# Supporting Information

Multifunctional cardanol-based room-temperature phosphorescent material with multi-stimulus-responsive shape-memory for anti-Counterfeiting and encryption

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#### **1. Experimental section**

# 1.1. Materials

Cardanol (~ 95%, Cardolite chemical Co., Ltd.), 3-Aminobenzeneboronic acid (Shanghai Macklin Biochemical Co., Ltd.) N, N-Bis(2-hydroxyethyl) ethylenediamine (98%, Wuhan Xinweiye Chemical Co., Ltd), N, N,N',N'-tetrakis(2hydroxyethyl)ethylenediamine(99%, Macklin). All other chemicals and reagents were reagent grade and used without further purification in this study.

# 1.2. Characterization

1.2.1. Fourier transform infrared spectroscopy analysis (FT-IR)

The FT-IR spectra were acquired on a Nicolet iS50 FTIR meter (Nicolet Instrument Crop., USA).

1.2.2. Nuclear magnetic resonance analysis (NMR)

<sup>1</sup>H nuclear magnetic resonance (NMR) spectra of samples in d-DMSO were recorded on a Bruker AV-300 Advance NMR spectrometer (Bruker Corporation, Germany) at 300 MHz

1.2.3. Thermogravimetric Analysis (TGA)

TGA was carried out on a STA 209F1 thermogravimetry instrument (Netzsch Corporation, Germany) within a temperature from 40  $^{\circ}$ C to 600  $^{\circ}$ C under N<sub>2</sub>.

1.2.4. Photoluminescence excitation (PLE) and photoluminescence (PL) analysis

Photoluminescence excitation, prompt emission and delayed emission spectra were measured on a FLS1000 fluorescence spectrophotometer (Edinburgh Instruments) under ambient condition.

1.2.5. General reprocessing procedure

The samples were first cut completely into fragments and then compressed at hot 80 °C, 10 MPa for 10 min. After cooling to room temperature, a recycled film was obtained.

#### 1.2.6. Mechanical property

Mechanical property values were presented as the mean and standard deviation based on at least three trials using an UTM6503 instrument.

1.2.7. Shape memory

Shape-memory behavior testing: The thermally-induced shape memory behaviors were determined by thermo-mechanical analysis were conducted on DMA800 according to the procedure described in ref <sup>[1-2]</sup>. All samples were cut in rectangular pieces of approximately 10 mm×6.0 mm×0.5 mm. First, the samples were heated to programming temperature  $T_{prog}$  at the rate of 3 °C/min and held for 5 min before being stretched to the maximum stress. Then, while keeping a constant stress, they were rapidly cooled to below transition temperature  $T_{low}$  at 3 °C/min and held for 5 min. Finally, the stress was released to recovery temperature  $T_{rec}$  at 3 °C/min for triggering the shape recovery. The most significant parameters to evaluate the shape memory performance are the shape-recovery ratio ( $R_r$ ) and shape-fixity ratio ( $R_f$ ). They can be calculated by the following equations:

$$R_r = \frac{\varepsilon_{u(N)} - \varepsilon_{p(N)}}{\varepsilon_{u(N)} - \varepsilon_{p(N-1)}} \times 100$$
(S1)

$$R_f = \frac{\varepsilon_{u(N)} - \varepsilon_{p(N-1)}}{\varepsilon_{m(N)} - \varepsilon_{p(N-1)}} \times 100$$
(S2)

Where  $\varepsilon_u$  represents the strain after unloading,  $\varepsilon_p$  is the permanent strain after the shape recovery, and  $\varepsilon_m$  represents the maximum strain during loading. N in the equation denotes the cycle number.

IR light induced shape recovery: The samples were exposed to the irradiation of IR light at 1.8 W/cm<sup>2</sup>, and the photothermal behavior have been investigated using a FLIR Pro thermal imaging camera.

### 1.2.8. Dynamic mechanical analysis (DMA)

DMA was performed on a Q800 solids analyzer (TA Corporation, USA) from -50 °C to 150 °C (3 °C/min, 1Hz). Cross-link density ( $v_e$ ) values of the cured materials can be calculated using the following equation<sup>[3]</sup>:

$$v_e = \frac{E}{3RT}$$
(S3)

Where *E* is the storage modulus at rubbery states ( $T_g+20$  °C), R is the gas constant (8.314 J/(mol·K)) and T is the Kelvin temperature of  $T_g+20$ °C.

### 1.2.9. Swelling tests

Samples were immersed in H<sub>2</sub>O, 1 mol/L NaOH, 1 mol/L HCl, hexane (HEX), EtOH, DMF, THF, acetonitrile (ACN), dichloromethane (DCM), ethyl

acetate (ACE), and toluene (TOL) for different times at ambient temperature.

Swelling ratio (%) = 
$$\frac{m_s - m_i}{m_i} \times 100$$
 (S4)

Insoluble fraction (%) = 
$$1 - \frac{m_i - m_d}{m_i} \times 100$$
 (S5)

Where  $m_i$ ,  $m_s$  and  $m_d$  represent the weight of initial, swollen, and dry samples.

# 1.2.10. Self-healing tests

The Self-healing tests of the materials were tested by Leica optical microscope (Germany, ICC50 W). The self-healing efficiency was calculated using the ratio of the reduced scratch width to the initial scratch width of the materials.

#### 1.2.11. Stress relaxation

The stress relaxation curves of the samples were conducted by DMA Q800 instrument with a strain value of 2% in "stress relaxation" mode. The activation energy  $(E_a)$  of the cured materials was calculated using the following equations <sup>[4-5]</sup>

$$\ln \tau^* = \frac{E_a}{RT} - \ln A \tag{S 6}$$

Where T is the absolute temperature, A is a pre-exponential factor, and R is the gas constant.

#### **1.3. Synthetic Procedure**

#### 1.3.1. Synthesis of card polyphenol glycidyl ether (CPGE)

45 g (~0.15 mol) of cardanol was added in a four-necked round-bottom flask equipped with a mechanical stirrer, thermometer sensor, and reflux condenser; then, 141.17g (1.5 mol) of phenol was added into the flask, followed by addition of 1.86 g of tetrafluoro boric acid. The resultant solution was allowed to react at 90 °C for 2 h. After the reaction was complete, the crude product was filtered and washed with excessive hot H<sub>2</sub>O. Finally, the organic phase was dried with anhydrous MgSO<sub>4</sub> and then filtered. Typically, card polyphenol reacted with epichlorohydrin under alkaline conditions to form card polyphenol glycidyl ether, The epoxy value of CPGE was 0.193 mol/ 100 g.



Scheme S1. Synthesis route of CPGE

1.3.2. Synthesis of N-coordinated bicyclic boronic ester amine compounds (BNAs)

Synthesis of BNA-1: N,N-Bis(2-hydroxyethyl)ethylenediamine (7.78 g, 52.50 mmol) and 3-aminobenzeneboronic acid (6.85 g, 50 mmol) were mixed and dissolved in DMF (100 mL) at 40 °C, and the mixture was stirred for 1 h. The resulting mixture was reduced in volume by rotary evaporation under reduced pressure. Then a white powder product with the yield of 82 % was obtained after washing.



Scheme S2. Synthesis route of BNA-1

*Synthesis of BNA-2*: N,N,N',N'-tetrakis(2-hydroxyethyl)ethylenediamine (6.20g, 26.24 mmol) and 3-aminobenzeneboronic acid (6.85g, 50 mmol) were mixed and dissolved in DMF (100 mL) at 40 °C, and the mixture was stirred for 1 h. The resulting mixture was reduced in volume by rotary evaporation under reduced pressure. Then a white powder product with the yield of 80 % was obtained after washing.



Scheme S3. Synthesis route of BNA-2

#### 1.3.3. Preparation of cardanol-based epoxy resin CPGE-BNAs

As shown in Scheme S4, a certain amount of CPGE and BNAs were dissolved in 10 mL DMF. The obtained solutions were stirred at 120 °C for 7 h and dried at 80 °C in vacuum oven remove the DMF to make a smooth film. By changing the molar ratios of epoxy and amino group (0.8, 1.0, 1.2, 1.5, 1.8 and 2.0 respectively), the obtained CPGE-BNA1 were named as CPGE-BNA1-0.8, CPGE-BNA1-1.0, CPGE-BNA1-1.2 and CPGE-BNA1-1.5, respectively. Epoxy resin CPGE-BNA2 was name through the same method.

# 2. Results and Discussion



Figure S1. FT-IR spectra of cardanol, card polyphenol and CPGE



Figure S2. <sup>1</sup>H NMR spectra of card polyphenol and CPGE



Figure S3. FT-IR spectra of BNA1 and BNA2

In the FT-IR spectra, BNAs show the characteristic absorption bands of typical boronic esters: 1454,1357,1240, 1307, 1040<sup>[6]</sup>.



Figure S4. <sup>1</sup>H NMR spectra of BNA1



Figure S5. <sup>1</sup>H NMR spectra of BNA2



Figure S6. FT-IR spectra of CPGE-BNAs



**Figure S7**. (a)The mechanical properties, (b,c) stress–strain curves of CPGE-BNA1 and CPGE-BNA2, (d,e) tan  $\delta$  and (f,g) *E* of CPGE-BNA1 and CPGE-BNA2

Comple	Tensile Strength	$T_{ m g}$	E'25	ve	
Sample	(MPa)	(°C)	(MPa)	$(10^{3} \text{mol/m}^{3})$	
CPGE-BNA1-0.8	21.35±3.45	78.99	949	0.16	
CPGE-BNA1-1.0	32.77±1.51	88.97	1249	0.33	
CPGE-BNA1-1.2	31.86±2.89	84.80	878	0.24	
CPGE-BNA1-1.5	21.09±5.58	82.45	711	0.05	
CPGE-BNA2-1.0	23.67±4.64	83.49	998	0.20	
CPGE-BNA2-1.2	26.03±7.30				
CPGE-BNA2-1.5	33.17±4.33				
CPGE-BNA2-1.8	39.67±2.88	89.72	1700	0.34	
CPGE-BNA2-2.0	31.79±4.40				

Table S1 Mechanical and thermal properties of CPGE-BNA1 and CPGE-BNA2



Figure S8. TGA of original and 3rd reprocessed CPGE-BNA1



Figure S9. TGA and DTG of CPGE-BNA2

Sample		$T_{-5\%}$	T <sub>max</sub> (°C)		Char yield
		(°C)	Ι	II	(%)
CPGE-BNA1-0.8	pristine	297.89		437.48	9.09
	3rd	290.65		439.40	8.10
CPGE-BNA1-1.0	pristine	284.81	311.71	443.63	9.26
	3rd	283.93	317.93	449.93	9.41
CPGE-BNA1-1.2	pristine	277.85	312.96	436.23	9.37
	3rd	261.11	308.11	430.11	8.56
CPGE-BNA1-1.5	pristine	271.91	290.26	444.76	10.25
	3rd	262.11	309.11	435.11	10.68

Table S2 Thermal degradation results of original and 3rd reprocessed CPGE-BNA1

Table S3 Thermal degradation results of CPGE-BNA2

Sample	<i>T</i> -5%(°C)	T <sub>max</sub> (°C)	Char yield (%)
CPGE-BNA2-1.0	362.53	435.53	9.12
CPGE-BNA2-1.2	347.85	433.85	7.24
CPGE-BNA2-1.5	334.89	435.89	6.69
CPGE-BNA2-1.8	332.85	432.85	4.49
CPGE-BNA2-2.0	313.86	435.86	8.30



**Figure S10**. Swelling ratio and insoluble fraction for CPGE-BNA1-1.0, CPGE-BNA2-1.0, and CPGE-BNA2-1.8 in H<sub>2</sub>O, NaOH, and HCl at different times



**Figure S11**. Swelling ratio and insoluble fraction for CPGE-BNA1-1.0, CPGE-BNA2-1.0, and CPGE-BNA2-1.8 in different solvents at different times



Figure S12. Afterglow images of CPGE-BNA2-1.0 excited at 365 nm immersed in  $H_2O$ , HCl, NaOH for four weeks



Figure S13. Afterglow images of CPGE-BNA2-1.0 excited at 365 nm in hexane at different times



Figure S14. Afterglow images of CPGE-BNA2-1.0 excited at 365 nm at different

temperatures



**Figure S15**. Consecutive shape memory cycles of CPGE-BNA1-1.0

Table S4 Shape fixity and recovery properties of CPGE-BNA1-1.0, CPGE-BNA2-1.0

		Cycle	CPGE-BNA1-1.0 (%)	CPGE-BNA2-1.0 (%)	CPGE-BNA2-1.8 (%)
		1	97.73	96.66	96.81
	$R_{\mathrm{f}}$	2	97.52	96.42	96.77
		3	97.94	97.70	96.76
-		1	53.48	87.75	95.84
	$R_r$	2	75.91	91.57	97.40
		3	82.10	~100	~100

and CPGE-BNA2-1.8



**Figure S16**. Recyclability and self-healing of CPGE-BNA1 system polymers: (a) Healing efficiency and mechanical properties of the recycled CPGE-BNA1 polymers after hot processing. (b) FT-IR spectra. (c) Images recording the reprocessing of CPGE-BNA1 system polymers from fractured pieces into a new film via thermal processing. (d) Scratch-repairing images of the CPGE-BNA1 system polymers. (e) Scratch-repairing images of the CPGE-BNA2-1.0 and CPGE-BNA2-1.8. (f) Images recording the reprocessing of CPGE-BNA2-1.0 from fractured pieces.



**Figure S17.** Stress relaxation curves and the relationship between  $ln(\tau^*)$  and temperature: (a) CPGE-BNA1-1.0, (b) CPGE-BNA2-1.0 and (c) CPGE-BNA2-1.8 at different temperatures. (d) Time-resolved emission-decay curves of reprocessed CPGE-BNA1-1.0, excited at 365 nm.

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