Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Solid-State Fluorescent Materials Based on Coumarin Derivatives: Polymorphism, Stimuli-Responsive Emission, Self-Assembly and Optical Waveguides

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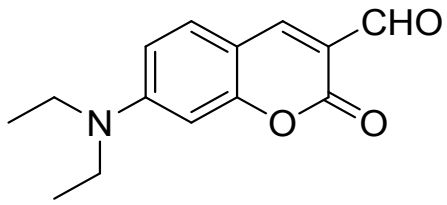
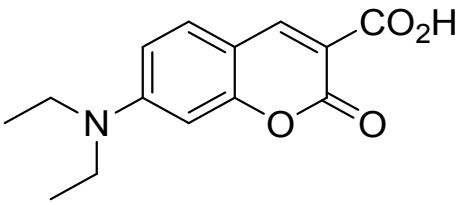
Table of Contents

1. General Information

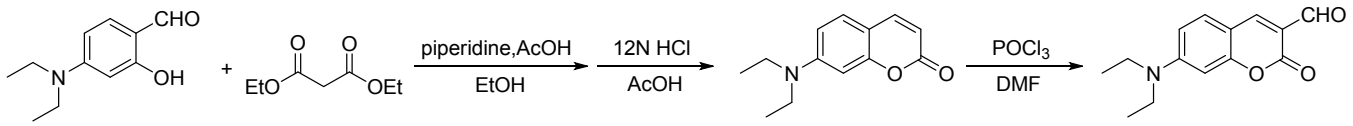
DMF was distilled over CaH_2. Petroleum ether and ethyl acetate for chromatography were distilled before used. All other reagents and solvents were used directly from the corresponding supplier without further purification. All starting materials were purchased from Aladdin, Energy, Accela, Tansoole and use directly. Analytical thin-layer chromatography (TLC) was carried out using commercial silica gel plated (GF254). Nuclear magnetic resonance spectra (^1H, ^{13}C NMR) were recorded on a Bruker Ascend 600 (^1H at 600 MHz, ^{13}C at 151 MHz). The chemical shifts are reported as ppm and solvent residual peaks were shown as following: $CDCl_3$ δ H (7.26 ppm) and δ C (77.16 ppm). UV-visible absorption spectra were measured on Purkinje TU-1950 spectrometer. Fluorescence spectra were recorded on a Hitachi F-7000 spectrometer. Fluorescence quantum yields were measured using Hamamatsu C9920-02G. Fluorescence lifetime was measured using Edinburgh FLS980 spectrometer. Single crystal was collected on Oxford diffraction Eos CCD detector or Bruker CMOS PHOTON 100 detector, respectively. Powder X-Ray diffraction (XRD) was performed on a Bruker D8 Advance. The single crystal pictures were taken on Olympus DP80 fluorescent microscopy. High-resolution Mass spectra (HRMS) were obtained on a Bruker Maxis and Microflex and reported as m/z (relative intensity). Accurate masses are presented as molecular ion $[M+Na]^+$.

2. Target Compounds Charts

Compound	Compound
	
Data NMR X-ray (O) X-ray (R)	Data NMR X-ray (G) X-ray (R)

3. Experimental Procedure and Characterization Data

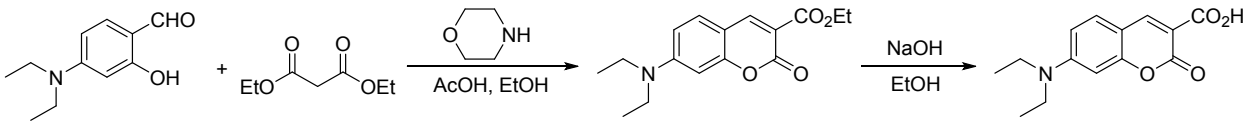
3.1 Reaction procedures



4-(diethylamino)salicylaldehyde (1.93 g, 10.00 mmol), diethyl malonate (3.03 mL, 20.00 mmol), piperidine (1.00 mL) and one drop of AcOH were combined in absolute EtOH (60.00 mL) and refluxed for 6 hours. All volatiles were evaporated under reduced pressure, then concentrated HCl (20.00 mL) and glacial acetic acid (20.00 mL) were added to cyclize, hydrolyze and decarboxylate the intermediate ester while stirring for another 24 hours at reflux. The solution was cooled to room temperature and poured into 100.00 mL of ice water. Then 40% NaOH solution was added dropwise to adjust the pH to 5.0, and a gray precipitate formed immediately. After stirring for 1 hour, the mixture was filtered, washed with water, and dried to give 7-(diethylamino)coumarin in 92% yield.

Freshly distilled DMF (1.60 mL) was added dropwise to $POCl_3$ (1.60 mL) at 25°C under N_2 atmosphere and stirred for 30 minutes to give a red solution. The solution was added to 7-(diethylamino)coumarin (1.10 g, 5.18 mmol) in 7.50 mL DMF to afford a scarlet suspension. The mixture was stirred at 60 °C for 24 hours and then poured into ice water. NaOH solution was added to adjust the pH to 5.2 to generate an abundant precipitate. The crude product was filtered to give desire product in 60% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.11 (s, 1H, CHO), 8.23 (s, 1H, Ar H), 7.39 (d, 1H, J = 9.0 Hz, Ar H), 6.63-6.61 (q, 1H), 6.47 (d, 1H, J = 1.9 Hz), 3.48-3.45 (q, 4H, CH_2), 1.24 (t, 6H, J = 7.1 Hz, CH_3); ^{13}C-NMR (151 MHz, $CDCl_3$) δ (ppm): 187.94, 161.93, 158.99, 153.57, 145.44, 132.60, 114.30, 110.30, 108.28, 97.19, 45.36, 12.53; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{14}H_{15}NO_3Na^+$, 268.0944,

found, 268.0948. Compounds chart X-ray NMR



4-(diethylamino)salicylaldehyde (1.93 g, 10.00 mmol) and diethyl malonate (5.20 mL, 34.00 mmol) was dissolved in anhydrous EtOH (50.00 mL). Then a mixture of morpholine (87.00 μL, 0.10 mmol) and acetic acid (40.00 μL) in 4.00 mL anhydrous EtOH were added to above solution. After stirring at 80°C for 8 hours, the reaction solution was concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 2 : 1) to give ethyl 7-(diethylamino)coumarin -3-carboxylate in 76% yield.

0.5 M NaOH (20.00 mL) were added to a solution of ethyl 7-(diethylamino)coumarin-3-carboxylate (0.87 g, 3.00 mmol) in EtOH (20.00 mL). After stirring for 12 hours at 25°C, the reaction solution was concentrated under reduced pressure. Hydrochloric acid was then added to adjust the pH to 2.0 and generated an abundant precipitate. The crude product was filtered to give 7-(diethylamino)coumarin-3-carboxylic acid in 60% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 12.32 (s, 1H, COOH), 8.61 (s, 1H, Ar H), 7.43 (d, 1H, J = 9.0 Hz, Ar H), 6.71-6.69 (m, 1H, Ar H), 6.51 (d, 1H, J = 2.3 Hz), 3.50-3.46 (q, 4H, CH_2), 1.26 (t, 6H, J = 7.1 Hz, CH_3); ^{13}C-NMR (151 MHz, $CDCl_3$) δ (ppm): 165.62, 164.52, 158.11, 153.90, 150.26, 132.03, 111.06, 108.60, 105.48, 96.87, 45.44, 12.47; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{14}H_{15}NO_4Na^+$, 284.0899, found, 284.0897. Compounds chart X-ray NMR

3.2 Preparation of Micromaterials

The micromaterials were prepared by injecting 100 μL of DCA or DCCA solution (3.0×10^{-2} M) in THF into 5 mL of ultrasonic water. The aggregated molecules DCA or DCCA occurred in consequence of the change in the solubility. The mixture solution was continually ultrasonic treated for 10 min and sequentially was aged for 9 hours at room temperature. The aged suspensions of microcrystals were transferred onto clean quartz substrates and dried for morphology and spectroscopy measurements.

4. Summary of the Optical Properties

Table S1 Optical properties for DCA and DCCA in different solvents at 298K[a].

Solvents	Δf	λ_{abs} [nm]	ε [cm^{-1} M^{-1}]	λ_{em} [nm]	$\Delta\nu$ [cm^{-1}]	Φ_F (%)	τ_{ave} (ns)
DCA							
Toluene	0.014	438	57200	465	1326	61.8	2.11
Ethyl acetate	0.200	438	64500	478	1910	34.8	1.49
Tetrahydrofuran	0.210	440	52900	478	1807	46.0	1.89
Acetone	0.285	442	54200	487	2091	4.5	0.27
Acetonitrile	0.305	443	51500	490	2165	2.7	0.49
DCCA							
Toluene	0.014	424	20300	450	1362	93.4	3.09
Ethyl acetate	0.200	423	44200	463	2042	13.3	13.90
Tetrahydrofuran	0.210	424	37300	466	2126	24.1	0.85
Acetone	0.285	427	36900	474	2322	3.2	20.65
Acetonitrile	0.305	429	36700	476	2302	2.1	16.04

[a]Abbreviation: Δf = solvent polarity parameters, λ_{abs} = absorption maximum, λ_{em} = emission maximum, Φ_F = solution fluorescence quantum yield estimated by using the calibrated integrating sphere system.

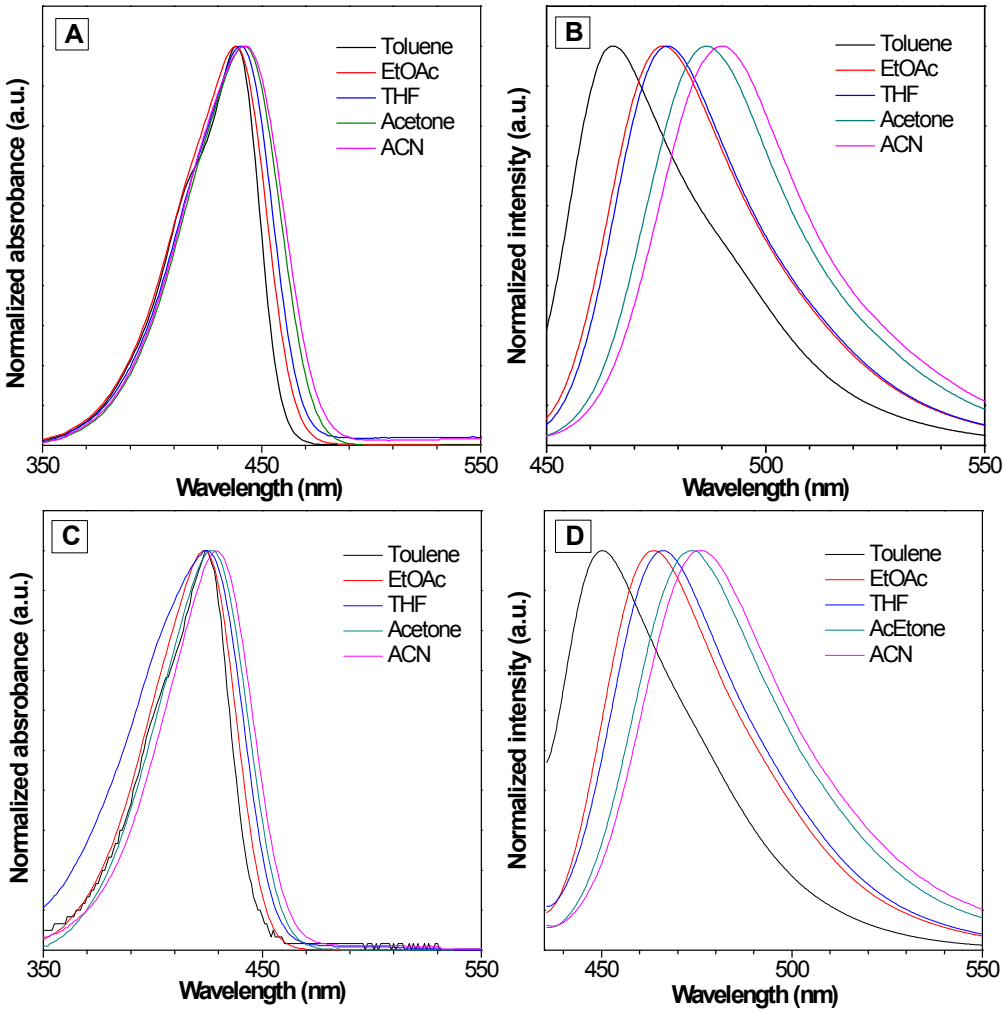


Fig. S1 Normalized absorption spectra of DCA (10 μM) (A) and DCCA (10 μM) (C) in different solvents. Normalized PL spectra of DCA (10 μM) (B) and DCCA (10 μM) (D) in different solvents.

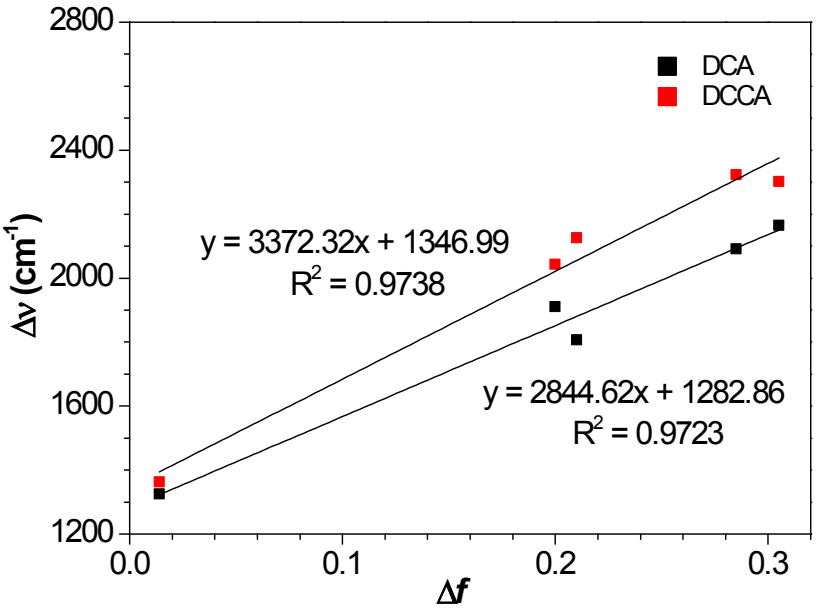


Fig. S2 Lippert-Mataga plot of DCA and DCCA.

5. PXRD Data

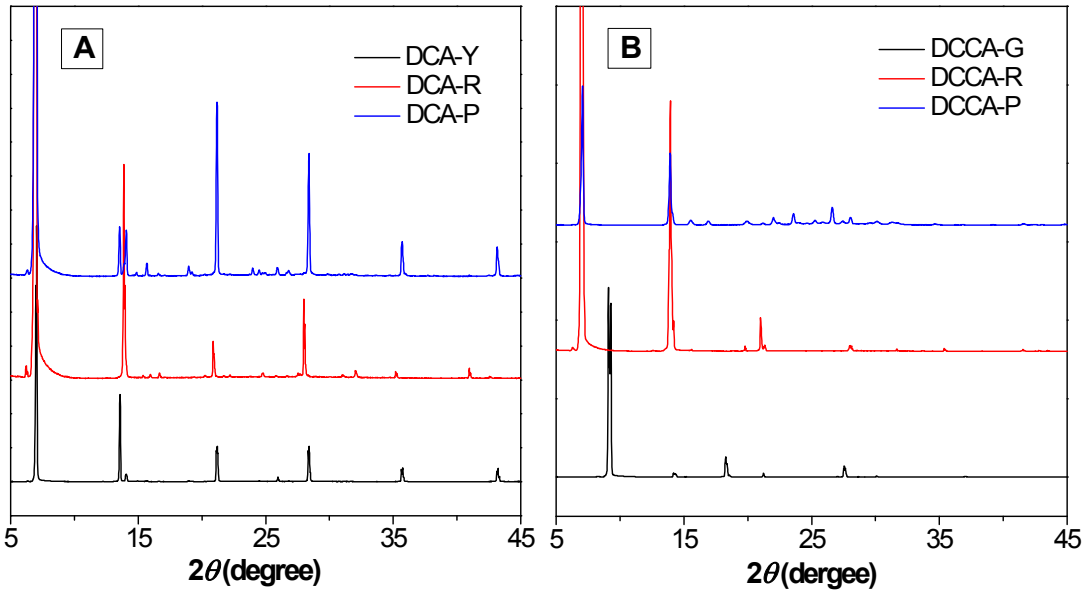
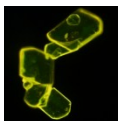
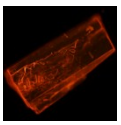
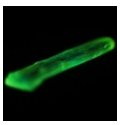
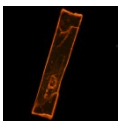


Fig. S3 PXRD of DCA and DCCA under different state.

6. X-ray Single Crystals Data

Table S2. Crystallographic data.

Crystal	**DCA-Y**[1]	**DCA-R**[2]	**DCCA-G**	**DCCA-R**[3]
formula	$C_{14}H_{15}NO_3$	$C_{14}H_{15}NO_3$	$C_{14}H_{15}NO_4$	$C_{14}H_{15}NO_4$
crystal system	triclinic	monoclinic	triclinic	monoclinic
space group	P -1	C 1 2/c 1	P-1	P2 (1) /c
a [Å]	7.1186 (4)	25.3417 (9)	5.0788 (3)	14.075 (5)
b[Å]	7.4835 (5)	7.6890 (3)	10.0610 (7)	7.9101 (15)
c[Å]	12.5900 (6)	12.5224 (4)	12.9069 (8)	12.694 (3)
β [deg]	85.720 (4)	94.012 (2)	80.914 (5)	116.62 (4)
V [Å^3]	613.46 (7)	2434.04 (15)	627.97 (7)	1263.5 (6)
Z	2	8	2	4
μ [mm^{-1}]	0.767	0.094	0.846	0.841
T [K]	293	153	293	293
θ_{min}-θ_{max}[deg]	0.686-1.000	0.628-0.746	0.756-0.785	0.775-0.817
R	0.0417	0.0425	0.0539	0.0599
wR_2	0.1298	0.1224	0.1811	0.1797
GOOF	1.059	1.047	1.074	1.075
crystal pictures[a]				
	Compounds chart Data NMR		Compounds chart Data NMR	

[a] The fluorescent pictures of corresponding single crystals were taken by Olympus DP-80 fluorescence microscopy under UV irradiation.

References:

1. X. C. Li, L. Yang, X. W. Zhang, L. F. Li, Y. Zhou and Y. A. Son, *Z. Kristallogr.-New Cryst. Struct.*, 2014, **229**, 241.
2. H. D. Li and B. Z. Yin, *Acta Crystallogr., Sect. E: Struct. Rep.*, 2011, **67**, o1713.
3. G. R. Bardajee, M. A. Winnik and A. J. Loung, *Acta Crystallogr., Sect. E: Struct. Rep.*, 2006, **62**, o3076.

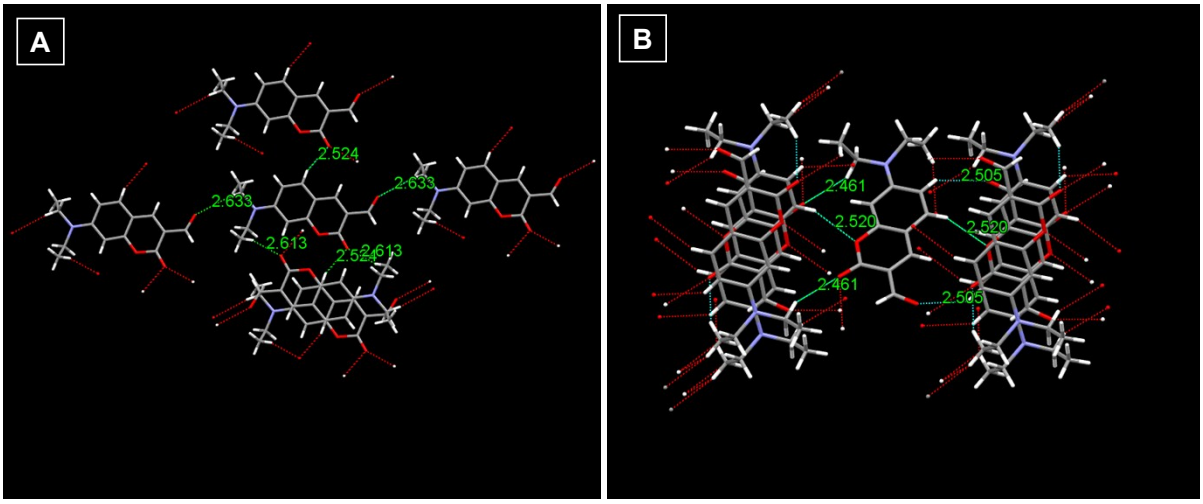


Fig. S4 View of the C–H···O interaction in DCA-Y (A) and DCA-R (B).

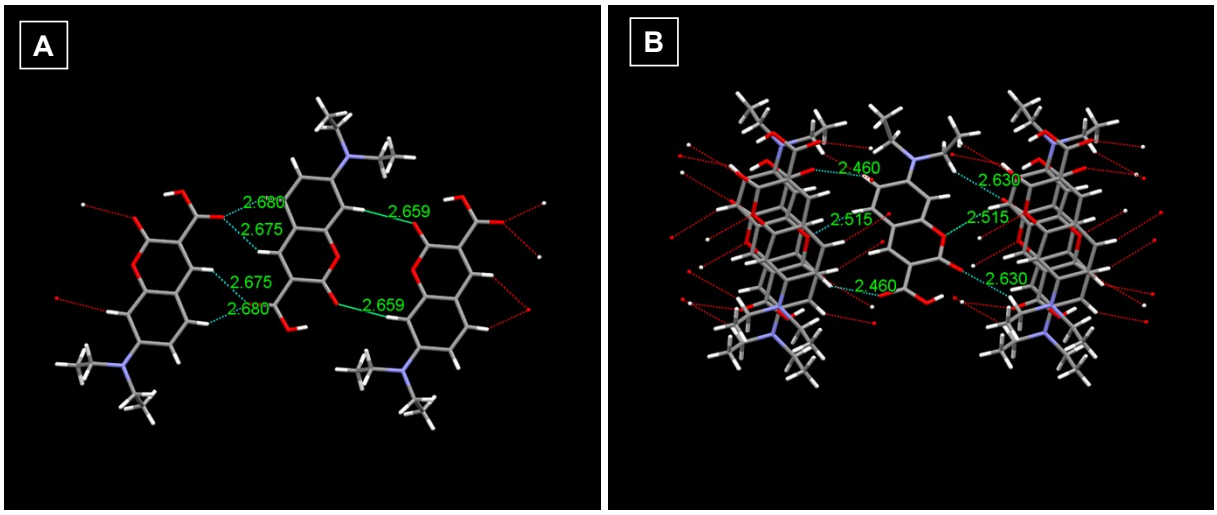


Fig. S5 View of the C–H···O interaction in DCCA-G (A) and DCCA-R (B).

7. Photoluminescence Properties under Thermal Stimuli

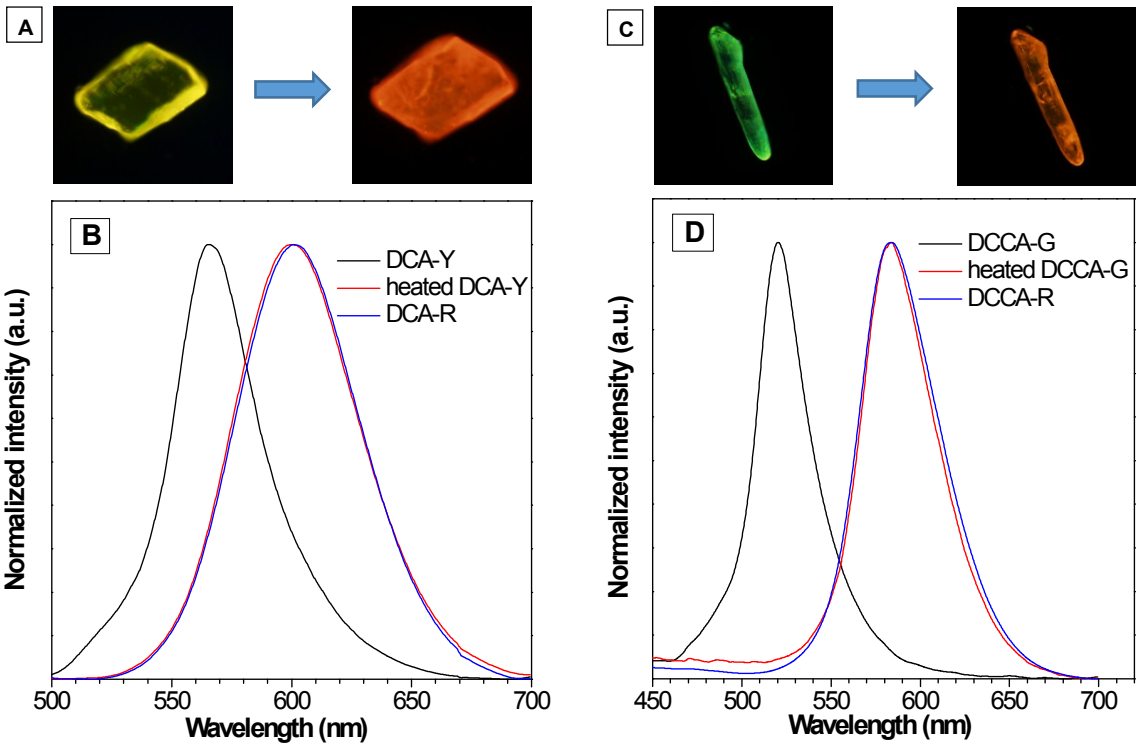


Fig. S6 The photographs of crystal to crystal transformation of DCA-Y into DCA-R (A) and DCCA-G into DCCA-R (C) under the fluorescence microscope. (B) Normalized PL spectra of crystal DCA-Y, heating treated DCA-Y and DCA-R. (D) Normalized PL spectra of crystal DCCA-G, heating treated DCCA-G and DCCA-R.

8. ^{1}H NMR analysis of DCA and DCCA under Acidic-Basic Condition

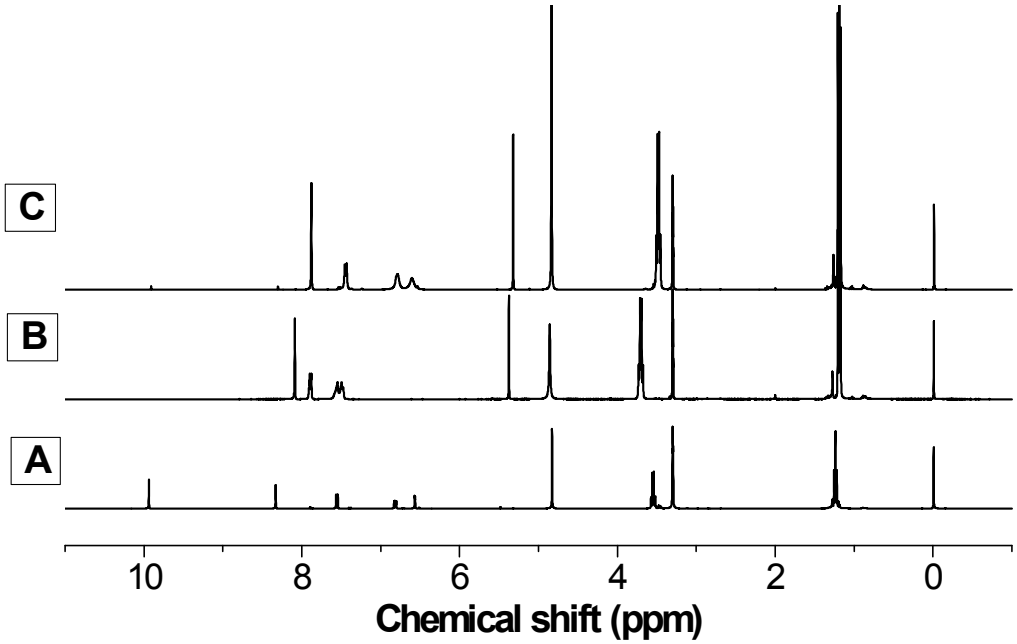


Fig. S7 (A) The ^{1}H NMR signal of DCA. (B) The ^{1}H NMR signal of DCA after treated with HCl gas. (C) The ^{1}H NMR signal of DCA after treated with NH_3 gas.

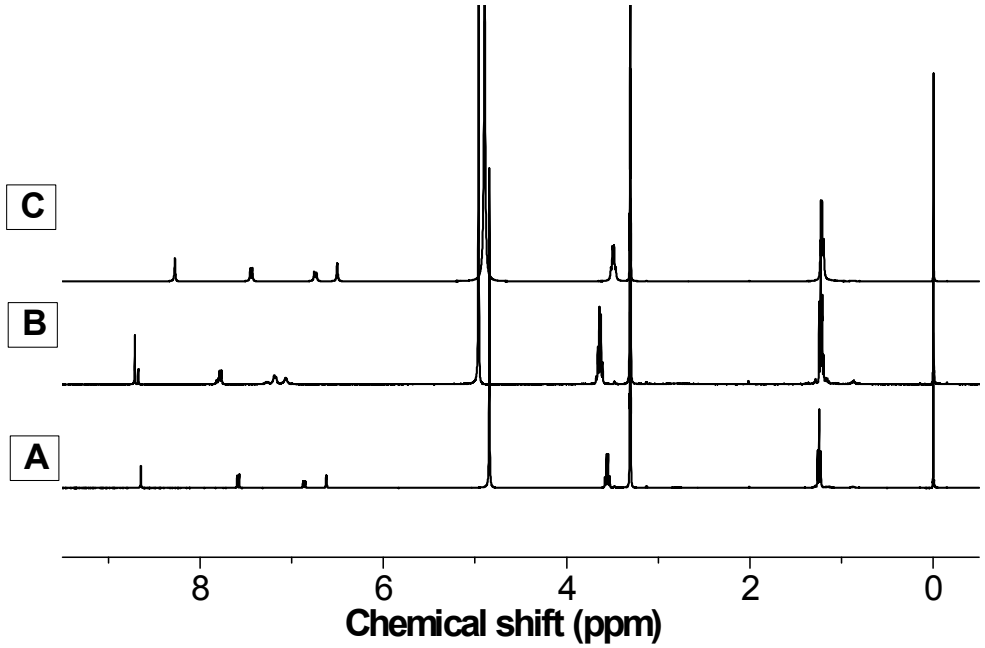


Fig. S8 (A) The ^{1}H NMR signal of DCCA. (B) The ^{1}H NMR signal of DCCA after treated with HCl gas. (C) The ^{1}H NMR signal of DCCA after treated with NH_3 gas.

9. Photoluminescence Properties of DCA and DCCA after Self-Assembly

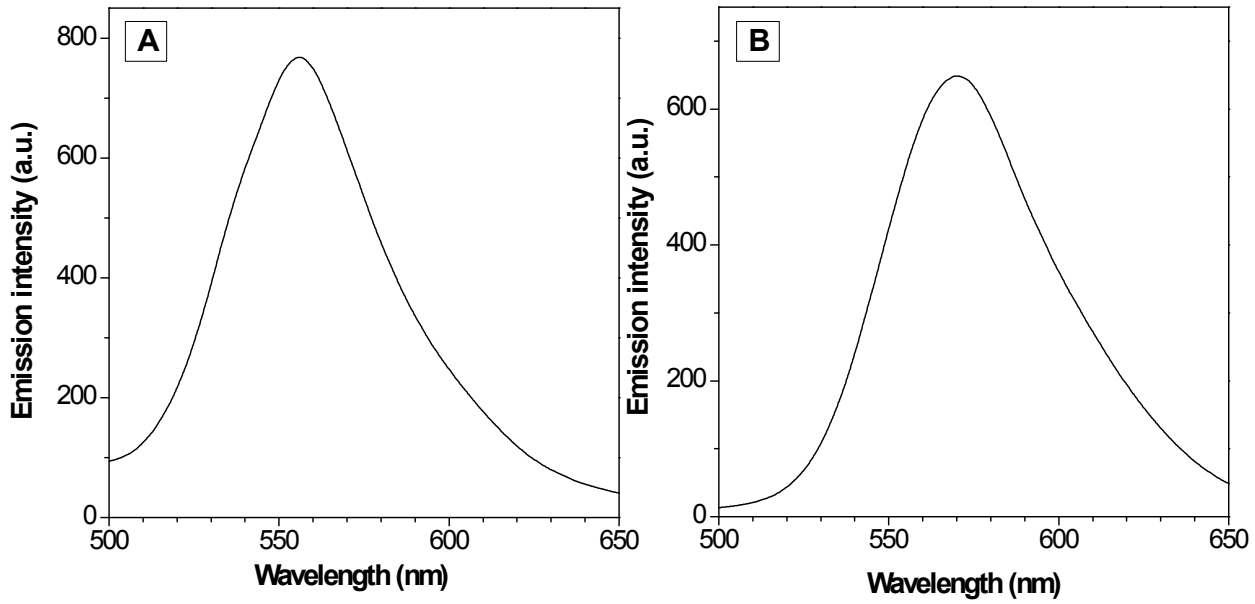
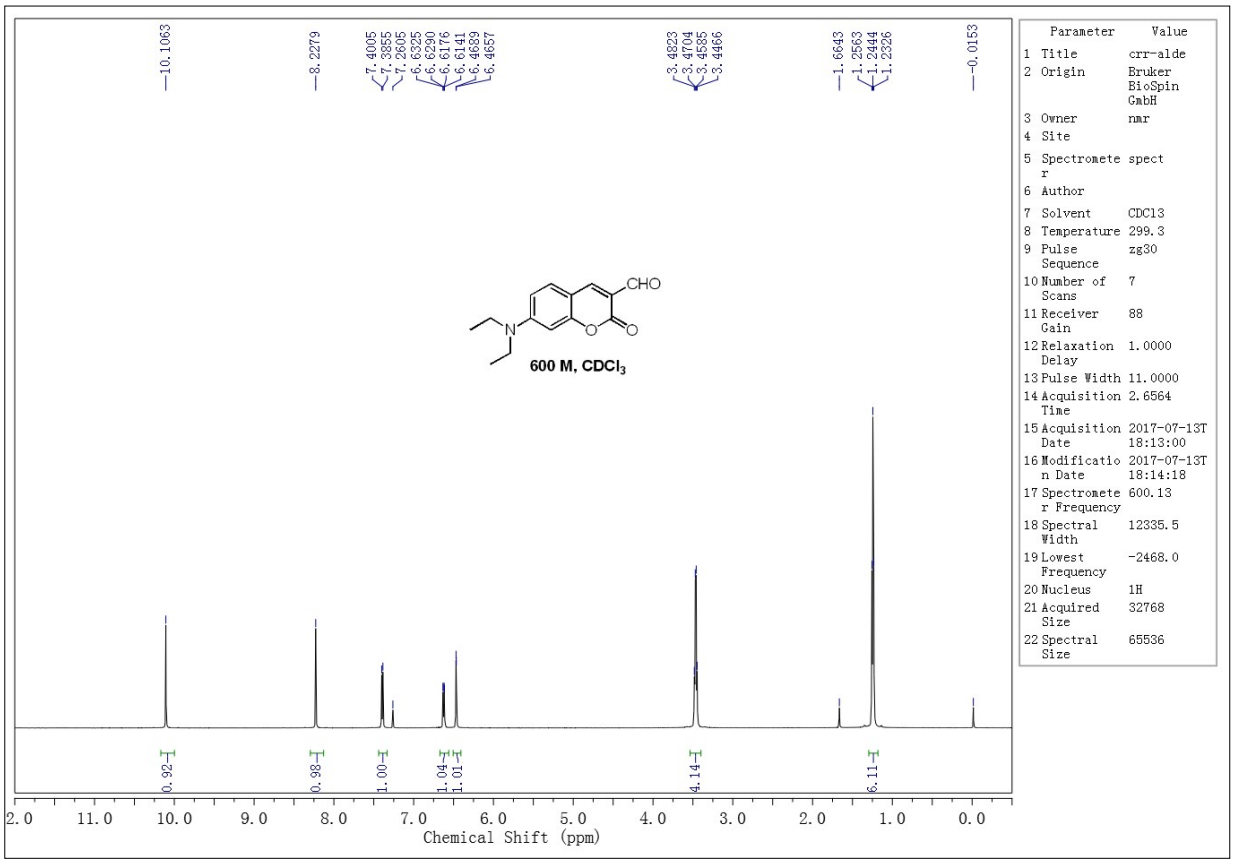
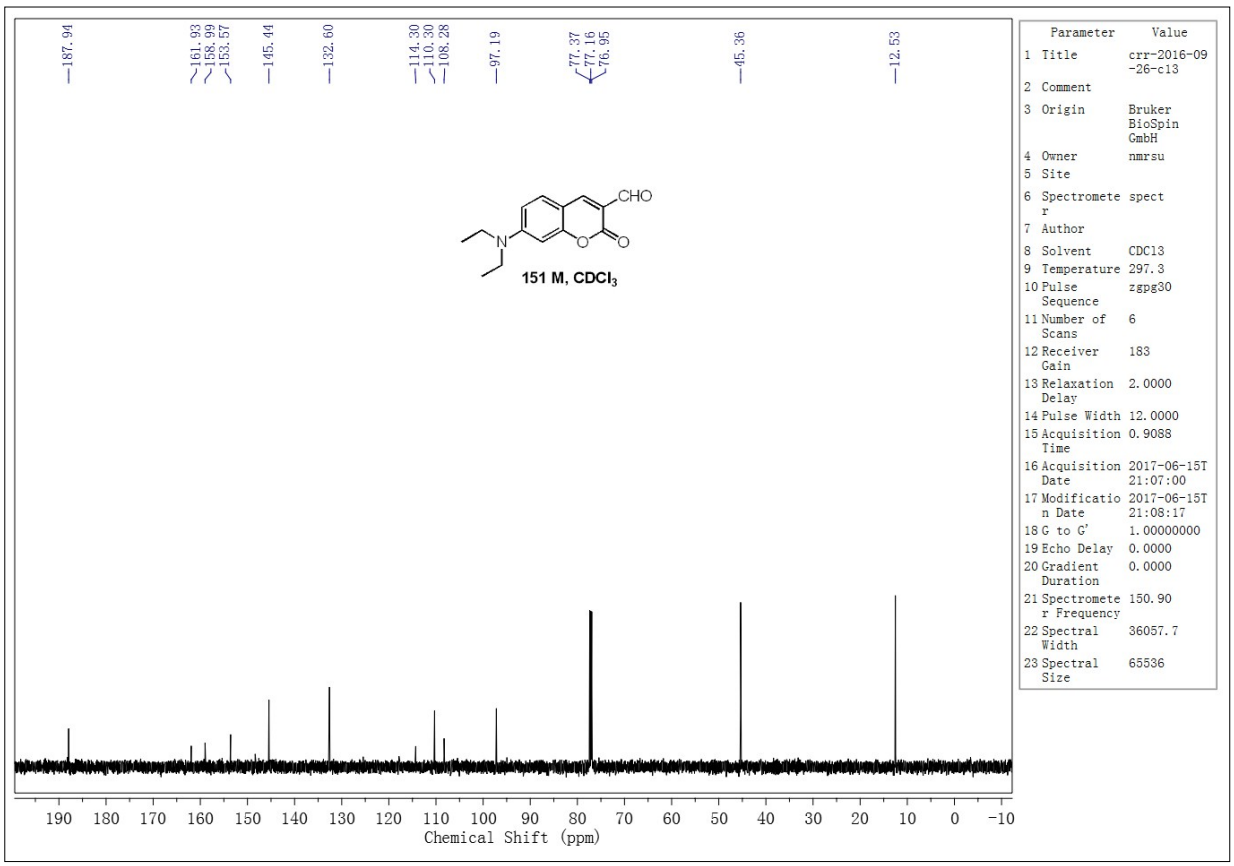


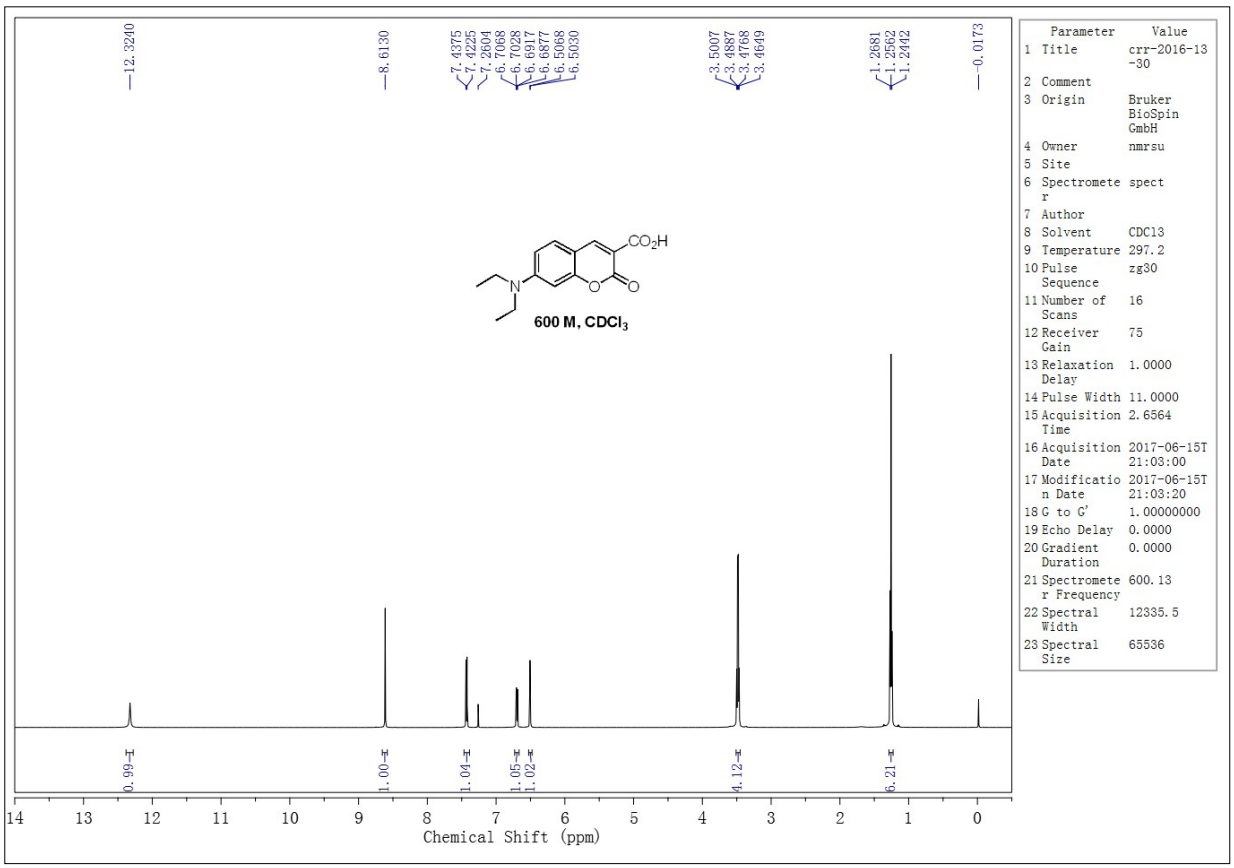
Fig. S9 (A) PL spectra of DCA after self-assembling into ordered structures. (B) PL spectra of DCCA after self-assembling into ordered structures.

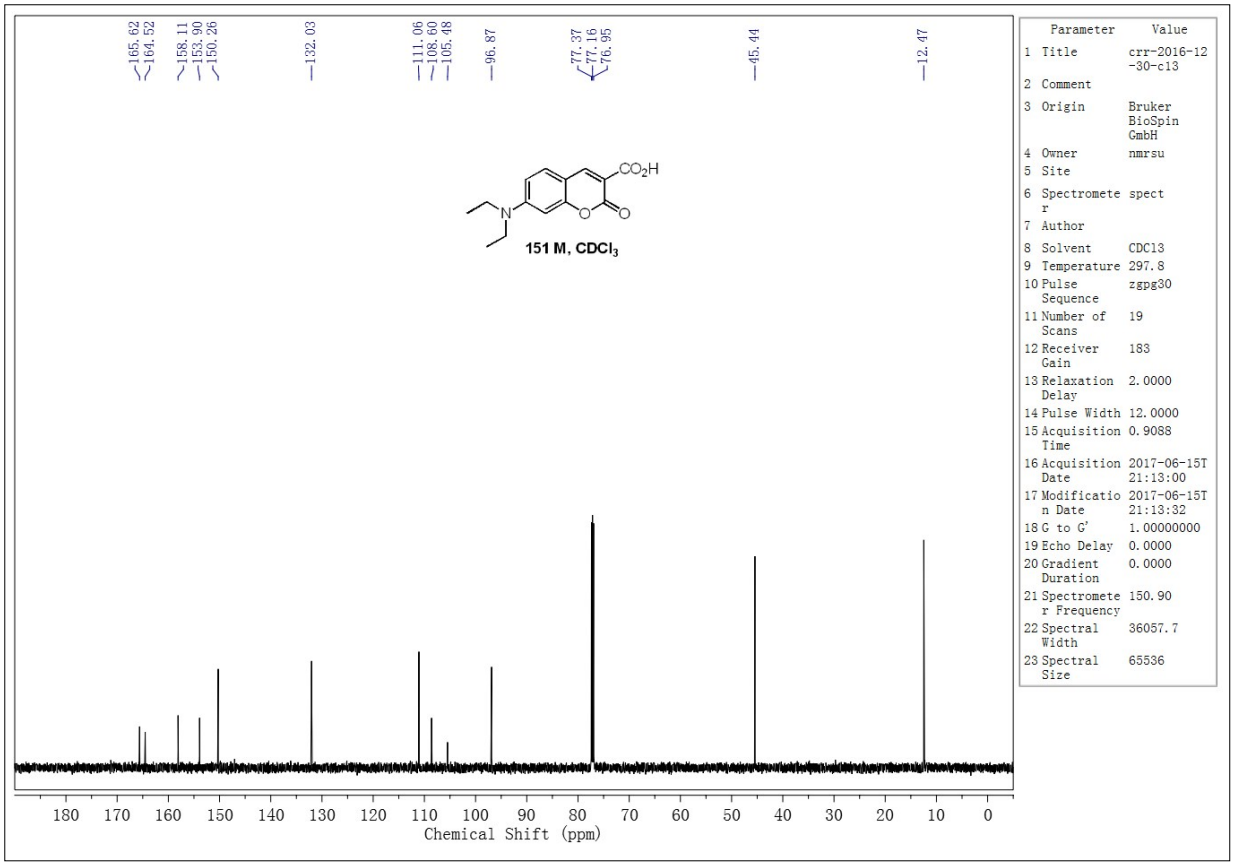
10. NMR Spectra





Compounds chart Data X-ray





Compounds chart Data X-ray