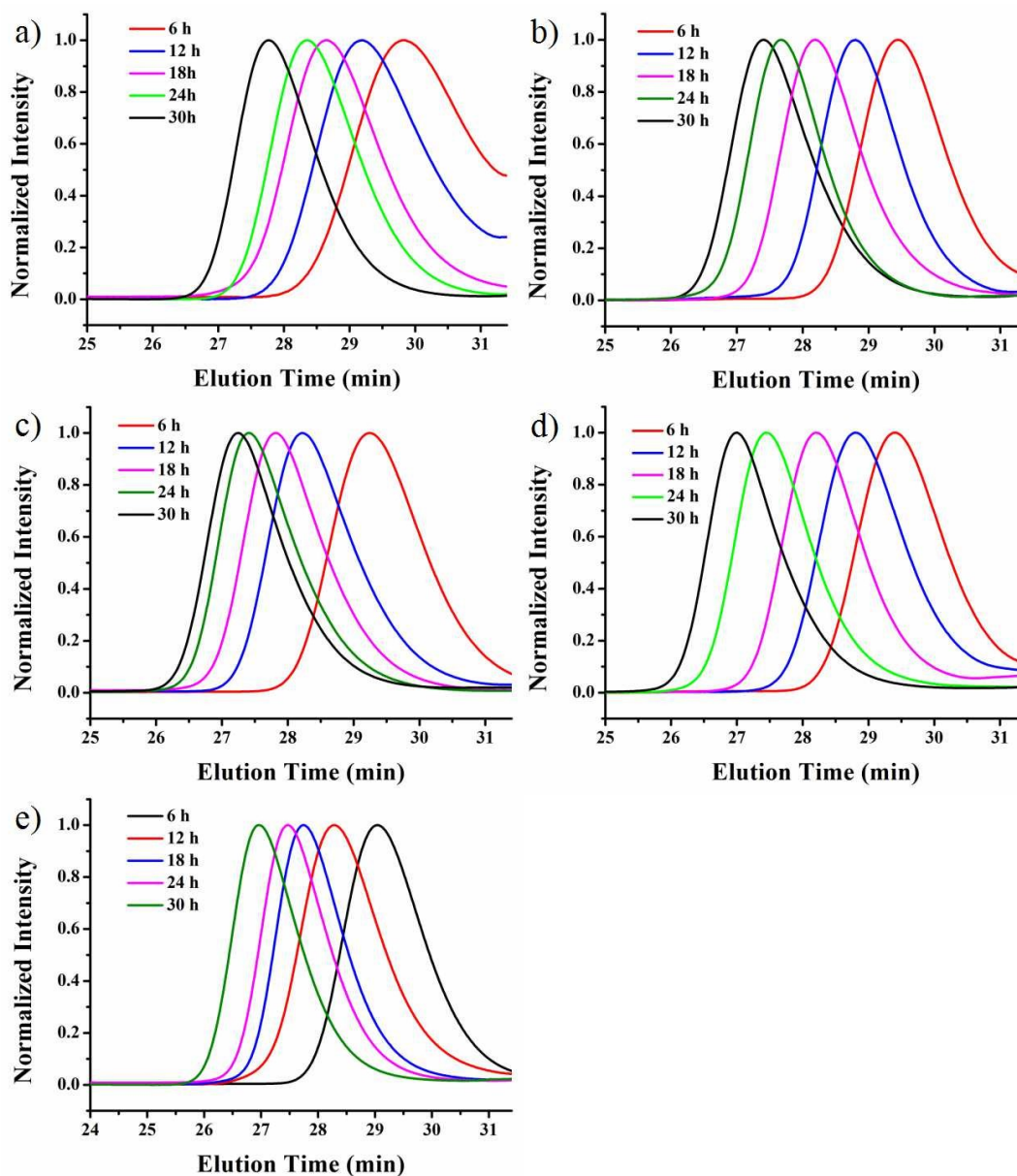| Au NCs	Length (nm)	Diameter (nm)	Aspect Ratio	SPR$_T$ (nm)	SPR$_L$ (nm)
NS-A	/	12±2	/	525	/
NS-B	/	19±2	/	531	/
NR-A	53±4	25±1	2.1	528	603
NR-B	64±6	21±2	3.0	520	741
NR-C	64±6	12±2	5.3	513	855
NR-D	89±6	9±2	9.9	506	1068
NR-E	90±6	8.0±1	11.2	505	1072

Fig. S1 GPC traces of PET-RAFT polymerization of MMA catalyzed by Au NRs: a) NR-A, b) NR-B, c) NR-C, d) NR-D, e) NR-E. Room temperature; Green light (λ_{max} = 532 nm, 1.5 mW/cm^2).

Table S2 Au NCs catalyzed PET-RAFT polymerization of MMA with different NCs amounts

Entry	Au NCs	[M]:[CTA][a]	m_{pc} (mg)	Conv.[b] (%)	$M_{n,th}$[c] (KDa)	$M_{n,GPC}$[d] (KDa)	M_w/M_n[d]

1	NR-C	200:1	0.25	23.6	5.0	6.3	1.16
2	NR-C	200:1	0.50	47.3	9.7	10.2	1.15
3	NR-C	200:1	0.75	56.1	11.5	12.5	1.16
4	NR-C	200:1	1.0	57.0	11.7	12.4	1.15
5	NR-D	200:1	0.25	47.4	9.8	10.6	1.15
6	NR-D	200:1	0.50	62.4	12.8	13.8	1.15

[a] The polymerizations were performed in DMF at room temperature using CPADB as CTA for MMA under green LED light irradiation (λ_{max} = 532 nm, 1.5 mW/ cm^2) for 30 hours; [b] Monomer conversion was calculated based on ^{1}H-NMR analysis; [c] Theoretical molecular weight was calculated according to the equation: $M_{n,th} = [M]_0/[CTA]_0 \times M_W^M \times \alpha + M_W^{CTA}$, where $[M]_0$, $[CTA]_0$, M_W^M, α, and M_W^{CTA} represent the initial monomer concentration, initial CTA concentration, molar mass of the monomer, conversion, and molar mass of CTA; [d] Molecular weight and dispersity were determined by GPC using THF as eluent.
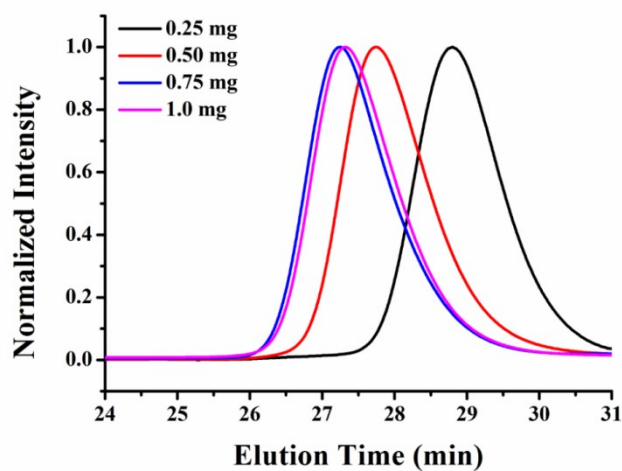

Fig. S2 GPC traces of PET-RAFT polymerization of MMA with different amounts of NR-C (Table S2, entries 1-4).
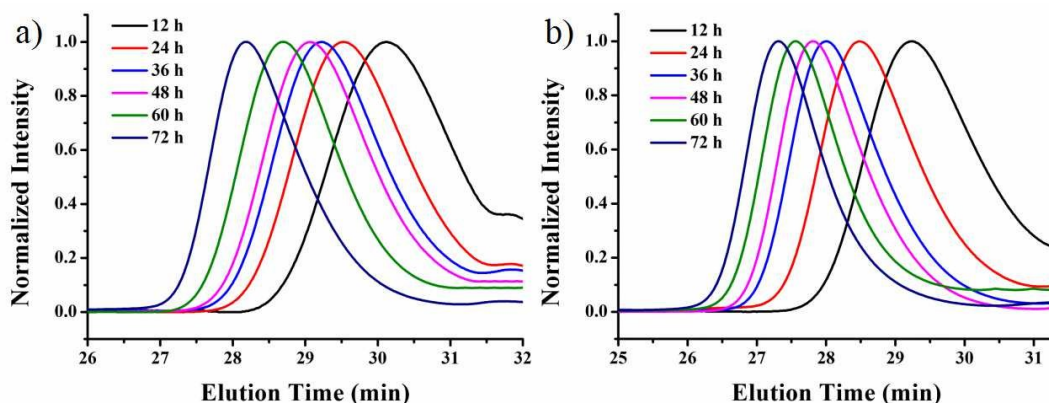
Fig. S3 GPC traces of PET-RAFT polymerization of MMA catalyzed by Au NRs (NR-B): a) No TEA, b) involving TEA. Room temperature; NIR light (λ_{max} = 740 nm, 0.7 mW/cm^2).
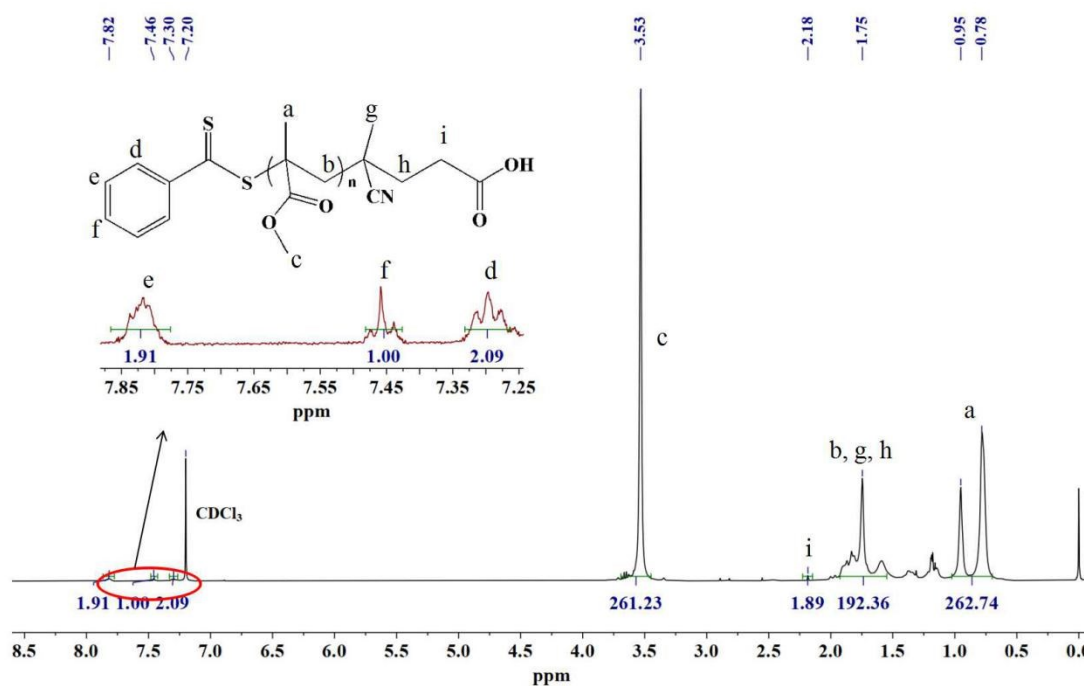

Fig. S4 ^{1}H-NMR spectrum of PMMA synthesized by PET-RAFT polymerization catalyzed by NR-D ($M_{n,th}$ = 8.8 KDa, $M_{n,GPC}$ = 8.7 KDa, $M_{n,NMR}$ = 9.0 KDa).

Note: Molecular weight determined by NMR analysis using $M_{n,NMR} = (I_c/3)/I_f \times M_W^{MMA} + M_W^{CPADB}$, where I_c and I_f correspond to integrals of signal at 3.53 ppm and 7.46 ppm attributed to OCH$_3$ of MMA and phenyl group of CPADB agent (Z-group).

Table S3 Au NCs catalyzed PET-RAFT polymerization of MMA in different solvents

Entry	Au NCs	[M]:[CTA][a]	Solvent	Conv.[b] (%)	$M_{n,th}$[c] (KDa)	$M_{n,GPC}$[d] (KDa)	M_w/M_n[d]
1	NR-D	300:1	DMSO	89.7	27.2	30.5	1.19
2	NR-D	300:1	DMF	77.7	23.6	23.4	1.12
3	NR-D	300:1	MeCN	50.5	15.4	19.0	1.16
4	NR-D	300:1	THF	42.7	13.1	15.9	1.14
5	NS-B	300:1	THF	18.8	5.9	9.5	1.21
6	NR-A	300:1	THF	22.6	7.1	10.3	1.13
7	NR-C	300:1	THF	31.4	9.7	13.2	1.11

[a] The polymerizations were performed at room temperature using CPADB as CTA for MMA under green LED light irradiation (λ_{max} = 532 nm, 1.5 mW/cm^2) for 30 hours; [b] Monomer conversion was calculated based on ^{1}H-NMR analysis; [c] Theoretical molecular weight was calculated according to the equation: $M_{n,th} = [M]_0/[CTA]_0 \times M_W^M \times \alpha + M_W^{CTA}$, where $[M]_0$, $[CTA]_0$, M_W^M, α, and M_W^{CTA} represent the initial monomer concentration, initial CTA concentration, molar mass of the monomer, conversion, and molar mass of CTA; [d] Molecular weight and dispersity were determined by GPC using THF as eluent.
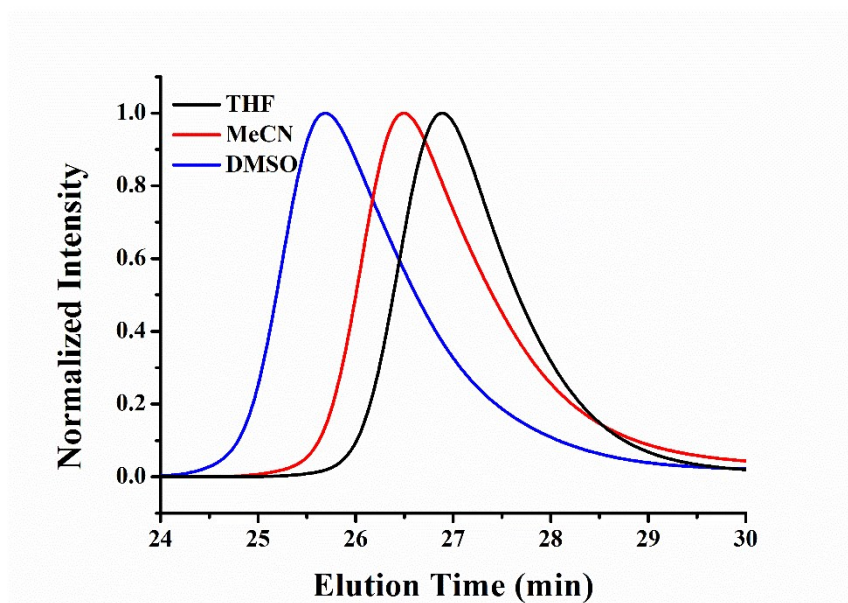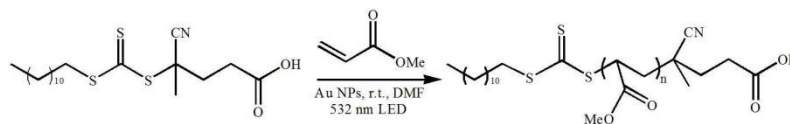
Fig. S5 GPC traces of PET-RAFT polymerization of MMA catalyzed by Au NRs (NR-D) in different solvents (Table S3, entries 1, 3, 4).

Table S4 Au NCs catalyzed PET-RAFT polymerization of different monomers

Entry	Au NCs	[M]:[CTA]^a	Monomer	Conv.^{b} (%)	$M_{\text{n,th}}{}^c$ (KDa)	$M_{\text{n,GPC}}{}^d$ (KDa)	$M_{\text{w}}/M_{\text{n}}{}^d$
1	NR-D	300:1	MA	68.5	18.0	19.6	1.16
2	NR-D	300:1	BA	45.3	17.7	19.0	1.18
3	NR-D	300:1	St	30.4	9.8	6.8	1.19

^{a} The polymerizations were performed in DMF at room temperature using CDTPA as CTA under green LED light irradiation ($\lambda_{\max}$ = 532 nm, 1.5 mW/cm^2) for 30 hours; ^{b} Monomer conversion was calculated based on ^{1}H-NMR analysis; ^{c} Theoretical molecular weight was calculated according to the equation: $M_{\text{n,th}} = [M]_0/[CTA]_0 \times M_{\text{W}}^{\text{M}} \times \alpha + M_{\text{W}}^{\text{CTA}}$, where $[M]_0$, $[CTA]_0$, M_{W}^{M}, α, and $M_{\text{W}}^{\text{CTA}}$ represent the initial monomer concentration, initial CTA concentration, molar mass of the monomer, conversion, and molar mass of CTA; ^{d} Molecular weight and dispersity were determined by GPC using THF as eluent.
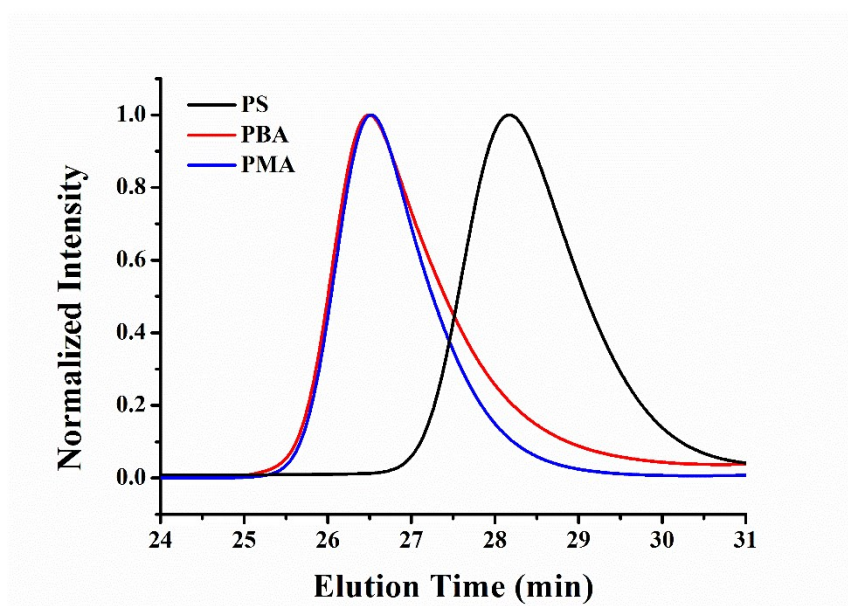
Fig. S6 GPC traces of PET-RAFT polymerization of different monomers catalyzed by Au NRs (NR-D) (Table S4).
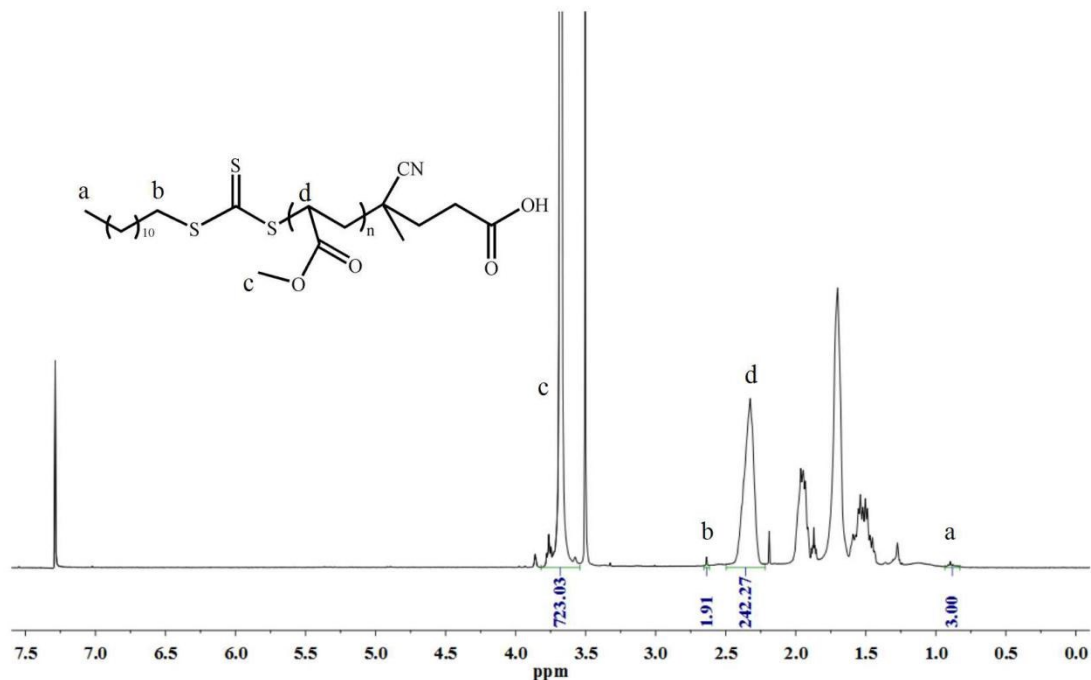

Fig. S7 ^{1}H-NMR spectrum of PMA synthesized by PET-RAFT polymerization catalyzed by NR-D (Table S4, entry 1) ($M_{n,NMR}$ = 21.1 KDa).

Note: Molecular weight determined by NMR analysis using $M_{n,NMR} = (I_c/3)/(I_a/3) \times M_W^{MA} + M_W^{CDTPA}$, where I_c and I_a correspond to integrals of signal attributed to OCH_3 of MA and methyl group of CDTPA agent (Z-group).
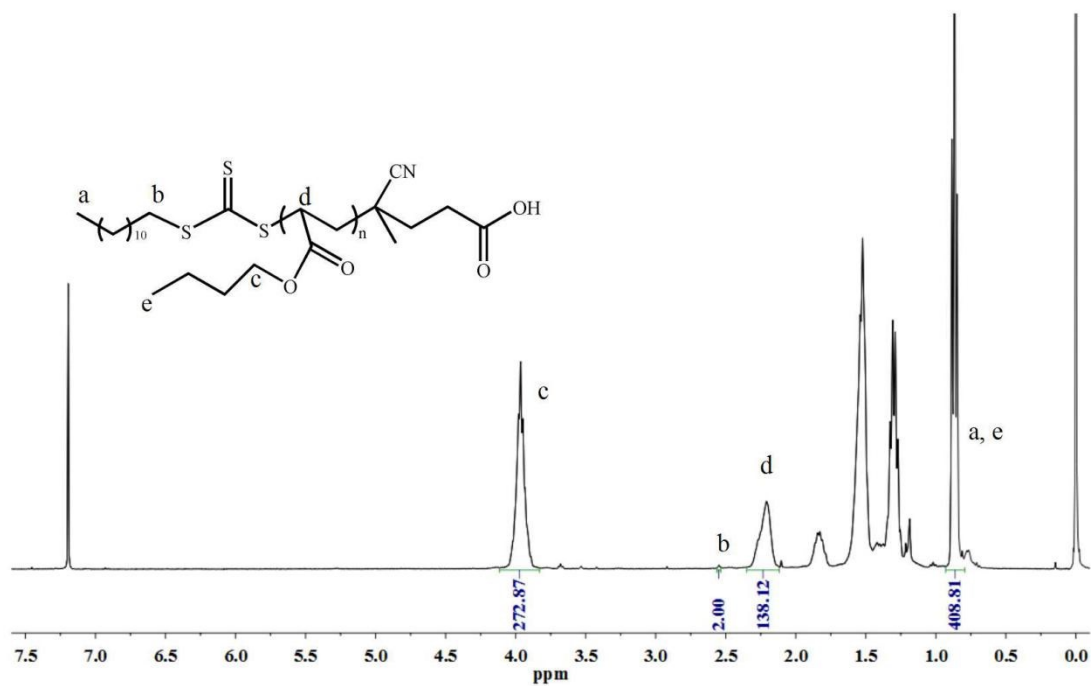
Fig. S8 ^{1}H-NMR spectrum of PBA synthesized by PET-RAFT polymerization catalyzed by NR-D (Table S4, entry 2) ($M_{n,NMR}$ = 17.9 KDa).

Note: Molecular weight determined by NMR analysis using $M_{n,NMR} = (I_c/2)/(I_b/2) \times M_W^{BA} + M_W^{CDTPA}$, where I_c and I_b correspond to integrals of signal attributed to CH_2O of BA and sulfur-linked methylene group of CDTPA agent (Z-group).
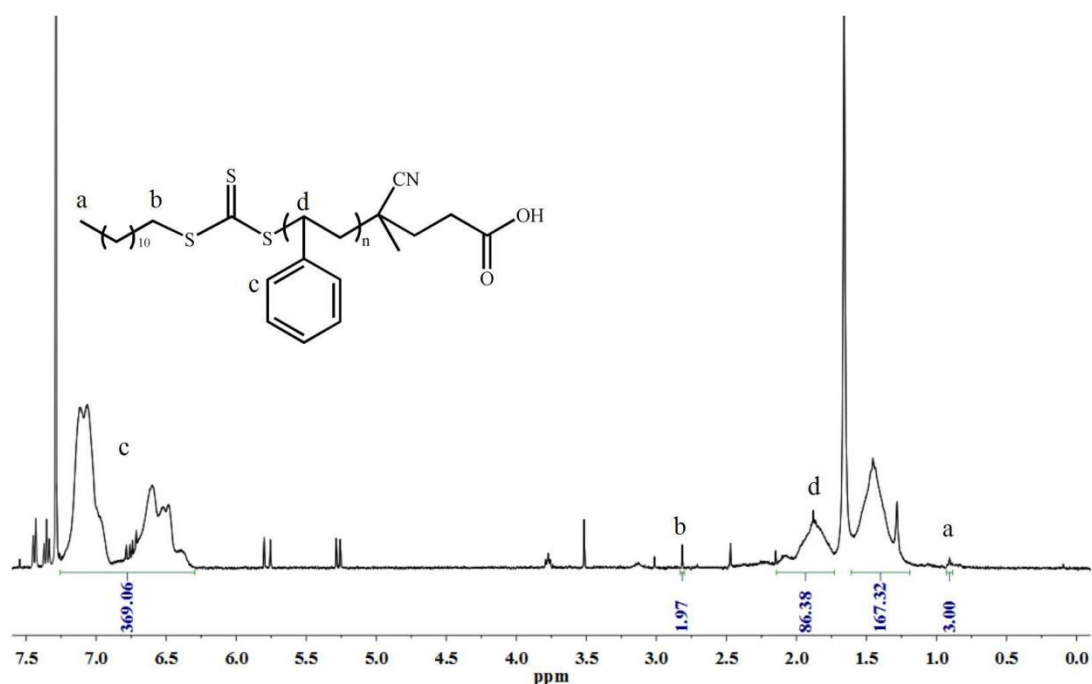
Fig. S9 ^{1}H-NMR spectrum of PS synthesized by PET-RAFT polymerization catalyzed by NR-D (Table S4, entry 3) ($M_{n,NMR}$ = 8.1 KDa).

Note: Molecular weight determined by NMR analysis using $M_{n,NMR} = (I_c/5)/(I_a/3) \times M_W^{St} + M_W^{CDTPA}$, where I_c and I_a correspond to integrals of signal attributed to phenyl group of St and methyl group of CDTPA agent (Z-group).

Table S5 Au NCs catalyzed PET-RAFT polymerization for MMA with different DP

Entry	Au NCs	[M]:[CTA]^a	Solvent	Conv.^{b} (%)	$M_{n,th}^c$ (KDa)	$M_{n,GPC}^d$ (KDa)	M_w/M_n ^{d}
1	NR-D	100:1	DMF	66.7	6.9	6.8	1.16
2	NR-D	200:1	DMF	66.3	13.6	14.7	1.15
3	NR-D	300:1	DMF	77.7	23.6	23.4	1.12
4	NR-D	400:1	DMF	73.8	29.8	33.9	1.15

^{a} The polymerizations were performed in DMF at room temperature using CPADB as CTA for MMA under green LED light irradiation (λ_{max} = 532 nm, 1.5 mW/cm^2) for 30 hours; ^{b} Monomer conversion was calculated based on ^{1}H-NMR analysis; ^{c} Theoretical molecular weight was calculated according to the equation: $M_{n,th} = [M]_0/[CTA]_0 \times M_W^M \times \alpha + M_W^{CTA}$, where $[M]_0$, $[CTA]_0$, M_W^M, α, and M_W^{CTA} represent the initial monomer concentration, initial CTA concentration, molar

mass of the monomer, conversion, and molar mass of CTA; [d] Molecular weight and dispersity were determined by GPC using THF as eluent.
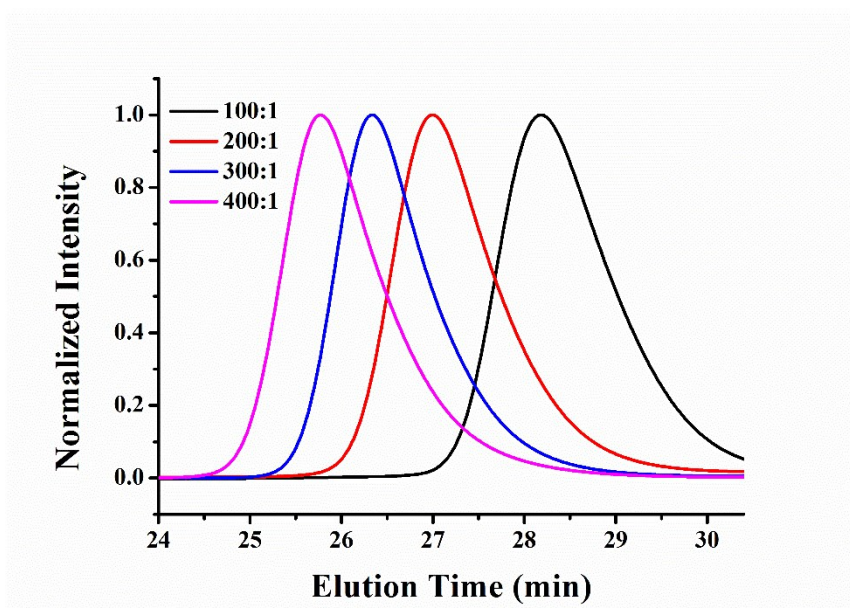

Fig. S10 GPC traces of PET-RAFT polymerization of MMA with different DP catalyzed by Au NRs (NR-D) (Table S5).
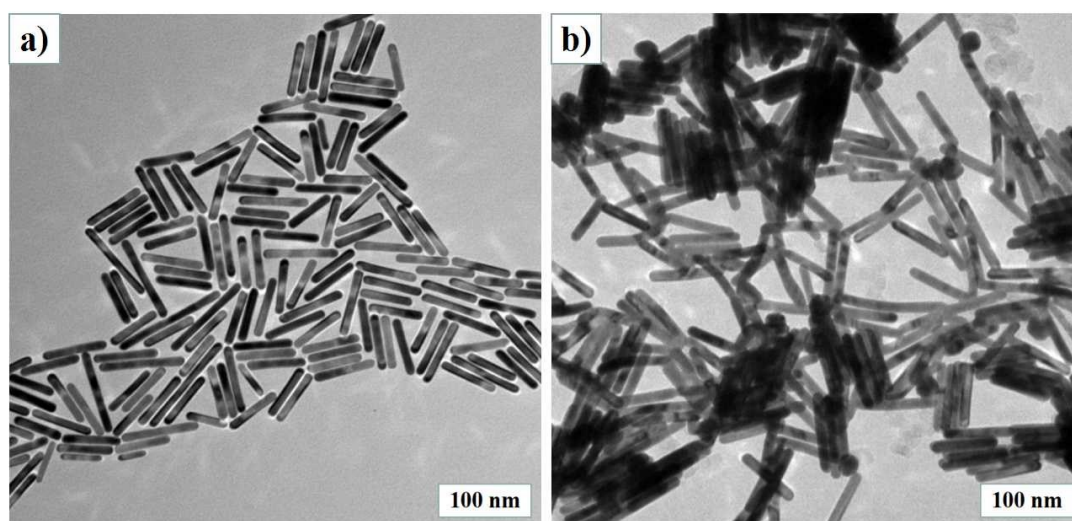

Fig. S11 TEM image of regenerated Au NR-D photocatalyst before a) and after b) RAFT polymerization under green LED light (λ_{max} = 532 nm, 1.5 mW/ cm^2) for 30 h in DMF.

References

S1 N. R. Jana, L. Gearheart, C. J. Murphy, *Langmuir*, 2001, **17**, 6782-6786.

S2 L. Vigderman, E. R. Zubarev, *Chem. Mater.*, 2013, **25**, 1450-1457.