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Electronic supplementary information

Strong CIE activity, multi-stimuli-responsive fluorescence and data storage application of new diphenyl maleimide derivatives

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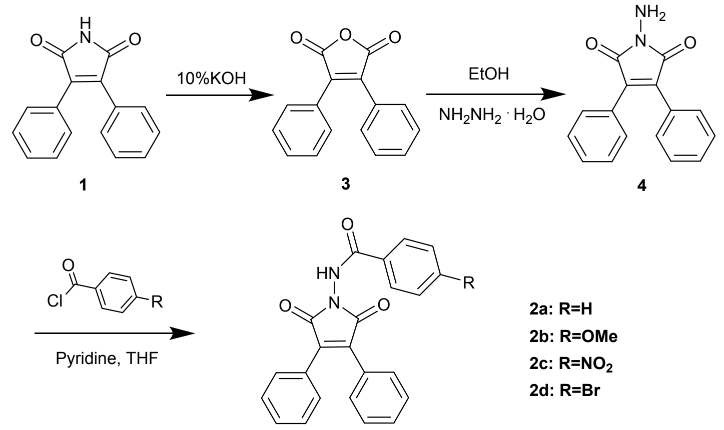
Synthesis



N-Amino-3,4-diphenylmaleimide (4)

The suspension of compound **1** (1 g, 4 mmol) in 150 ml 10% sodium hydroxide solution was refluxed for 6 h. Then the reaction mixture was cooled to room temperature, and treated with 3 N HCl until precipitates formed. The solid was filtered and washed with water, and dried in vacuo to give pale yellow compound **3** in a 90% yield (0.9 g).

To a suspension of compound **3** (0.9 g, 3.6 mmol) in 45 ml anhydrous ethanol was slowly added hydrazine hydrate (1.06ml, 18mmol). After stirred at room temperature for 20 minutes, the organic layer was separated, and aqueous layer was extracted with ethyl acetate. The combined organic solution was purified by column chromatography using EA/PE (1:3) as the eluent, affording a yellow solid of **4** in an 85% yield (0.77 g). mp: 209 ℃. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.46 (d, J = 4 Hz, 4H), 7.36 (m, 6H), 4.08 (s, 2H).

Benzamide substituted diphenyl maleimide derivatives (2)

To a solution of compound **4** (0.1 g, 0.38 mmol) and pyridine (0.3 ml, 3.73 mmol) in THF (5 ml), was added dropwise 1.1 equivalent of benzoyl chloride dissolved in THF (3 ml). After stirred at room temperature for 5 h, the solution was extracted with ethyl acetate and purified by column chromatography using EA/PE (1:4) as the eluent, affording a yellow solid of **2** in a 70-81% yield.

Compound **2a**. Yield: 81%. mp: 242 ℃. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.83 (s, 1H), 7.83 (d, J = 7.6 Hz, 2H), 7.48 (t, J = 7.8 Hz, 5H), 7.42-7.29 (m, 8H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 168.08, 165.92, 135.57, 132.88, 130.62, 130.26, 130.02, 128.81, 128.66, 128.17, 127.73. MALDI MASS m/z [M]$^+$ calcd 368.116, found 368.204.

Compound **2b**. Yield: 75%. mp: 275 ℃. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.02 (s, 1H), 7.87 (d, J =

8.7 Hz, 2H), 7.51 (d, J = 6.9 Hz, 4H), 7.37 (dd, J = 16.1, 8.6 Hz, 6H), 6.96 (d, J = 8.7 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.18, 165.44, 163.35, 135.55, 130.22, 130.02, 129.74, 128.64, 128.23, 122.87, 114.07, 55.51. MALDI MASS m/z $[M]^+$ calcd 398.127, found 398.255.

Compound **2c**. Yield: 74%. mp: 249 ℃. 1H NMR (CDCl3, 400 MHz): δ 9.05 (s, 1H), 8.25-8.11 (m, 2H), 8.00 (d, J = 8.8 Hz, 2H), 7.57-7.47 (m, 4H), 7.46-7.34 (m, 6H). 13C NMR (CDCl3, 100 MHz): δ 167.98, 164.18, 150.24, 135.79, 135.64, 130.53, 129.95, 129.01, 128.77, 127.87, 123.87. MALDI MASS m/z [M-H]+ calcd 412.093, found 412.216.

Compound **2d**. Yield: 70%. mp: 267 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.21 (s, 1H), 7.75 (d, J = 7.9 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 7.0 Hz, 4H), 7.38 (d, J = 7.2 Hz, 6H). ^{13}C NMR (DMSO, 100 MHz): δ 168.33, 165.21, 135.74, 132.42, 130.66, 130.34, 130.22, 130.16, 129.16, 128.53, 127.27. MALDI MASS m/z $[M]^+$ calcd 446.027, found 446.182.

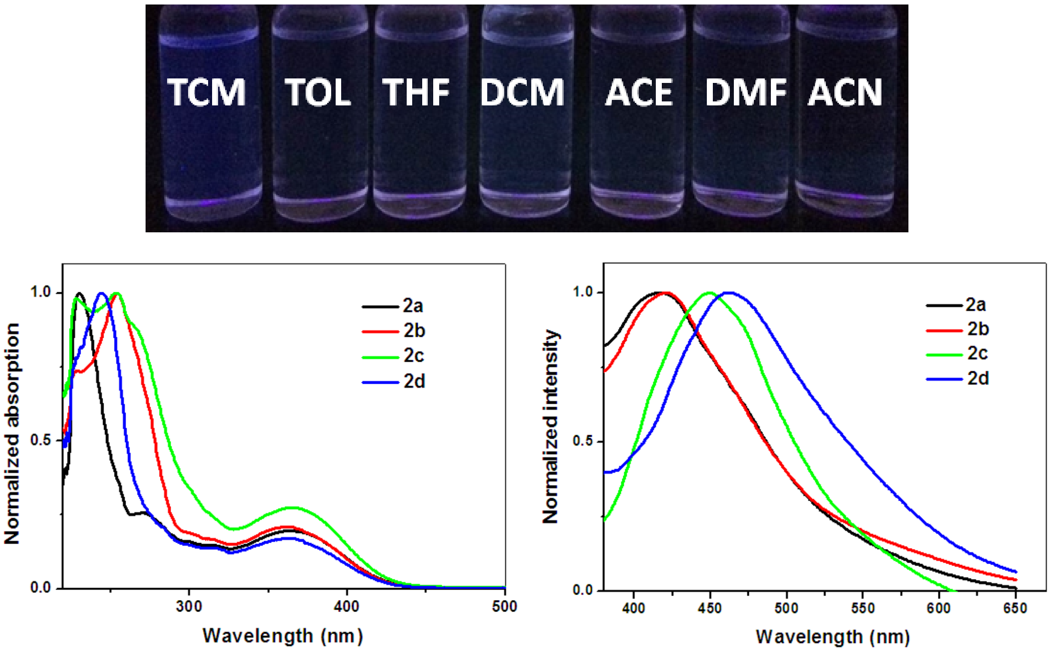


Fig. S1 (Upper) Photo of 2d in various solutions (50 µM) under UV light. (Bottom) Absorption and emission specra (λ_{ex} = 365 nm) of 2 in DMF solutions (50 µM). TCM= tetrachloromethane; TOL= toluene; THF= tetrahydrofuran; DCM= dichloromethane; ACE= acetone; DMF= dimethyl formamide; ACN= acetonitrile.

Table S1 Experimental data of photophysical properties of 2 in solution

Compounds	λ_{ab}, nm		λ_{em}, nm		Stokes shift [a] (nm)	Φ_F, % [a]
	CCl_4	DMF	CCl_4	DMF		
1	356	351	490	497	146	21[b]
2a	361	365	445	418	53	<0.1
2b	361	364	446	422	58	<0.1
2c	364	366	447	450	84	<0.1
2d	363	365	446	462	97	<0.1

[a] in DMF. [b] From Ref. 40.

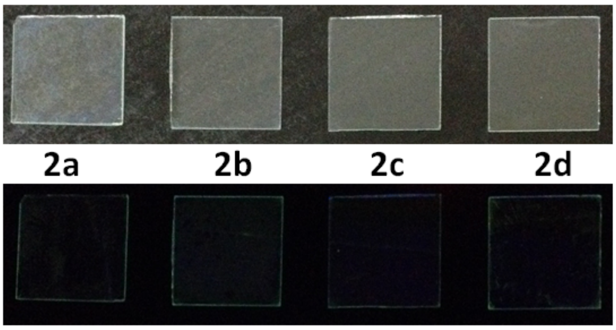


Fig. S2 Photos of 2 in thin films prepared by spin-coating of dichloromethane solution (4 mg/ml) under natural light (upper) and UV light (bottom).

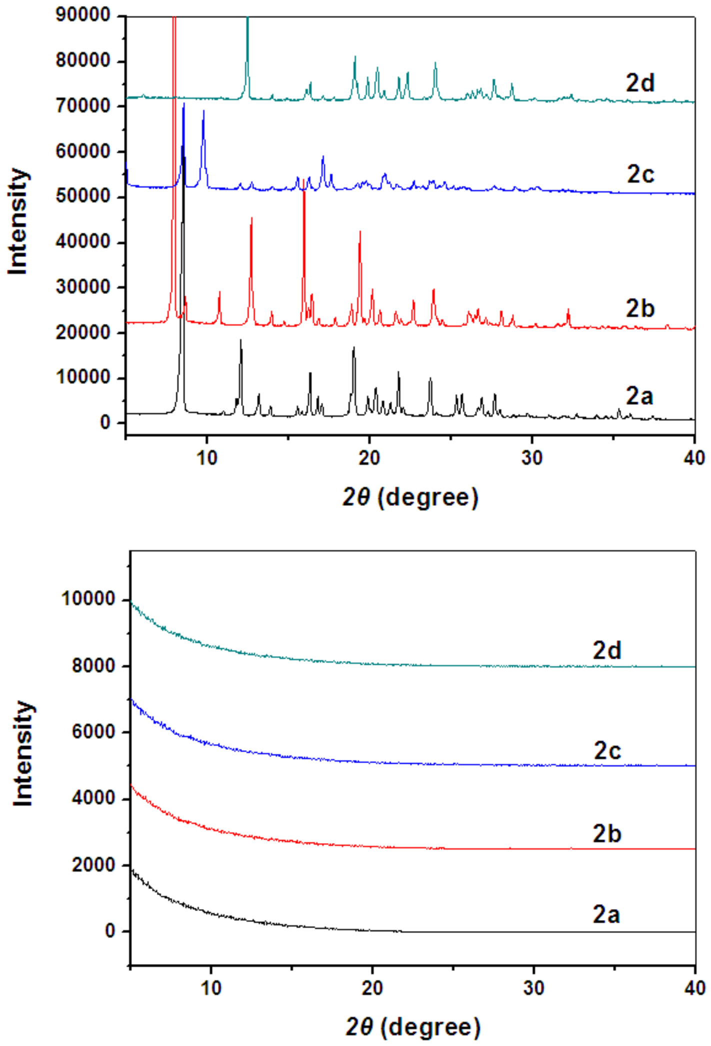


Fig. S3 Powder XRD patterns of 2a-d in powders (upper) and Grazing incidence XRD patterns of 2a-d in films (bottom).

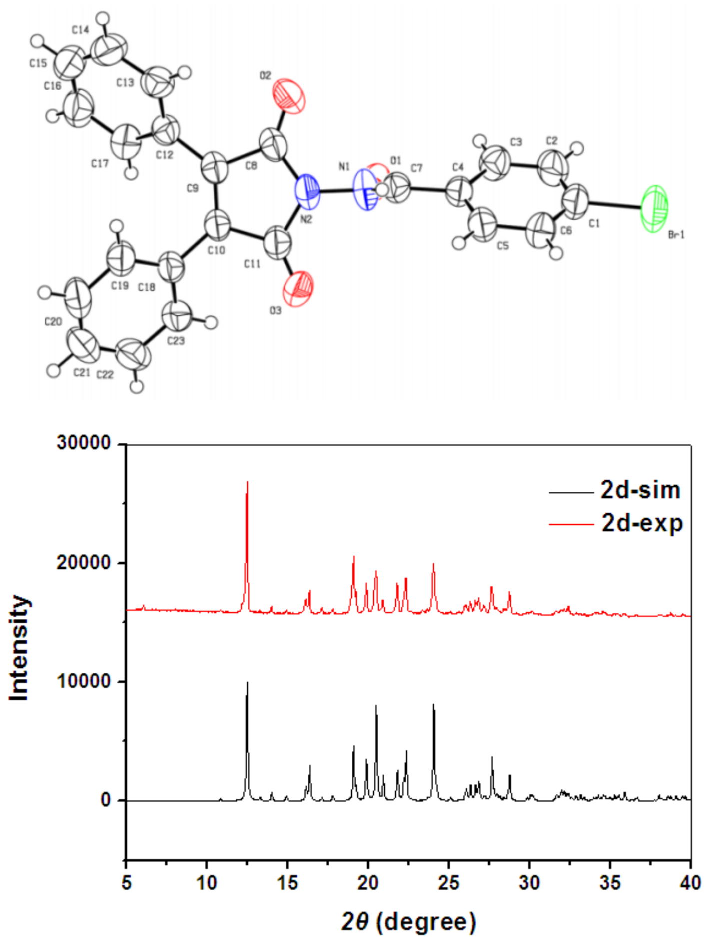


Fig. S4 (Upper) The single molecular structure of 2d in single crystals. (Bottom) The simulated and experimental powder XRD patterns of 2d.

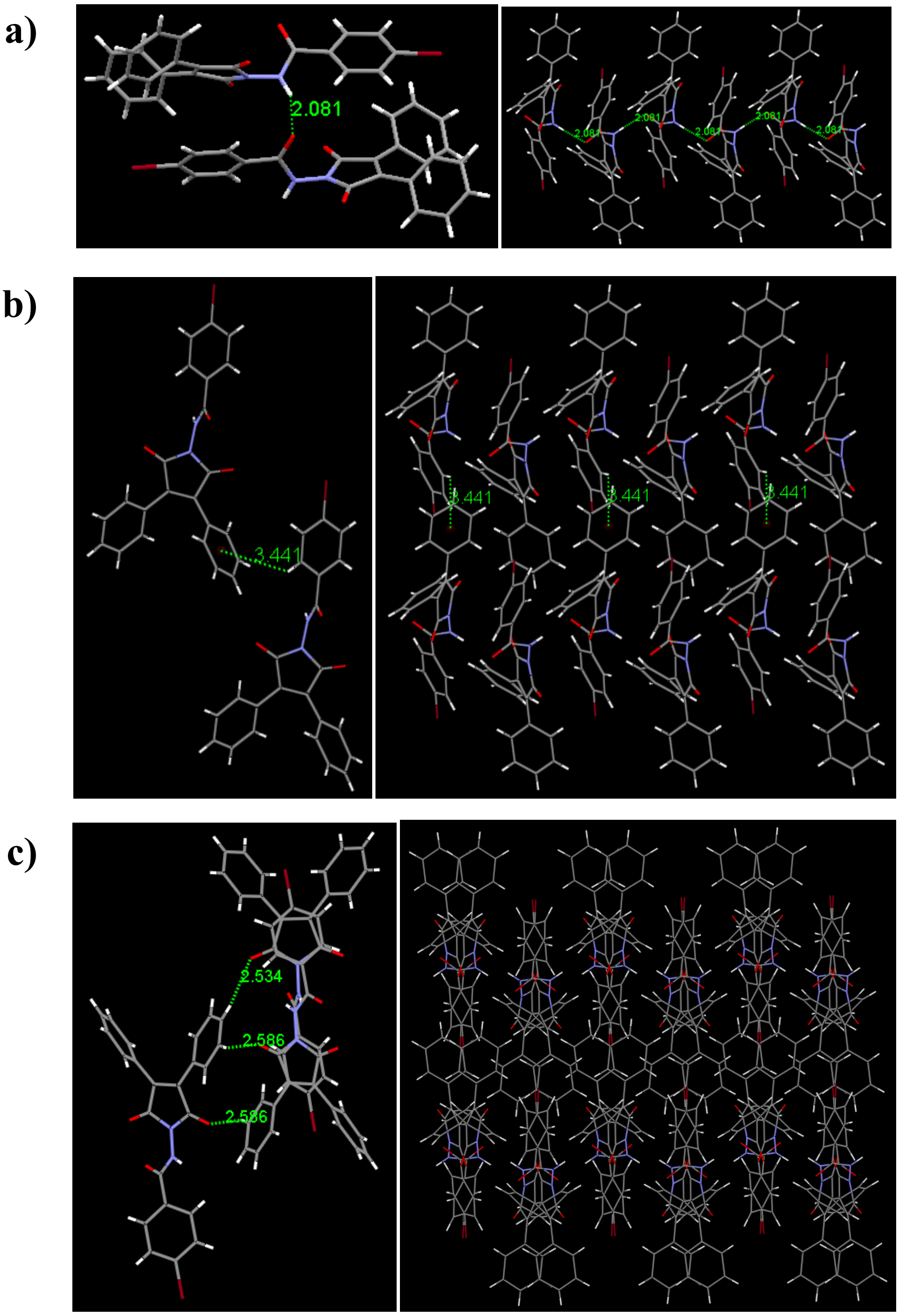


Fig. S5 Weak intermolecular interaction and molecular packing pattern of 2d in the crystalline state.

Table S2 Hydrogen bonds parameters for 2d crystal.

D-H…A	d (D-H) (Å)	d (H…A) (Å)	d (D…A) (Å)	∠DHA (°)
N1-H1…O1[a)]	0.86	2.08	2.825(3)	144.3
C14-H14…O1[b)]	0.93	2.86	3.456(4)	123.2
C22-H22…O3[c)]	0.93	2.59	3.481(4)	161.7
C21-H21…O2[d)]	0.93	2.53	3.442(3)	165.2
C15-H15…O1[b)]	0.93	2.77	3.410(4)	127.1

Symmetry codes: [a] 2-x,1/2+y,1/2-z; [b] 3-x,1/2+y,1/2-z; [c] 2-x,-y,-z; [d] +x,1/2-y,-1/2+z.

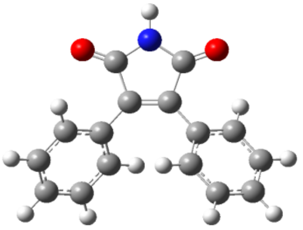
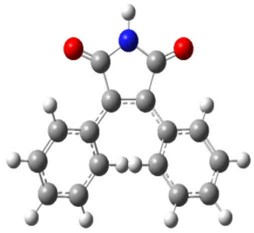
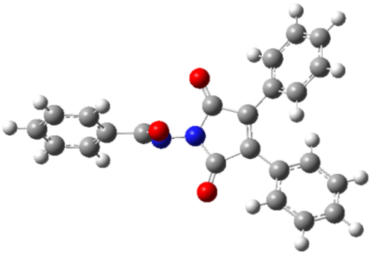
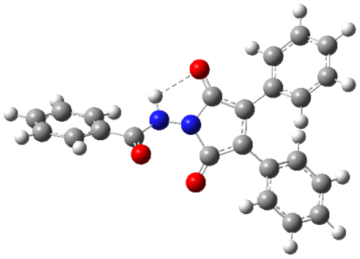
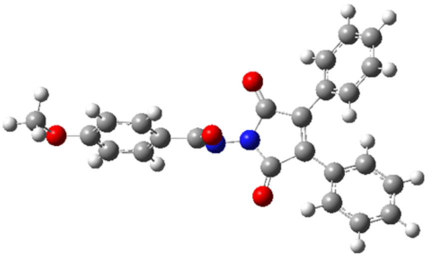
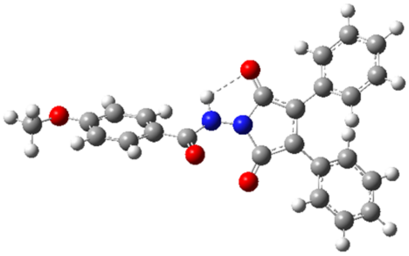
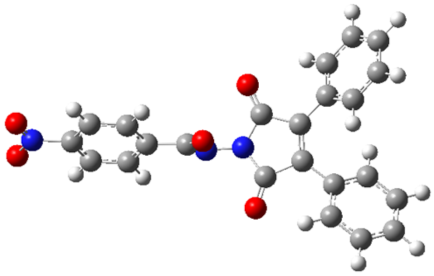
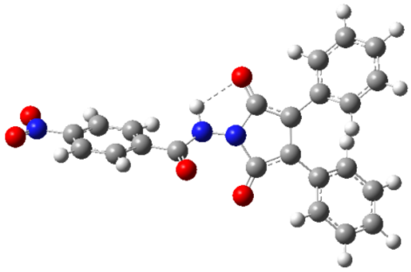
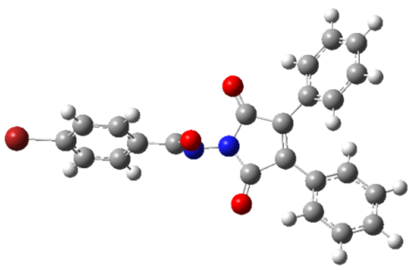
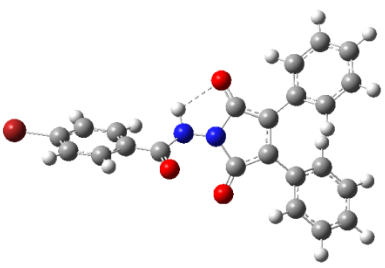
	Ground state	**Excited state**
1		
2a		
2b		
2c		
2d		

Fig. S6 The optimized geometry of 1 and 2a-d in ground state and excited state.

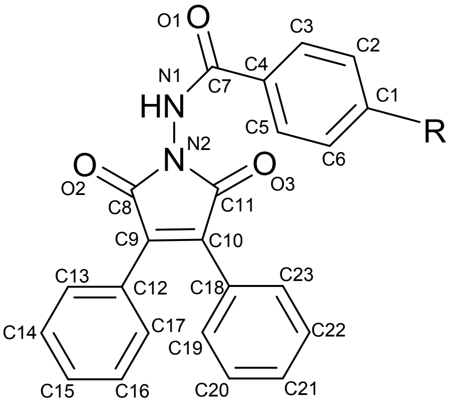


Table S3 Partial torsion angels and bond length in the molecule of 2.

Compounds	$T_{C8N2N1H}$ (°)		$T_{C11N2C4C5}$ (°)		**d (N2-N1) (Å)**	
	G[a]	**E**[b]	**G**	**E**	**G**	**E**
2a	77.9	1.3	99.7	74.8	1.37	1.32
2b	76.0	0.7	95.9	71.5	1.37	1.32
2c	80.5	2.1	102.8	75.2	1.37	1.32
2d	78.2	1.5	100.5	73.3	1.37	1.32

[a] Ground state. [b] Excited state

Table S4 Hydrogen bond parameters of N1-H···O18 of 2 in the excited state.

Compounds	**d (N-H) (Å)**	**d (H…O) (Å)**	**d (N…O) (Å)**	**∠NHO (°)**
2a	1.028	2.118	2.650	109.8
2b	1.028	2.117	2.652	110.1
2c	1.029	2.111	2.645	109.9
2d	1.029	2.114	2.648	110.0

Table S5 Calculated wavelength (λ) and oscillator strength (f) for absorption of 1, and 2.

Compounds		**Main orbital transition[a] (CIC)**	**λ, nm**	**f**
1	$S_0 \rightarrow S_1$	HOMO→LUMO (0.69)	402	0.1623
	$S_0 \rightarrow S_2$	HOMO-3→LUMO (0.55) HOMO-1→LUMO (-0.43)	376	0.0091
	$S_0 \rightarrow S_3$	HOMO-3→LUMO (0.43) HOMO-1→LUMO (0.55)	337	0.0156
2a	$S_0 \rightarrow S_1$	HOMO→LUMO (0.67)	407	0.1304
	$S_0 \rightarrow S_2$	HOMO-4→LUMO (-0.39) HOMO-1→LUMO (0.42)	378	0.0329
	$S_0 \rightarrow S_3$	HOMO-4→LUMO (0.32) HOMO-1→LUMO (0.53)	341	0.0084
2b	$S_0 \rightarrow S_1$	HOMO→LUMO (0.66)	407	0.1196
	$S_0 \rightarrow S_2$	HOMO-3→LUMO (0.32) HOMO-2→LUMO (-0.36) HOMO-1→LUMO (0.39)	380	0.0384
	$S_0 \rightarrow S_3$	HOMO-2→LUMO (0.26) HOMO-1→LUMO (0.58)	371	0.0047
2c	$S_0 \rightarrow S_1$	HOMO→LUMO (0.45) HOMO→LUMO+1 (0.51)	411	0.1427
	$S_0 \rightarrow S_2$	HOMO→LUMO (0.54) HOMO→LUMO+1 (-0.46)	385	0.0066
	$S_0 \rightarrow S_3$	HOMO-3→LUMO (0.32) HOMO-3→LUMO+1 (-0.43)	376	0.0241
2d	$S_0 \rightarrow S_1$	HOMO→LUMO (0.68)	408	0.1367
	$S_0 \rightarrow S_2$	HOMO-4→LUMO (0.50) HOMO-1→LUMO (0.33)	377	0.0283
	$S_0 \rightarrow S_3$	HOMO-2→LUMO (0.47)	342	0.0098

[a] CI expansion coefficients for the main orbital transitions.

Table S6 Calculated wavelength (λ) and oscillator strength (f) for emission of 1, and 2.

Compounds		**Main orbital transition[a] (CIC)**	**λ, nm**	**f**
1	$S_1 \rightarrow S_0$	LUMO→HOMO (0.70)	556	0.1227
	$S_2 \rightarrow S_0$	LUMO→HOMO-3 (0.65) LUMO→HOMO-1 (0.24)	420	0.0133
	$S_3 \rightarrow S_0$	LUMO→HOMO-3 (0.25) LUMO→HOMO-1 (-0.65)	395	0.0297
2a	$S_1 \rightarrow S_0$	LUMO→HOMO (-0.71)	1050	0.0074
	$S_2 \rightarrow S_0$	LUMO→HOMO-2 (-0.31) LUMO→HOMO-1 (0.46)	472	0.0286
	$S_3 \rightarrow S_0$	LUMO→HOMO-4 (-0.23) LUMO→HOMO-2 (-0.21) LUMO→HOMO-1 (-0.50)	447	0.1253
2b	$S_1 \rightarrow S_0$	LUMO→HOMO (0.71)	1090	0.0065
	$S_2 \rightarrow S_0$	LUMO→HOMO-1 (0.70)	532	0.0013
	$S_4 \rightarrow S_0$	LUMO→HOMO-3 (-0.38) LUMO→HOMO-2 (0.50)	446	0.1292
2c	$S_1 \rightarrow S_0$	LUMO→HOMO (-0.70)	940	0.0119
	$S_2 \rightarrow S_0$	LUMO+1→HOMO (-0.70)	465	0.1186
	$S_3 \rightarrow S_0$	LUMO→HOMO-2 (0.35) LUMO→HOMO-1 (0.56)	460	0.0709
2d	$S_1 \rightarrow S_0$	LUMO→HOMO (-0.70)	1005	0.0089
	$S_2 \rightarrow S_0$	LUMO→HOMO-1 (-0.46)	465	0.0413
	$S_3 \rightarrow S_0$	LUMO→HOMO-4 (-0.25) LUMO→HOMO-3 (-0.29) LUMO→HOMO-2 (0.17) LUMO→HOMO-1 (-0.49)	447	0.1082

[a] CI expansion coefficients for the main orbital transitions.

Table S7 Calculated absorption and emission wavelength (λ) of 1 and 2a-d.

Compounds	**λ_{ab} nm[a]**	**λ_{em} nm[a]**
1	402 (356)	556 (490)
2a	407 (361)	447 (445)
2b	407 (361)	446 (446)
2c	411 (364)	465 (447)
2d	408 (363)	447 (446)

[a] The data in parentheses is the experimental value in CCl_4 solution.

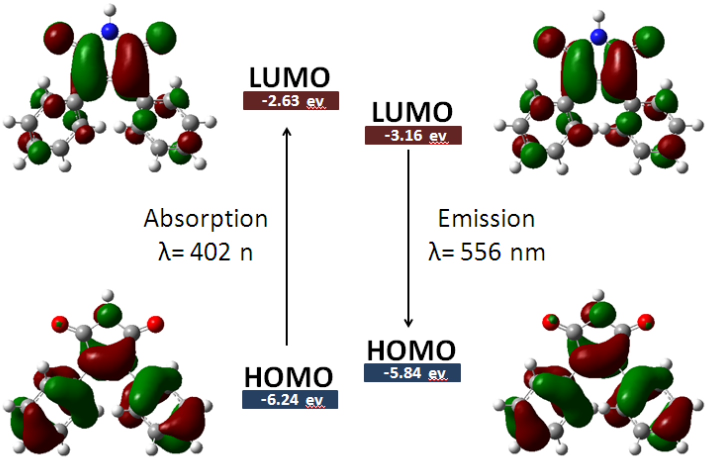


Fig. S7 The main electronic transition contributing to the absorption and emission processes of 1.

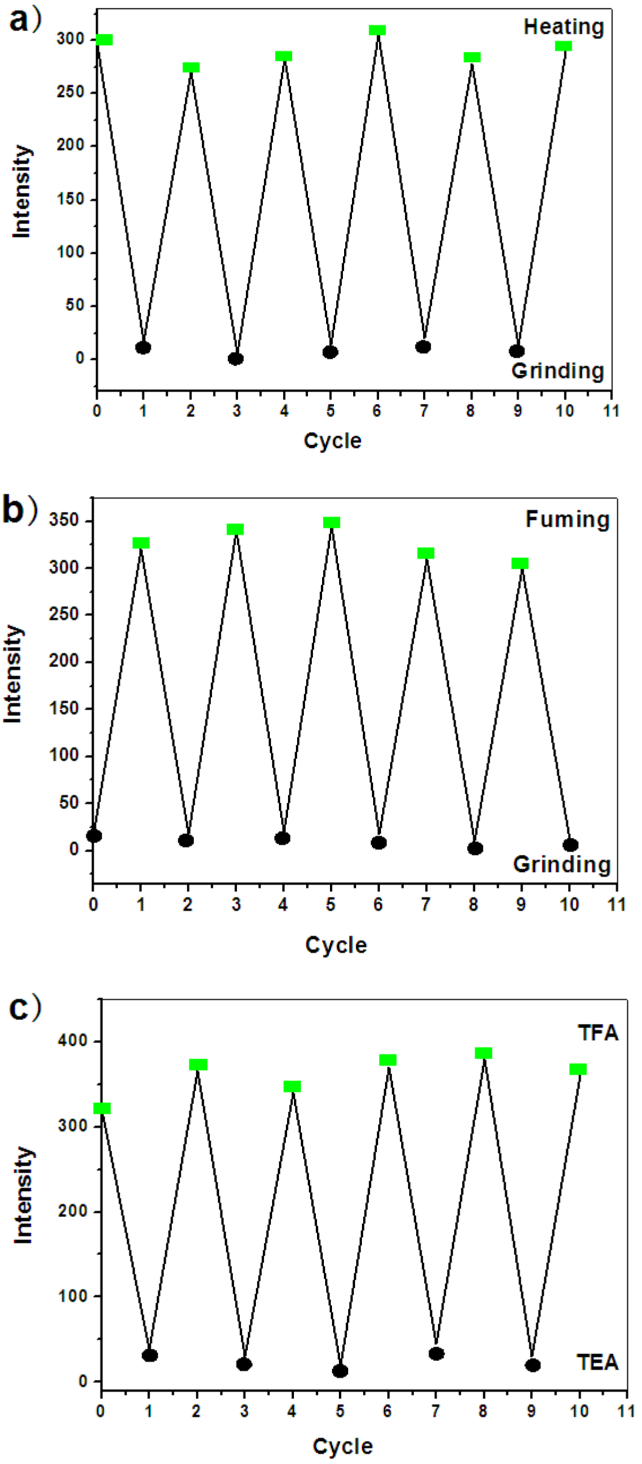


Fig. S8 Repeated switching between on/off emission of 2d by grinding-heating cycles (a), fuming-grinding cycles (b) and TEA-TFA stuimuli cycles (c).

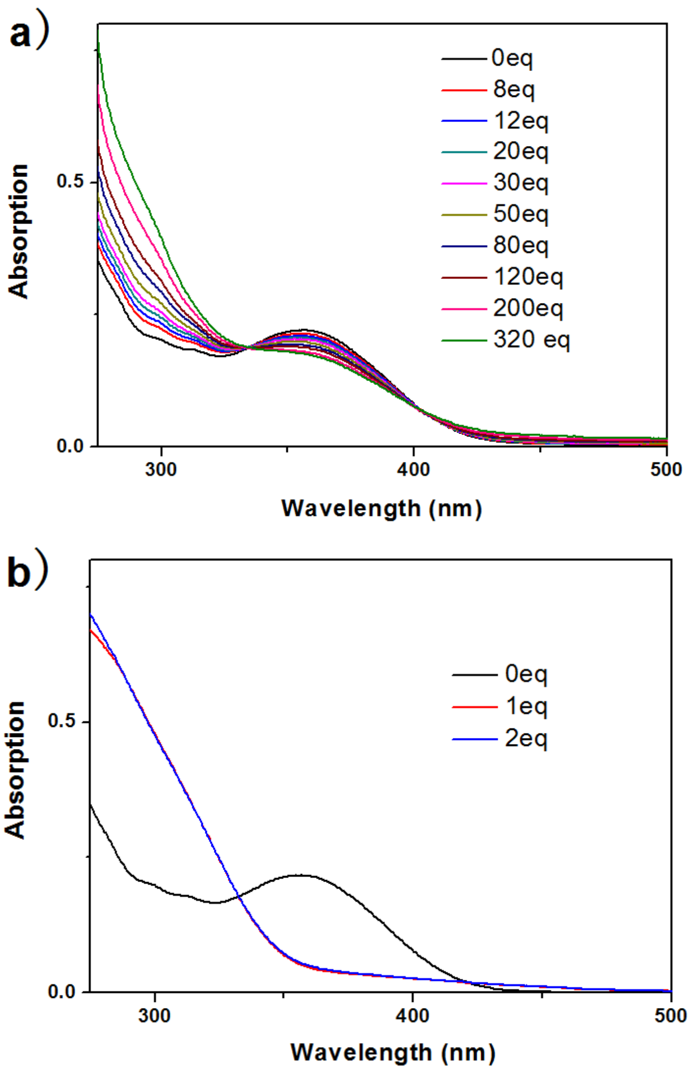


Fig. S9 Absorption spectra of 2d (50 uM in ACN) upon the addition of TEA (a) and TBAOH (b).

Table S8 Crystal data and structure refinement for 2d.

EmpiricaL formula	$C_{23} H_{15} Br N_2 O_3$
Formula weight	447.29
Temperature	292 K
Crystal system	monoclinic
Space group	P 1 21/c 1
a (Å)	11.1280(3)
b (Å)	8.6691(2)
c (Å)	21.0368(4)
α(deg)	90.00
β(deg)	97.996(2)
γ(deg)	90.00
V (Å^3)	2009.68(8)
Z	4
$D_{calcd.}$(g/cm^3)	1.4782
F(000)	903.8311
Limiting indices	-13<=h<=12, -10<=k<=9, -26=l<=20
R (int)	0.0259
GOF on F^2	1.0428
R1[I > 2σ(I)]	0.0472
wR2[I>2σ(I)]	0.1321
R1 (all data)	0.0600
wR2(all data)	0.1490