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Supporting Information

Ag-In-Zn-S Alloyed Nanocrystals as Photocatalysts of Controlled Light-Mediated Radical Polymerization

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EXPERIMENTAL

Materials. Silver nitrate (99%), indium(II) chloride (99%), zinc stearate (technical grade), 1-dodecanethiol (DDT, 98%), sulfur (99%), 1-octadecene (ODE, 90%), oleylamine (OLA, 70%), methyl methacrylate (MMA, 99%), trietylamine (Et_3N, 99.5%), methyl α-bromophenylacetate (MBP, 97%), 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (CPADB) and benzene-d_6 (100%, 99.6 atom % D) were supplied by Sigma-Aldrich (Merck KGaA, Darmstadt, Germany).

Preparation of the S/OLA Precursor. Sulfur powder (15 mg, 0.47 mmol) and OLA (1.0 mL) were loaded into a glass vial, which was then immersed in an ultrasonic bath. The mixture was sonicated at room temperature (for about 10 min) until a clear red solution was formed.

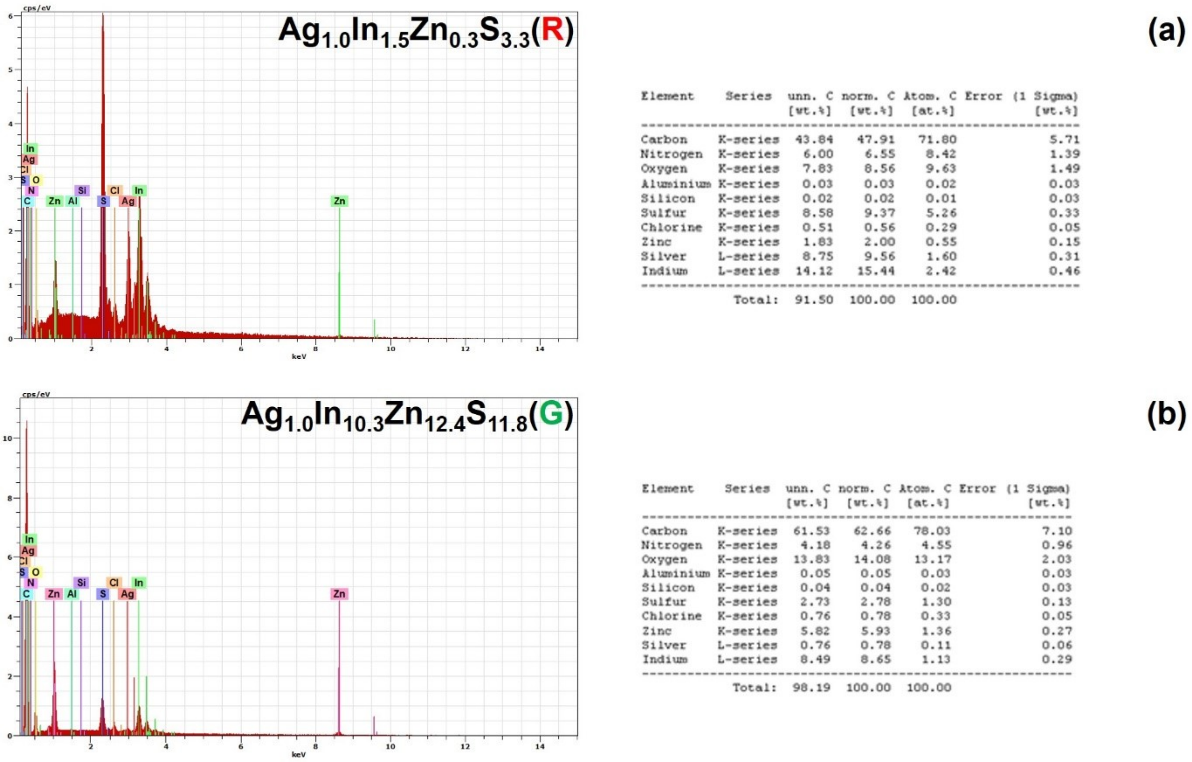
Preparation of Ag-In-Zn-S Nanocrystals (Red and Green). All operations were carried out under a constant dry argon flow. Silver nitrate (0.03 g, 0.18 mmol), indium(II) chloride (0.11 g, 0.59 mmol), DDT (0.20 g, 1.0 mmol), and zinc stearate (0.11 g, 0.18 mmol for **R** or 1.10 g, 1.62 mmol for **G**) were mixed with ODE (15 mL) in a three-neck flask. The mixture was heated to 150 °C until a homogeneous solution was formed. Then, 1 mL of the S/OLA precursor was quickly injected into the reaction solution. The temperature was increased to 180 °C, and the mixture was kept at this temperature for 60 min. After the mixture was cooled to room temperature, toluene (10 mL) was added, and the reaction mixture was centrifuged; the isolated black precipitate consisting of organic waste and agglomerated particles was separated. The supernatant was treated with 30 mL of acetone, leading to the precipitation of the desired fraction of nanocrystals. The nanocrystals were separated by centrifugation (7000 rpm, 5 min) and then redispersed in benzene-d_6.

Procedures for the Bulk Photopolymerization of Methyl Methacrylate. To a mixture of methyl methacrylate (8 mL), trietylamine (0.13 mL, 0.96 mmol) and methyl α-bromophenylacetate (0.1 mL, 0.60 mmol) was added $Ag_{1.0}In_{1.5}Zn_{0.3}S_{3.3}$ (**R**) (~1.4 mg in 0.1 mL of benzene-d_6) or $Ag_{1.0}In_{10.3}Zn_{12.4}S_{11.8}$ (**G**) (2.1 mg in 0.1 mL of benzene-d_6). The vial was sealed and purged with argon for 10 min before illumination by either ultraviolet (8 × 5.6 W LEDs, $\lambda = 365$ nm) or blue (16 × 4.3 W LEDs, $\lambda = 457$ nm) or green (16 × 16.4 W LEDs, $\lambda = 523$ nm) light using THALESNano photoreactor. After stirring at room temperature for 6 h, a small amount of the reaction mixture (0.1 mL) was diluted in benzene-d_6 or dichloromethane (0.5 mL) and analyzed *via* NMR spectroscopy or GPC respectively.

Procedure for the Solution Photopolymerization of Methyl Methacrylate. To a solution of methyl methacrylate (8 mL), trietylamine (0.13 mL, 0.96 mmol) and methyl α-bromophenylacetate (0.1 mL, 0.60 mmol) in benzene-d_6 (8 mL) was added $Ag_{1.0}In_{1.5}Zn_{0.3}S_{3.3}$

(**R**) (~1.4 mg in 0.1 mL of benzene-d_6) or $Ag_{1.0}In_{10.3}Zn_{12.4}S_{11.8}$ (**G**) (2.1 mg in 0.1 mL of benzene-d_6). The vial was sealed and purged with argon for 10 min before illumination by either blue (16 × 4.3 W LEDs, λ = 457 nm) light using THALESNano photoreactor. After stirring at room temperature for 1, 2, 3, 4 and 5 h, a small amount of the reaction mixture (0.1 mL) was diluted in benzene-d_6 or dichloromethane (0.5 mL) and analyzed *via* NMR spectroscopy or GPC respectively.

Characterization Methods. Elemental analysis was carried out with a multichannel Quantax 400 energy-dispersive X-ray spectroscopy (EDS) system with a 125 eV xFlash detector 5010 (Bruker) using a 15 kV electron beam energy. X-ray powder diffractograms were recorded at room temperature on a Bruker D8 Advance diffractometer equipped with a LYNXEYE position-sensitive detector using Cu Kα radiation (λ = 0.15418 nm). The data were collected in the Bragg-Brentano ($\theta/2\theta$) horizontal geometry (flat reflection mode) between 10° and 70° (2θ) in a continuous scan, using 0.04° steps at 960 s/step. The incident-beam path in the diffractometer was equipped with a 2.5° Soller slit and a 1.14° fixed divergence slit, whereas the path of the diffracted beam was equipped with a programmable antiscatter slit (fixed at 2.20°), a Ni β-filter, and a 2.5° Soller slit. The sample holder was rotated at an angular speed of 15 rpm. The data were collected under standard conditions (temperature and relative humidity). High-resolution images were acquired by a Tecnai TF20 X-TWIN (Thermo Fisher Scientific) microscope operated at 200 kV. UV-vis-NIR spectra were registered using a Cary 5000 (Varian) spectrometer. Steady-state PL spectra of toluene solutions of samples were measured with FLS-980 fluorescence spectrophotometer equipped with a 450 W Xe lamp and photomultiplier (Hamamatsu, R928P) detector with a standard 10 mm cuvette (λ_{exc} = 375 nm).[1] The quantum yields were examined using integrating sphere absolute method with solvent used as blank. The compounds were excited with wavelengths in each case corresponding to the obtained excitations. The emission correction file was used to take into account the sensitivity of the monochromator, detector, sphere coating and optics to wavelength. Each scans were conducted with 0.25 nm steps, 0.2 Dwell time as well as repeated 2 times. The FLS-980 software was used to designate the quantum yield values. The PL lifetime measurement was performed with a time correlated single photon counting (TCSPC) method on FLS-980 fluorescence spectrophotometer. The excitation wavelength (405 nm) was obtained using the picosecond pulsed diode laser (EPL - 405 nm, Edinburgh Instruments). The system was aligned at the emission wavelengths. Additionally, for the analysis of a fluorescence decay lower than 50ns, an instrument response function (IRF) was obtained. The IRF contains the information about the time response of the overall optical and electronic system. The IRF was designated using solutions of LUDOX® as a standard at excitation wavelength. The decay components were evaluated using the FLS-980 software. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance (500 MHz) spectrometer and referenced with respect to tetramethylsilane (TMS) and solvents. To record the 150 MHz ^{13}C NMR spectra a gated decoupling sequence was applied to avoid the nuclear Overhauser effect, and a good signal-to-noise ratio was achieved after 12000 scans. The spectra were obtained with a 4s delay (D1). The number-average molar mass (M_n) and the molecular weight distribution (Đ) of the samples were determined by Size Exclusion Chromatography (SEC). The system was composed of a Viscotek GPCmax unit (pumping and degassing of solvent, sample injection with autosampler), a 305TDA detection unit (consisting of column, a UV measuring cell, RI detector, hybrid Right-Angle Light Scattering/Low-Angle Light Scattering (RALS/LALS) detector, and a viscometer), and a PDA UV detector (190-500 nm). The system was equipped with a Jordi Labs DVB column (mixed bed, 5 μm), which worked with dichloromethane at 30 °C, with a flow rate of 1 cm^3/min. The MALDI-ToF mass spectra were recorded on a Bruker UltraFlex (Bremen, Germany) spectrometer using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as a matrix and analyzed with flexAnalysis v.3.3 (Bruker Daltonik GmbH) and Polymerix v. 2.0 (Sierra Analytics Inc.) software. The solutions for MALDI-ToF analyses were prepared by dissolving 5 mg of the sample in 1 mL of methylene chloride. Electron paramagnetic resonance (EPR) spectra were obtained with a Bruker EMX EPR spectrometer (Bruker-Biospin, Germany) operating at the X-band frequency (9.7 GHz) at room temperature. Typical instrument parameters were as follows: central field, 3480 G; modulation amplitude, 1.0 G; gain, 4.48×104 G; microwave power, 31.81 mW; sweep width, 100 G.



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Element    Series   unn. C  norm. C Atom. C Error (1 Sigma)
                    [wt.%]  [wt.%]  [at.%]          [wt.%]
-----------------------------------------------------------
Carbon    K-series  43.84   47.91   71.80           5.71
Nitrogen  K-series   6.00    6.55    8.42           1.39
Oxygen    K-series   7.83    8.56    9.63           1.49
Aluminium K-series   0.03    0.03    0.02           0.03
Silicon   K-series   0.02    0.02    0.01           0.03
Sulfur    K-series   8.58    9.37    5.26           0.33
Chlorine  K-series   0.51    0.56    0.29           0.05
Zinc      K-series   1.83    2.00    0.55           0.15
Silver    L-series   8.75    9.56    1.60           0.31
Indium    L-series  14.12   15.44    2.42           0.46
-----------------------------------------------------------
             Total: 91.50  100.00  100.00
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Element    Series   unn. C  norm. C Atom. C Error (1 Sigma)
                    [wt.%]  [wt.%]  [at.%]          [wt.%]
-----------------------------------------------------------
Carbon    K-series  61.53   62.66   78.03           7.10
Nitrogen  K-series   4.18    4.26    4.55           0.96
Oxygen    K-series  13.83   14.08   13.17           2.03
Aluminium K-series   0.05    0.05    0.03           0.03
Silicon   K-series   0.04    0.04    0.02           0.03
Sulfur    K-series   2.73    2.78    1.30           0.13
Chlorine  K-series   0.76    0.78    0.33           0.05
Zinc      K-series   5.82    5.93    1.36           0.27
Silver    L-series   0.76    0.78    0.11           0.06
Indium    L-series   8.49    8.65    1.13           0.29
-----------------------------------------------------------
             Total: 98.19  100.00  100.00
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Fig. S1 Energy-dispersive spectra of alloyed $\mathbf{Ag_{1.0}In_{1.5}Zn_{0.3}S_{3.3}}$ (**R**) (**a**) and $\mathbf{Ag_{1.0}In_{10.3}Zn_{12.4}S_{11.8}}$ (**G**) (**b**) nanocrystals.

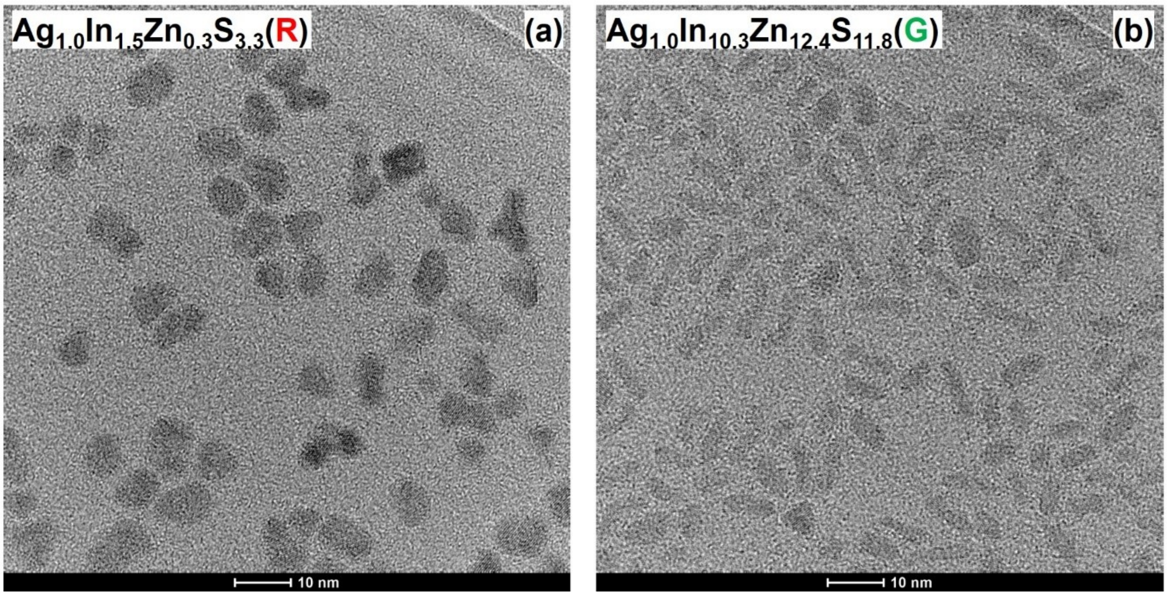

Fig. S2 HR-TEM images of alloyed $\mathbf{Ag_{1.0}In_{1.5}Zn_{0.3}S_{3.3}}$ (**R**) (**a**) and $\mathbf{Ag_{1.0}In_{10.3}Zn_{12.4}S_{11.8}}$ (**G**) (**b**) nanocrystals.

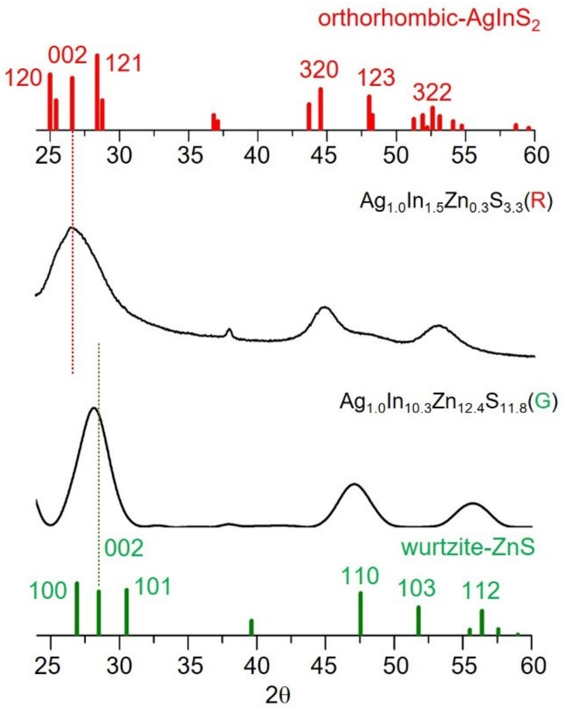

Fig. S3 X-ray diffraction (XRD) patterns of alloyed $\mathbf{Ag_{1.0}In_{1.5}Zn_{0.3}S_{3.3}}$ (**R**) and $\mathbf{Ag_{1.0}In_{10.3}Zn_{12.4}S_{11.8}}$ (**G**) nanocrystals. The red and green bars indicates respectively the diffraction pattern of orthorhombic $AgInS_2$ (JCPDS 00-025-1328) and wurtzite ZnS (JCPDS 00-036-1450).

Table S1. Photo-mediated polymerization of MMA (8 mL)

Entry	Nanocrystals (mL)	Solvent (mL)	Et_3N (mmol)	MBP (mmol)	Light (nm)	Time (h)	Conversion[a] (%)	$M_{n,theo}$[b] (kDa)	M_{nGPC}[c] (kDa)	Đ
1	A-1 (0.1)	-	-	-	365	6	24.0	-	313.8	2.53
2	A-4 (0.1)	-	-	-	365	6	25.0	-	134.9	3.07
3	A-1 (0.1)	-	-	-	457	6	14.5	-	-	-
4	A-4 (0.1)	-	-	-	457	6	0.0	-	-	-
5	A-1 (0.1)	-	1.0	-	457	6	41.3	-	318.7	2.90
6	A-4 (0.1)	-	1.0	-	457	6	13.8	-	-	-
7	A-1 (0.1)	-	-	0.6	457	6	5.0	-	-	-
8	A-4 (0.1)	-	-	0.6	457	6	7.7	-	-	-
9	A-1 (0.1)	C_6D_6 (8 mL)	1.0	0.6	457	1 (on)	45.6	5.9	4.9	1.32
						2 (off)	45.9	5.9	5.3	1.38
						3 (on)	85.3	10.9	13.9	1.41
						4 (off)	85.9	10.9	15.6	1.39
						5 (on)	94.5	12.0	17.8	1.45
10	A-4	C_6D_6 (8 mL)	1.0	0.6	457	1 (on)	35.0	4.6	3.6	1.21
						2 (off)	35.9	4.7	3.6	1.28
						3 (on)	59.3	7.6	14.2	1.15
						4 (off)	59.4	7.6	15.5	1.18
						5 (on)	85.9	10.9	18.3	1.29
11	A-1 (0.1)	-	-	-	523	6	0.0	-	-	-
12	A-4 (0.1)	-	-	-	523	6	0.0	-	-	-
13	A-1 (0.1)	-	1.0	-	523	6	15.0	-	-	-
14	A-4 (0.1)	-	1.0	-	523	6	0.0	-	-	-
15	A-1 (0.1)	-	-	0.6	523	6	9.3	-	-	-
16	A-4 (0.1)	-	-	0.6	523	6	0.0	-	-	-
17	A-1 (0.1)	-	1.0	0.6	523	6	98.0	12.5	86.9	1.75
18	A-4 (0.1)	-	1.0	0.6	523	6	63.0	8.1	93.4	1.82

[a]Determined by ^{1}H NMR analysis. [b]$M_{n,theo}$ = [monomer] /[initiator] × conversion × MW (monomer) + MW (initiator). [c]M_n measured by SEC in dichloromethane, based on linear polystyrene as the calibration standard.

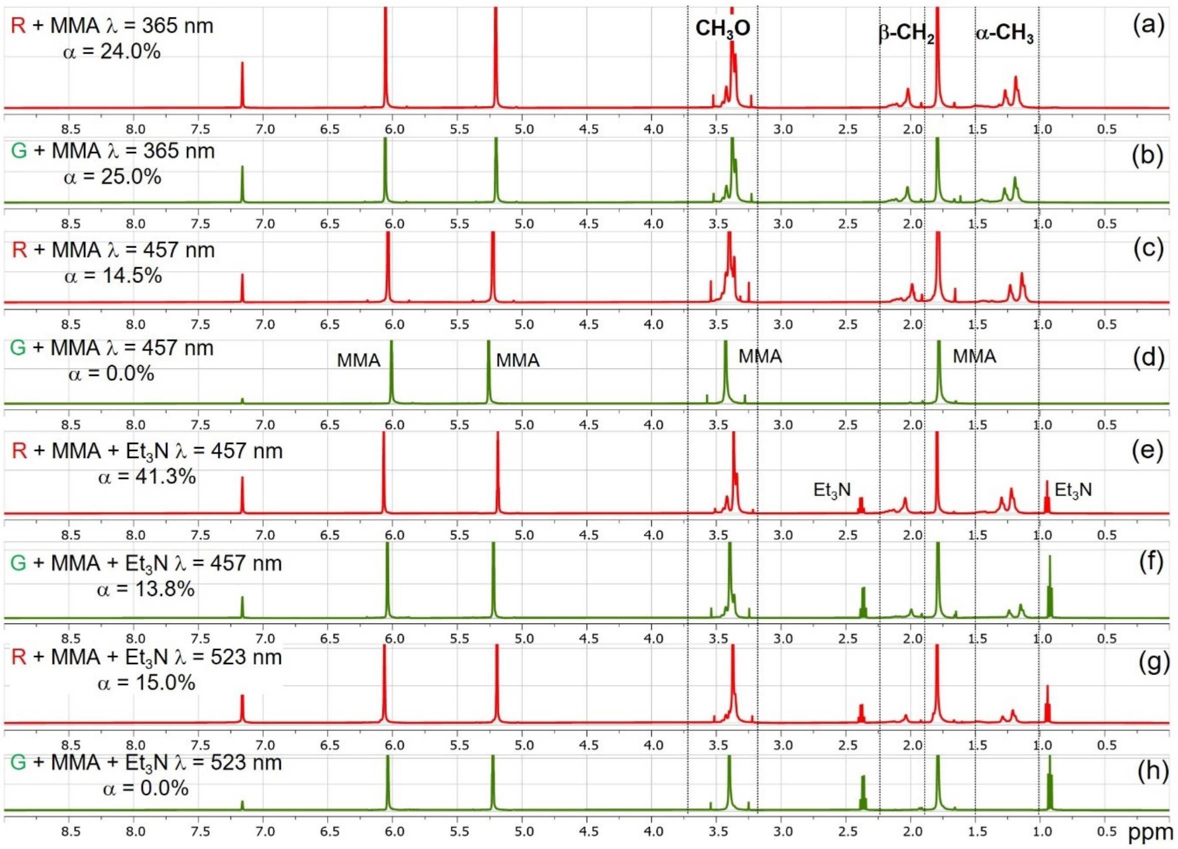

Fig. S4 ^{1}H NMR spectra (in benzene-d_6) of the reaction mixture used for the photocatalytic bulk polymerization of MMA with **R** (**a**,**c**,**e**,**g**) and **G** (**b**,**d**,**f**,**h**) nanocrystals as a photocatalyst.

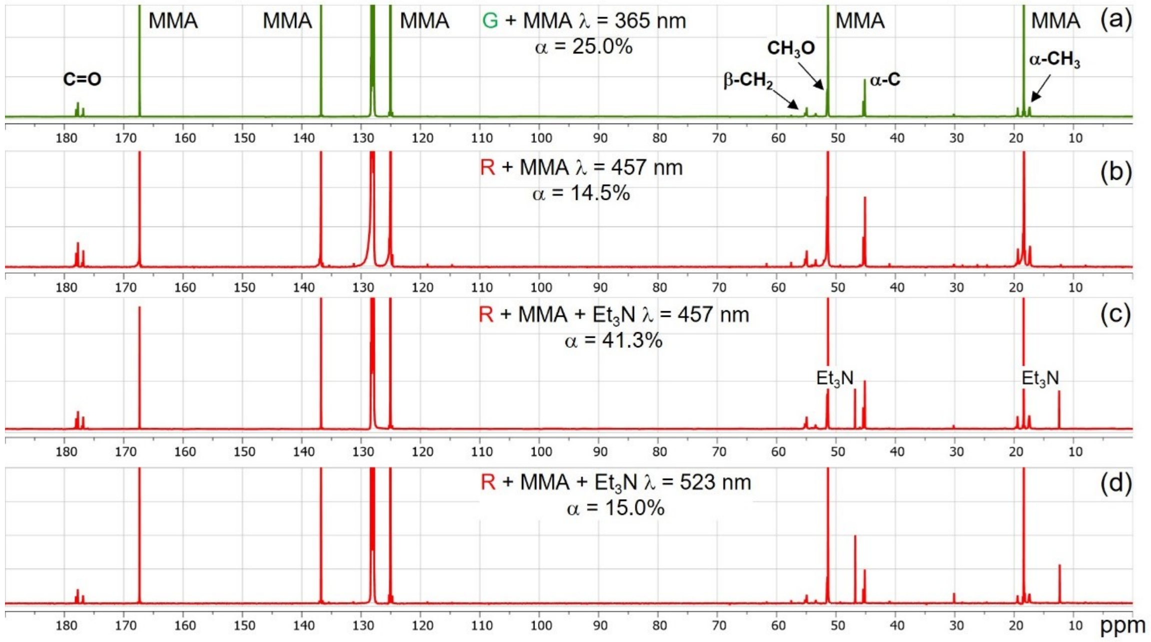

Fig. S5 ^{13}C NMR spectra (in benzene-d_6) of the reaction mixture used for the photocatalytic bulk polymerization of MMA with **G** (**a**) and **R** (**b**,**c**,**d**) nanocrystals as a photocatalyst.

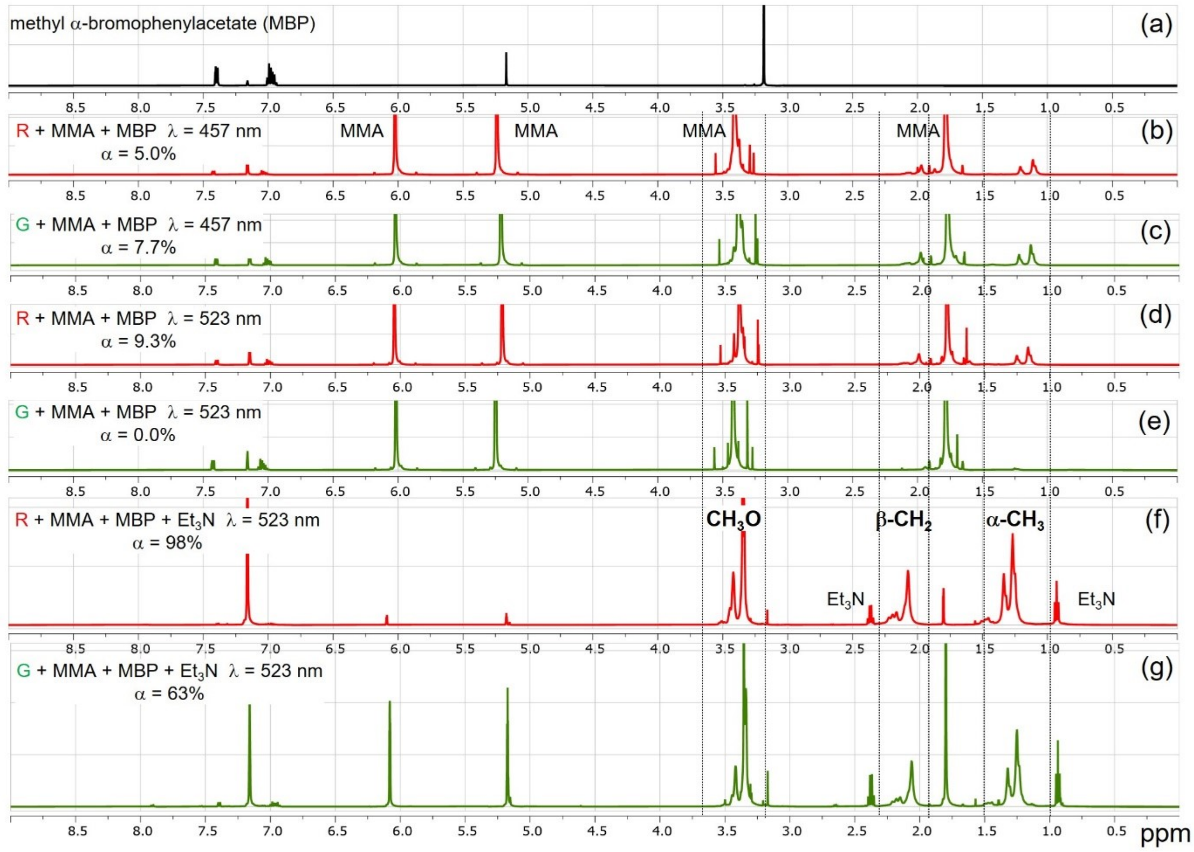

Fig. S6 ^{1}H NMR spectra (in benzene-d_6) of methyl α-bromophenylacetate (**a**) and the reaction mixture used for the photocatalytic bulk polymerization of MMA with **R** (**b**,**d**,**f**) and **G** (**c**,**e**,**g**) nanocrystals as a photocatalyst.

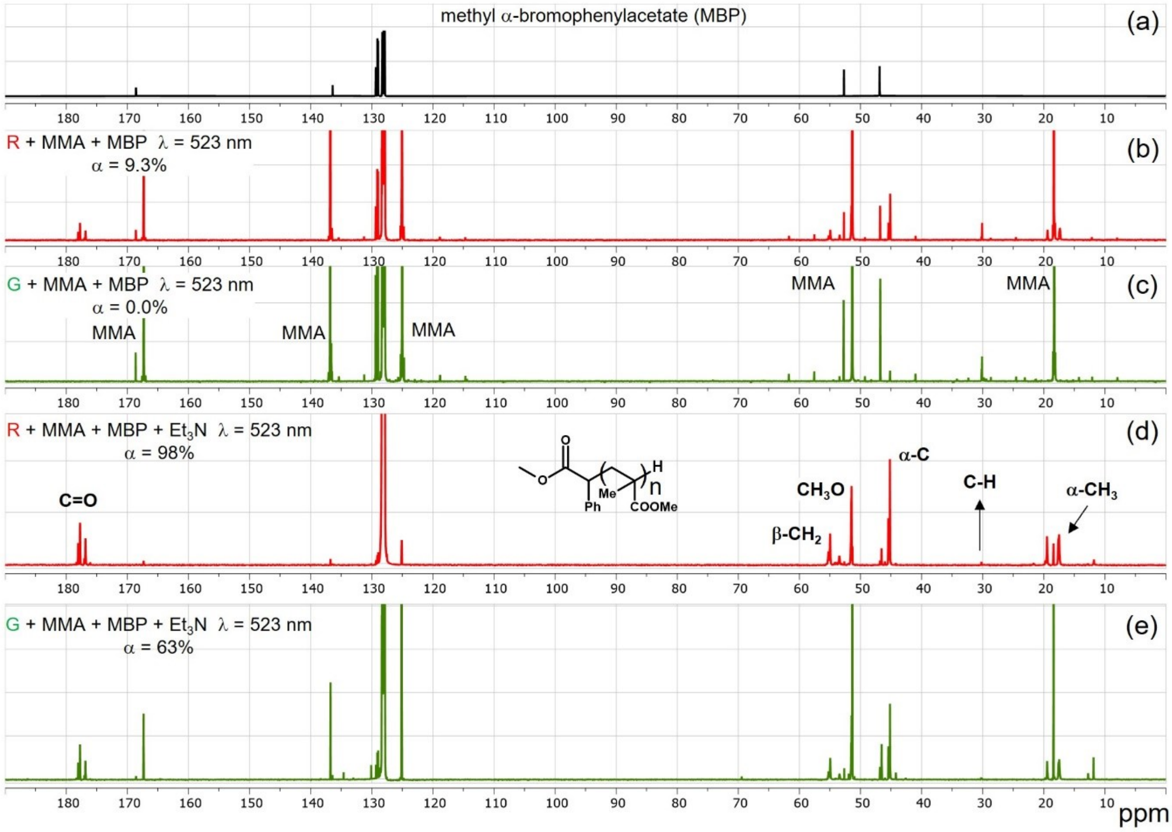

Fig. S7 ^{13}C NMR spectra (in benzene-d_6) of methyl α-bromophenylacetate (**a**) and the reaction mixture used for the photocatalytic bulk polymerization of MMA with **R** (**b**,**d**) and **G** (**c**,**e**) nanocrystals as a photocatalyst.

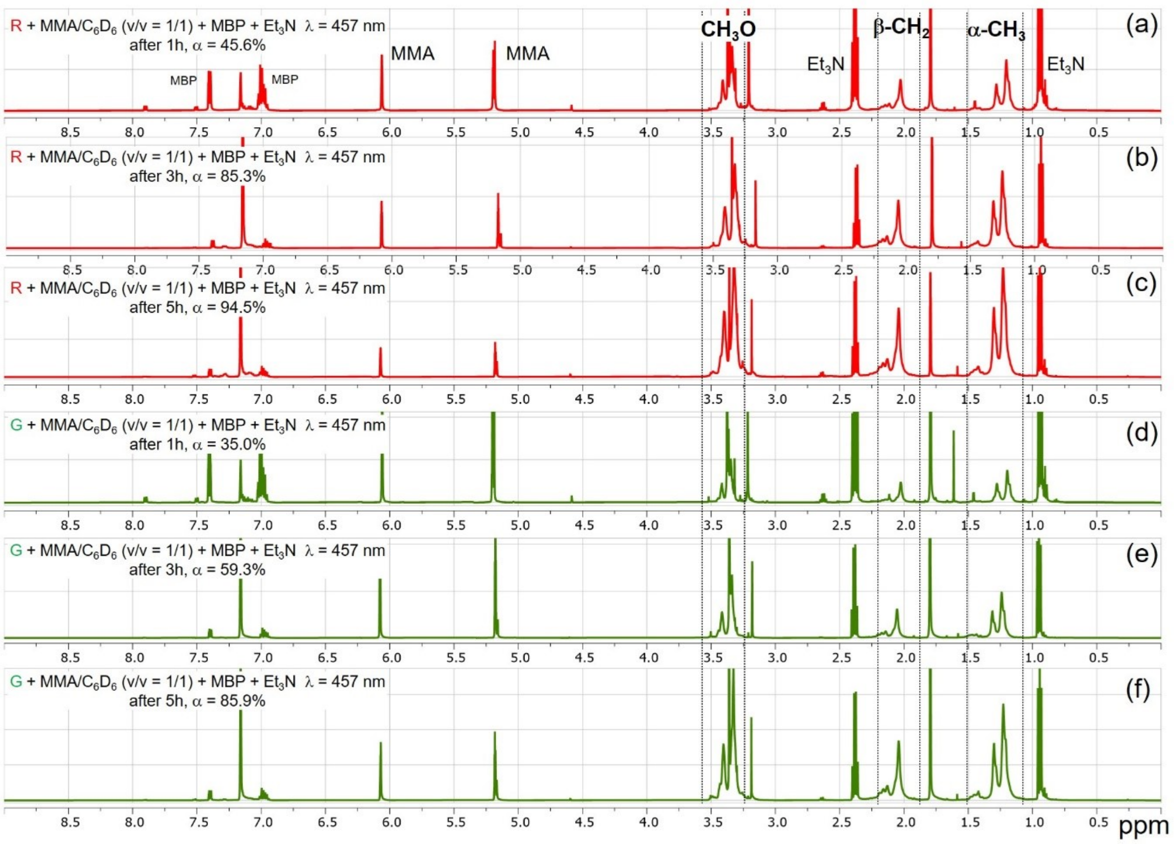

Fig. S8 ^{1}H NMR spectra (in benzene-d_6) of the reaction mixture used for the photocatalytic solution polymerization of MMA with **R** (**a**,**b**,**c**) and **G** (**d**,**e**,**f**) nanocrystals as a photocatalyst in the presence ("on") of blue light.

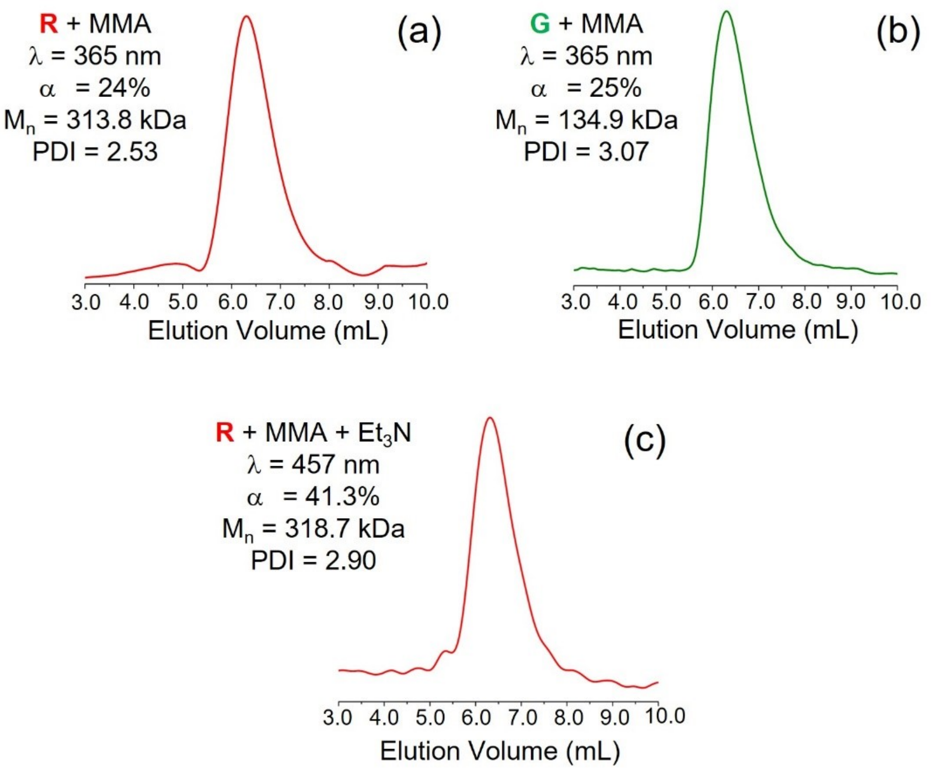

Fig. S9 SEC profiles of PMMA prepared in bulk polymerization under UV and blue light.

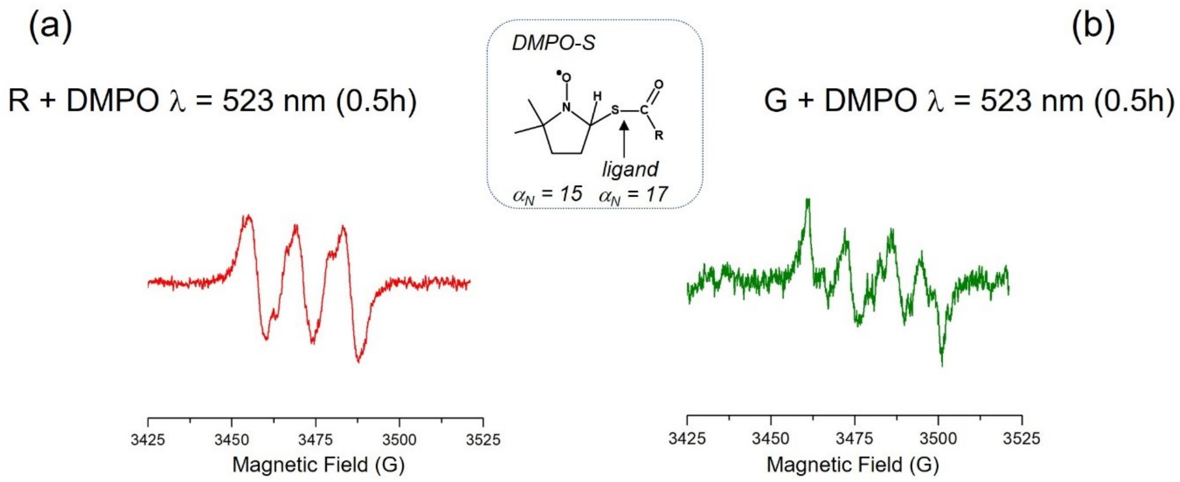

Fig. S10 Experimental EPR spectra of adducts generated for **R** (**a**) and **G** (**b**) nanocrystals + 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) under illumination by a green LED (λ = 523 nm).

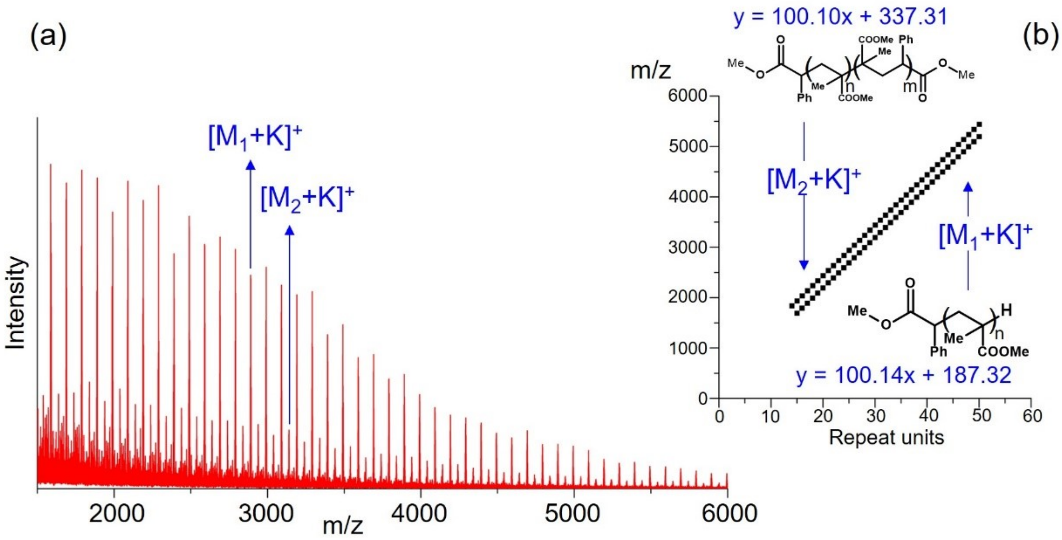

Fig. S11 (**a**) MALDI-TOF of PMMA and structural assignment of the polymer chains; (**b**) plot of mass-to-charge ratio (m/z) *vs* number of monomer repeat from the results of MALDI-TOF analysis of PMMA synthesized in the presence of **R** nanocrystals.

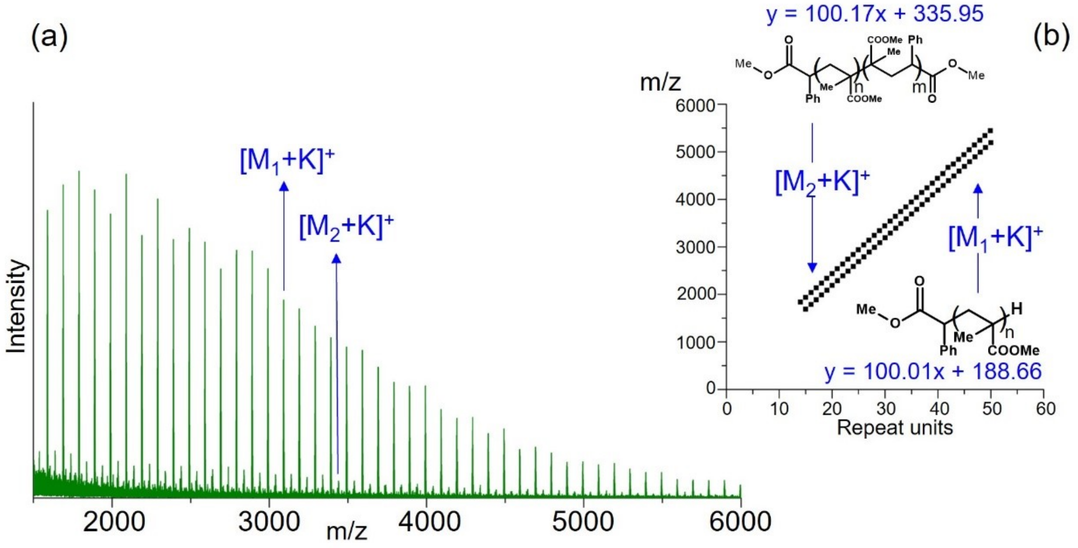

Fig. S12 (**a**) MALDI-TOF of PMMA and structural assignment of the polymer chains; (**b**) plot of mass-to-charge ratio (m/z) *vs* number of monomer repeat from the results of MALDI-TOF analysis of PMMA synthesized in the presence of **G** nanocrystals.

RAFT polymerizations of MMA in bulk were performed using quaternary Ag-In-Zn-S nanocrystals (sample **R** ~1.4 mg in 0.1 mL of benzene-d$_6$) as photocatalysts. A typical RAFT initiator was used in these experiments, namely 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (CPADB) and Et$_3$N as an electron donor (the same as that used in ATRP processes). The reaction mixtures consisted of 8 mL of MMA mixed with 25 mg (0.089 mmol) of CPADB and 0.15 mL (1.076 mmol) of Et$_3$N (CPABD/Et$_3$N molar ratio = 1:12). The polymerizations were carried out for 2 h under blue light (457 nm). PMMA with conversion of 95% were obtained as confirmed by ^{1}H NMR spectrum (see **Fig. S13**). The RAFT mechanism was confirmed by MALDI-TOF spectra in the low and high molecular weight ranges (see **Fig. S14 a** and **b**). The observed peaks correspond to PMMA chains capped with end groups originating from the fragmentation of the CPADB initiator.

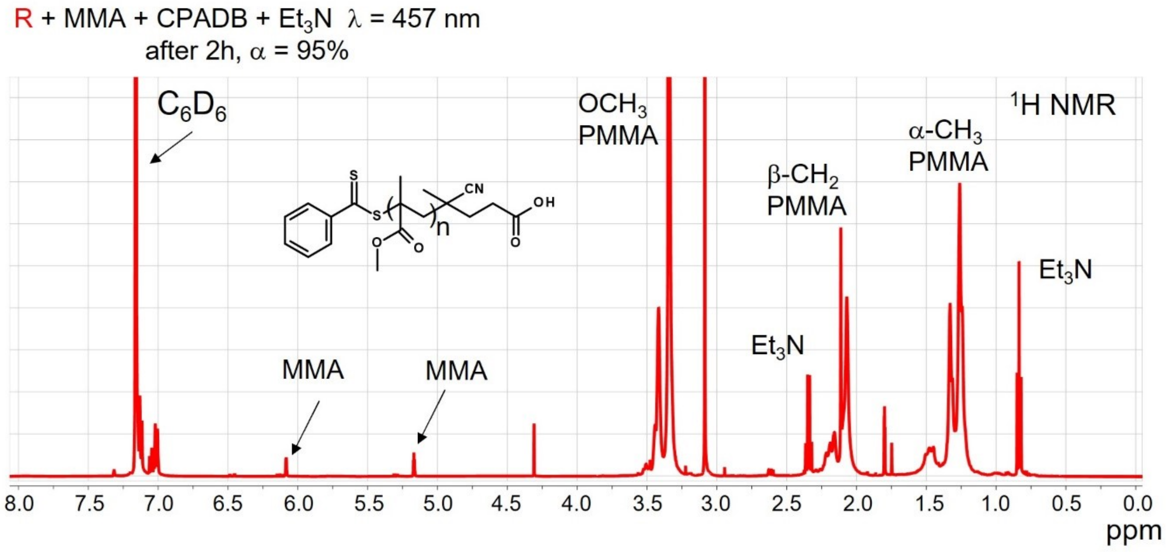

Fig. S13 ^{1}H NMR spectrum (in benzene-d_6) of the reaction mixture used for the photocatalytic bulk RAFT polymerization of MMA with **R** nanocrystals as a photocatalyst.

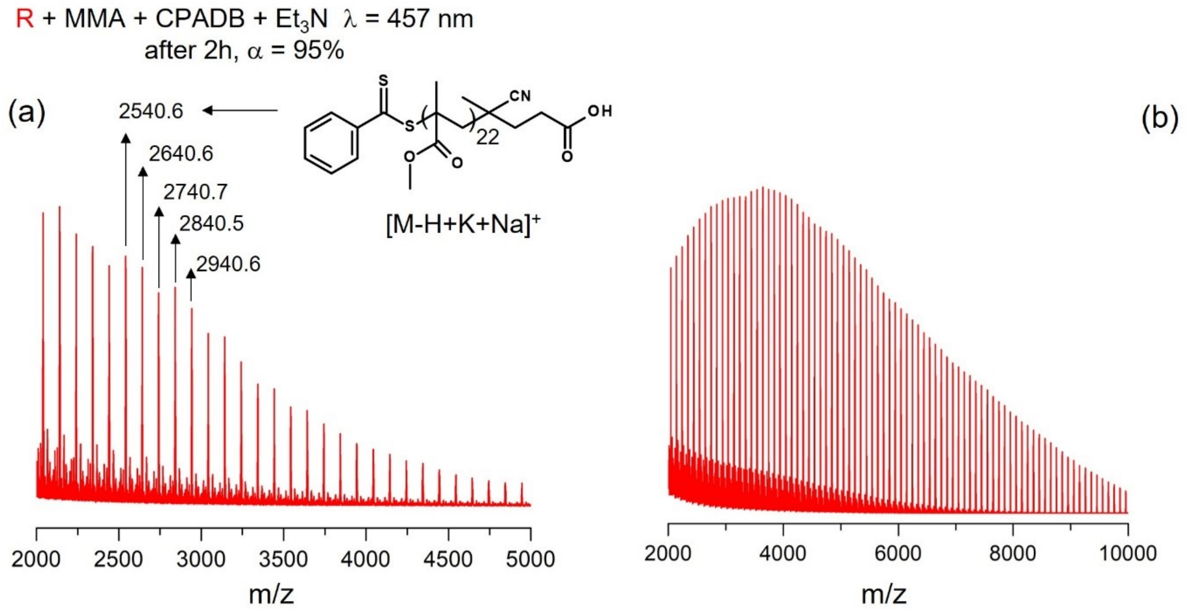

Fig. S14 MALDI-TOF spectra in the low (**a**) and high (**b**) molecular weight ranges of PMMA synthesized in the presence of **R** nanocrystals as photocatalysts for RAFT polymerization.

REFERENCES

(1) A. M. Maron, A. Szłapa-Kula, M. Matussek, R. Kruszyński, M. Siwy, H. Janeczek, J. Grzelak, S. Mackowski, E. Schab-Balcerzak, B. Machura, *Dalton Trans.,* 2020, **49**, 4441-4453.