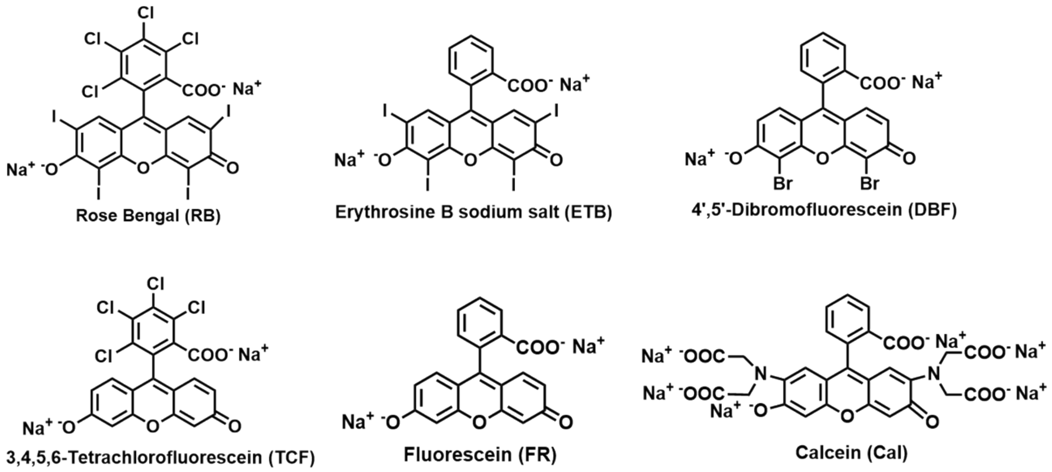
Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for

Hyperbranched Poly (ether amine) Nanomicelles as Nanoreactors for the Unexpected Ultrafast Photolysis of Fluorescein Dyes

Materials and Methods

Polyethylene glycol diglycidyl ether (PEO, Mn = 500 g/mol Aldrich), polypropylene glycol diglycidyl ether (PPO, Mn = 640 g/mol Aldrich), 1,2-Epoxydodecane (EPO, TCI), allyl glycidyl ether (AGE, Aldrich), (3-mercaptopropyl)trimethoxysilane (TMS, Aldrich), photoinitiator I-907 (Tronly. Changzhou, China), Rose Bengal (RB), Erythrosine B sodium salt (ETB), 4’,5’-Dibromofluorescein (DBF), 3,4,5,6-Tetrachlorofluorescein (TCF), Fluorescein (FR), Calcein (Cal), Nethylethylenediamine (NEED), acrylamide (AM), triethanolamine (TEOA), tetrahydrofuran (THF), methanol and ethanol (from Sinopharm Chemical Reagent). All of the reagents were used as received. Other chemicals are of analytical grade except as noted.



Scheme S1. Structure and Abbreviation of six fluorescence dyes.

Synthesis of Hyperbranched poly (ether amine) (hPEA)

Hyperbranched poly(ether amine) (hPEA) was synthesized according to our previous works.[1-2] NEED, PEO and PPO were dissolved in ethanol in a ratio of 2：1：1, and then stirred at 0 °C for 48 h. Then the mixture was heated to 80 °C for 24 h. And then the most of solvent was removed by rotary evaporation. The residue was dropped into 10-fold hexane. After removing the supernatant, the sediment was dried in vacuum oven to get the product (hPEA).

Synthesis of dodecane ended hPEA(EP-hPEA)

Typically, hPEA (2.0 g) was firstly added to a three-necked flask and dissolved in 20 ml ethanol, then 1,2-Epoxydodecane(EPO) was added in proportion (molar ration of the secondary amino groups in hPEA/the epoxy groups of EPO is 1/1). After refluxed at 80 °C for 24 h under protection of nitrogen gas, the mixture was poured into 10-fold hexane. After the supernatant was removed, the precipitate was dried in vacuum oven to obtain the product of EP-hPEA, which was confirmed by ^{1}H NMR successfully.
^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.25 (16H, CH_2), 1.31 (2H, CH_2), 0.86 (3H, CH_3)

Synthesis of hPEA containing trimethoxysilyl moieties (TMS-hPEA)

hPEA containing trimethoxysilyl moieties (TMS-hPEA)was synthesized according to our previous works.[3] Allyl glycidyl ether (0.015 mol) and hPEA (0.01 mol in term of its structure units) were refluxed in ethanol (20 mL) for 20 h with nitrogen protect. The mixture was poured into n-hexane and the precipitate was dried in vacuum to get hPEA-AGE.
^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.89 (1H, CH=), 5.25 (1H, =CH_2), 5.15 (1H, =CH_2), 4.01 (2H, CH_2).
To the solution of CH_2Cl_2 with trace of photoinitiator I-907, hPEA-AGE and (3-mercaptopropyl) trimethoxysilane (thiol/double bond = 1.3:1) were added. The mixture was irradiated by 365 nm ultraviolet light for 12 h. Then the mixture was poured into n-hexane. After removing the supernatant, the graft polymer containing trimethoxysilyl moiety (TMS-hPEA) was collected and dried.
^{1}H NMR (400 MHz, $CDCl_3$, δ): 3.57 (9H, CH_3), 2.62 (4H, $COCH_2$), 2.53 (4H, SCH_2), 2.07 (3H, $COCH_3$), 1.83 (2H, CH_2), 1.69 (2H, CH_2), 0.74 (2H, $SiCH_2$).

Measurements

^{1}H NMR spectra were carried out on a Mercury Plus 400 MHz spectrometer with $CDCl_3$ as the solvent.

UV–*vis* spectra were recorded in aqueous solution by Shimadzu UV-2550 spectrophotometer.

Steady state photolysis experiments: The mixed solution of dyes and amines were irradiated with a LED bulb at wavelength of 450 nm whose intensity is approximately 8 mW/cm^2. In order to ensure the consistency of the experimental conditions, the molar concentration of amines in the solution of hPEA and TEOA was equal. [Dye] = 1×10^{-5} mol L^{-1}, [TEOA] = 2×10^{-3} mol L^{-1}, [EP-hPEA] = 0.83 mol L^{-1}, [$SiO_{1.5}$-hPEA] = 0.95 g L^{-1}. The UV-*vis* spectra were recorded by the Shimadzu UV-2550 spectrophotometer at different irradiation times.

The first-order reaction dynamic model: As shown in Equation (1), the photobleaching rate is related to the concentration of the dye and amine:

$$\frac{d(C_0 - C)}{dt} = k\,C\,C_{Am} \qquad (1)$$

where C_0 is the initial dye concentration, C is the dye concentration after t minutes irradiation, C_{Am} is the amine concentration after t minutes irradiation, and k is a constant.

Because the amine concentration is much higher than that of the fluorescence dye and remains almost unchanged, it can be regarded as a constant. Therefore, the photobleaching rate is only related to the dye concentration, Equation (1) can be simplified to Equation (2):

$$\frac{d(C_0 - C)}{dt} = k^{'}C \qquad (2)$$

where $k^{'}$ is constant and $k^{'} = k\,C_{Am}$According to Lambert-Beer's law, the absorbance of a dye at a certain wavelength is proportional to the concentration, Equation (2) can be simplified to Equation (3) through the integral:

$$ln\frac{1}{A} = K\,t + d \qquad (3)$$

where A is the absorbance of the dye at λ_{max}, K is the kinetic constant of the first-order reaction and d is a constant.

DLS measurements were performed in $SiO_{1.5}$-hPEA and EP-hPEA nanomicelles solutions (concentration was 1g L^{-1}) using a Zetasizer Nano ZS90 instrument (Malvern Instruments) equipped with a 4 mW He-Ne laser ($\lambda = 633$ nm) at an angle of 90 °, an avalanche photodiode detector with high quantum efficiency, and an ALV/LSE-5003 multiple τ digital correlator electronics system. A regularized Laplace inversion (CONTIN algorithm) was applied to analyze the obtained autocorrelation functions. The size of the nanoparticles was determined using the volume-weighted distribution of particle sizes.

Electron spin-resonance spectroscopy (ESR-ST) experiments were carried out by the Freilberg Instruments ms-5000. The radicals were formed upon LED (365nm) irradiation for 60s at room temperature and trapped by 5, 5-dimethyl-1-pyrroline-N-oxide (DMPO). [RB] = 1×10^{-2} mol L^{-1}, [EP-hPEA] = 42.1 g L^{-1}, [TEOA] = 0.1 mol L^{-1}, [DMPO] = 1 mol L^{-1}.

TEM measurements were carried out using a JEOL JEM-2100 microscope, operating at 200 kV. A drop of 0.1 g L^{-1} $SiO_{1.5}$-hPEA or EP-hPEA nanomicelles aqueous solution was placed onto a copper grid and the excess solution was removed by a filter paper.

Adsorption Experiment: A EP-hPEA nanomicelles solution and a small amount of

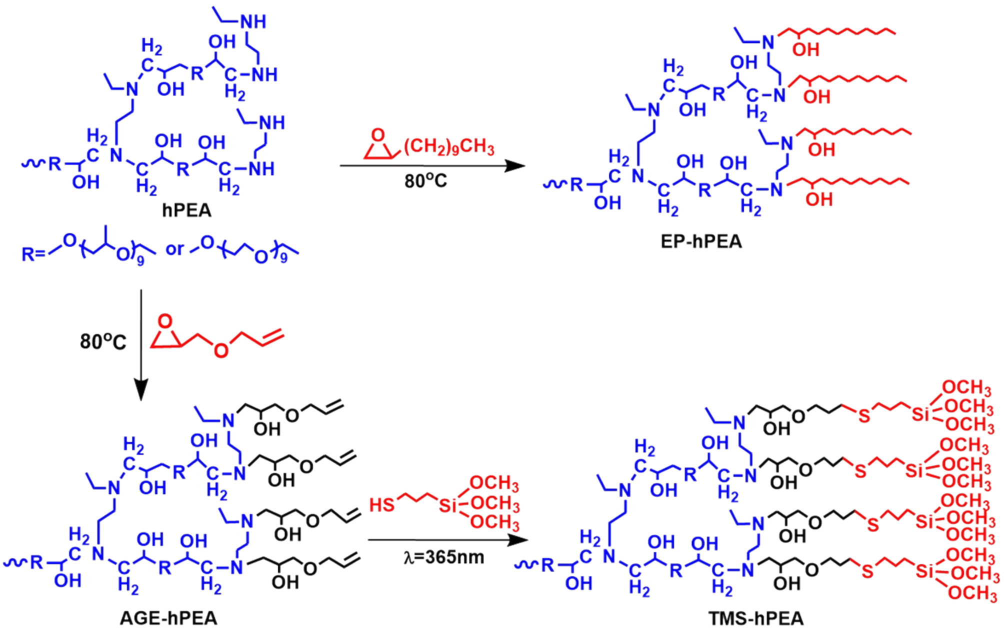
NaCl were added to dye in aqueous solution in a centrifuge tube. The concentration of the nanoparticles in water (5 mL) is 10 g L^{-1}, the concentration of the dye in water (5 mL) is 2×10^{-5} mol L^{-1}; the concentration of the NaCl in water (5 mL) is 5 g L^{-1}. The mixed solution was heated above the 75℃ for 10 min to ensure full separation of two phases. Then the turbid solution was centrifuged at 2000 rpm for 5 min. The distribution coefficient (D) is shown in Equation (1):

$$D = \frac{[Dye]_{hPEA}}{[Dye]_{aq}} \qquad (4)$$

where $[\mathrm{Dye}]_{\mathrm{NP}}$ (mmol/L) is the molar concentration of the dye in the hPEA nanomicelles and $[\mathrm{Dye}]_{\mathrm{aq}}$ (mmol/L) is the molar concentration of the dye in the aqueous phase. During the process, the UV-vis spectra of the dye in the initial aqueous solution with hPEA nanomicelles, as well as in supernatant after centrifugation, were recorded with a Shimadzu UV-2550 spectrophotometer. The dye concentration was calculated from the absorbance at maximum absorption wavelength ($\Delta\lambda_{\mathrm{max}}$).

Photopolymerization kinetic studies of Acrylamide（AM）in aqueous solution were performed dilatometerically in a recording dilatometer[4] by irradiating about 10 mL AM at 25 °C. The experimental conditions are as follows: [AM] = 2.9 mol L^{-1}, [Dye] = 1×10^{-2} mol L^{-1}, [TEOA] = 5×10^{-2} mol L^{-1}, [EP-hPEA] = 21.05 g L^{-1}. The light source was a LED bulb at wavelength of 450 nm with a LED bulb at wavelength of 450 nm whose intensity is approximately 8 mW/cm^2. The polymerization rate (R_p) was determined below 10% conversion where R_p is almost independent of the conversion. The produced polymer was precipitated with methanol, filtered, and dried in vacuo. The experiment in the sunlight was carried out in November 10, 2017 at 121 ° N, 31 ° E.

Bonding performance test: A mixed solution of RB, EP-hPEA and acrylamide in water was prepared and coated on the glass. Another piece of glass was covered on the coating and exposed to sunlight irradiation for 1 hour. The experimental conditions are as follows: [AM] = 5.57 mol L^{-1}, [RB] = 1×10^{-2} mol L^{-1}, [EPO-hPEA] = 42.1g L^{-1}. This experiment was carried out in October 15, 2017 at 121 ° N, 31 ° E.



Scheme S2. Synthesis of EP-hPEA and TMS-hPEA.

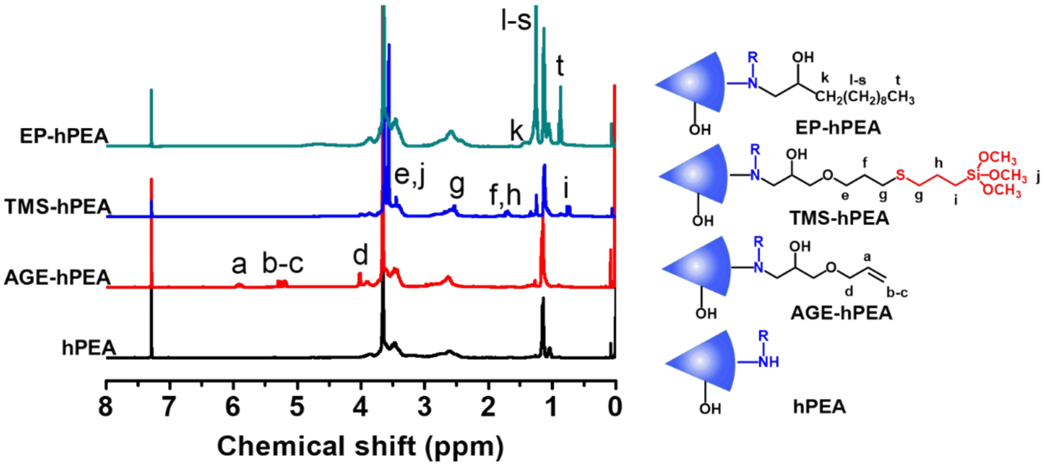
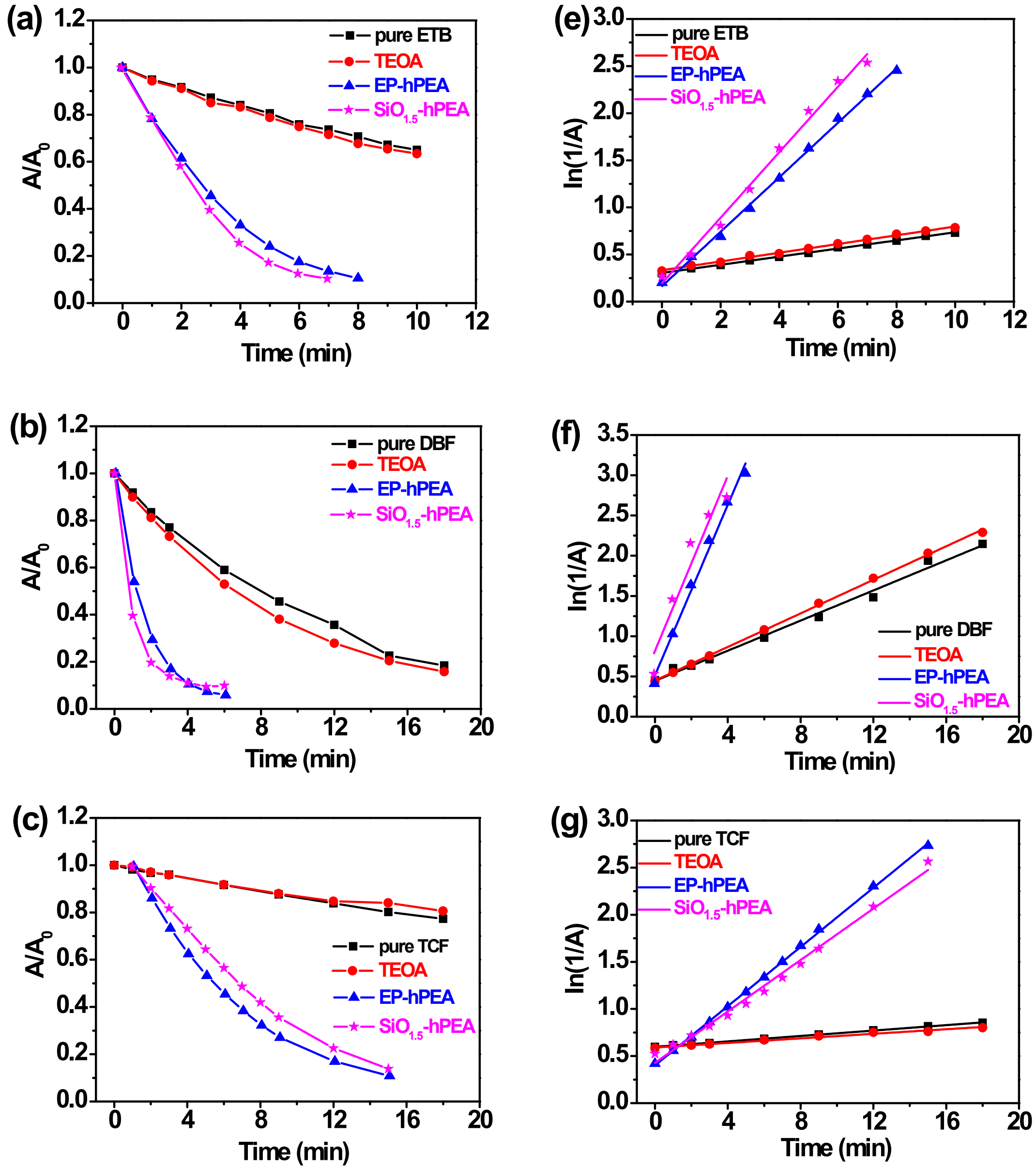


Fig. S1 ^{1}H NMR spectra of EP-hPEA, AGE-hPEA and TMS-hPEAs.

Table S1 The molecular weight Data of EP-hPEA and TMS-hPEA.

Polymer	Percentage of grafting	Mn ($\times 10^4$) (g/mol)	Mw/Mn
hPEA	-	1.8	1.30
EP-hPEA	81.2%	2.2	-
TMS-hPEA	30.5%	2.1	-



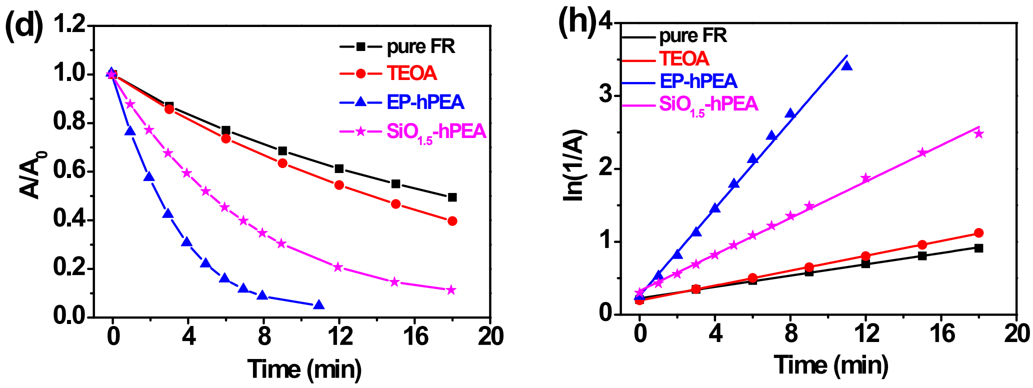


Fig. S2 The maximum UV absorption wavelength variation in ETB (a), DBF (b), TCF (c) and FR (d) with different amines as a function of visible light irradiation time. Plot of $ln\frac{1}{A}$ vs. time for the photodecolorization of ETB (e), DBF (f), TCF(g) and FR (h) with different amines.

Table S2 The first order rate constant (K = $\frac{ln(1/A)}{t}$) for six fluorescein dyes with different amines in aqueous solution under the irradiation of LED.

photobleaching rate coefficient K (min^{-1}) $\times 10^2$	RB	ETB	DBF	TCF	FR	Cal[a]
Pure dye	1.90	4.32	9.36	1.44	3.88	<0.1
TEOA	1.13	4.64	10.43	1.21	5.10	<0.1
EPO-hPEA	18.14	28.91	52.93	15.72	29.94	<0.1
$SiO_{1.5}$-hPEA	20.69	34.74	54.39	13.65	12.45	<0.1

[a] Cal can scarcely be photobleached.

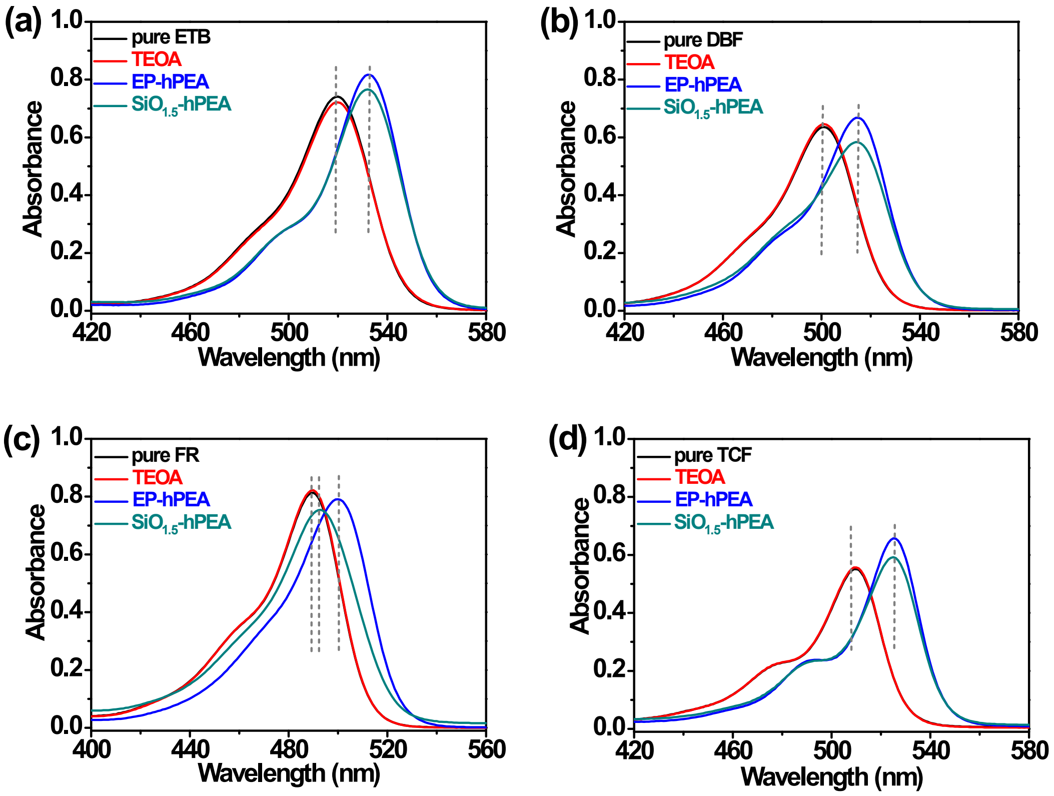
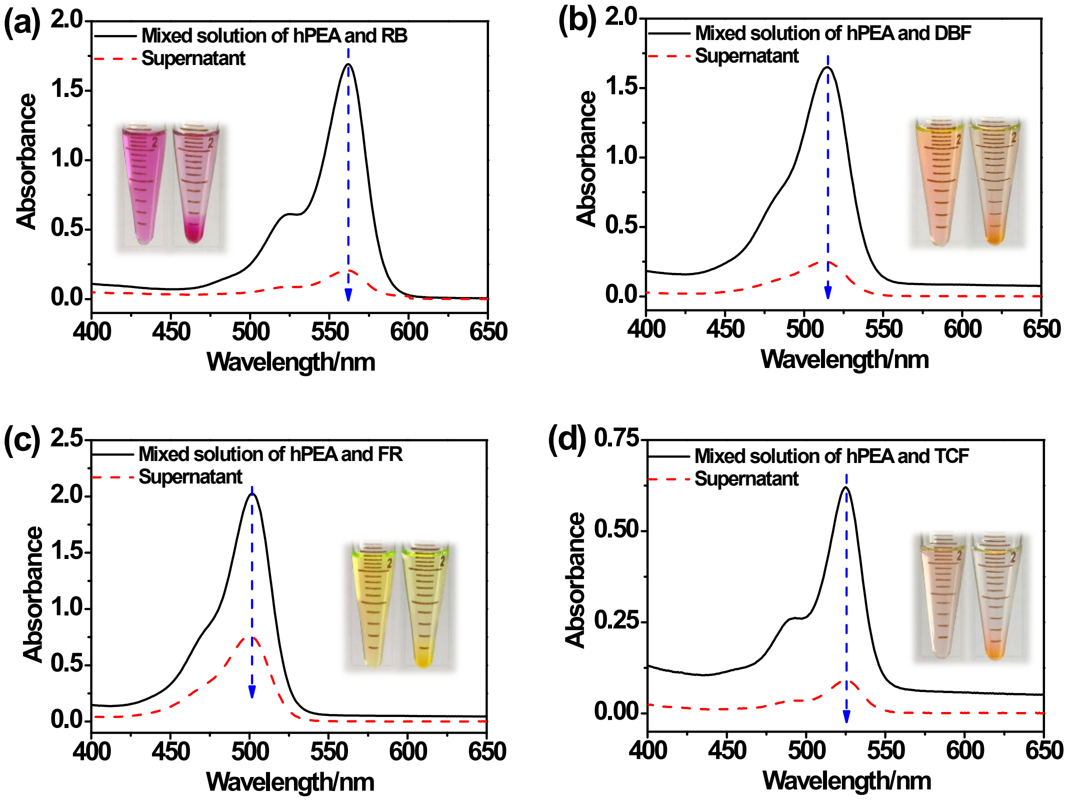


Fig. S3 UV-vis spectra of ETB (a), DBF (b), FR (c) and TCF (d) with different amines in aqueous solution.



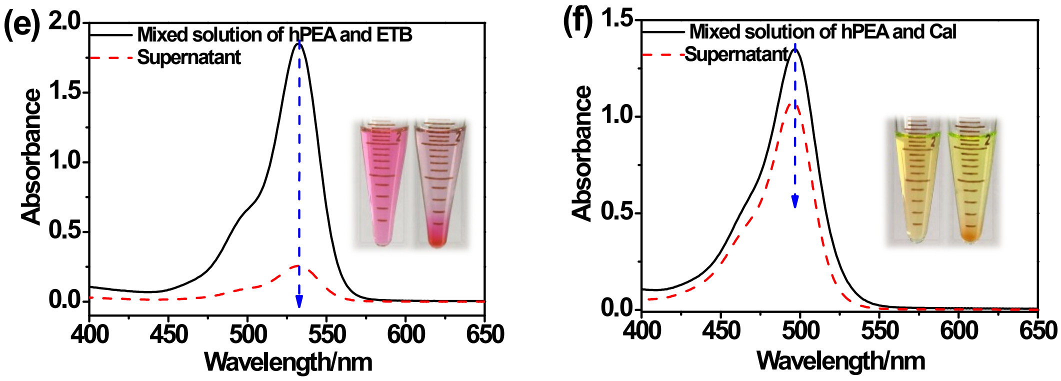


Fig. S4 Separation of different dyes in aqueous solution: photographs of dye encapsulation before (left) and after (right) precipitation; UV-vis spectra of (a) RB, (b) DBF, (c) FR, (d) TCF, (e) ETB and (f) Cal in hPEA nanomicelles (black solid line) and supernatant (red dashed line) after precipitation.

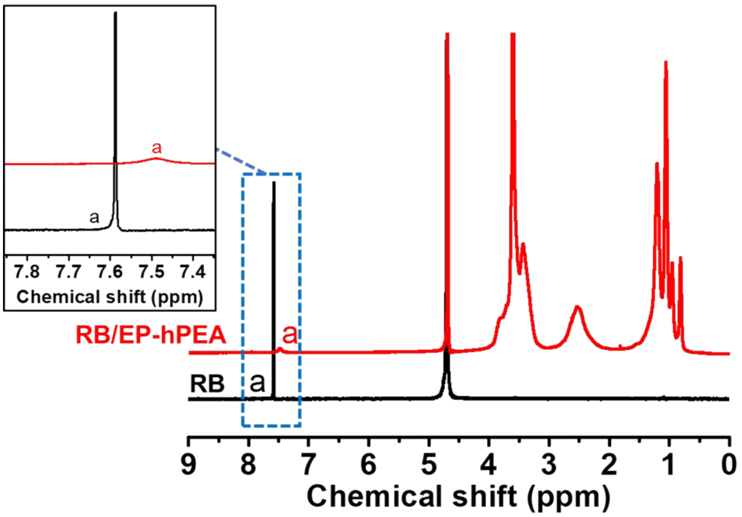


Fig. S5 ^{1}H NMR spectra of RB and RB/EP-hPEA (using D_2O as solvent).

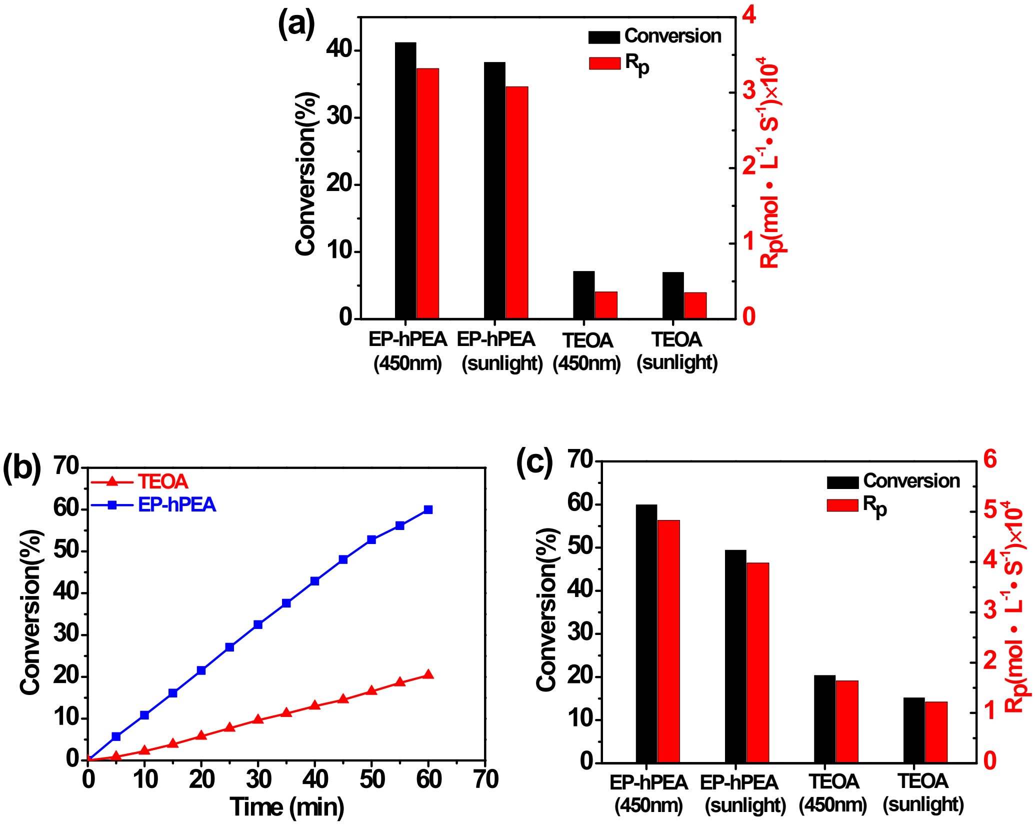


Fig. S6 Conversion and polymerization rates (R_p) of AM photoinitiated by RB (a) and ETB (c) with different co-initiators under 1 h 450 nm LED or sunlight irradiation. (b) Conversion vs. time curves for the polymerization of AM in aqueous solution photoinitiated by ETB with different co-initiators at 25 °C. The experiment in the sunlight was carried out in November 10, 2017 at 121 ° N, 31 ° E.

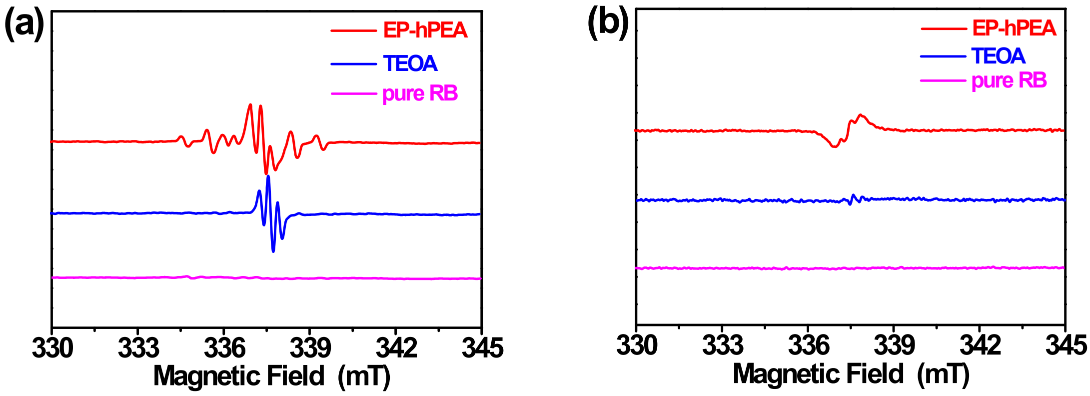


Fig. S7 ESR spectra of RB with different amines after 30s (a) and 10 minutes (b) of irradiation.

Movie S1. Video of RB in aqueous solution with different amine-containing samples after 10 minutes irradiation by sunlight.

References

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