Electronic Supplementary Information for

Tricolor fluorescent switching in the three crystal polymorphs of tetraphenylethylene modified fluorenone AIEgen

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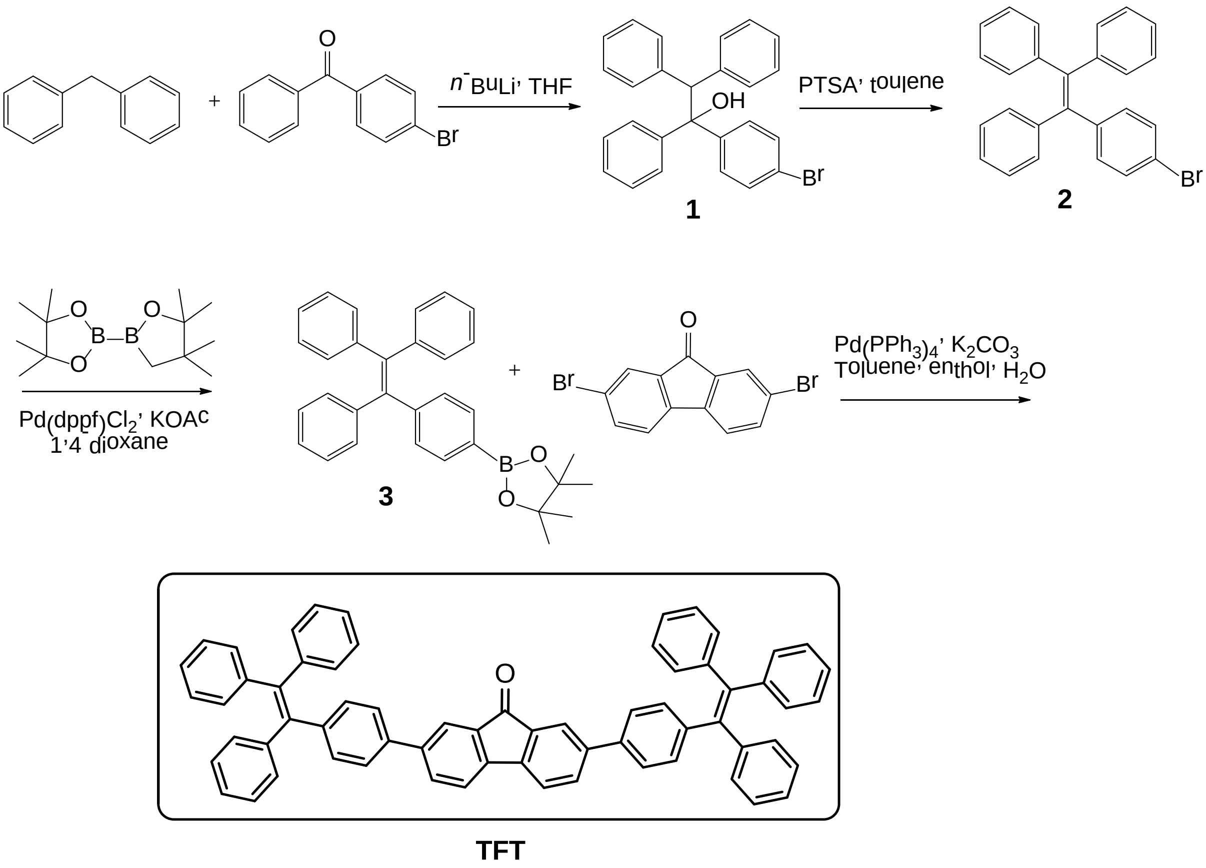
Table of contents

1. Synthesis and the single-crystal preparation



Scheme S1 Synthetic routes to **TFT**.

Synthesis of 1-(4-bromophenyl)-1, 2, 2-triphenylethene (compound 2) [1]

To a 250 mL three-necked flask, diphenylmethane (1.53 mL, 9.04 mmol) and 30 mL dry THF was added. Evacuated replacement and then 2.9 mL (7.00 mol) of n-butyllithium (2.4 mol/L solution in hexane) was injected to the solution slowly with a syringe at 0°C under nitrogen. After stirring for 30 min, 40 mL dry THF solution of 4-bromobenzophenone (1.56 g, 5.99 mmol) was added dropwise to the reaction mixture. Stirred over night at room temperature and then quenched by adding an aqueous solution of ammonium chloride into the mixture. Extracted with DCM, the DCM phase was alternately washed with deionized water and saturated sodium chloride aqueous for three times, and then dried over anhydrous magnesium sulfate. After filtration followed by solvent evaporation, the intermediate (**compound 2**) was obtained. Then, the intermediate 1 and 0.21 g anhydrous p-toluenesulfonic acid were dissolved in 30 mL toluene and refluxed for 8 h. After evaporating to remove toluene, the obtained solid was dissolved in DCM and then alternately washed with deionized water and saturated sodium chloride aqueous for three times. The DCM phase was dried over anhydrous magnesium sulfate and the blue-white crude TPE-Br was obtained after filtration followed by solvent evaporation. Purified by silica gel column chromatography using hexane/DCM (v/v=4:1) as eluent, **compound 2** was obtained as a white solid in 56.14% yield. The resulting product was directly synthesized into **compound 3.**

Synthesis of 4, 4, 5, 5-tetramethyl-2-(4-(1, 2, 2-triphenylvinyl) phenyl)-1, 3, 2-dioxaborolane (compound 3)[2]

In a 100 mL three-necked flask, B_2Pin_2 (1.14 g, 4.5 mmol), TPE-Br (1.5 g, 3.6 mmol) and potassium acetate (1.46 g, 14.9 mmol) were dissolved in 20 mL dioxane, and then Pd(dppf)Cl_2 (30 mg, 0.04 mmol) was added to the solution under nitrogen. The resulting mixture was stirred at 90 ℃ for 16 h. After filtration with silica gel, the filtrate was evaporated under reduced pressure to remove dioxane. Then, the slight-yellow residue was purified by silica gel column chromatography, using PE/DCM (V/V=3:1) as eluent to give **compound 3** in yield of 66.42% (1.02 g). ^{1}H NMR (DMSO-d_6, 500 MHz, ppm) δ 7.46 (d, J = 7.6 Hz, 2H), 7.15 (dq, 9H), 7.05 – 6.96 (m, 8H), 3.37 (s, 12H).

The synthesis of 2,7-bis(4-(1,2,2-triphenylvinyl)phenyl)-9H-fluoren-9-one (TFT)

A mixture of **compound 3** (733.7 mg, 1.6 mmol), 2,7-bis(4-bromophenyl)-9H-fluoren-9-one (264.3 mg, 0.78 mmol), Pd(PPh_3)$_4$ (56 mg, 0.047 mmol), K_2CO_3 (431.2mg, 3.12 mmol) in toluene (15 mL) and water (2 mL) was heated to reflux and stirred under nitrogen overnight. After cooling down to room temperature, the organic layer was separated and the water layer was extracted with dichloromethane (DCM). The combined organic solution was dried with Na_2SO_4. After filtration, the resulting solution was concentrated on a rotary evaporator. The residue was purified by column chromatography on silica gel using DCM/PE (v/v: 1: 2) as the eluent to obtain **TFT** (86.67%, yield) as an orange powder. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.91 (s, 2H), 7.72 (dd, J = 7.6, 1.8 Hz, 2H), 7.58 (d, J = 7.8 Hz, 2H), 7.42 (d, J = 8.1 Hz, 4H), 7.23 – 7.06 (m, 34H). ^{13}C NMR ($CDCl_3$, 101 MHz, ppm) δ 193.79, 143.64, 143.61, 143.56, 143.54, 142.92, 141.71, 141.46, 140.29, 137.49, 135.15, 132.97, 131.96, 131.40, 131.32, 127.81, 127.74, 127.65, 126.63, 126.55, 126.49, 125.89, 122.82, 120.66. HRMS (ESI) m/z calcd for $C_{65}H_{45}O^+$ $(M+H)^+$ 841.34649, found 841.34644.

The preparation of yellow single crystals Y-TFT

The yellow single crystals **Y-TFT** were obtained by slow evaporation. Firstly, the compound **TFT** was dissolved in DCM to prepare a saturated solution, then *n*-hexane was slowly added along the bottle wall and the bottle mouth was sealed. Finally, the culture bottle was placed in a quiet and vibration free environment and volatilized slowly at room temperature over a week to obtain yellow single crystals **Y-TFT.**

The preparation of orange single crystals O-TFT

The orange single crystals **O-TFT** were also obtained by slow evaporation. Firstly, the compound **TFT** was dissolved in DCM to prepare a saturated solution, then methanol was slowly added along the bottle wall and the bottle mouth was sealed. Finally, the culture bottle was placed in a quiet and vibration free environment and volatilized slowly at room temperature over a week to obtain orange single crystals **O-TFT.**

The preparation of red single crystals R-TFT

Similar to the preparation of yellow single crystals **Y-TFT** and orange single crystals **O-TFT**, the red single crystals **R-TFT** was prepared by using tetrahydrofuran and methanol mixed system, sealing and static, and slowly evaporating at room temperature over a week.

2. ^{1}H NMR, ^{13}C NMR and MS.

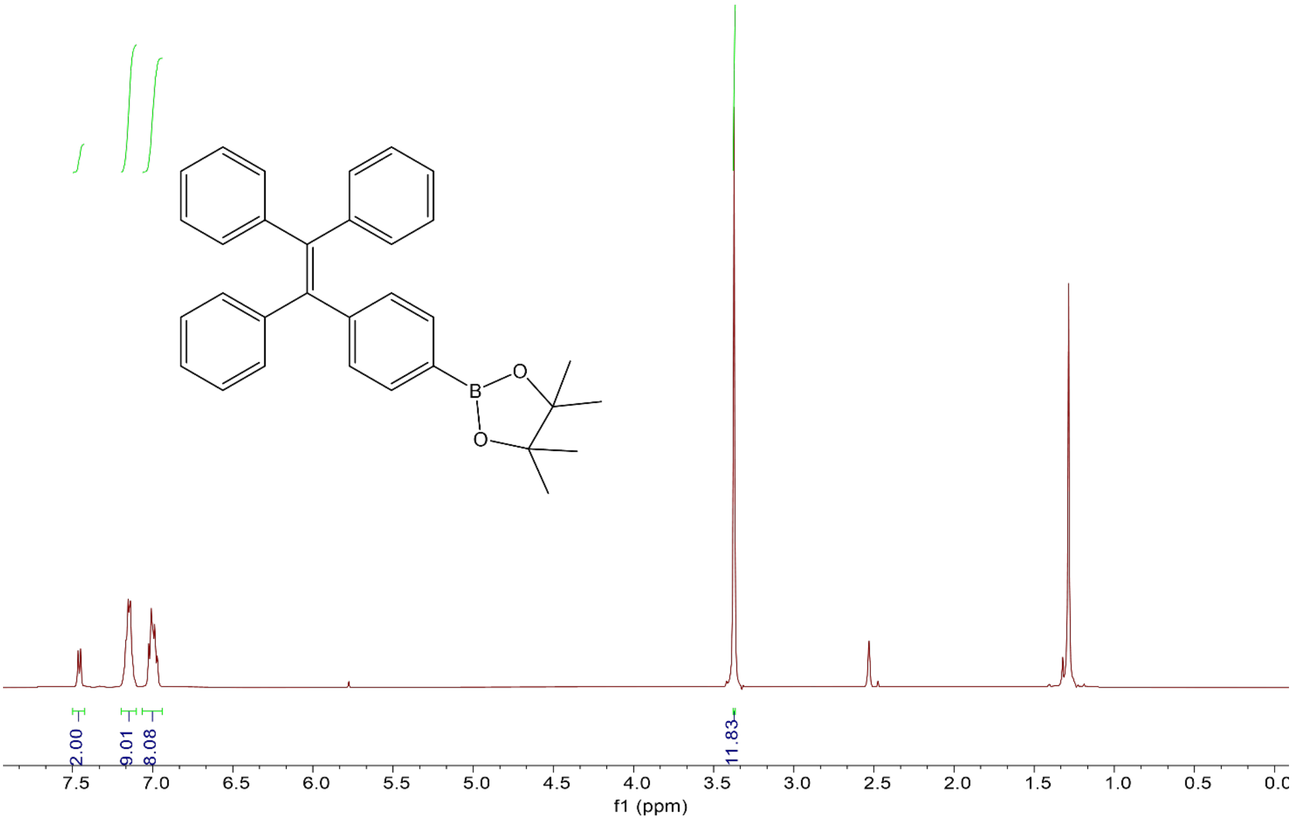


Figure S1 ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of **compound 3**

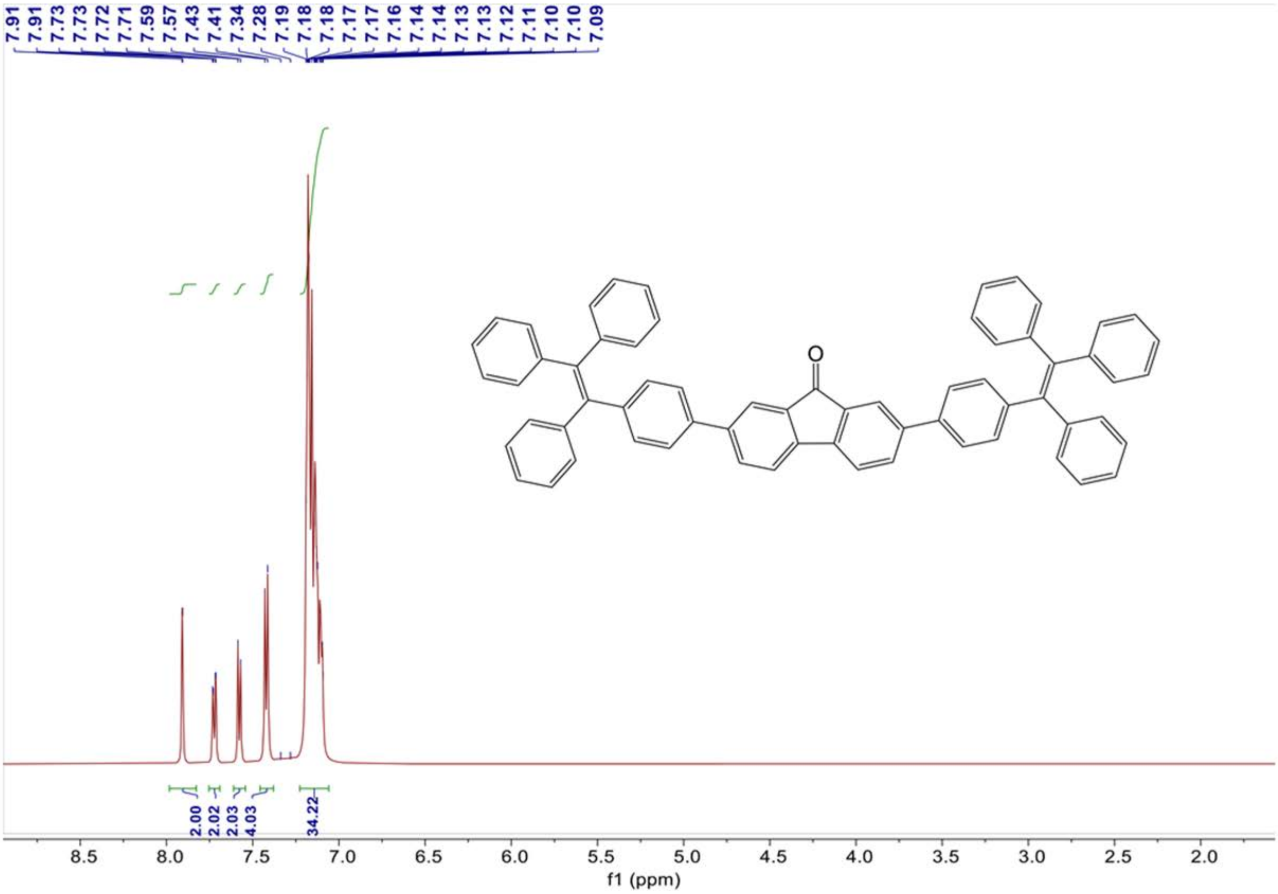


Figure S2 ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **TFT**

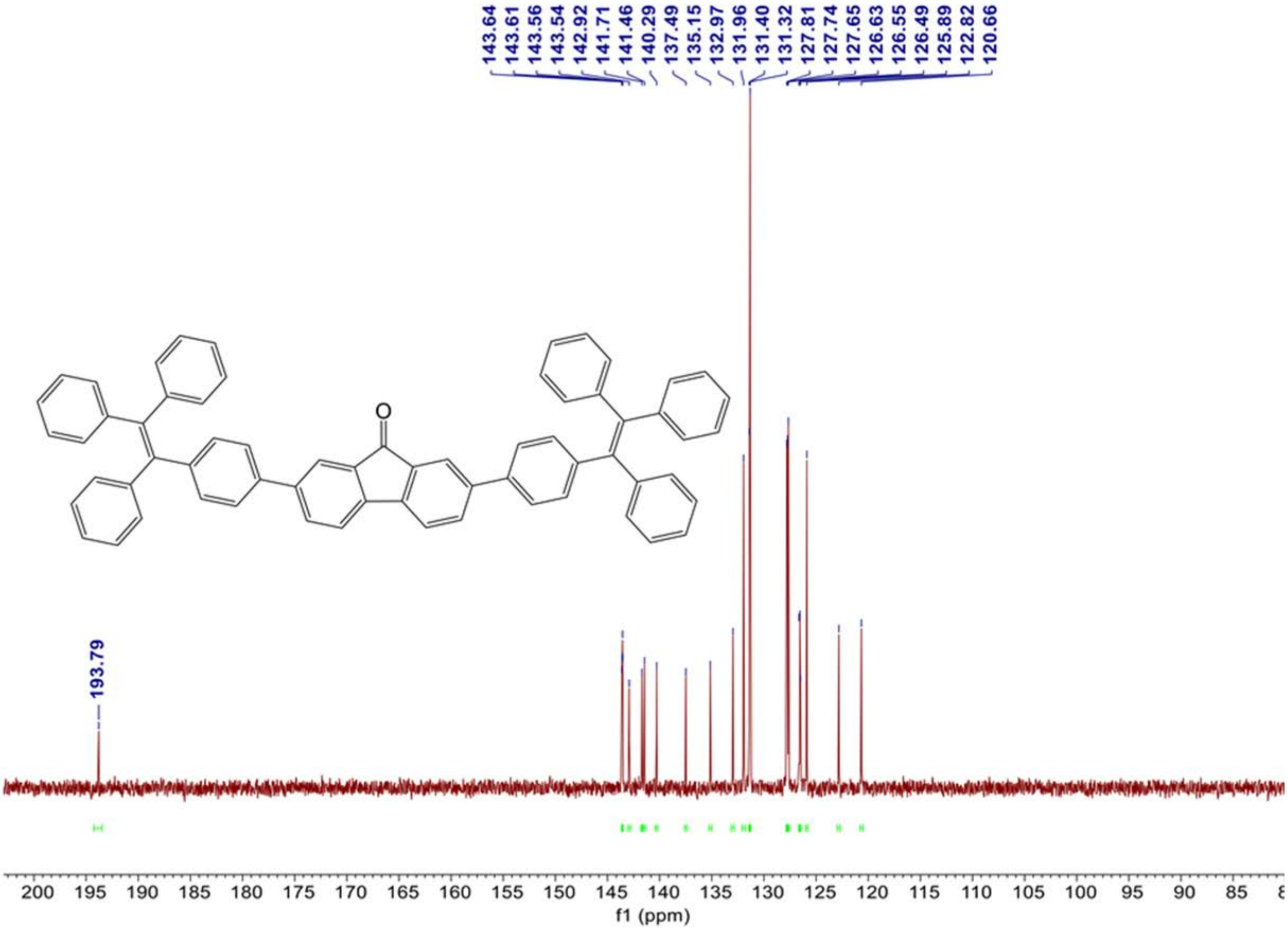


Figure S3 ^{13}C NMR spectrum (101 MHz, CDCl$_3$) of compound **TFT**

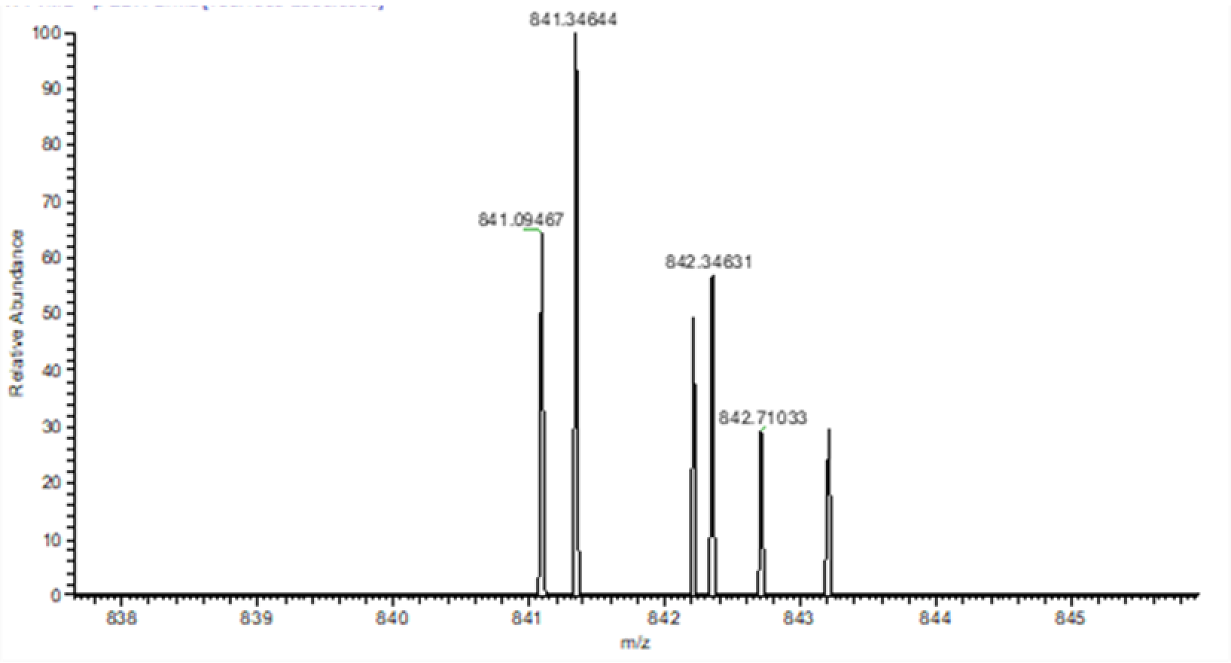


Figure S4 HRMS (ESI) spectrum of **TFT**

3. PL and Absorption Spectra of TFT solution

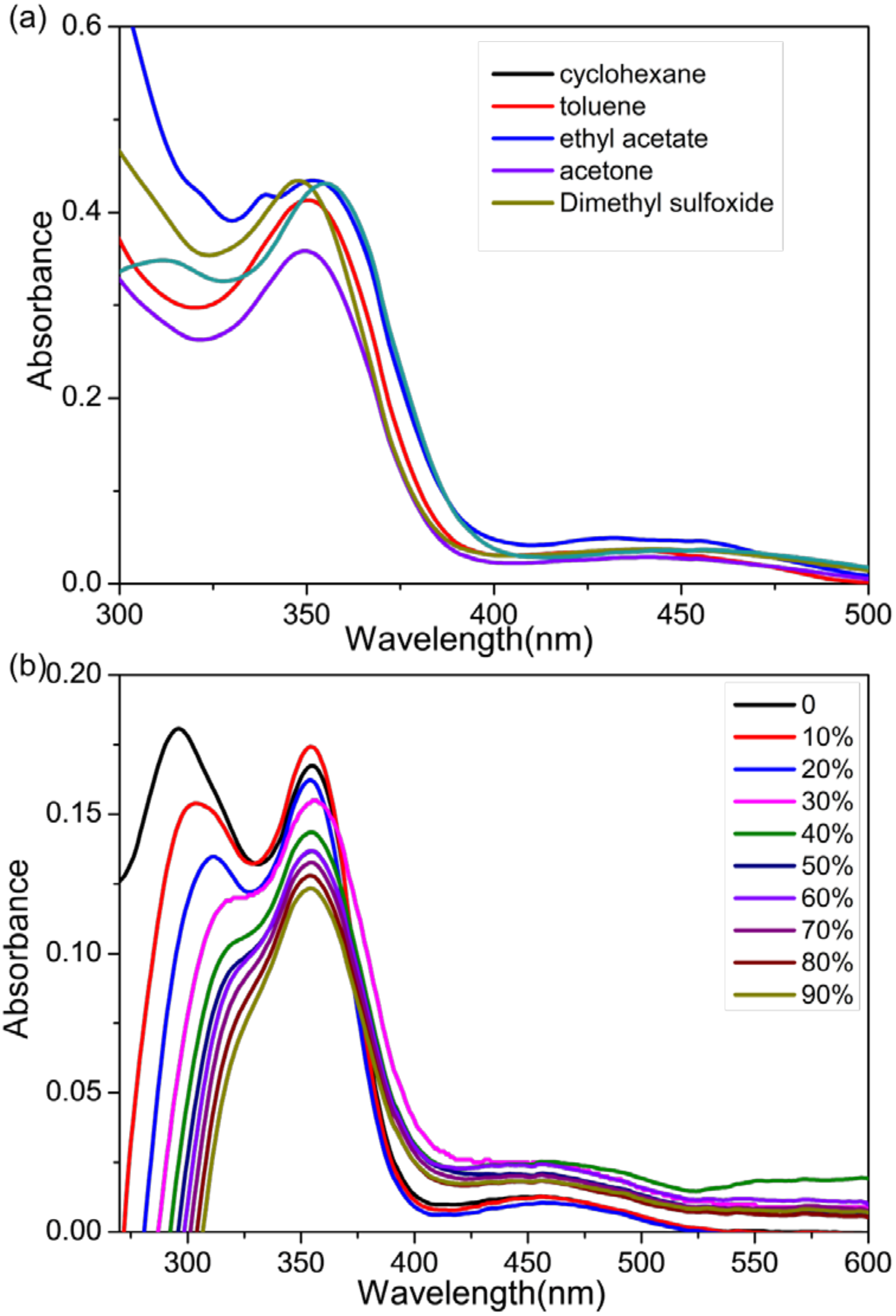


Figure S5 (a) UV-Vis absorption spectra of **TFT** in varying solvents; (b)UV-Vis absorption spectra of **TFT** in DMSO–water mixtures with different water fractions (2μM)

4.Single crystal structure

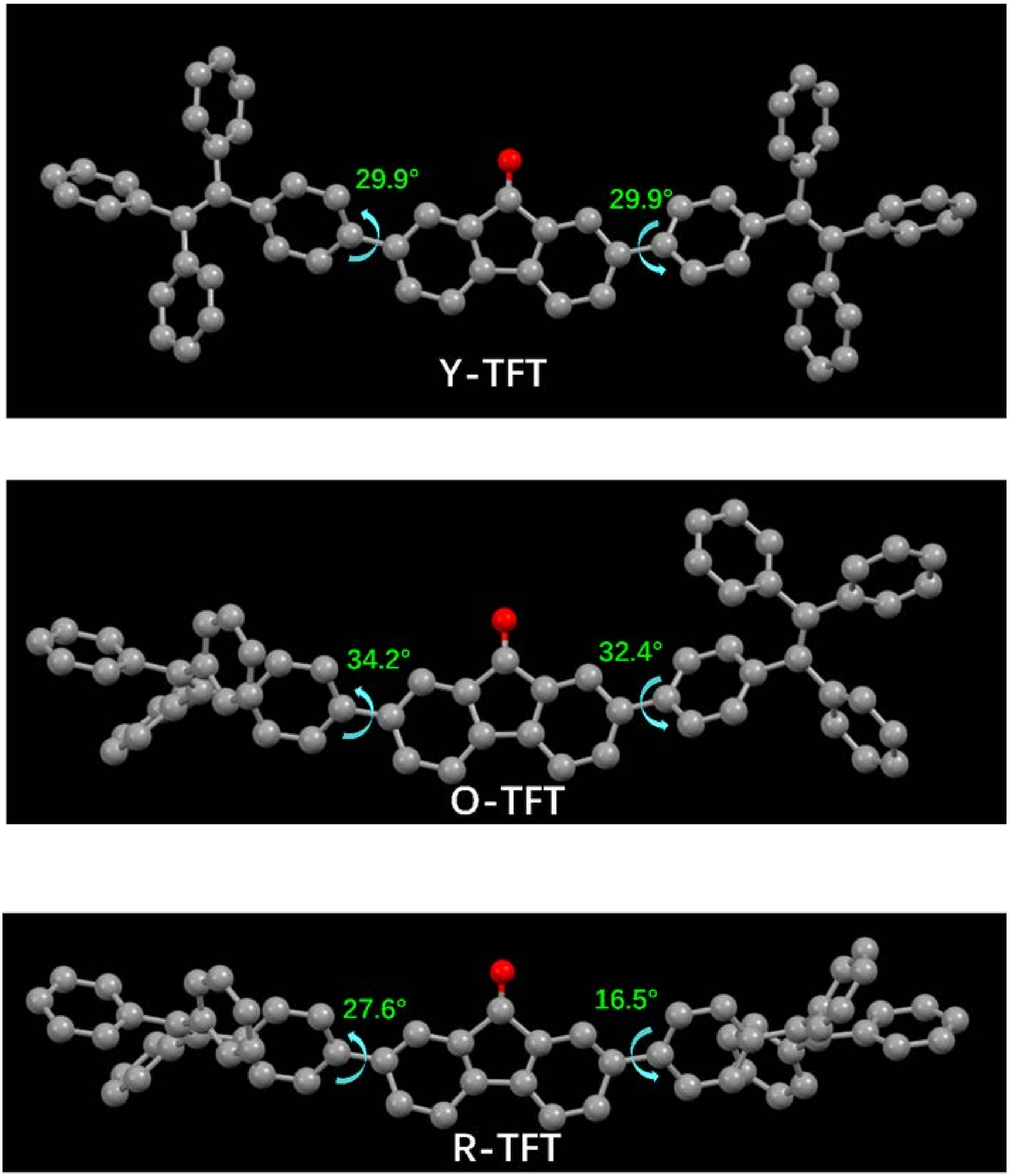


Figure S6 The single crystal structure of **Y-TFT, O-TFT** and **R-TTF**

5. PL, Absorption Spectra and XRD of TFT powders

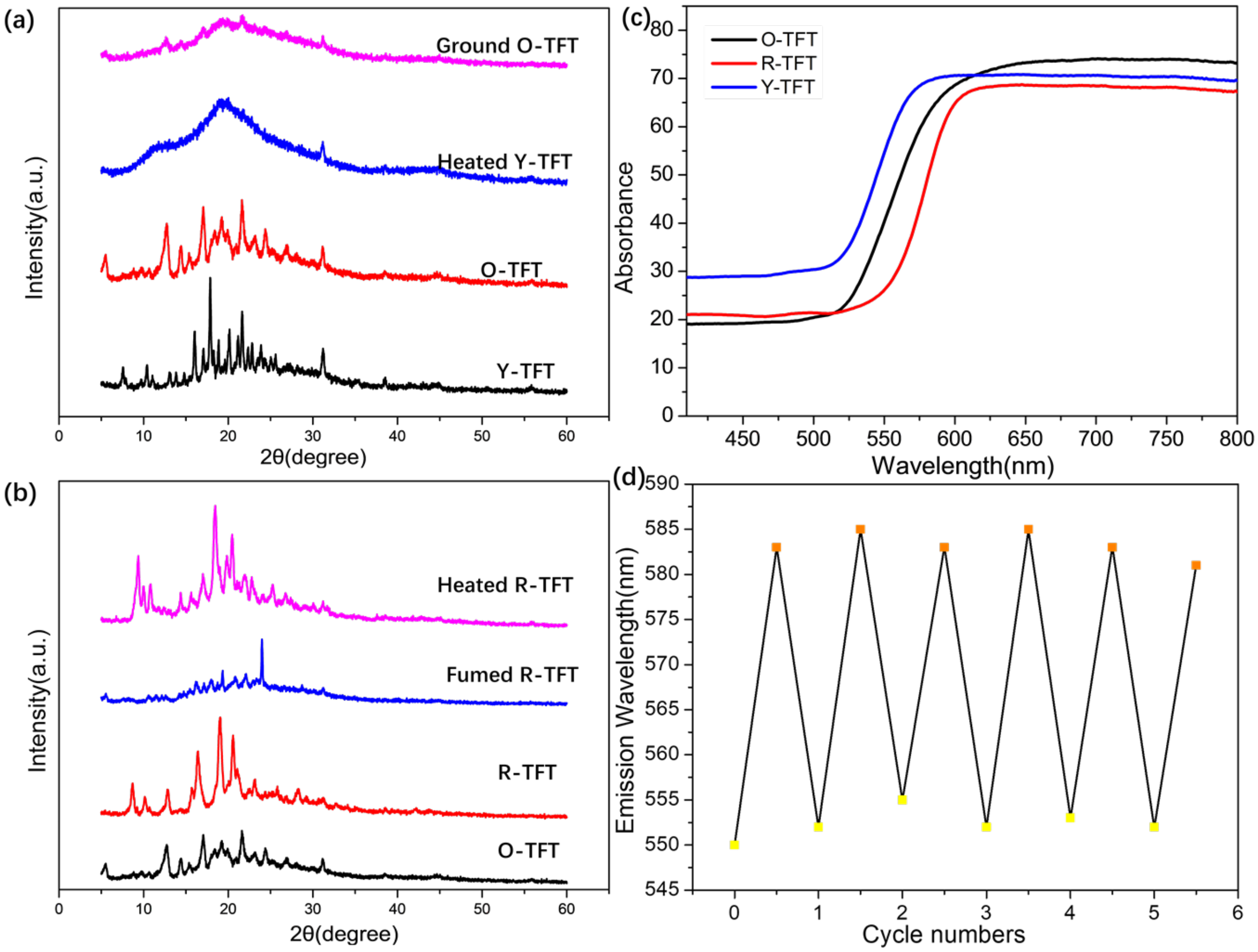


Figure S7 (a) (b)Powder XRD profiles of the yellow crystal **Y-TFT**、orange crystal **O-TFT** and red crystal **R-TFT**; (c)The absorbance spectra of **Y-TFT**、**O-TFT** and **R-TFT**; (d)Repeated switching of the solid-state fluorescence of **Y-TFT** and **O-TFT** by repeated grinding and heating cycles.

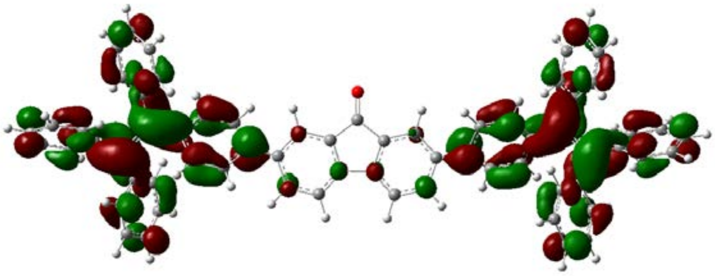
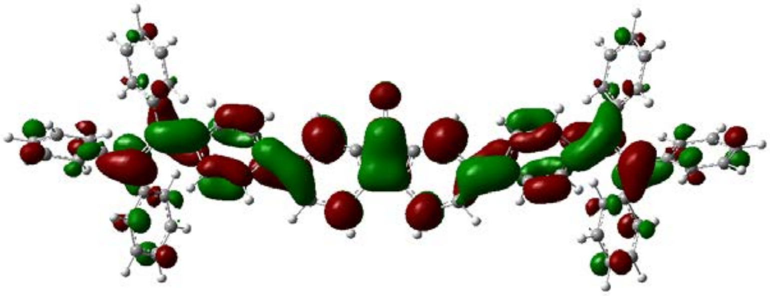
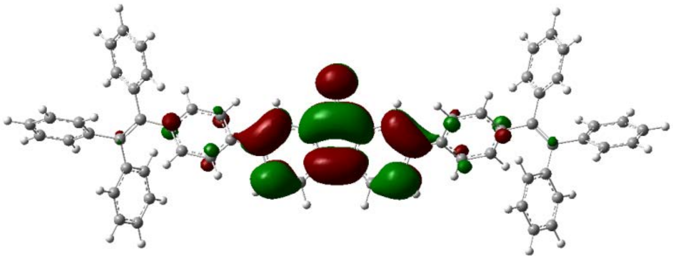
6. X-ray Crystal Data

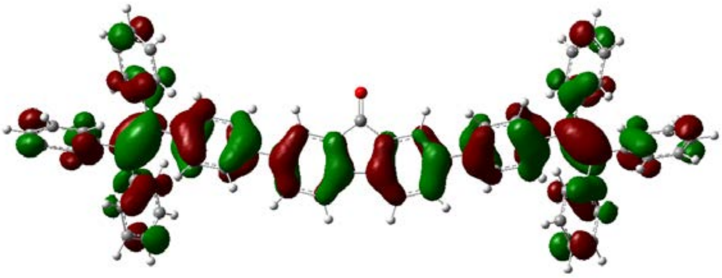
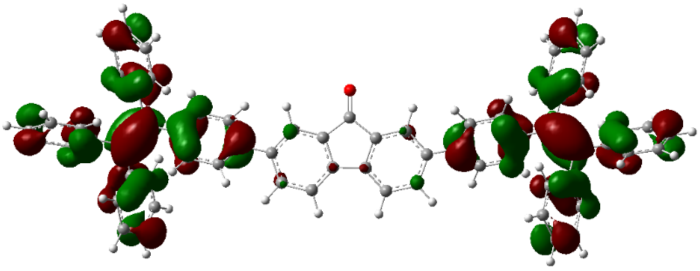
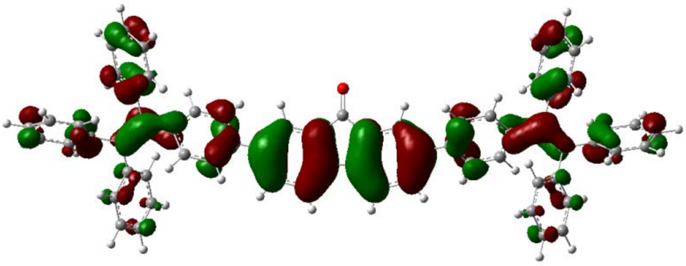
Table S1. Selected crystallographic data for **Y-TFT**, **O-TFT** and **R-TFT**

Crystals	**Y-TFT**	**O-TFT**	**R-TFT**
formula	$C_{65}H_{44}O$	$C_{65}H_{44}O$	$C_{65}H_{44}O$
Fw [g/mol]	841.00	841.00	841.00
Crystal color	yellow	orange	red
Crystal system	orthorhombic	triclinic	monoclinic
Space group	*Pbcn*	P_1	P_12_1/c_1
a[Å]	15.467(2)	10.1631(15)	29.085(3)
b[Å]	16.015(3)	12.8711(18)	9.7598(9)
c[Å]	20.695(4)	19.294(3)	19.4264
β[°]	90	99.038(4)	99.500(4)
V[Å^3]	5126.2(15)	2445.2(6)	5438.8(9)
z	4	2	4
ρ_{calcd}[g/cm^3]	1.310	1.258	1.027
μ [mm^{-1}]	1.615	1.007	0.289
T[K]	150(2)	150(2)	150(2)
θmin-θmax[°]	3.46-54.81	3.04-54.98	2.68- 54.82
R/wR[I>2$\sigma_{(1)}$]	0.074/0.1326	0.038/0.1027	0.0703/0.2106

7. Theoretical Calculations

Table S2 The graphic representations of the frontier molecular orbits of QB-Zn. Geometric optimization was performed using the B3LYP functional.

LUMO+2 No.224 -1.342 eV		Excited State 1: 2.5603 eV 484.26 nm f=0.0102 221->222 0.67836
LUMO+1 No.223 -1.502 eV		Excited State 2: 3.1312 eV 395.96 nm f=0.0000 211 -> 222 0.37194 212 -> 222 0.55799 212 -> 223 0.10643 218 -> 222 0.10259
LUMO No.222 -2.242 eV		Excited State 3: 3.3197 eV 373.48 nm f=1.3692 219 -> 222 0.11093 220 -> 224 -0.21109 221 -> 223 0.65653

HOMO No.221 -5.244 eV	
HOMO-1 No.220 -5.365 eV	
HOMO-2 No.219 -5.916 eV	

8. Reference

1. Zhang S, Cui H, Gu M, Zhao N, Cheng M, Lv J. *Small*, 2019, 15:1804662-4804670
2. Jiang Y, Duan Q, Zheng G, Yang L, Zhang J, Wang Y, Zhang H, He J, Sun H, Ho D. *Analyst*, 2019, 144:1353-1360