

SUPPORTING INFORMATION

Fluorescent Aliphatic Hyperbranched Polyether: chromophores-free and without any N and P Atoms

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Experimental section

Materials

Ether, sodium hydroxide (NaOH), hydrochloric acid (HCl), and tetrahydrofuran (THF) were purchased from Beijing reagent Co., China. 1,4-butanediol and tetrabutylammonium bromide (TBAB) was purchased from Tianjin Fuchen Chemical Reagents Factory (Tianjin, China). 1,1,1-Trihydroxymethylpropane triglycidyl ether (TMPGE) (99%) was purchased from Titanchem Co. Ltd. (Shanghai, China). All solvents and reagents are analytical pure and were used as received.

Measurements

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV-600 spectrometer (600 MHz) using CDCl₃ as the solvent. The chemical shifts of ¹H NMR were reported in ppm. FTIR spectrum was obtained with a Bruker Tensor 37 spectrophotometer using potassium bromide (KBr) disc technique. Weight-average molecular weight (*M_w*) of the hyperbranched molecules were determined using a Waters 515-2410 gel permeation chromatography (GPC) system which is calibrated with linear polystyrene calibration standards, THF was used as the mobile phase.

Luminescence experiments were carried out using a Varian Cary Eclipse fluorescence spectrophotometer. It has to be bear in mind the samples were given 0.5 h to equilibrate at given temperature before the fluorescence measurements. Unless otherwise stated, EHBPE solutions are ethanol solutions, the obtained fluorescence spectra were obtained at an excitation wavelength of 365 nm, and the mass concentrations of EHBPE in different solutions are maintained at 10 mg/mL. Fluorescence lifetime of EHBPE solutions were recorded on a LifeSpec-red time-resolved spectrometer from Edinburgh Instruments Ltd., which can resolve lifetimes down to 30 ps. The fluorescence decay traces were collected in the range of 0 to 50 ns, and the results were fitted using the commercial software package (F900) provide by Edinburgh Instruments, Ltd. Optical fluorescence microscope images of EHBPE (excited at 488 nm) was carried out on a Leica confocal microscope (TCS SP5) which is controlled by the Leica LAS-AF software.

Characterization of EHBPE2

The ^1H NMR spectrum shows several peaks at 3.4-4.0, 3.1, 2.8, 2.6, 1.4-1.2, and 0.8 ppm, which correspond to the hydrogen in $-\text{OCH}_2-$, $-\text{CH}_2-(\text{epoxy ring})$, $-\text{OCH}_2-(\text{epoxy ring})$, $-\text{OCH}-(\text{epoxy ring})$, $-\text{CH}_2-$, and $-\text{CH}_3$.

The ^{13}C NMR spectrum shows several peaks at 69.8-74.4, 62.8, 52.3, 44.2, 39.0, 28.5-29.2, 23.2, and 7.9 ppm, which correspond to the carbon in $-\text{C}-\text{C}-\text{O}-$, $-\text{C}-\text{O}-$, $-\text{OCH}-(\text{epoxy ring})$, $-\text{OCH}_2-(\text{epoxy ring})$, $-\text{C}(\text{CH}_3)_3-$, $-\text{CH}_2-(\text{A}_2)-\text{CH}_2-(\text{B}_3)$, and $-\text{CH}_3$.

The FTIR spectrum shows several peaks at 3456-3380, 2948-2880, 1710, 1654, 1460, 1361, 1248, 1110, 840, 760 cm^{-1} . The broad peak at 3456-3380 cm^{-1} correspond to the stretching vibrations of $-\text{OH}$; the broad peak at 2948-2880 cm^{-1} correspond to the stretching vibrations of $-\text{CH}_2-$ and $-\text{CH}_3$, the peak at 1460 cm^{-1} correspond to the deformation vibration of $-\text{CH}_2-$ and $-\text{CH}_3$, the peak at 1361 cm^{-1} correspond to the deformation vibration of $-\text{CH}_3$, the peak at 1248 cm^{-1} correspond to the stretching vibration of $-\text{C}-\text{O}-\text{C}-$; the peak at 1110 cm^{-1} correspond to the stretching vibration of $-\text{C}-\text{O}-\text{H}$; the peak at 840 and 760 cm^{-1} correspond to the ring vibration of epoxy.

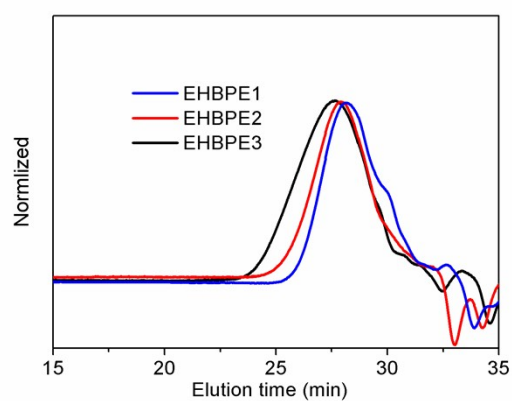


Fig. S1 GPC curves of EHBPEs.

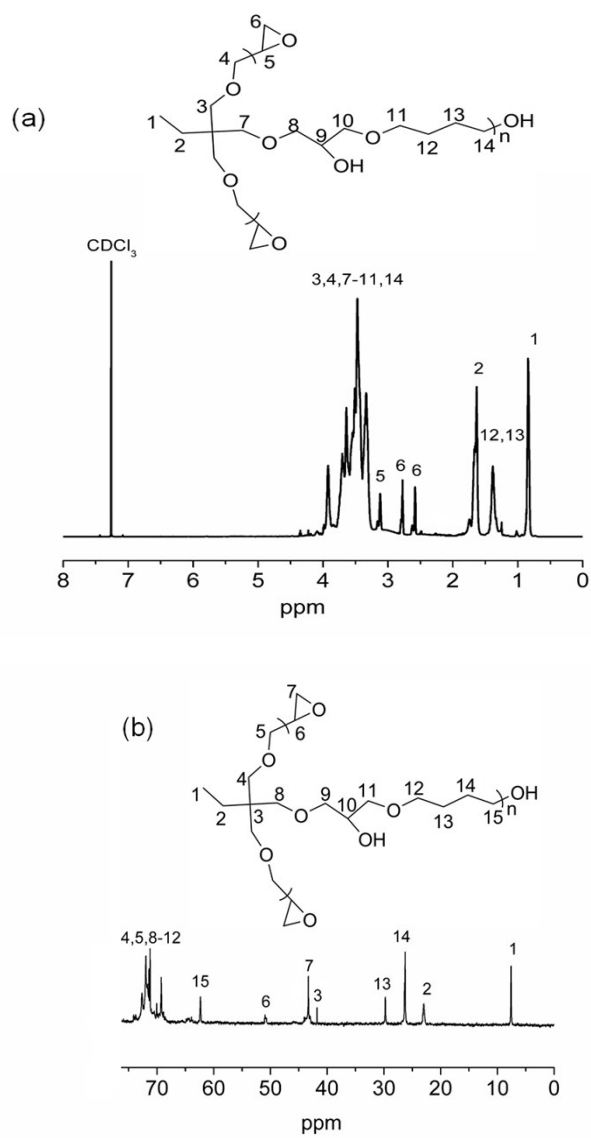


Fig. S2 (a) ^1H NMR of EHBPE2; (b) ^{13}C NMR of EHBPE2.

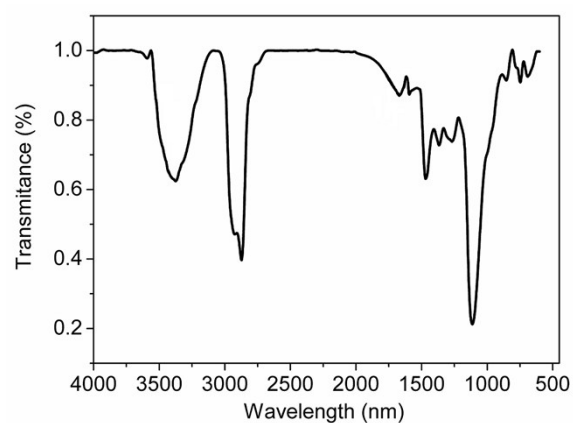


Fig. S3 FTIR of EHBPE2.

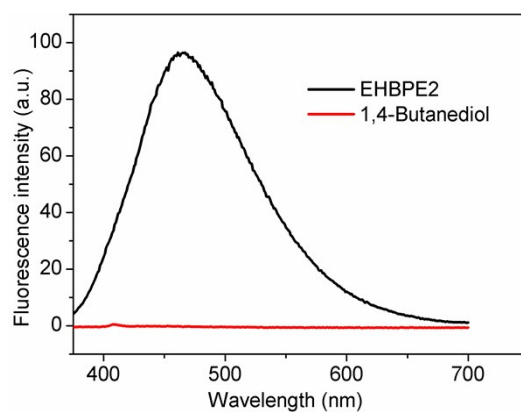


Fig. S4 Emission spectra of EHBPE2 and 1,4-butanediol.

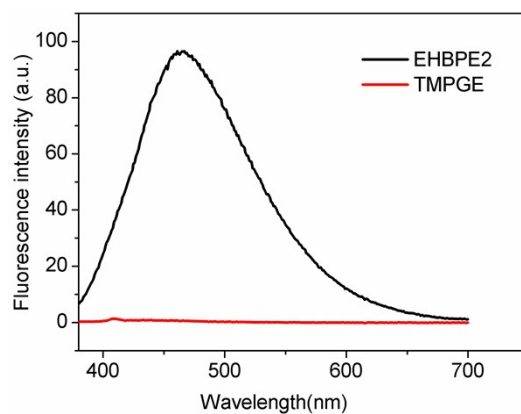


Fig. S5 Emission spectra of EHBPE2 and TMPGE.

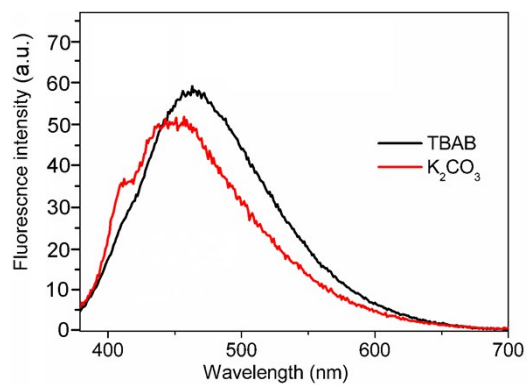


Fig. S6 Effects of catalyst on the emission spectra of EHBPE.

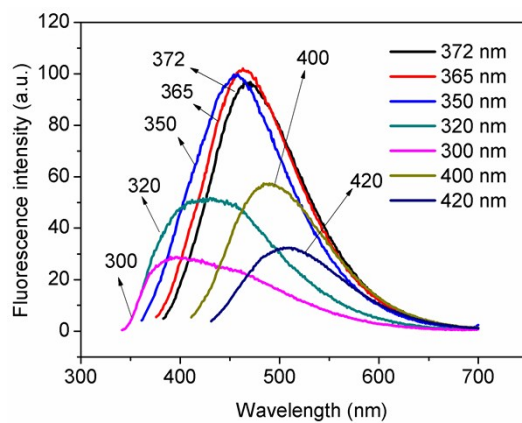


Fig. S7 Emission spectra of EHBPE2 excited at various wavelengths.

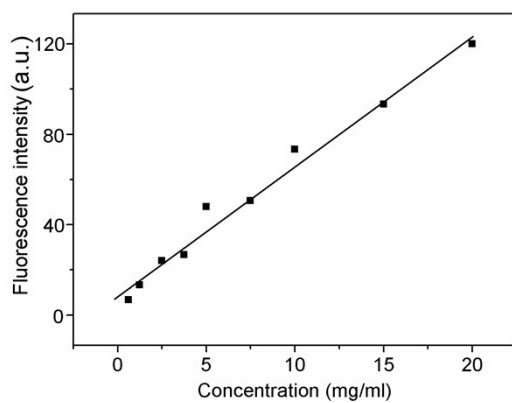


Fig. S8 Fluorescence intensity of EHBPE2 as a function of concentration.

Table S1 Characterization results of EHBPEs.

Sample code	M _n (g/mol)	M _w (g/mol)	PDI	DB	T _g (°C)	T _{d5%} (°C)
EHBPE1	931	1481	1.6	0.53	-42.4	315.2
EHBPE2	1685	3055	1.8	0.52	-29.5	326.8
EHBPE3	2510	5625	2.2	0.50	-25.8	329.1

Table S2 Element analysis results of EHBPEs

Element	Mass	Conc	Units
Na	23	<0.0001	mg/mL
Mg	24	<0.0001	mg/mL
Al	27	<0.0000	mg/mL
Si	29	<0.0001	mg/mL
K	39	<0.0001	mg/mL
Ca	43	<0.0000	mg/mL
Cr	53	<0.0001	mg/mL
Mn	55	<0.0001	mg/mL
Fe	57	<0.0000	mg/mL
Co	59	<0.0001	mg/mL
Ni	60	<0.0001	mg/mL
Cu	63	<0.0000	mg/mL
Zn	66	<0.0001	mg/mL

Table S3 Fluorecence characterization results of EHBPEs.

Sample code		EHBPE1	EHBPE2	EHBPE3
Y _U (%)		19.71	39.00	11.20
τ^{avg} (ns)		3.27	4.59	3.21
τ (ns)	τ_1	0.35	0.42	0.39
	τ_2	1.68	2.20	1.91
	τ_3	6.65	7.55	6.57