

Electronic Supporting information

**Construction of Tetraphenylethene Derivative Exhibiting High
Contrast and Multicolored Emission Switching**

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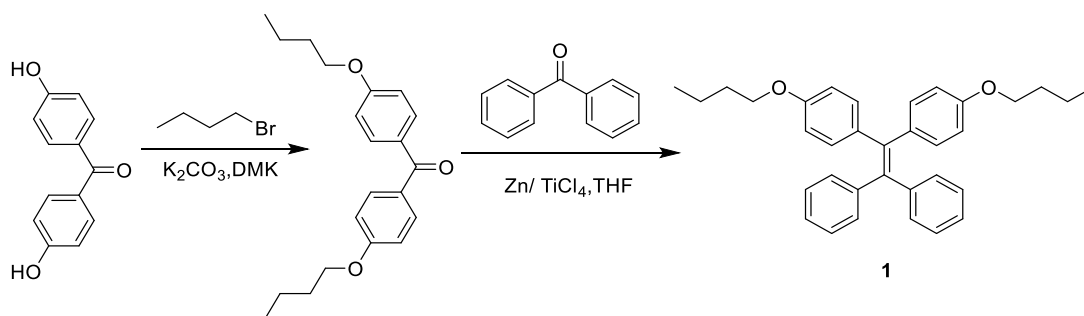
Experimental Section

Materials and Instrumentations

4,4'-dihydroxybenzophenone was purchased from Alfa Aesar. Potassium carbonate, titanium tetrachloride, acetone, zinc dust, 1-bromobutane, acetone, 1-bromobutane, ammonium chloride, and anhydrous magnesium sulfate were purchased from Sinopharm Chemical Reagent Co.Ltd. THF was purchased from Aldrich and distilled under normal pressure from sodium benzophenone under argon immediately prior to use.

All the reactions were carried out under a nitrogen atmosphere using Schlenk technique. ^1H NMR and ^{13}C NMR spectra were recorded using a Bruker AV 400 Spectrometer at 400 and 100 MHz in DMSO- d_6 solutions, respectively. Tetramethylsilane was used as the internal standard. An LCT Premier XE time-of-flight mass spectrometer (Micromass), equipped with a dual sprayer orthogonal electrospray source (LockSpray), was used to obtain exact mass measurements. Fluorescence spectra of all samples were measured by a Cary Eclipse spectrofluorometer. Fluorescence quantum yields of solid were recorded on Hamamatsu Quantaurus-QY C9220-02 at room temperature with a calibrated integrating sphere system, and the machine was revaluated using standard sample before measurement. Fluorescence lifetimes were measured with Hamamatsu Quantaurus-Tau C11367-11 at room temperature. Infra-red (IR) spectra were obtained on a Nicolet Fourier spectrofluorometer. Differential scanning calorimetry (DSC) was carried out using a Mettler DSC 1 instrument at a scanning rate of 10 K min^{-1} . Powder X-Ray diffraction (PXRD) patterns were performed on an X'Pert PRO MPD diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at 25°C (scan range: 4.5-50°). Single crystals data was collected on a Bruker Smart APEXII CCD diffractometer using graphite monochromatic Mo $K\alpha$ radiation ($\lambda=0.71070 \text{ \AA}$). Melting points were measured by DSC analysis. All photographs were recorded on a FinePix S7000 digital camera. The thermal annealing processes were carried out in oven. The amorphous solid of luminogens were prepared by heating the luminogens to melt with a heating gun and quenching the melt with liquid nitrogen.

Synthesis Procedures and Characterization Data



Synthesis routes of luminogen **1**.

A mixture of 4, 4'-dihydroxybenzophenone 6.52 g (30 mmol), 1-bromobutane 60 mL, potassium carbonate 12.44 g (90 mmol) and 60 mL of acetone were added into 500 mL two-neck flask. The mixture was refluxed under nitrogen atmosphere until TLC exhibited complete conversion. The cooled mixture was poured into 300 mL of water and extracted with diethyl ether (3×100 mL). The organic layers were dried over anhydrous magnesium sulfate and filtered. The solvent of filtrate was removed with a rotary evaporator to gain dibutoxy benzophenone as white powder (26.1 mmol, 87%).

As a universal McMurry coupling reaction, a 250 mL two-necked flask equipped with a magnetic stirrer was charged with zinc powder (3.09 g, 48 mmol) and 60 mL THF under nitrogen atmosphere. The mixture was cooled to 0°C, and TiCl₄ (2.55 mL, 24 mmol) was added slowly by a injector. The mixture was refluxed for 2.5 h and cooled to room temperature. Then pyridine (1.33 mL) was added dropwise. Then dibutoxy benzophenone (4.95 g, 10 mmol) in THF (100 mL) was added to the mixture. Then the mixture was refluxed until TLC showing complete conversion. The reaction was quenched with saturated aqueous NH₄Cl solution, and extracted with diethyl ether. The organic layer was desiccated with anhydrous magnesium sulfate for two hours, and then filtered. The solvent were removed by evaporation. Finally the resulting residue was purified by column chromatography (1.90 g, 40%).

1: M.p.89.9°C-92.0°C. ¹HNMR (400 MHz, DMSO-d₆) δ: 0.91(t,6H,CH₃), 1.41(m, 4H,CH₂), 1.62(m,4H,CH₂), 3.86(t,4H,OCH₂), 6.66(d,4H,Ar-H), 6.83(d,4H,Ar-H), 6.94(d,4H,Ar-H), 7.09(m,6H,Ar-H); ¹³CNMR (100 MHz, DMSO-d₆) δ: 13.62, 18.66, 66.93, 113.58, 126.10, 127.73, 130.63, 131.90, 138.63, 139.88, 143.79, 157.16; HRMS (ESI): *m/z* calcd. 477.2715 for C₃₄H₃₆O₂, found 477.2791; Elemental analysis: calcd. for C₃₄H₃₆O₂ (%): C, 85.71, H, 7.56; found (%) C, 85.46, H, 7.92.

Table S1 Summary of crystal data and intensity collection parameters for **1CA**.

Sample	1CA	
Empirical formula	C ₃₄ H ₃₆ O ₂	
Formula weight	476.27	
Temperature	110(2) K	
Wavelength,	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Ibca	
Unit cell dimensions	a = 16.6206(18) Å	alpha = 90 deg.
	b = 17.1087(18) Å	beta = 90 deg.
	c = 18.788(2) Å	gamma = 90 deg.
Volume	5342.5(10) Å ³	
Z, Calculated density	8, 1.185 Mg/m ³	
Absorption coefficient	0.072 mm ⁻¹	
F(000)	2048	
Crystal size	0.48 x 0.33 x 0.11 mm	
Theta range for data collection	2.17 to 27.59 deg.	
Limiting indices	-21<=h<=19, -21<=k<=21, -20<=l<=24	
Reflections collected / unique	15015 / 3092 [R(int) = 0.0422]	
Completeness to theta = 27.59	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9922 and 0.9664	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3092 / 0 / 165	
Goodness-of-fit on F ²	1.038	
Final R indices [I > 2sigma(I)]	R1 = 0.0392, wR2 = 0.0840	
R indices (all data)	R1 = 0.0597, wR2 = 0.0925	
Largest diff. peak and hole	0.251 and -0.192 e.Å ⁻³	

Table S2 Summary of crystal data and intensity collection parameters for **1CB**.

Sample	1CB
Empirical formula	C ₃₄ H ₃₆ O ₂
Formula weight	476.27
Temperature	180(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 13.6584(13) Å alpha = 90 deg. b = 5.7107(6) Å beta = 100.414(2) deg. c = 36.606(4) Å gamma = 90 deg.
Volume	13.6584(13) Å ³
Z, Calculated density	4, 1.127 Mg/m ³
Absorption coefficient	0.068 mm ⁻¹
F(000)	1024
Crystal size	0.18 x 0.16 x 0.10 mm
Theta range for data collection	2.26 to 25.25 deg.
Limiting indices	-16<=h<=12, -5<=k<=6, -42<=l<=43
Reflections collected / unique	13347 / 5072 [R(int) = 0.0309]
Completeness to theta = 25.25	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9932 and 0.9878
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5072 / 190 / 379
Goodness-of-fit on F ²	1.026
Final R indices [I > 2sigma(I)]	R1 = 0.0552, wR2 = 0.1384
R indices (all data)	R1 = 0.0841, wR2 = 0.1596
Largest diff. peak and hole	0.374 and -0.305 e.Å ⁻³

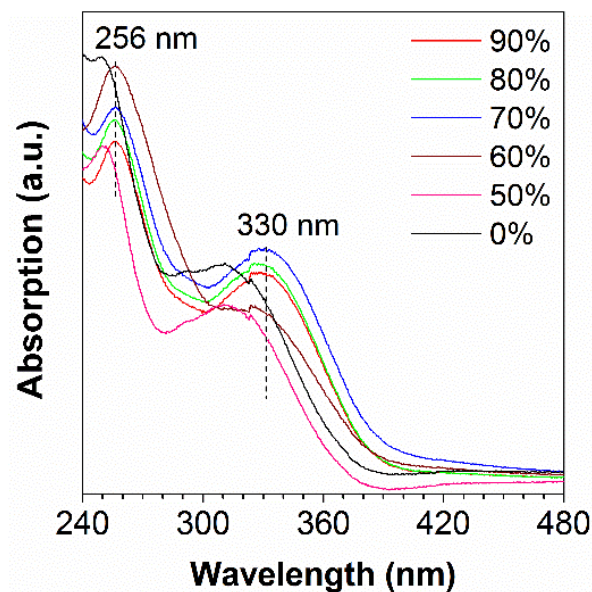


Fig. S1 UV-vis absorption of luminogen **1** in water/acetonitrile mixtures; Concentration: 10 μM .

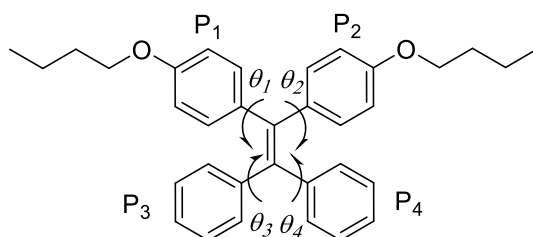
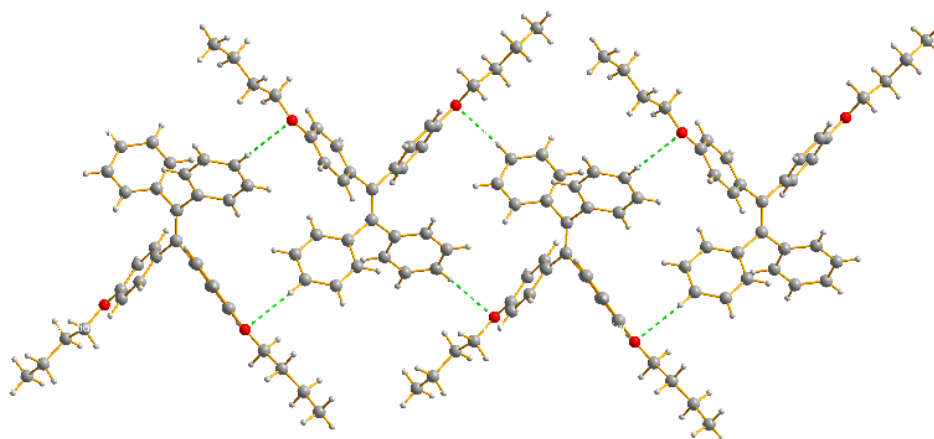


Table S3 Torsion angle of phenyl rings in two single crystals of compound **1**.

Samples	λ_{em}	θ_1	θ_2	θ_3	θ_4	θ_A
1CA	420 nm	48.22	49.51	53.27	52.72	50.93
1CB	460 nm	50.98	51.16	53.28	51.62	51.76

θ_1 , dihedral angle between benzene ring P₁ and double bond plane. θ_2 , dihedral angle between benzene ring P₂ and double bond plane. θ_3 , dihedral angle between benzene ring P₃ and double bond plane. θ_4 , dihedral angle between benzene ring P₄ and double bond plane. θ_A , average value of θ_1 , θ_2 , θ_3 , and θ_4 .



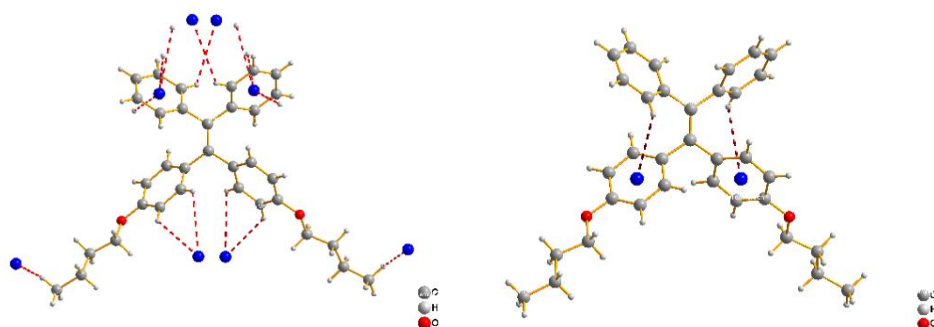


Fig. S2 View of C-H...O (green dashed line) and C-H... π (red dashed line) between molecules and intramolecular C-H... π (dark-red dashed line) interactions in single crystal of **1CA**. The blue dots refer to the center of benzene rings.

Table S4 Summarization of the C-H...O and C-H... π interactions in the crystal of **1CA** (intermolecular interactions: 1-5; intramolecular interactions: 6).

Interactions	d /Å [a] ^[N] [b]	A/° [c]
1C-H...O	2.560(4)	151.484(84)
2C-H... π	2.978(4)	128.764(70)
3C-H... π	3.435(4)	112.285(70)
4C-H... π	3.447(4)	119.569(75)
5C-H... π	3.474(2)	121.787(75)
6C-H... π	3.442(2)	106.499(71)

[a] Distance of C-H... π or C-H...O interaction. [b] Number of the intermolecular or intramolecular interactions. [c] Angel of C-H... π or C-H...O interaction.

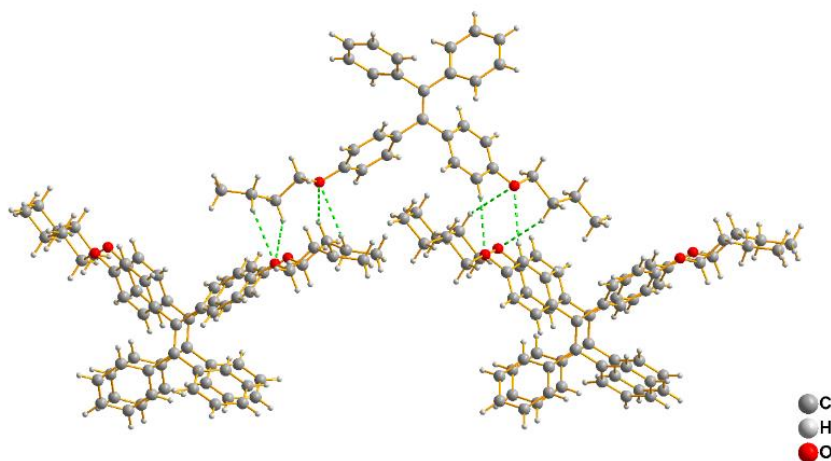
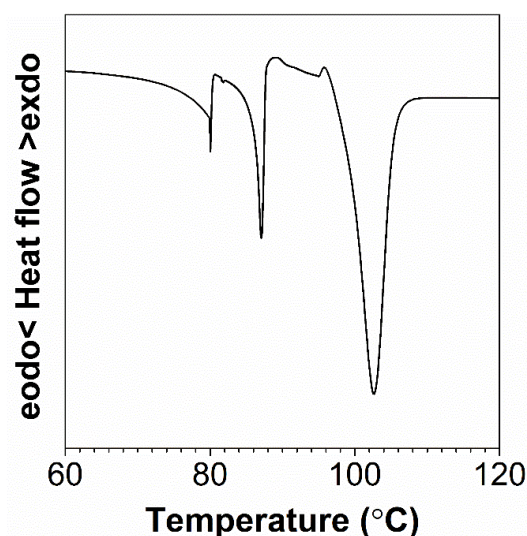


Fig. S3 View of C-H...O (green dashed line) interactions between molecules in single crystal of **1CB**.

Table S5 Summarization of the C-H...O interactions in the crystal of **1CB**.

Interactions	$d / \text{\AA}$ [a](N) ^[b]	$A/^\circ$ [c]
1C-H...O	2.595(2)	138.684(587)
2C-H...O	2.711(2)	135.638(553)
3C-H...O	2.814(2)	169.032(174)
4C-H...O	2.939(2)	150.676(236)

[a] Distance of C-H...O interaction. [b] Number of the intermolecular interactions. [c] Angel of C-H...O interaction.

**Fig. S4** DSC curves of **1CA** heating at a rate of 10 K/min from 60°C to 85°C; then heat at a rate of 0.5 K/min from 85°C to 120°C.**Table S6** Optical Properties of Samples a-g in Fig. 3

Samples	^a Φ_F (%)	A_1/A_2 ^b	τ_1 (ns)	τ_2 (ns)	$\langle \tau \rangle$ ^c (ns)
a	7.6	96/4	0.4	2.65	0.49
b	5.1	88/12	0.53	3.22	0.85
c	42.1	17/83	1.12	2.06	1.90
d	48.3	47/53	1.41	2.24	1.85
e	6.4	88/12	0.48	2.50	0.72
f	8.3	75/25	0.43	2.39	0.92
g	50.4	100/0	2.27		2.27

^a Φ_F = Fluorescence quantum yield determined using a calibrated integrating sphere, excited at 350 nm. ^bFraction (A , %) and lifetime (τ , ns) of shorter (1) or longer-lived species (2). ^cThe mean lifetime $\langle \tau \rangle$ was calculated according to $\langle \tau \rangle = (A_1\tau_1 + A_2\tau_2)/(A_1 + A_2)$

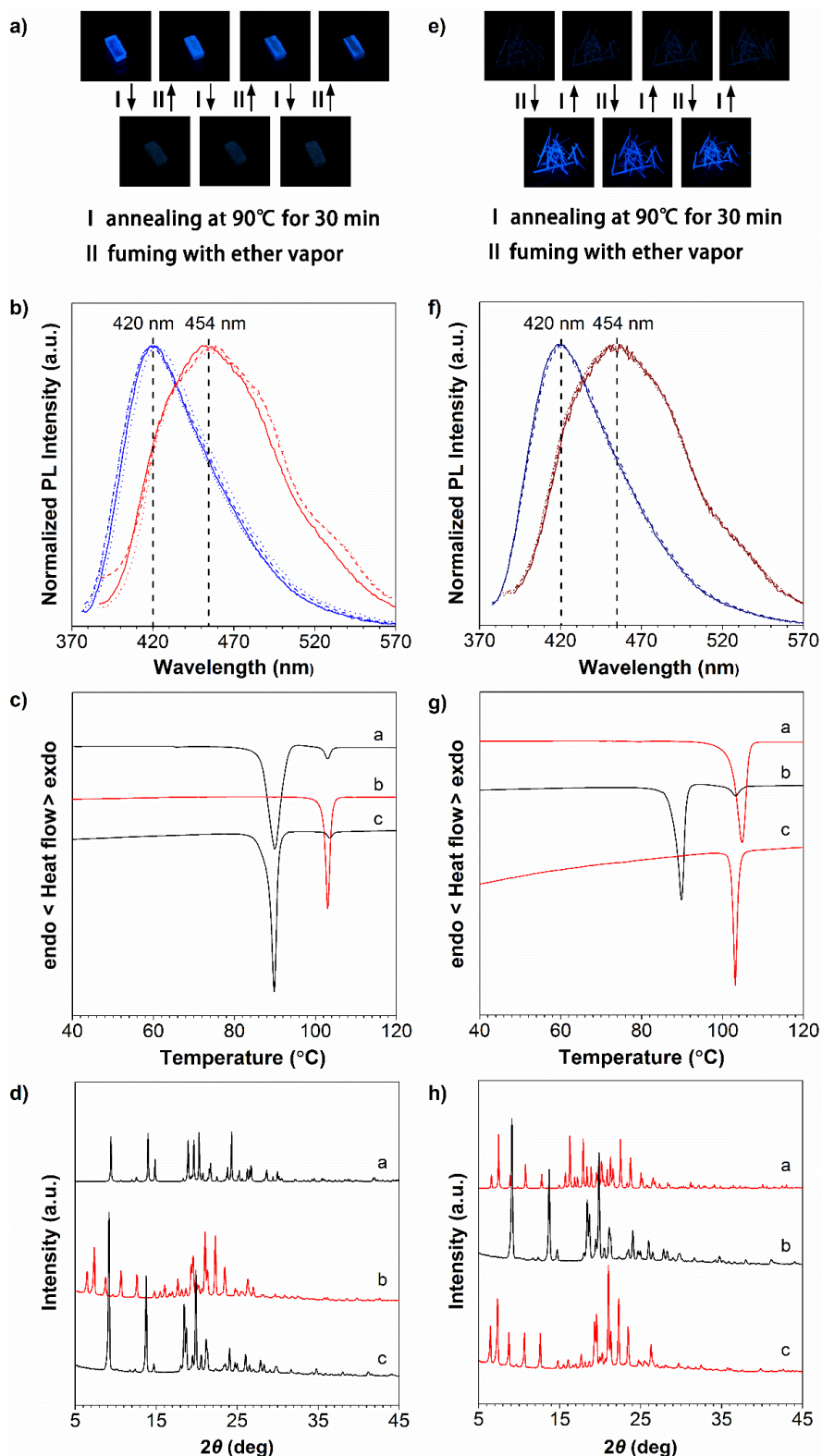


Fig. S5 (a) Photos of **1CA** in the three repeating cycles. (b) Normalized PL spectra of samples in the picture of a, (c) DSC curves and (d) powder XRD patterns of **1CA** in the first cycle. (e) Photos of **1CB** in the three repeating cycles. (f) Normalized PL spectra of samples in the picture of e, (g) DSC curves and (h) powder XRD patterns of **1CB** in the first cycle. Excitation wavelength: 350 nm; Photos were taken under 365 UV illumination, expose time: 1/25 s.

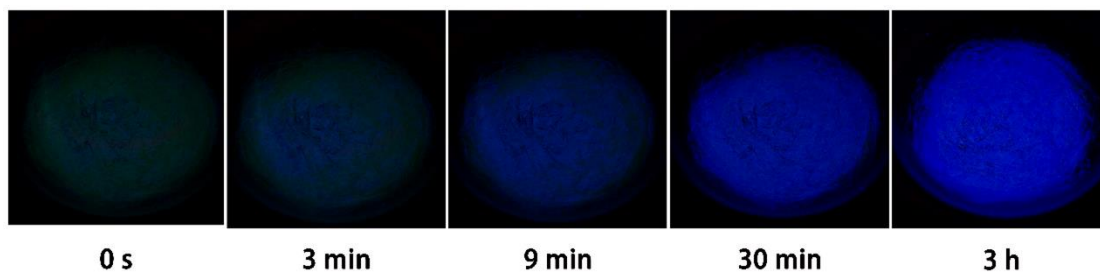


Fig. S6 Spontaneously recovering of **1CA** at room temperature (30°C) after ground in mortar. Photos are taken under 365 UV illumination at different time; exposed time: 1/8 s.

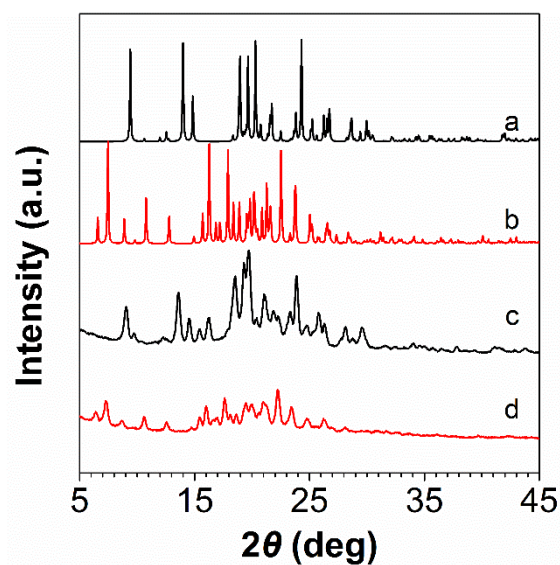


Fig. S7 Powder XRD patterns of **1** in different states; a: **1CA**; b: **1CB**; c: ground from **1CA**; d: ground from **1CB**.

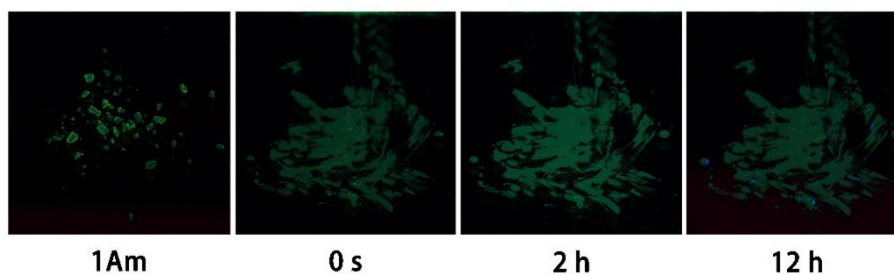


Fig. S8 Spontaneously recovering of ground amorphous solid of **1** at room temperature (30°C) after ground in mortar. Photos are taken under 365 UV illumination at different time; exposed time: 1/8 s.

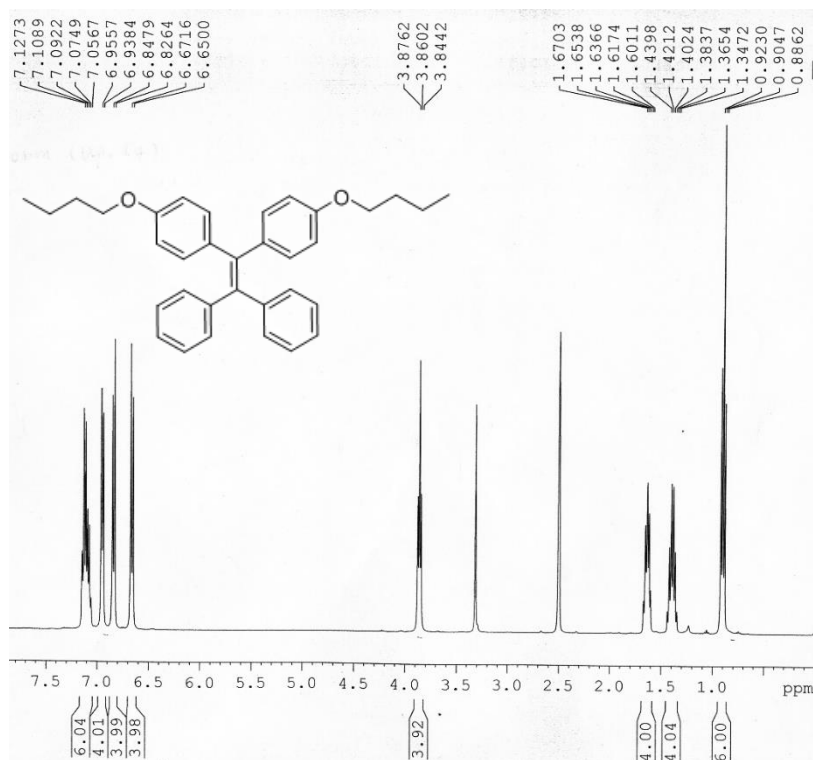


Fig. S9 The ¹H NMR spectrum of **1** in DMSO-d₆ solution.

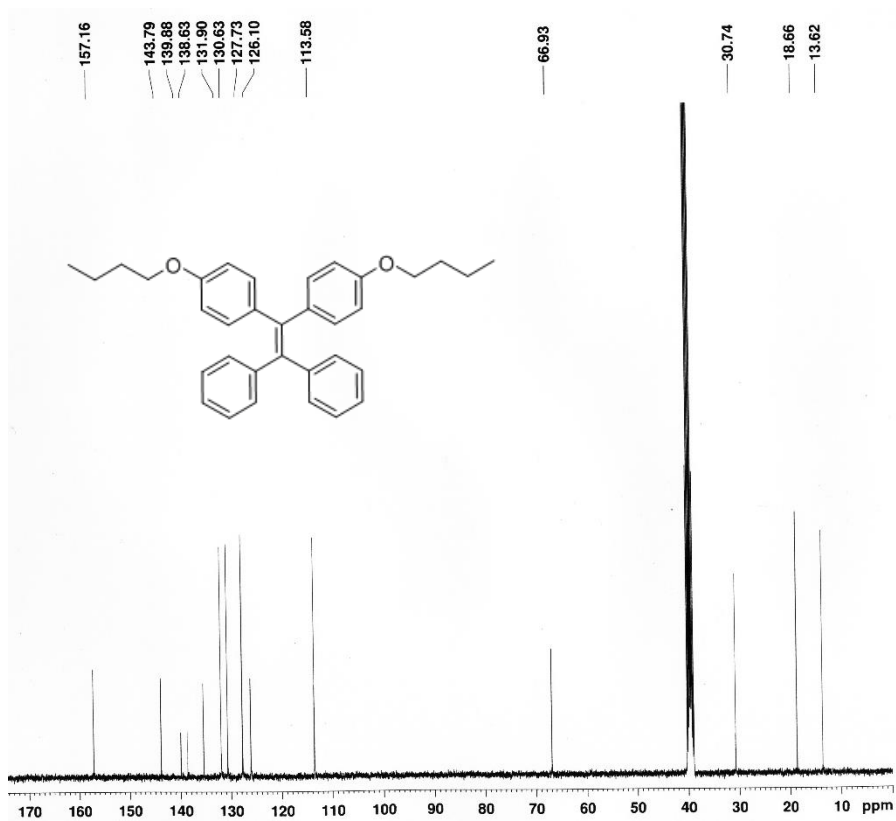


Fig. S10 The ¹³C NMR spectrum of **1** in DMSO-d₆ solution.

Mass Spectrum SmartFormula Report

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Comment				

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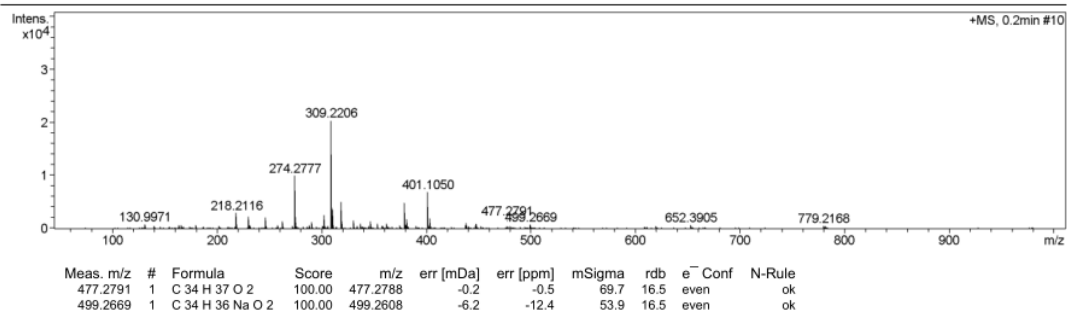


Fig. S11 The HRMS spectrum of compound **1**.