MechanochromismTriggered Fluorescent Color Switching among Polymorphs of Natural Fluorescence Pigment

Supporting Information

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EXPERIMENTAL SECTION

Materials and the preparations of different solid forms

Materials. The raw material of Emodin (MH used in the present study was obtained from Sun Chemical & Technology (Shanghai) Co., Ltd., with 98% purity. All analytical grade solvents were purchased from Sinopharm Chemical Reagent Company and were used without any further purification.

Preparation of form I. The Emodin monohydrate (MH) was heated to 90 $^{\circ}$ C for one hour to lose water completely. The yellow powder was obtained for further identification. Form I (2 mg) was dissolved in ether (2 mL). The resulting solution was filtered and placed in 4 mL glass vial sealed by parafilm with only one hole at room temperature under low humidity condition (RH < 43 %) for evaporation. After two weeks, yellow needle crystals were harvested for crystal structure identification.

Preparation of HH. The mix solvent we used contained 1:1 (v/v) mixture of acetonitrile and toluene or 1:1 (v/v) mixture of acetone and toluene (1 mL). 5 mg Emodin form I was dissolved in the mix solvent. The solution was filtered and placed under low humidity conditions (25 % < RH < 50 %) at 25 °C for slow evaporation. After 72 hours, orange needle crystals were obtained and identified as HH.

Preparation of form II. Form II was prepared by heating HH powder at 90 °C for one hour as orange powder. The single crystal of form II was obtained by heating high quality single crystal of HH at 60 °C for 3 days *via* a single-crystal-to-single-crystal transformation process to desolvate water molecules moderately.

Preparation of DH. MH (20 mg) was dissolved in tetrahydrofuran (4 mL). The solution was filtered, placed in a 4 mL glass vial and evaporated at 50 °C in ambient condition for one day to give DH as red powder.

Preparation of form III. MH (20 mg) was dissolved in tetrahydrofuran (4 mL). The solution was filtered, placed in a 4 mL glass vial and evaporated at 50 °C in ambient condition for one day to gain red powder. Form III can only be obtained by desolvation process through heating this red powder (DH, 25 mg) at 130 °C for 5 minutes as orange powder.

Preparation of amorphous. 100 mg form I was put into a ball mill. After milling for two hours, amorphous of Emodin was obtained as orange powder (67.5 mg, 67.5% yield).

Solid State Characterization

X-ray Powder Diffraction (XRPD). All these solid forms were characterized by X-ray Powder Diffraction (XRPD). XRPD patterns were measured at ambient temperature on a D8 Advance (Bruker) diffractometer using copper radiation (Cu K_{α}) at the wavelength of 1.54180 Å. The voltage and current of generator were set to 40 kV and 40 mA, respectively. All data were obtained at ambient temperature over the range 3-40° 2 θ with a scan rate of 5 °/min. Data were imaged and integrated with RINT Rapid and peak-analyzed with Jade 6.0 from Rigaku.

Single Crystal X-ray Diffraction (SCXRD). X-ray diffraction measurements of all single

crystals were executed at 100(2) K on a Bruker Apex II CCD diffractometer using Mo K α radiation (λ = 0.71073 Å) with a graphite monochromator. The integration and scaling of intensity data was attained using the SAINT program. The data were corrected for the effects of absorption using SADASB. The structures were solved by direct methods and refined with the full-matrix least-squares technique using SHELX-2014 software. Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were placed in calculated positions and refined with a riding model. Crystallographic data in cif format have been deposited in the Cambridge Crystallographic Data Center, CCDC No.1482005-1482008 for form I, form II, DH, HH, respectively. In the final refinement, the contributions of disordered solvent to the structure factors were removed by the SQUEEZE program and the crystal structure was further refined with new hkl file generated by the SQUEEZE calculation. Based on the SQUEEZE calculation results, and the TG analysis, water molecules were added directly to the final molecular formula. And some disorder were existed in the main molecule of DH, which did not make a massive difference modelling.

Thermalgravimetric Analysis. Thermogravimetric analysis (TGA) was carried out in a Netzsch TG 209F3 equipment, using dry air with a flow of 20 mL/min and a scan rate of 10 °C/min.

Differential Scanning Calorimetry (DSC). DSC experiments were performed on a PerkinElmer DSC 8500 instrument under a nitrogen gas flow of 20 mL/min purge. Ground samples weighting 3-5 mg were heated in sealed nonhermetic aluminum pans. Two-point calibration using indium and tin was carried out to access the temperature axis and heat flow of the equipment.

Hot-stage microscopy (**HSM**). All HSM examinations were performed on a XPV-400E polarizing microscope and a XPH-300 hot stage coupled with a JVC TK-C9201 EC digital video

recorder (Shanghai Changfang Optical Instrument Company Ltd.). Crystals of polymorphs and hydrates of Emodin were filmed under microscope $(10\times)$ and set to capture images periodically over time during the heating program.

Scanning Electron Microscopy (SEM). The surface morphology of all of the samples was viewed using a scanning electron microscopy (Agilent 8500) operated at a beam voltage of 700 V. The samples were mounted on a steel stage using double-sided adhesive tape before the analysis.

Fluorescence microscopy. In the experiment, we picked a single crystal of HH, put it on a glass slide and sealed it with Dako S302380 mount on the edge of the coverslip. All of the crystal photos were filmed under the excitation wavelength of 460-495 nm $(20\times)$ used Olympus IX51.

UV-vis spectroscopy. UV-vis spectra of solid-state polymorphs and hydrates were recorded on Agilent Cary 500 spectrometer.

The discussion of IR spectra: The Fourier-Transform Infrared (FT-IR) spectroscopy was employed to demonstrate the differences in the carbonyl group and hydrogen bonding in the solid states. As Shown in the Fig. S3, the IR spectra of EM in the range of 400 - 3700 cm⁻¹ were compared. The significant differences observed in the region of 3300 - 3600 cm⁻¹ indicated that O-H stretching were affected by different hydrogen bonding in these forms. The O-H stretching frequency (v_{O-H}) in form I showed relative sharp peak at 3386.4 cm⁻¹. While in form II, form III, HH, MH and DH, the v_{O-H} broadened and red-shifted respectively. In MH, v_{O-H} was split corresponding to the multiple interaction conditions of hydroxyl groups. It is obvious that C-H stretching frequency (v_{C-H}) was relatively strong only in DH. Moreover, the stretching vibration of carbonyl groups were slightly different in IR spectra due to different environment of carbonyl groups in EM. The discussion of DSC diagrams: According to the DSC experiments (Fig. S5a), form I melted at an onset temperature of 260.6 °C. Form II partially transformed to I during the heating ramp, a melting event of form II was observed at an onset temperature of 257.9 °C with melting of form I embedded. Form III melted at an onset temperature of 255.4 °C. The loss of HH channel water in the crystal lattices could be seen in the magnifying DSC diagram in Fig. S5b. As we already confirmed in TGA and VT-XRPD, after desolvation, HH transformed to form II was observed at the onset temperature of 258.1 °C with melting of form I embedded. A broad endothermic event was observed at the region of 90 - 150 °C on the DSC diagram of MH, corresponding to the dehydration process and subsequently transformation to form I. As the temperature ramping up, a melting event at an onset temperature of 256.6 °C was observed. While DH undergwent an endothermic transition at a region of 105 - 123 °C, corresponding to the desolvation process and followed by a melting endothermit at an onset temperature of 256.2 °C.

The transition process of MH. According to the DSC diagrams (Fig. S5) and VT-XRPD patterns of MH (Fig. S15), MH transformed to form I via heating at 90 °C. Since the emission colors of form I and MH showed no obvious differences, the bulk powder transition process was not monitored under 365 nm UV light.

The transition process of DH. According to DSC (Fig. S5) and VT-XRPD patterns (Fig. S16), DH presented a complex transition process. It underwent an endothermic transition process at the region of 105 - 123 °C which corrresponded to the desolvation process of DH. The VT-XRPD patterns of DH confirmed that after desolvation, DH transformed to form III and subsequently transformed to form I under heating process.

Bulk sample phase transition process of HH monitored under 365 nm UV light. HH powder was molded into letter "EM" and it was put under 365 nm UV light. The tangerine HH powder was put at 90 °C for two hours, the color change from tangerine to light orange was monitored by digital camera under the same condition. After heated, the powder wasbalanced at 25 °C under 60% RH for one day, the tangerine was re-emerged. The reversible color changes before and after balanced demonstrate the reversible transition process of two isomorphs under different stress conditions. The conversion between tangerine and light orange was repeated two times without fatigue as these stimuli are non-destructive. The color discrepancy between powder and single crystal of HH and form II may be caused by different wavelength of irradiation source and the fast absorption of channel water in form II powder in the process of filming. Subsequently, the "EM" powder was heated from 90 °C to 190 °C. The "EM" started to turn yellow gradually as heating temperature increased, which corresponded to the solid-state conversion from form II to form I. However, the unchanged XRPD patterns when cooling to 90 °C indicates that the transition process from form II to form I is irreversible.

Bulk sample phase transition process of DH monitored under 365 nm UV light. In Fig. S17, DH powder was molded into letter "EM" and it was put under 365 nm UV light. The transition process was monitored by digital camera. The dark red DH powder was heated at 130 °C for 8 minutes, the color changed from dark red to orange. Subsequently, the "EM" powder was heated to 170 °C for 8 minutes. The "EM" started to turn yellow gradually as heating temperature increased, corresponding to the solid-state conversion from form III to form I.

Diagrams:



Scheme. S1 Chemical structures of Emodin



Fig. S1 XRPD patterns of different solid states of Emodin



Fig. S2 Experimental and simulated XRPD patterns of Emodin polymorphs and hydrates



Fig.S3 IR spectra of Emodin polymorphs and hydrates



Fig. S4 TGA diagrams of Emodin polymorphs and hydrates



(a)



Fig. S5 (a) DSC diagrams of Emodin polymorphs and hydrates, (b) a comparison of DSC patterns for form II and HH



Fig. S6 Solid-state UV-Vis spectra of Emodin solid forms



Fig. S7 Photos of Emodin different solid states under room light (up) and UV light under 365 nm

(down)



Fig. S8 Solid-State fluorescence spectra of Emodin solid forms



Fig. S9 Overlay of EM molecules in form I (green), form II(cyan), HH (magenta), MH (yellow)





Fig. S10 XRPD patterns of HH and form II



Fig. S11 XRPD patterns of solid-state transition from HH to form I by heating



Fig. S12 HSM photos of Emodin HH inter-conversion (a) HH, (b) 90 °C, (c) 130 °C, (d) 140 °C, (e) 140 °C 3 min, (f) 140 °C 6 min, (g) 140 °C 9 min, (h) 140 °C 18 min, (i) 140 °C 36 min, (j) 140 °C

54 min, (k) 140 °C 90 min, (l) 140 °C 180 min, (m) 140 °C 300 min, (n) 140 °C 420 min



Fig. S13 Photos of (a) Powder sample under UV (365 nm) and (b) molecular arrangement

transformation from EM HH to form I.



Fig. S14 XRPD patterns for heated form I cooling to 90 °C-combined with figure S11, form II

heat from room temperature to 140 °C, then cool to room temperature.



Fig. S15 XRPD patterns of the desolvation process of MH



Fig. S16 XRPD patterns of the desolvation process of DH

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Guest molecule	HH	MH	DH		
Calculated weight loss (%)	3.23	6.25	11.76		
Observed weight loss (%) in TGA	3.31	5.98	11.70		

Table S1. TGA data for the hydrates of Emodin

Table S2. Unit Cell Comparison for the Polymorphs and Hydrates of Emodin

	Form I	Form II	НН	DH	MH(known)
Empirical	$C_{15}H_{10}O_5$	$C_{15}H_{10}O_5$	$C_{15}H_{10}O_5$	$C_{15}H_{10}O_5$	$C_{15}H_{10}O_5$
Formula			0.5H ₂ O	2H ₂ O	H ₂ O
Mr	270.23	270.23	278.87	302.23	288.24
Crystal	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
System					
Space	C 2/c	P 21/n	P 21/n	P 21/n	P 21/c
Group					

a (Å)	27.783(4)	16.4721(10)	16.6384(6)	12.6343(6)	9.5881(6)
b (Å)	4.6822(8)	3.6915(2)	3.6887(2)	3.6437(2)	15.1776(8)
c (Å)	20.212(3)	19.4294(12)	19.4060(7)	31.2026(14)	9.2655(6)
a(deg)	90	90	90	90	90
β(deg)	118.891(8)	96.188(4)	95.544(3)	95.706(3)	113.115(3)
γ(deg)	90	90	90	90	90
V(Å ³)	2302.1(6)	1174.56(12)	1185.45(9)	1429.31(12)	1240.11(13)
$Dx(g \cdot cm^{-3})$	1.559	1.528	1.508	1.404	1.544
Z/Z'	8	4	2	4	4
T,K	100(2)	100(2)	100(2)	100(2)	100(2)
wR	14.04	30.6	21.58	23.33	13.47
Rint	5.62	9.06	4.15	5.56	4.72
Gof	1.062	1.014	1.032	1.050	1.027

Table S3.List of intermolecular H-bonding lengths and angles for five different solid forms

Crystal	Interactions	H····A/Å	D…A/Å	<d-h····a th="" °<=""><th>Symmetry code</th></d-h····a>	Symmetry code
form					
Form I	O4-H2····O2	1.784	2.789	168.84	-x+2, -y+3, -z+2
	C8-H4····O4	2.52	3.394	157	-x,y,-1/2-z
	С10-Н5…О2	2.56	3.252	132	-x,-1-y,-z
Form II	O4-H2····O2	2.155	2.900	151.22	-x+1, -y+2, -z
	О5-Н3…О3	2.557	3.135	128.66	-x+1/2, y-1/2,
					-Z+1/2

	С10-Н5…О2	2.58	3.305	135	-x,-1-y,-z
НН	04-H2···O6A	1.878	2.627	151.40	x, y+1, z
	O5-H3····O3	2.555	3.115	121.88	-x+1/2, y-1/2, -z+1/2
MH	O4-H2···O6	1.79	2.620	172	• -x+1,-y+1,-z+1
	O6-H12····O2	1.99	2.804	158	1-x,-1/2+y,1/2-z
	O6-H11····O3	2.11	2.879	149	$x, -y + \frac{1}{2}, z - \frac{1}{2}$
	С7-Н8••••О4	2.51	3.434	163	$x+1,-y+\frac{1}{2},z-\frac{1}{2}$
	O3-H1…O5	2.55	3.090	123	-x+2,-y,-z+1
DH	С15-Н10О2	2.16	3.012	147	-x,1-y,-z



Fig.S17 The transition process of DH powder ("EM") under 365nm UV irradiation.



Fig. S18 XRPD patterns for the ball milling process of EM form I.