

Supporting Information

Achieving Long Lifetime of Room-Temperature Phosphorescence via Constructing Vitrimer Networks

Yulei Gao^a, Zhou Deng^a, Fenfen Wang^{a,*} and Pingchuan Sun^{a,*}

Key Laboratory of Functional Polymer Materials of Ministry of Education and College of Chemistry,
State Key Laboratory of Medicinal Chemical Biology, Nankai University, Tianjin 300071, P. R.
China.

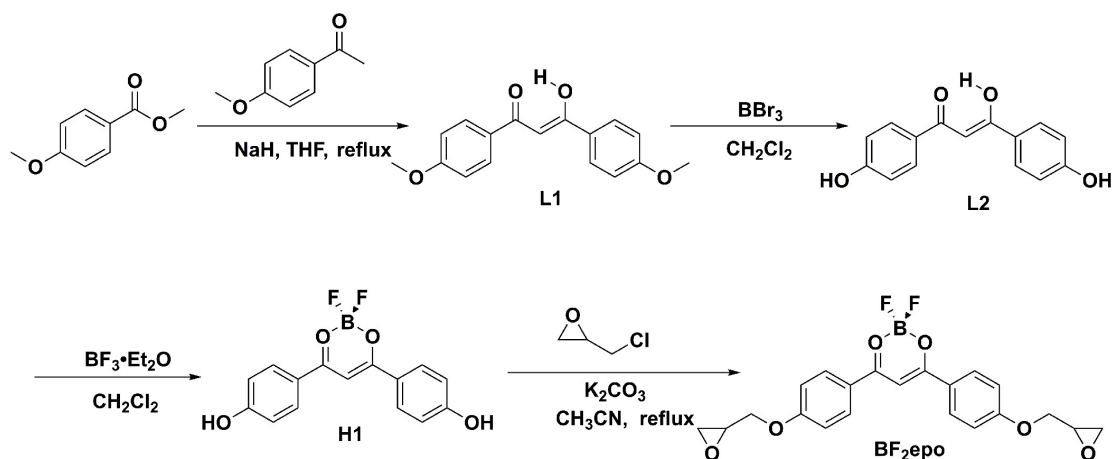
E-mail: wff@mail.nankai.edu.cn; spclbh@nankai.edu.cn

Table of Contents

1. Experimental details
2. Supporting Figures and Tables
3. References

1. Experimental details

1.1. Synthetic routes of BF₂epo and BF₂L1.



Scheme S1. Synthetic route of BF₂epo.

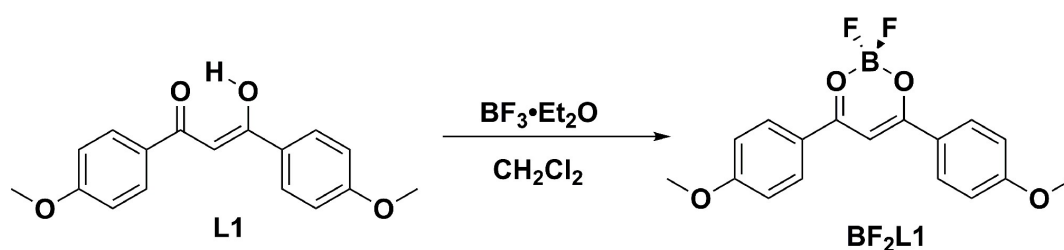
Compound 1,3-bis(4-methoxyphenyl)propane-1,3-dione (L1) was synthesized according to the method which has been reported in the earlier literature with the same structure.¹

Synthesis of 1,3-bis(4-hydroxyphenyl)propane-1,3-dione (L2): To a solution of L1 (3.46 g, 12.2 mmol) in CH₂Cl₂ (50 mL) cooled with an ice-salt bath was added dropwise a 1 M CH₂Cl₂ solution of

BBr_3 (36.5 mL, 36.5 mmol). This solution was stirred for 30 min at ice-salt bath, 30 min at 0 °C, 5 h at room temperature, and afterward quenched by dropwise addition of H_2O (50 mL). Add 2 M NaOH (50 mL). The aqueous was adjusted to pH = 6 with conc. HCl (aq) caused the formation of a yellow precipitate which was then extracted with ethyl acetate 3 times, and the combined organic phase was washed with brine (20 mL), dried (MgSO_4), filtrated and concentrated under vacuum to afford L2 as a yellow solid (2.77 g, 88.8% yield). ^1H NMR (400 MHz, in Acetone- d_6): δ 17.58 (s, 0.9H), 9.12 (s, 2H), 8.04 (d, 4H), 7.04 (s, 1H), 6.97 (d, 4H), 4.60 (s, 0.1H).

Synthesis of difluoroboron-1,3-bis(4-hydroxyphenyl)propane-1,3-dione (H1): To a solution of L2 (2.56 g, 10.0 mmol) in CH_2Cl_2 (50 mL) added dropwise $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (2.5 mL, 20.0 mmol) by a syringe. The mixture was heated slowly to 60 °C for 5.5 h under nitrogen atmosphere. After cooled to room temperature, the mixture was concentrated under reduced pressure. The desired pure product was obtained by recrystallization from ethyl acetate as a yellow solid (2.18 g, 71.7% yield). ^1H NMR (400 MHz, in Acetone- d_6): δ 9.69 (s, 1.5H), 8.25 (d, 4H), 7.51 (s, 1H), 7.06 (d, 4H).

Synthesis of difluoroboron-1,3-bis(4-(oxiran-2-ylmethoxy)phenyl)propane-1,3-dione (BF_2epo): H1 (1.0 g, 3.29 mmol), epichlorohydrin (12.17g, 131.6 mmol) and potassium carbonate (1.82 g, 13.16 mmol) were added into 20 mL of acetonitrile and the mixture was heated to 120 °C for 16 h. After cooled to room temperature, the mixture was filtrated, washed with CH_2Cl_2 (3×10 mL) and concentrated under vacuum to yield the BF_2epo (0.54 g, 39.5% yield). ^1H NMR (400 MHz, in CDCl_3): δ 8.12 (d, 2H), 7.04 (d, 2H), 7.01 (s, 0.5H), 4.39 (dd, 1H), 4.04 (dd, 1H), 3.40 (dt, 1H), 2.97 – 2.92 (m, 1H), 2.79 (dd, 1H). ^{13}C NMR (101 MHz, in CDCl_3 , δ ppm): 181.02, 164.24, 131.41, 129.27, 125.11, 115.25, 114.70, 91.85, 69.32, 49.90, 44.67.



Scheme S2. Synthetic route of $\text{BF}_2\text{L1}$.

Synthesis of difluoroboron-1,3-bis(4-methoxyphenyl)propane-1,3-dione ($\text{BF}_2\text{L1}$): To a solution of L1 (0.8 g, 2.81 mmol) in CH_2Cl_2 (30 mL) was added dropwise $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.5 mL, 4.22 mmol) by

a syringe. The mixture was heated slowly to 60 °C for 5 h under nitrogen atmosphere and was monitored by TLC at the same time (EA: n-hexane = 1:3, v:v). After cooled to room temperature, the mixture was concentrated under vacuum to produce a yellow solid. The desire pure product was obtained by washing with ethyl acetate 2-3 times (0.74 g, 80% yield). ¹H NMR (400 MHz, in DMSO-d₆): δ 8.36 (d, 4H), 7.75 (s, 1H), 7.19 (d, 4H), 3.93 (s, 6H).

1.2. Preparation of ER/BF₂epo vitrimer.

The hybrid vitrimers were synthesized via curing DGEBA, sebacic acid (SA) and BF₂epo with triazabicyclodecene (TBD) as the transesterification catalyst, obtaining a crosslinked epoxy resin labeled as ER/BF₂epo-x (x denotes the mole percentage of BF₂epo in total epoxy monomers).

Table S1. Formulations and gel contents of ER/BF₂epo vitrimer.

Sample	DGEBA [g]	BF ₂ epo [g]	SA [g]	TBD [g]	Gel content [%]
ER/BF ₂ epo-0	1.01	0	0.6	0.041	96.0 ± 0.5
ER/BF ₂ epo-1	1.00	0.012	0.6	0.041	94.6 ± 0.9
ER/BF ₂ epo-10	0.91	0.123	0.6	0.041	95.5 ± 1.1
ER/BF ₂ epo-20	0.81	0.247	0.6	0.041	95.8 ± 0.7
ER/BF ₂ epo-50	0.51	0.617	0.6	0.041	94.1 ± 0.4
ER/BF ₂ epo-100	0	1.235	0.6	0.041	93.7 ± 0.8

2. Supporting Figures and Tables

2.1. Characterization of monomers.

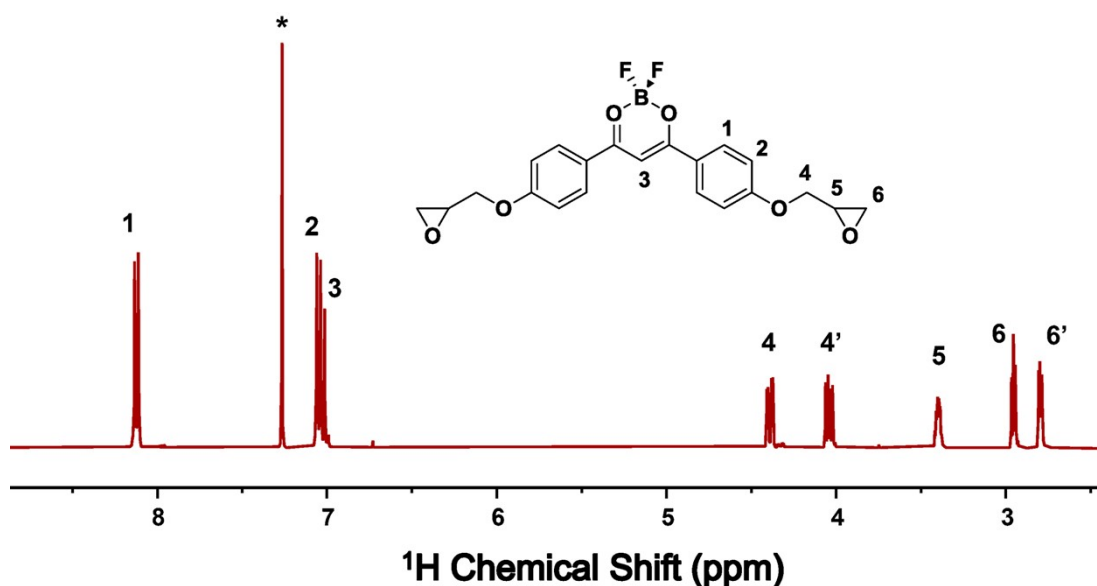


Figure S1. The ^1H NMR spectrum of compound BF_2epo in CDCl_3 .

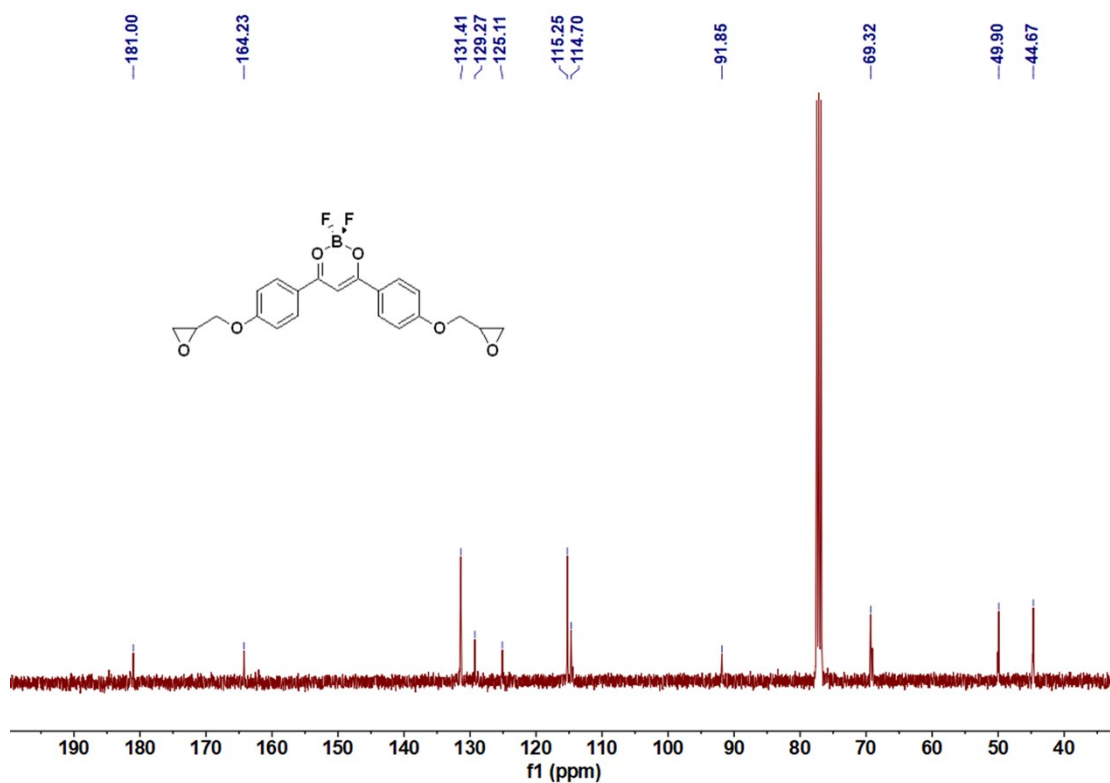


Figure S2. The ^{13}C NMR spectrum of compound BF_2epo in CDCl_3 .

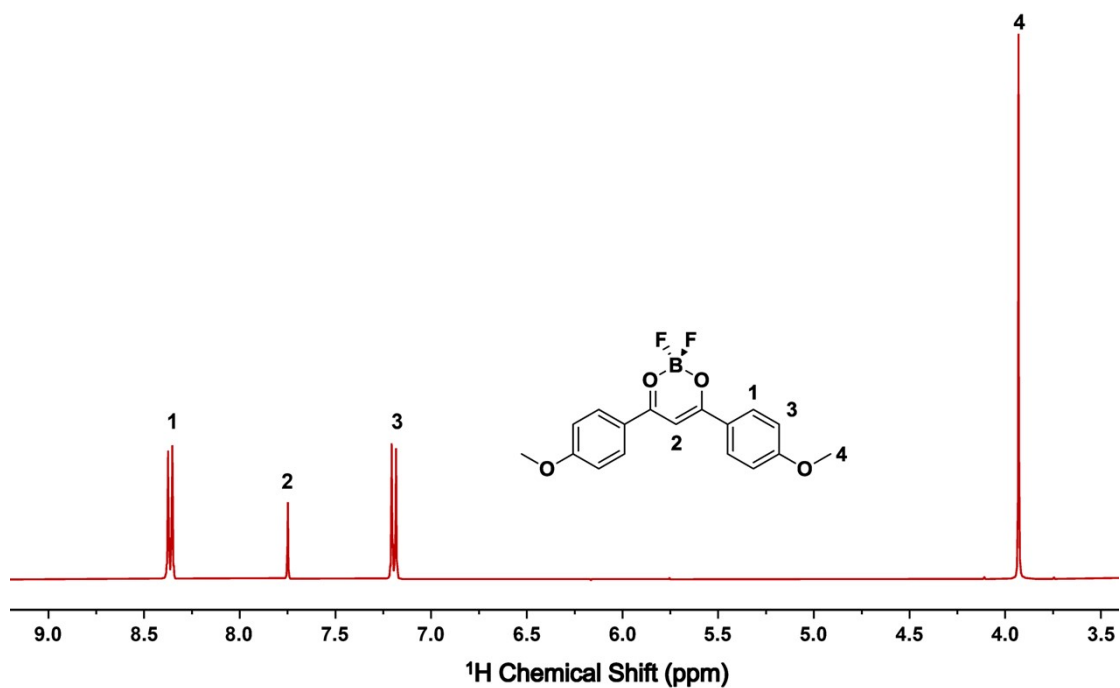


Figure S3. The ^1H NMR spectrum of compound $\text{BF}_2\text{L1}$ in DMSO-d_6 .

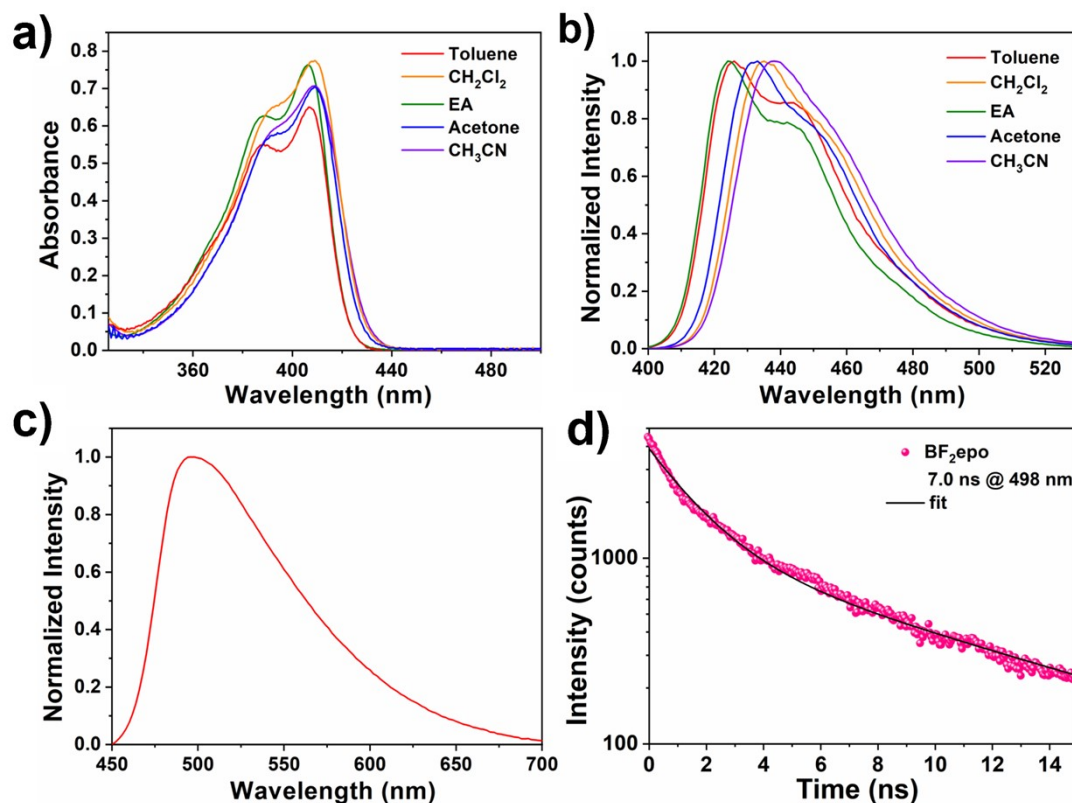


Figure S4. (a) UV-vis absorption and (b) normalized fluorescence emission spectra of BF₂epo in various solvents with 409 nm excitation (293 K, 10 μM). (c) Normalized fluorescence emission spectrum and (d) time-resolved photoluminescence decay of BF₂epo in the solid state with 369 nm excitation.

Figure S4 shows the UV-vis absorption and fluorescence emission spectra of BF₂epo in different solvents with varied polarities and the detailed data were listed in Table S2. UV-vis absorption spectra show that BF₂epo has intense absorption peaks over 400 nm and varying the polarity of the solvent has little effect on the maximum absorption wavelength. BF₂epo has a high fluorescence quantum yield in all solvents, manifesting a strong fluorescence emission under excitation at the maximum absorption wavelength (409 nm) and the emission red-shifted with increasing solvent polarities, which point to charge-transfer excited-state transitions. Exceptionally, an abnormal red-shifted emission was observed in CH₂Cl₂, which is possibly caused by the interaction between the π-electrons of the BF₂epo molecules and the surrounding solvent.² Besides, owing to the molecular interaction, the maximum emission wavelength red-shifted to 498 nm in the solid state with a fluorescence lifetime of 7.0 ns.

Table S2. Photophysical data of BF₂epo in different solvents.

Solvent	λ_{abs} [nm]	ϵ [M ⁻¹ cm ⁻¹]	λ_{em} [nm]	Φ_f^a	τ_f^b [ns]	τ_{rad}^c [ns]	k_r^d [10 ⁹ s ⁻¹]	k_{nr}^e [10 ⁹ s ⁻¹]
Toluene	407	55400	427	0.67	2.04	3.04	0.33	0.16
CH ₂ Cl ₂	409	80000	436	0.91	1.96	2.15	0.46	0.05
EA ^f	406	77400	410	0.85	2.00	2.35	0.43	0.08
Acetone	409	72600	432	0.72	2.51	3.49	0.29	0.11
CH ₃ CN	409	69800	438	0.74	2.13	2.88	0.35	0.12

^a Fluorescence quantum yield versus 9,10-diphenylanthracene in benzene ($\Phi_f = 0.85$, $\lambda_{\text{ex}} = 390$ nm). ^b Fluorescence lifetime. ^c Radiative lifetime: $\tau_{\text{rad}} = \tau_f / \Phi_f$. ^d Radiative rate constant: $k_r = \Phi_f / \tau_f$; ^e Nonradiative rate constant: $k_{\text{nr}} = (1 - \Phi_f) / \tau_f$. ^f Ethyl acetate.

2.2. Characterization of ER/BF₂epo vitrimer.

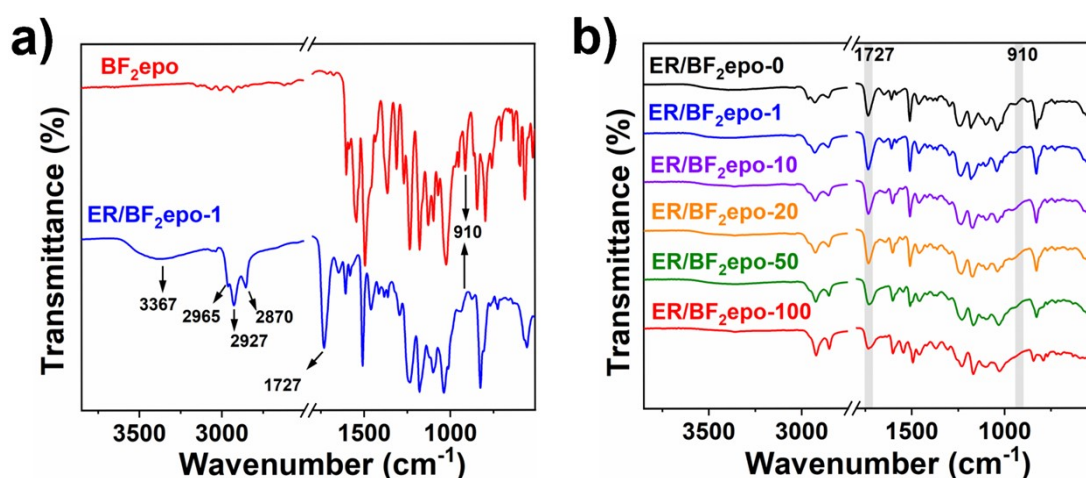


Figure S5. (a) FT-IR spectra of BF₂epo and ER/BF₂epo-1 vitrimer. (b) FT-IR spectra of ER/BF₂epo vitrimer with different contents of BF₂epo.

Figure S5 shows the spectra of ER/BF₂epo vitrimers. In the spectrum of BF₂epo, a distinct peak at 910 cm⁻¹ was observed which was assigned to the typical absorption of the epoxy group. Whilst in the case of ER/BF₂epo-1 vitrimer the epoxy group peak disappeared with the vibration absorption peaks of -OH (3367 cm⁻¹) and ester bonds (1727 cm⁻¹) emerged, the stretching vibration peaks of methyl groups and methylene groups (2965, 2927 and 2870 cm⁻¹) increased. Other ER/BF₂epo vitrimers also showed the same characteristics.

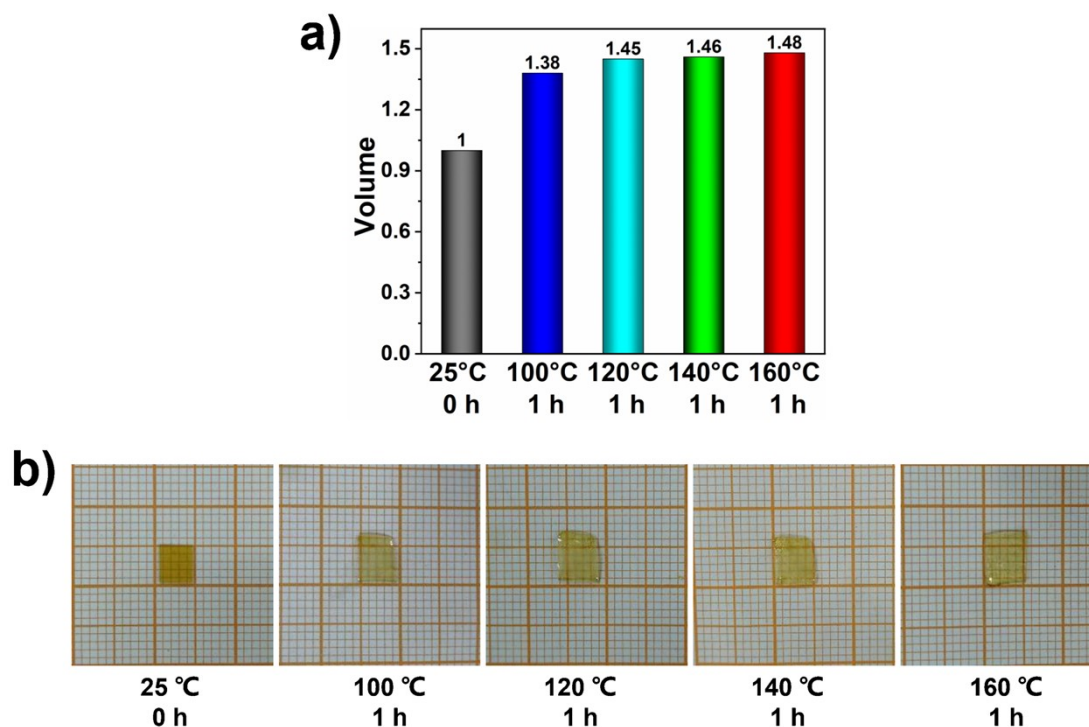


Figure S6. (a) Volume changes and (b) photographs of ER/BF₂epo-10 vitrimer film after swelled in DMAc at different temperatures.

To further verify that ER/BF₂epo vitrimer has successfully cured into a chemically crosslinked network, the swelling experiments were conducted using N, N-dimethylacetamide (DMAc) as the solvent (Figure S6). The volume of the film increased by 45% after 1 h at 120 °C and increased slowly after swelling for 1 h at 140 °C and 160 °C, which showed the sample had basically reached swelling equilibrium at 120 °C. It is worth noting that the film was merely swelled during the whole process without dissolving at elevated temperatures, revealing the formation of crosslinking structure.

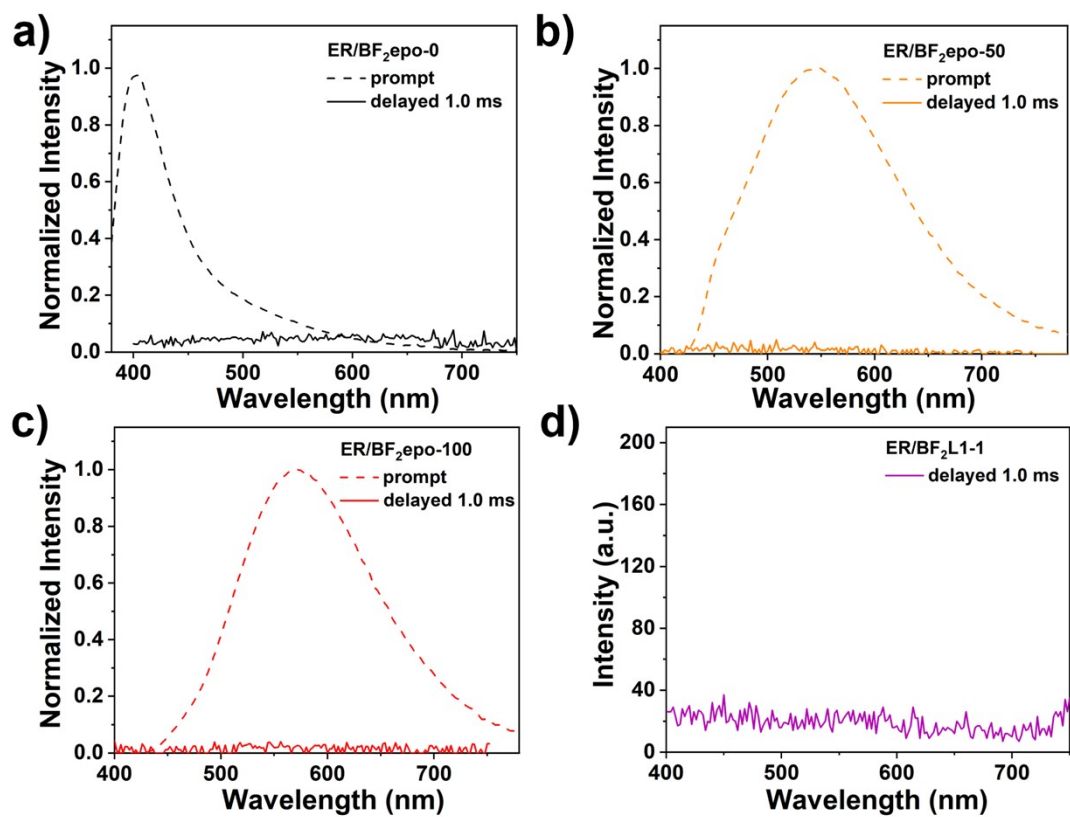


Figure S7. Prompt and delayed PL emission spectra of (a) ER/BF₂epo-0, (b) ER/BF₂epo-50 and (c) ER/BF₂epo-100 samples. (d) Delayed emission spectra of ER/BF₂L1-1 vitrimer.

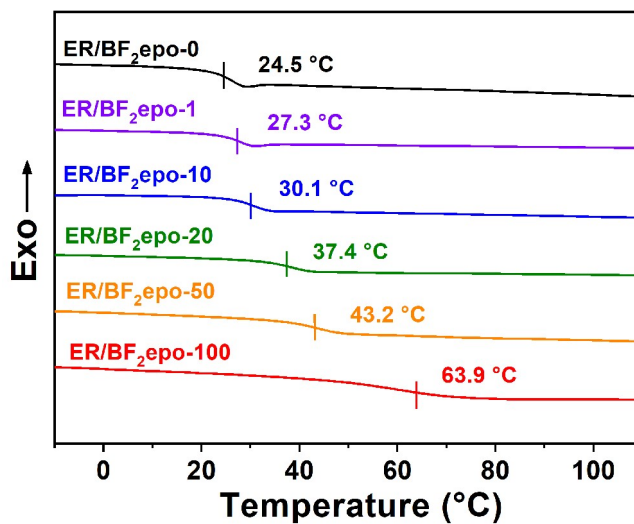


Figure S8. DSC curves. The peak temperatures are labeled on the curves.

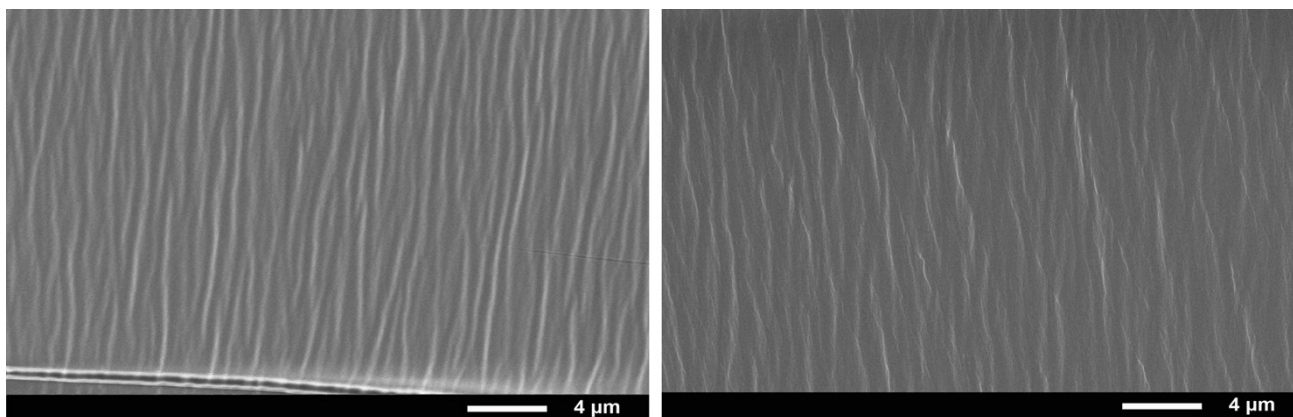


Figure S9. SEM micrographs of fracture surfaces of ER/BF₂epo-0 vitrimer (left) and ER/BF₂epo-10 vitrimer (right).

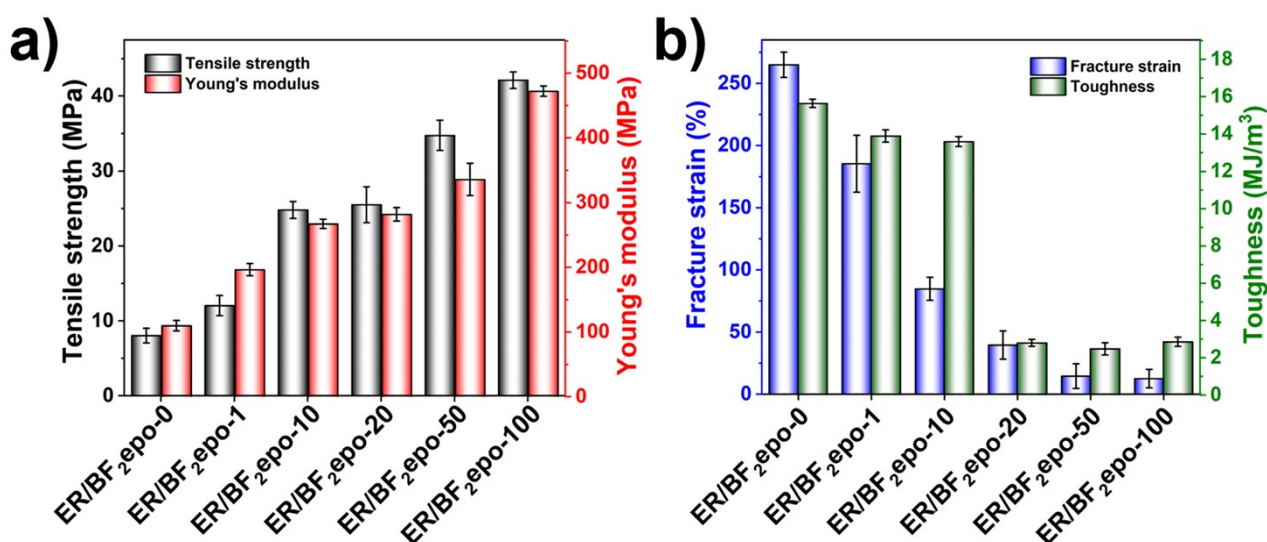


Figure S10. (a) The corresponding tensile strength and Young's modulus, and (b) the corresponding fracture strain and toughness of ER/BF₂epo vitrimer.

3. References

1. J. L. Howard, Y. Sagatov, L. Repusseau, C. Schotten and D. L. Browne, Controlling reactivity through liquid assisted grinding: the curious case of mechanochemical fluorination, *Green Chem.*, 2017, **19**, 2798-2802.
2. H. Zhang, P. Z. Chen, L. Y. Niu and Q. Z. Yang, A difluoroboron β -diketonate-based luminescent material with tunable solid-state emission and thermally activated delayed fluorescence, *Mater. Chem. Front.*, 2020, **4**, 285-291.