Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information for

Difluoroboron β-Diketonate Based Luminescent Material with Tunable Solid-state Emission and Thermally Activated Delayed Fluorescence

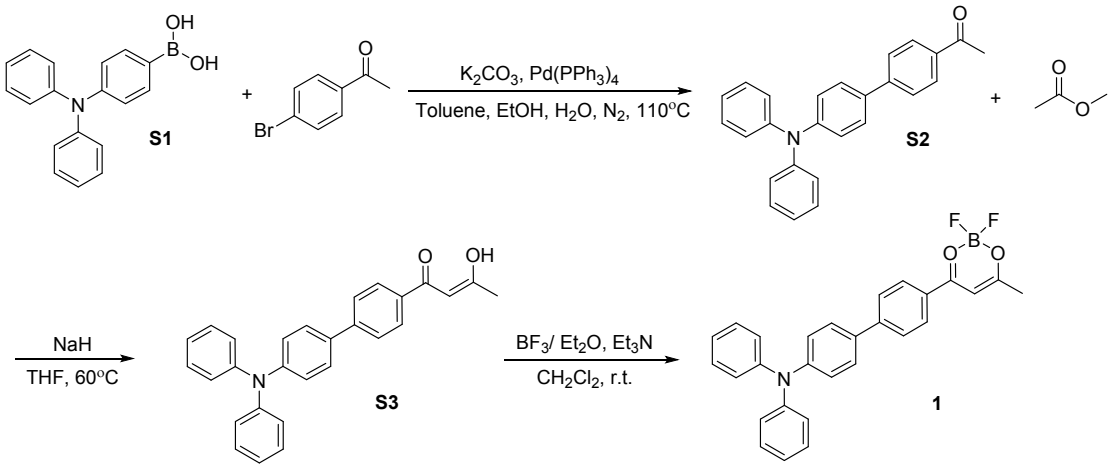
1. Materials and Methods.

All chemicals were commercially available and were used without further purification. The anhydrous solvents were from the solvent treatment system.

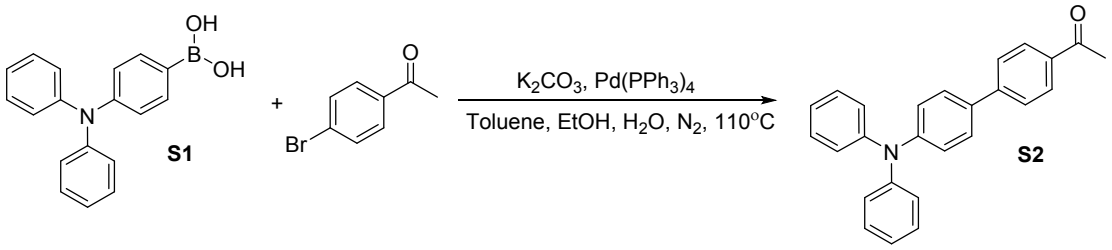
The absorbance spectra were recorded on Hitachi U-3900 UV-Vis spectrophotometer at room temperature. The fluorescence spectra were recorded on Hitachi F-4600 (solution) or Edinburgh instruments FLS-980 (solid, film). Fluorescence quantum yields were recorded on Edinburgh instruments FLS-980 with an integrating sphere system. The time-resolved fluorescence spectra were recorded by Edinburgh instruments FLS-980 with time-correlated single photon counting method, and the values of lifetime were analyzed by exponential function fitting with software F900. The values of delayed fluorescence lifetime and lifetime in Ar bubbled solutions were analyzed by Horiba ultrafast lifetime spectrofluorometer. The photographs were shot by Nikon D7100. X-ray diffraction (XRD) patterns were recorded at room temperature with a Shimadzu XRD-7000. The NMR spectra were analyzed by JEOL 400 MHz, 600 MHz nuclear resonance spectrometer. The differential scanning calorimetry (DSC) analysis were recorded on Mettler differential scanning calorimeter.

In SEM studies, the samples were centrifuged and washed by water twice to remove the interference of surfactants. The samples were examined after Au spraying with Hitachi SU8010 at an accelerating voltage of 5 or 10 kV.

2. Synthesis, NMR spectra and crystal data of compound 1.



Scheme S1. The synthetic route of compound **1**.



To a two-necked flask was added compound 1-(4-bromophenyl)ethan-1-one (100 mg, 0.5 mmol) and 1g potassium carbonate in a mixed solution of 20 mL toluene, 5 mL ethyl alcohol and 5 mL water under N_2 protection. Then to the reaction mixture was added **S1** (145 mg, 0.5 mmol) and tetrakis(triphenylphosphine)palladium (6 mg, 0.005 mmol). The reaction mixture was heated to 110℃ with stirring for 4 hours under N_2 protection. After cooling to room temperature, the solution was washed with brine and was extracted with dichloromethane thrice. The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, 1:2 v/v, petroleum

ether/dichloromethane) to afford product **S2** (140 mg, 77%) as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 8.1 Hz, 2H), 7.65 (d, J = 8.2 Hz, 2H), 7.50 (d, J = 8.6 Hz, 2H), 7.34 – 7.20 (m, 4H), 7.21 – 7.10 (m, 6H), 7.05 (dd, J = 10.9, 3.8 Hz, 2H), 2.61 (s, 3H).

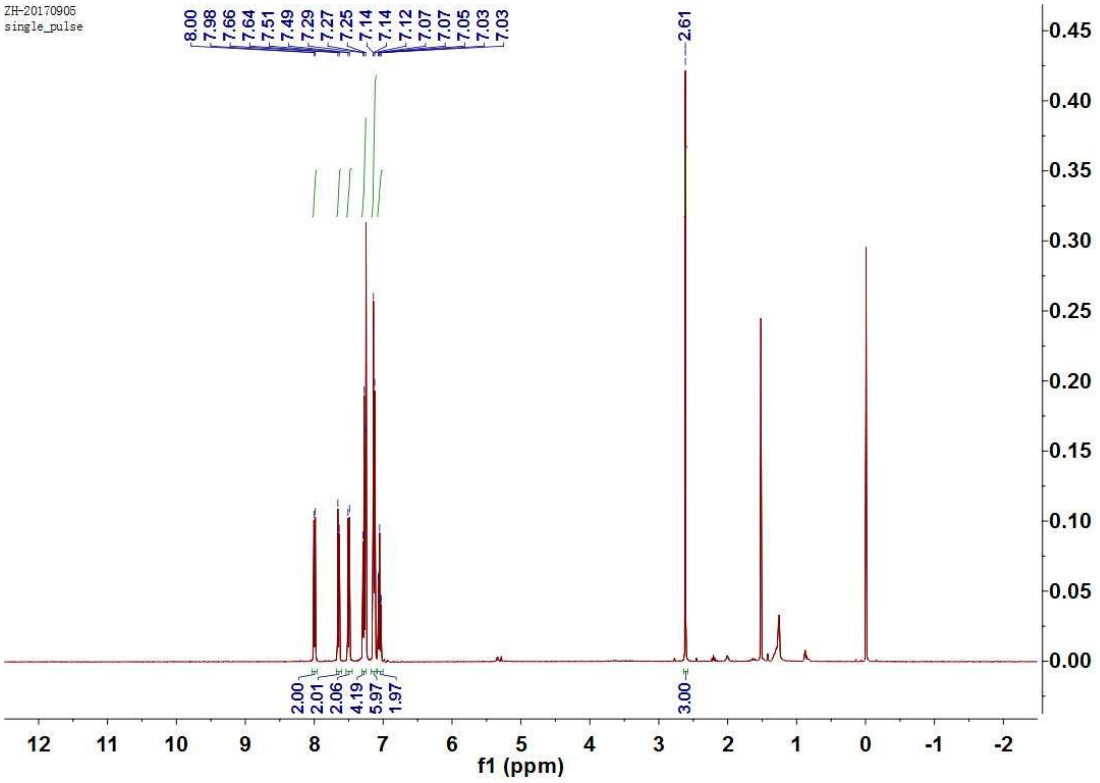
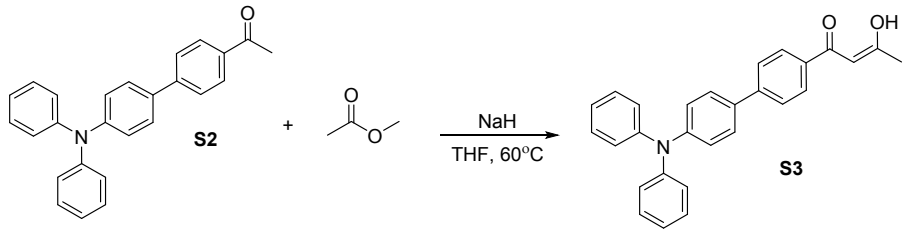


Figure S1. The ^{1}H NMR spectrum of compound **S2** in $CDCl_3$.



Added compound **S2** (182 mg, 0.5 mmol) and NaH (57-63％ oil dispersion, 100 mg, 2.5 mmol) in 3 mL anhydrous THF under N_2 protection. Then to the reaction mixture was added methyl acetate 1mL. The reaction mixture was heated to 60℃ with stirring for 24 hours. After cooling to room temperature, the water was dropped slowly into the mixture to react with excessive NaH, adjust pH to 7 with diluted hydrochloric acid. The

solution was washed with water and then extracted with dichloromethane thrice. The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, 1:1 v/v, petroleum ether/dichloromethane) to afford compound **S3** (138 mg, 68%) as yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 16.19 (s, 1H), 8.00 – 7.80 (m, 2H), 7.69 – 7.55 (m, 2H), 7.49 (t, *J* = 11.6 Hz, 2H), 7.34 – 7.20 (m, 4H), 7.13 (dd, *J* = 8.6, 2.3 Hz, 6H), 7.08 – 6.92 (m, 2H), 6.19 (d, *J* = 15.0 Hz, 1H), 2.20 (s, 3H).

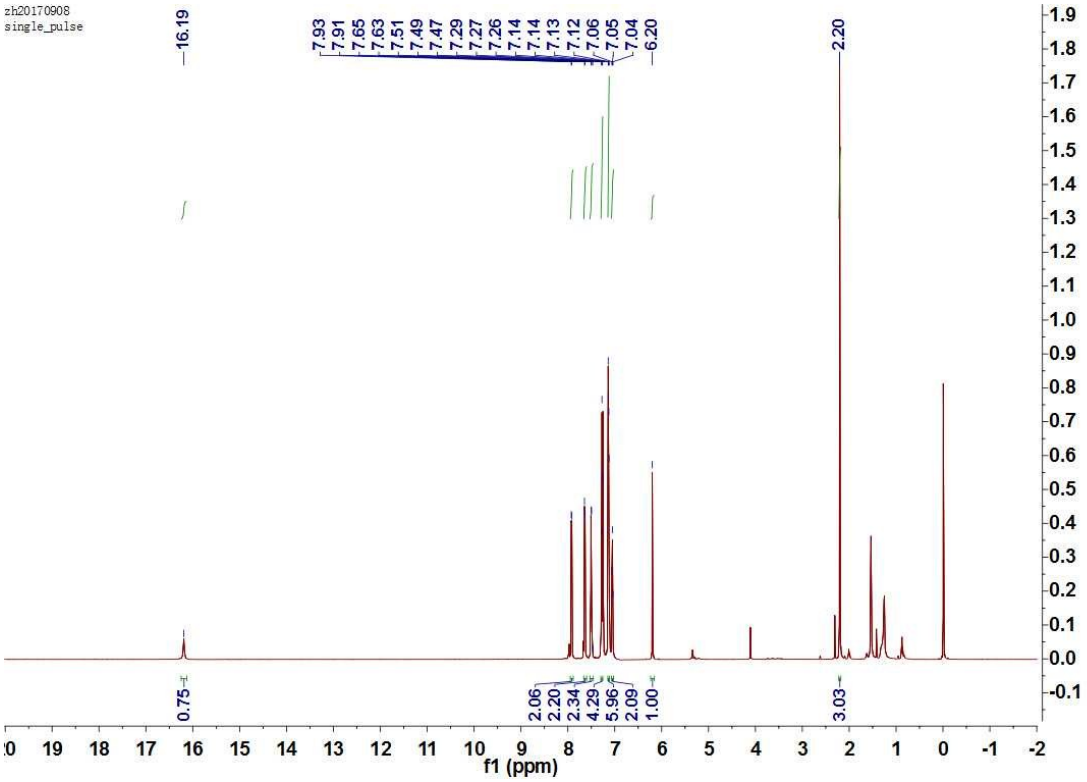
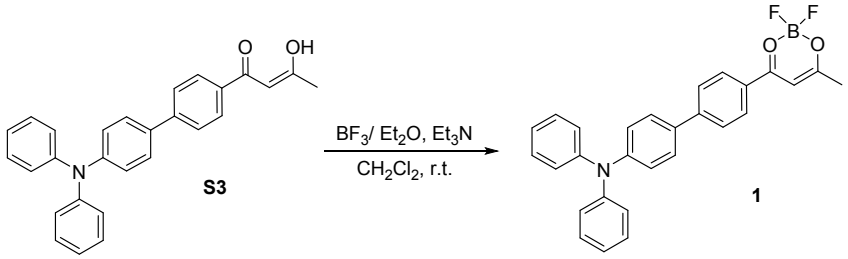


Figure S2. The ^{1}H NMR spectrum of compound **S3** in $CDCl_3$.



Compound **S3** (101 mg, 0.25 mmol) in 10 mL CH_2Cl_2 was added Et_3N (104 μL, 0.75

mmol). After stirring for 5 minutes at room temperature, BF_3/Et_2O (95 μL, 0.75 mmol) was added. The reaction mixture was stirred at room temperature in the dark for 24 h. The solution was washed with saturated $NaHCO_3$ solution, saturated NH_4Cl solution and brine thrice respectively, the organic layer was then dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, 1:1 v/v, petroleum ether/dichloromethane) to afford product **1** (80mg, 71%) as orange solid. ^1H NMR (600 MHz, $CDCl_3$): δ 8.11 (d, J = 8.5 Hz, 2H), 7.72 (d, J = 8.2 Hz, 2H), 7.53 (dd, J = 14.8, 8.4 Hz, 2H), 7.29 (dd, J = 19.2, 11.0 Hz, 4H), 7.14 (t, J = 8.2 Hz, 6H), 7.08 (d, J = 7.1 Hz, 2H), 6.57 (s, 1H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 191.57, 182.35, 148.99, 147.79, 147.24, 131.90, 129.86, 129.54, 129.06, 128.10, 126.87, 125.15, 123.80, 122.86, 97.22, 24.79. HR-ESI-MS: m/z [M + H] calculated for $C_{28}H_{23}BF_2NO_2$, 454.1790; found, 454.1789.

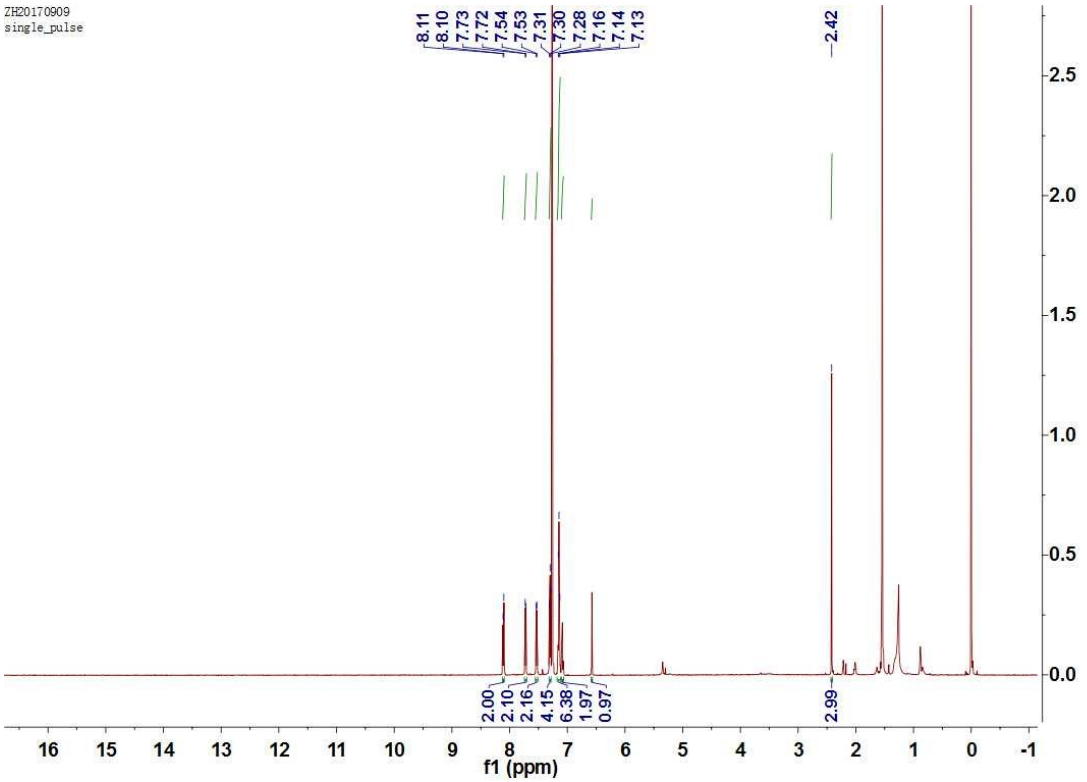


Figure S3. The ^1H NMR spectrum of compound **1** in $CDCl_3$.

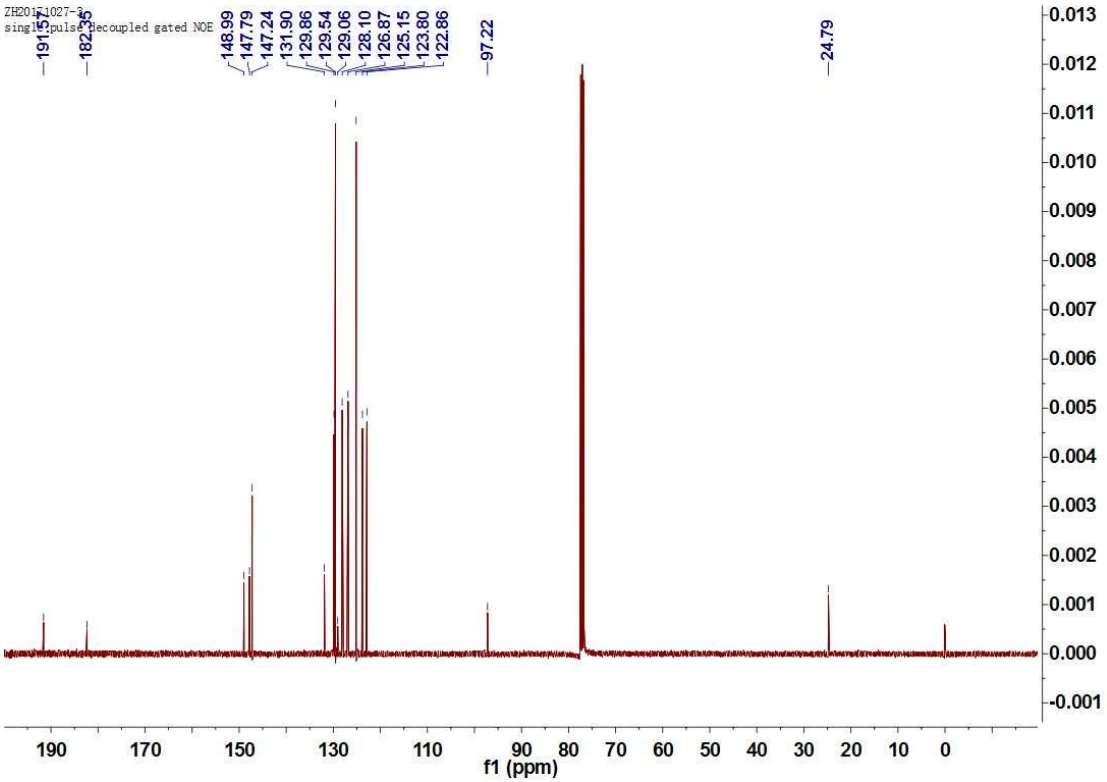


Figure S4. The ^{13}C NMR spectrum of compound **1** in $CDCl_3$.

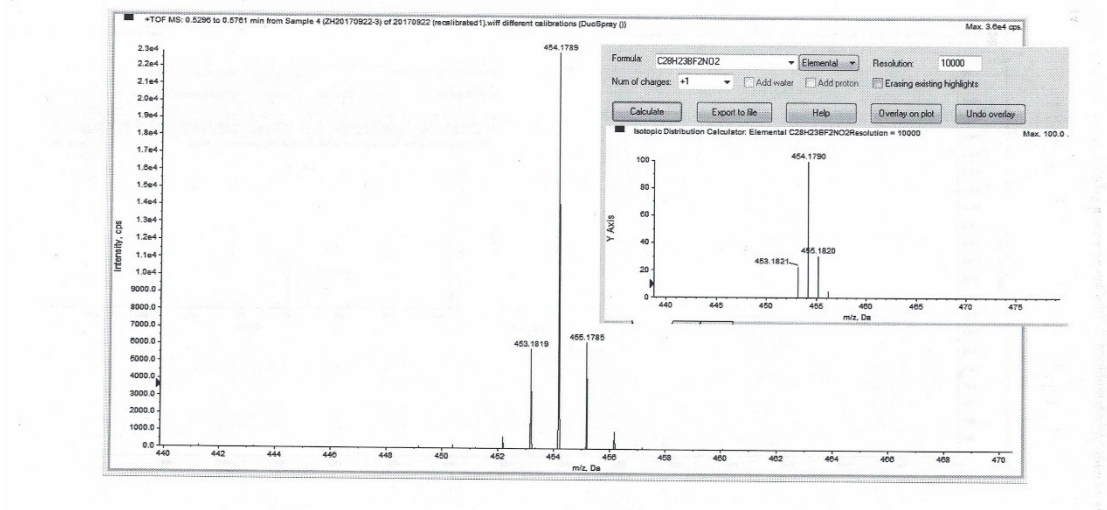


Figure S5. The HRMS spectrum of compound **1**.

Table S1. Crystal data and structure refinement for compound 1.

Identification code	bww18369
Empirical formula	$C_{28}H_{22}BF_2NO_2$
Formula weight	453.27
Temperature/K	153.15
Crystal system	triclinic
Space group	P-1
a/Å	9.6654(19)
b/Å	10.237(2)
c/Å	23.230(5)
α/°	95.58(3)
β/°	93.98(3)
γ/°	96.58(3)
Volume/Å^3	2265.0(8)
Z	4
ρ_{calc}g/cm^3	1.329
μ/mm^{-1}	0.094
F(000)	944.0
Crystal size/mm^3	0.21 × 0.13 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.028 to 55.036

Index ranges	$-12 \leq h \leq 12$, $-13 \leq k \leq 11$, $-27 \leq l \leq 30$
Reflections collected	23569
Independent reflections	10272 [$R_{int} = 0.0676$, $R_{sigma} = 0.0726$]
Data/restraints/parameters	10272/120/652
Goodness-of-fit on F^2	1.208
Final R indexes [I>=2σ (I)]	$R_1 = 0.0855$, $wR_2 = 0.1563$
Final R indexes [all data]	$R_1 = 0.1085$, $wR_2 = 0.1687$
Largest diff. peak/hole / e $Å^{-3}$	0.28/-0.32

Table S2. The lifetime and quantum yield of compound 1 in Ar bubbled organic solvents.

	hexane	**toluene**	**THF**	**CH_2Cl_2**	**$CHCl_3$**	**EA**
τ_f	2.8ns/2.8ms	3.7ns/5.2ms	1.3ns	0.7ns	3.7ns/3.6ms	1.2ns/1.2ms
Φ_f	0.99	0.99	0.55	0.09	0.82	0.31

3. Preparation of nanocrystals.

In a typical preparation of the nanocrystals, a solution of compound **1** (1 mM) in THF (good solvent, 0.5, 1, 1.5 mL) was injected into 5.0 mL water/ SDS (1.0 mg/mL)/ CTAB (0.3 mg/mL)/ F127 (1.0 mg/mL) aqueous solution (poor solvent) with stirring. After stirring for 2 minutes, the sample was placed for about 3 days for stabilization. The morphology of the nanostructures could be observed by SEM studies.

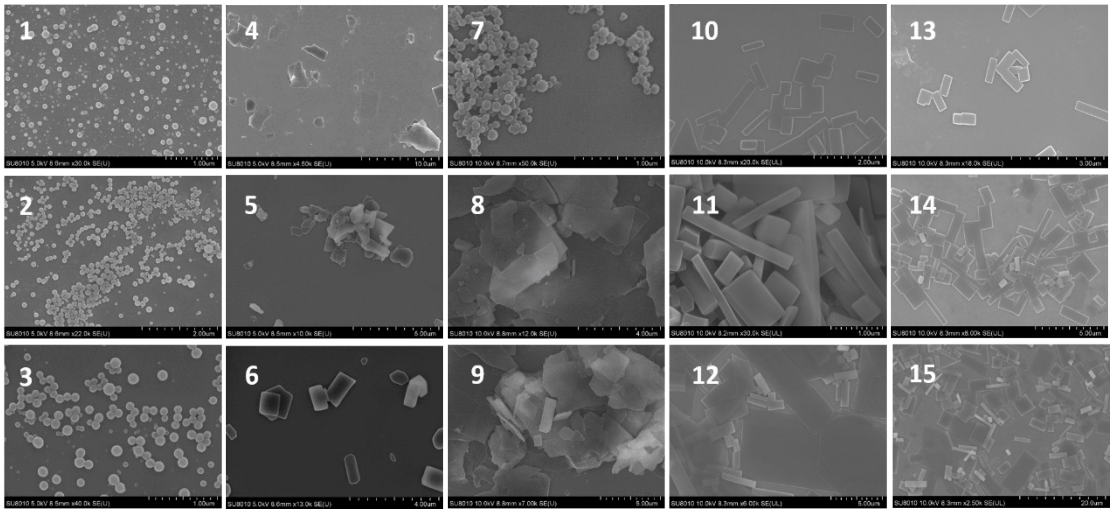


Figure S6. The SEM images of compound **1** nanocrystals prepared in 5 mL water from 0.5 mL (1), 1 mL (2) and 1.5 mL (3) THF, in 5 mL water with 1 mg/mL SDS from 0.5 mL (4), 1 mL (5) and 1.5 mL (6) THF, in 5 mL water with 0.3 mg/mL CTAB from 0.5 mL (7), 1 mL (8) and 1.5 mL (9) THF, in 5 mL water with 1 mg/mL F127 from 0.5 mL (10), 1 mL (11) and 1.5 mL (12) THF, in 5 mL water with 0.5 mg/mL F127 from 0.5 mL (13), 1 mL (14) and 1.5 mL (15) THF.

4. Other experiments.

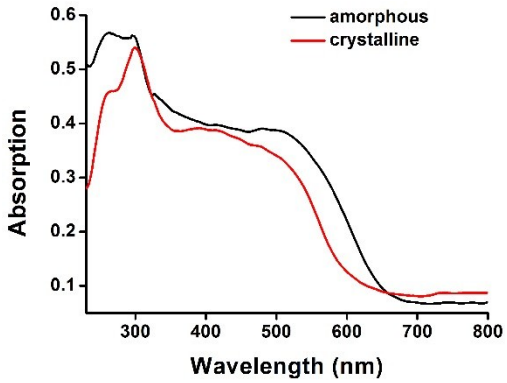


Figure S7. The absorption spectra of compound **1** in amorphous and crystalline state.

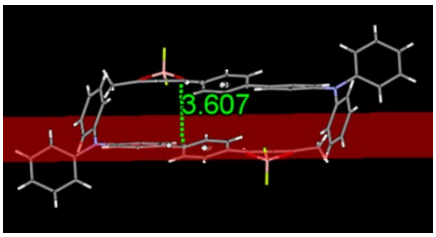


Figure S8. The distance between the layers of the crystal of compound **1**.

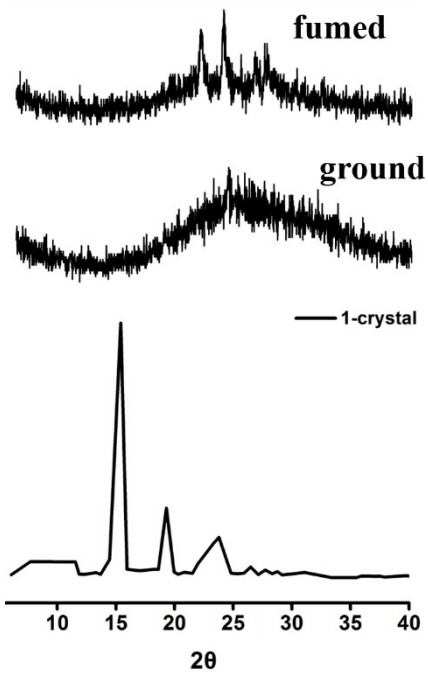


Figure S9. (a) The PXRD patterns of compound **1** upon external stimuli.

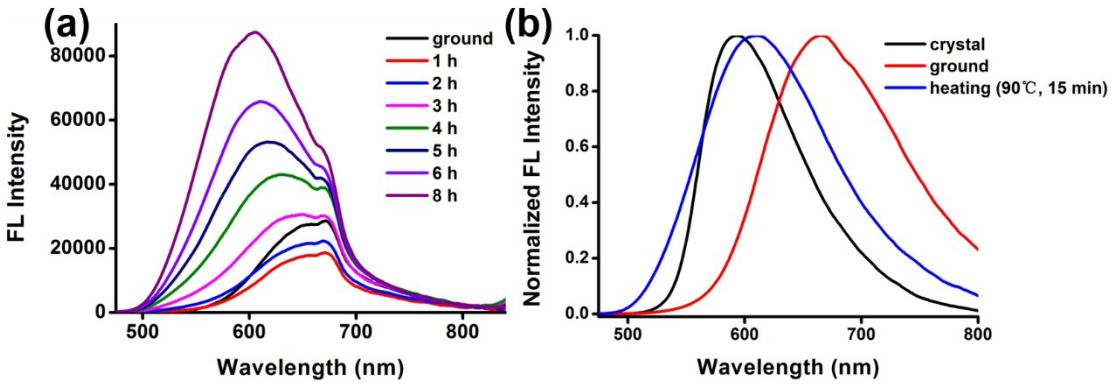


Figure S10. The normalized emission spectra of the compound **1** upon external stimuli.

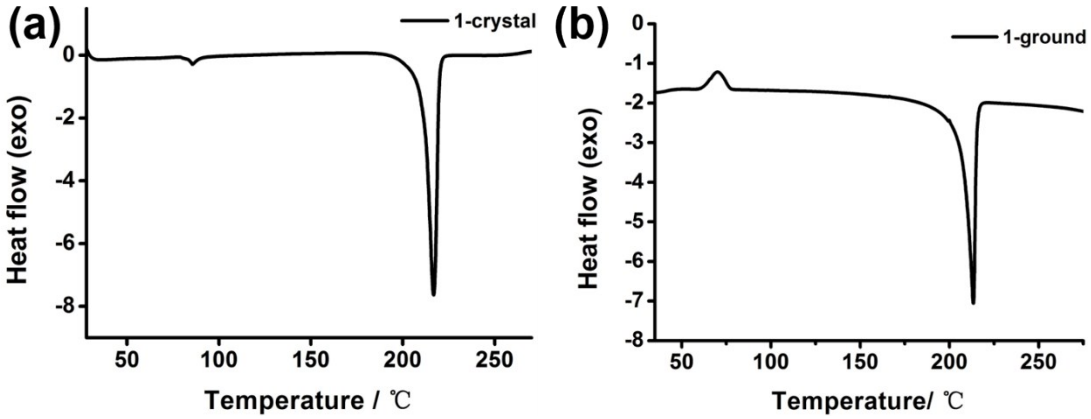


Figure S11. The DSC thermograms of compound **1** in (a) crystalline state and (b) crystalline state.

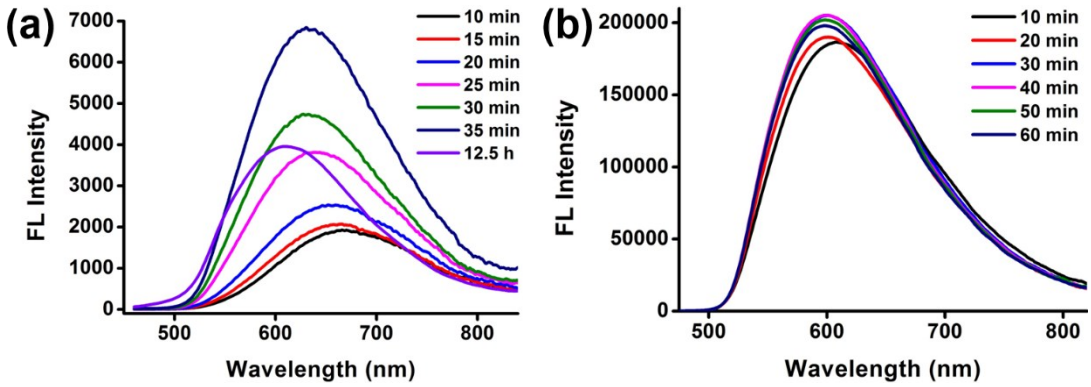


Figure S12. The emission changes of compound **1** during the formation of the nanorods prepared in 5 mL water with 1 mg/mL F127 from 0.5 mL (a) and 0.8 mL (b) THF. The spectra were recorded every 5 minutes for (a) and every 10 minutes for (b) except for the spectrum labeled by 12.5 h.

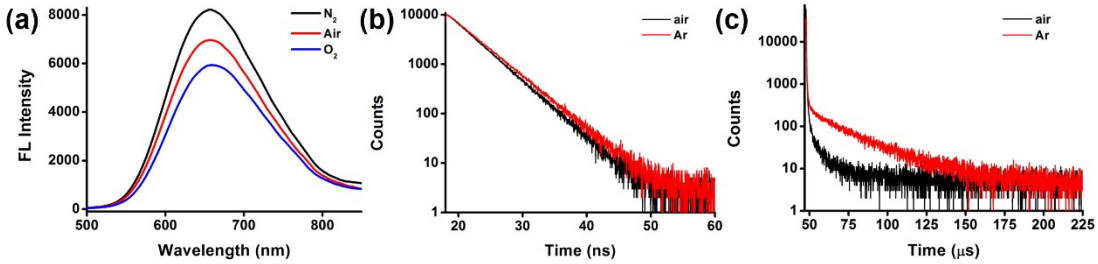


Figure S13. (a) The fluorescence of compound **1** in $CHCl_3$ (10 μM) at N_2, air and O_2 atmosphere. (b), (c) The transient decay of compound **1** in $CHCl_3$ at air and Ar atmosphere.