Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

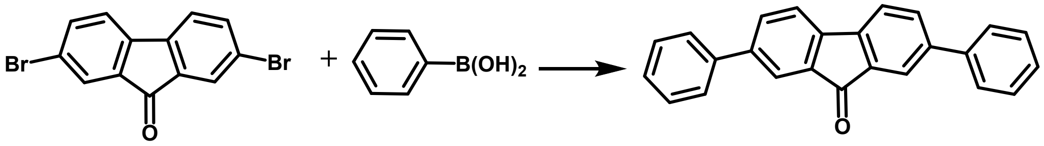
Electronic Supplementary Information

Reversible luminescence color switching in the crystal polymorphs of 2,7-bis(2′-methyl-[1,1′-biphenyl]-4-yl)-fluorenone by thermal and mechanical stimuli

Xianchao Du, Fan Xu, Mao-Sen Yuan, Pengchong Xue, Lei Zhao, Dong-En Wang, Wenji Wang, Qin Tu, Shu-Wei Chen, and Jinyi Wang

1. Synthesis

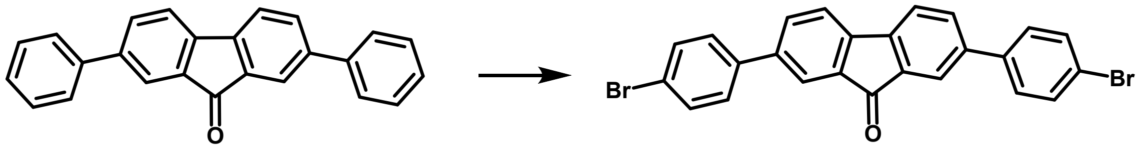
Synthesis of 2,7-diphenyl-9*H*-fluoren-9-one (1).



1

A mixture of 2,7-dibromo-9*H*-fluoren-9-one (0.60 g, 1.77 mmol), phenylboronic acid (0.55 g, 4.51 mmol), $Pd(PPh_3)_4$ (20 mg, 0.02 mmol), toluene (20 mL), ethanol (5 mL) and 2 M K_2CO_3 aqueous solution (2 mL) was heated to 80 °C with stirring under an argon atmosphere for 8 h. The mixture was then cooled to room temperature and poured into water (100 mL). After extraction with dichloromethane (DCM), the organic phase was dried over Na_2SO_4. Purification by column chromatography on silica gel and elution with dichloromethane-petroleum ether (1:1, v/v) yielded compound **1** (0.53 g, 91%) as a yellow-green powder. Compound **1** was dissolved in DCM, and yellow single crystals were formed upon slow evaporation at room temperature over a week. Melting point (m.p.): 235 °C–236 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.29 (s, 1 H), 7.40–7.45 (t, J = 7.4, 2 H), 7.48–7.52 (t, 4 H), 7.62–7.67 (m, 6 H), 7.75–7.76 (d, 1 H), 7.77–7.78 (d, 1 H) and 7.95–7.96 (d, J = 7.9, 1 H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 193.8, 143.1, 142.3, 139.9, 135.2, 133.4, 129.0, 128.0, 126.8, 123.1 and 120.8. TOF-MS-EI: m/z 332.1 $[M]^+$. Elemental anal. calcd. for $C_{25}H_{16}O$: C, 90.33; H, 4.85; and O, 4.81. Found: C, 90.17 and H, 4.92.

Synthesis of 2,7-bis(4-bromophenyl)-9*H*-fluoren-9-one (2).

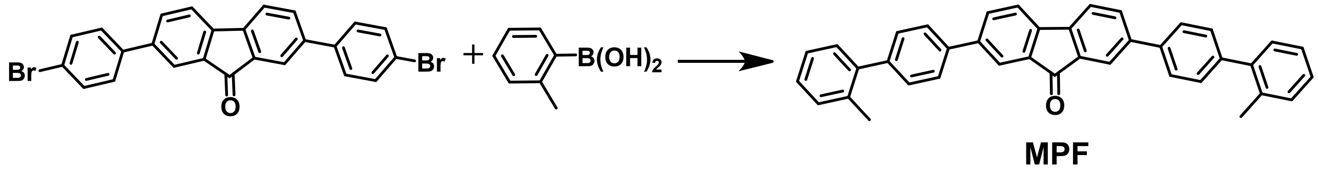


2

A mixture of compound 1 (0.30 g, 0.90 mmol), Br_2 (0.20 mL, 3.9 mmol) and H_2O (10 mL) were heated to reflux and stirred for 10 h. Afterwards, the mixture was cooled to room temperature and filtered off under suction, washed with water. The residue was recrystallized from THF to yield 2,7-

bis(4-bromophenyl)-9H-fluoren- 9-one **2** (0.25 g, 57%) as an orange crystal. Melting point (m.p.): 283 °C -284 °C. IR (KBr, cm-1): 3414, 3048, 1714, 1605, 1582, 1458, 1296, 1177, 1070, 1003, 815, 782, 744. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): d 7.51-7.53 (m, 4H), 7.61-7.65 (m, 6H), 7.72-7.74 (d, *J* =7.7 Hz, 2H) and 7.90 (s, 2H). ^{13}C NMR (CDCl3, 125 MHz, ppm): d 193.5, 143.3, 141.1, 138.7, 135.3, 133.2, 132.1, 128.4, 122.9, 122.3 and 121.0. TOF-MS-EI: m/z 488.3 [M]$^+$.

Synthesis of 2,7-bis(2'-methyl-[1,1'-biphenyl]-4-yl)-9*H*-fluoren-9-one (MPF).



A mixture of **2** (0.20g, 0.4 mmol), o-tolylboronic acid (0.136 g, 1.0mmol), Pd(PPh$_3$)$_4$ (6 mg, 0.005 mmol), toluene (6 mL), ethanol (2 mL) and 1M K$_2$CO$_3$ aqueous solution (1 mL) was heated to 80 °C with stirring under an argon atmosphere for 8 h. The mixture was then cooled to room temperature and poured into water (100 mL). After extraction with dichloromethane (DCM), the organic phase was dried over Na$_2$SO$_4$. Purification by column chromatography on silica gel and elution with dichloromethane-petroleum ether (1:1, v/v) yielded compound MPF (0.184 g, 90%) as a yellow-green powder. Melting point (m.p.): 259 °C -261 °C. ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.05 (s, 1H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.75 (d, *J* = 7.3 Hz, 2H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 7.4 Hz, 2H), 7.34 (s, 4H), 2.39 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 193.83, 143.15, 141.92, 141.73, 141.28, 138.24, 135.41, 133.26, 132.19, 130.49, 129.88, 128.60, 127.50, 126.50, 125.92, 123.02, 120.88, 20.59. TOF-MS-EI: m/z 511.8 [M]$^+$.

2. X-ray single-crystal structure

Table S1. Selected crystallographic data for **G-MPF** and **O-MPF**.

crystals	**G-MPF**	**O-MPF**
formula	$C_{39}H_{28}O$	$C_{39}H_{28}O$
fw[g·mol^{-1}]	512.61	512.61
crystal color	Green-yellow	Orange
crystal system	Monoclinic	Monoclinic
space group	$C2$	$P2_1/c$
a [Å]	27.852(3)	7.6772(6)
b[Å]	5.1630(4)	15.0035(13)
c [Å]	20.8582(18)	47.276(3)
β[º]	115.19(13)	95.0780(10)
V [Å^3]	2714.2(4)	5424.1(7)
Z	4	8
ρ_{calcd} [g/cm^3]	1.254	1.255
μ[mm^{-1}]	0.073	0.074
T[K]	298(2)	298(2)
θ_{min}-θ_{max} [º]	2.94-25.02	2.55-25.02
$R/wR[I > 2\sigma_{(1)}]$	0.0631/0.1393	0.1421/0.2996

3. PL spectra changes of MPF depending on temperature in THF

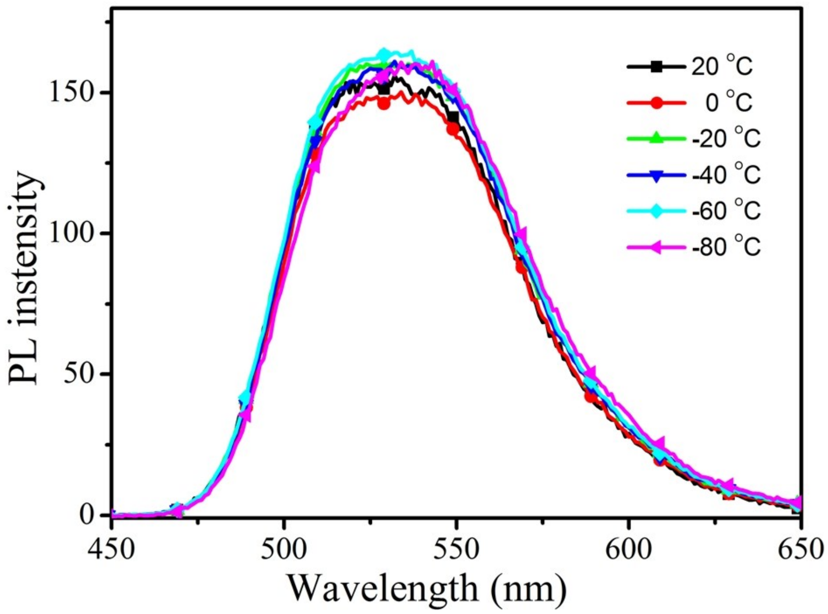


Fig. S1 PL spectra changes of **MPF** depending on the change of solution temperature in THF (10 μM).

4. Determination of repeated luminescence switching behavior

The reversible ability of heating- and grinding-induced luminescence switching of the two crystal polymorphs **G-MPF** and **O-MPF** was examined. Starting from polymorph **G-MPF**, the crystals **G-MPF** were kept at 225 °C for approximately 5 sec to convert them to the orange-emitting state. They were then ground in a mortar for approximately 2 min to give the green-emitting state. The switching cycle was performed 5 times.

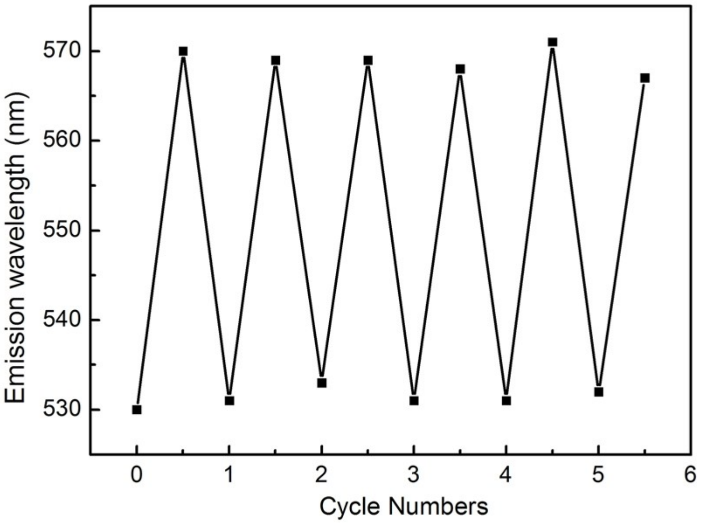


Fig. S2 Emission wavelength of the repeated luminescence switching behavior of compound **MPF** by heating the green-yellow crystal **G-MPF** and grinding crystal **O-MPF** treatments (excited at 360 nm).

5. UV−visible absorption spectra of the crystal polymorphs

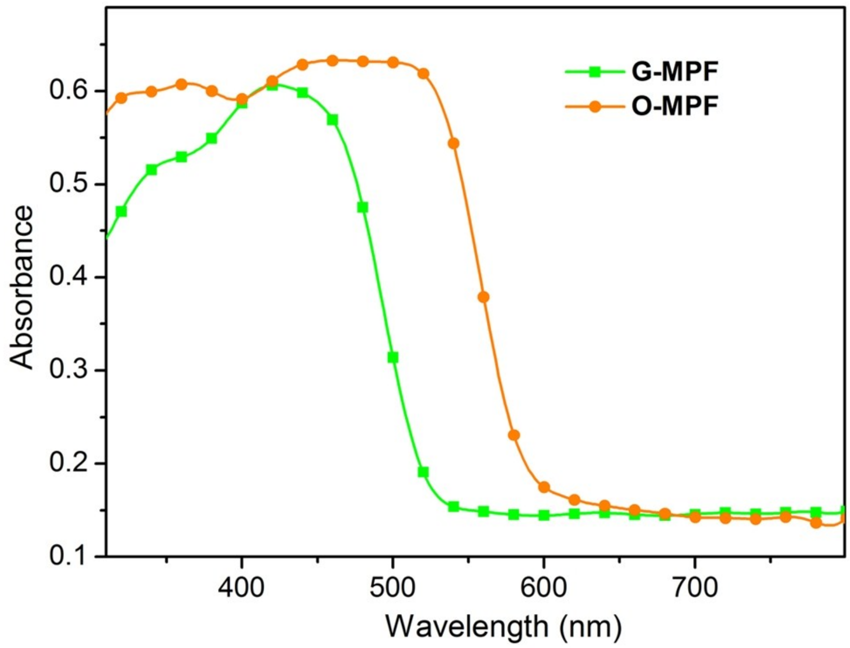


Fig. S3 UV−visible absorption spectra of **G-MPF** and **O-MPF** crystalline powders.

6. Fluorescence decay profiles of MPF in THF with different concentration

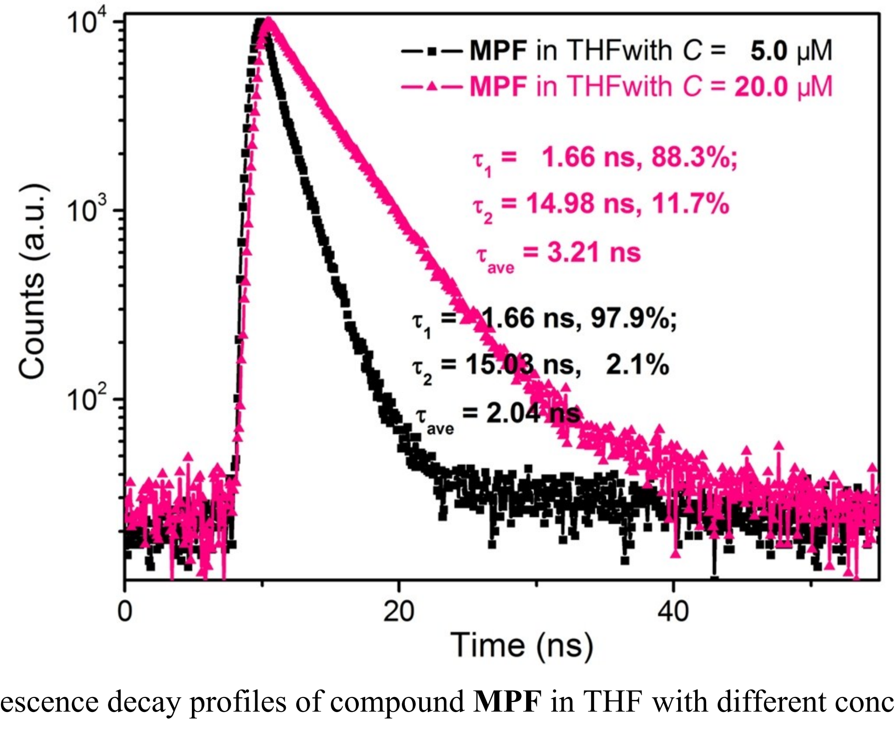


Fig. S4 Fluorescence decay profiles of compound **MPF** in THF with different concentration.

7. Theoretical calculation

To insight into the luminescent mechanisms and the formation of the static excimers of **O-MPF**, the orbital energy of the single molecule of **G-MPF** and both single molecule and dimer (static excimer) of **O-MPF** were respectively calculated by using the Gaussian 09 program at the B3LYP Time-Dependent Density Functional Theory (TD-DFT). The geometries of both the single molecule and the dimers for electronic structure calculation were obtained directly from their respective determined X-ray single crystal structures.

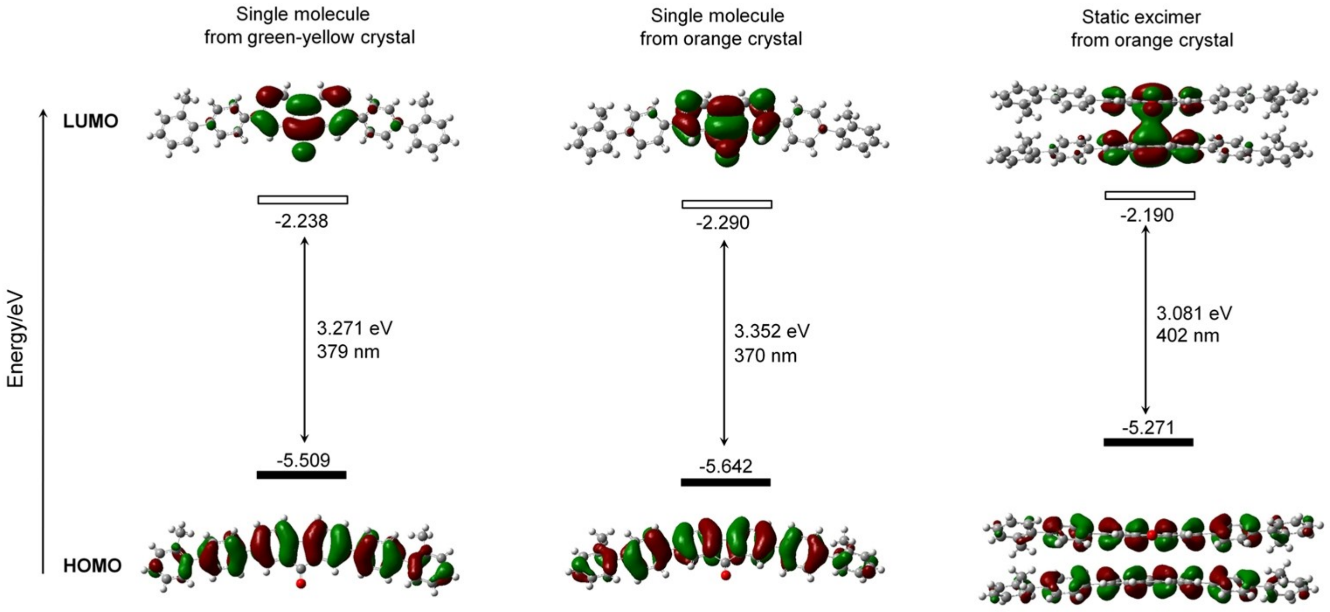


Fig. S5 Molecular orbital diagrams of HOMO and LUMO of the single molecule and the dimers (static excimer) for green-yellow crystal **G-MPF** and orange crystal **O-MPF** with their relative energy according to TD-DFT calculation.

8. ^{1}H NMR and ^{13}C NMR of compound MPF

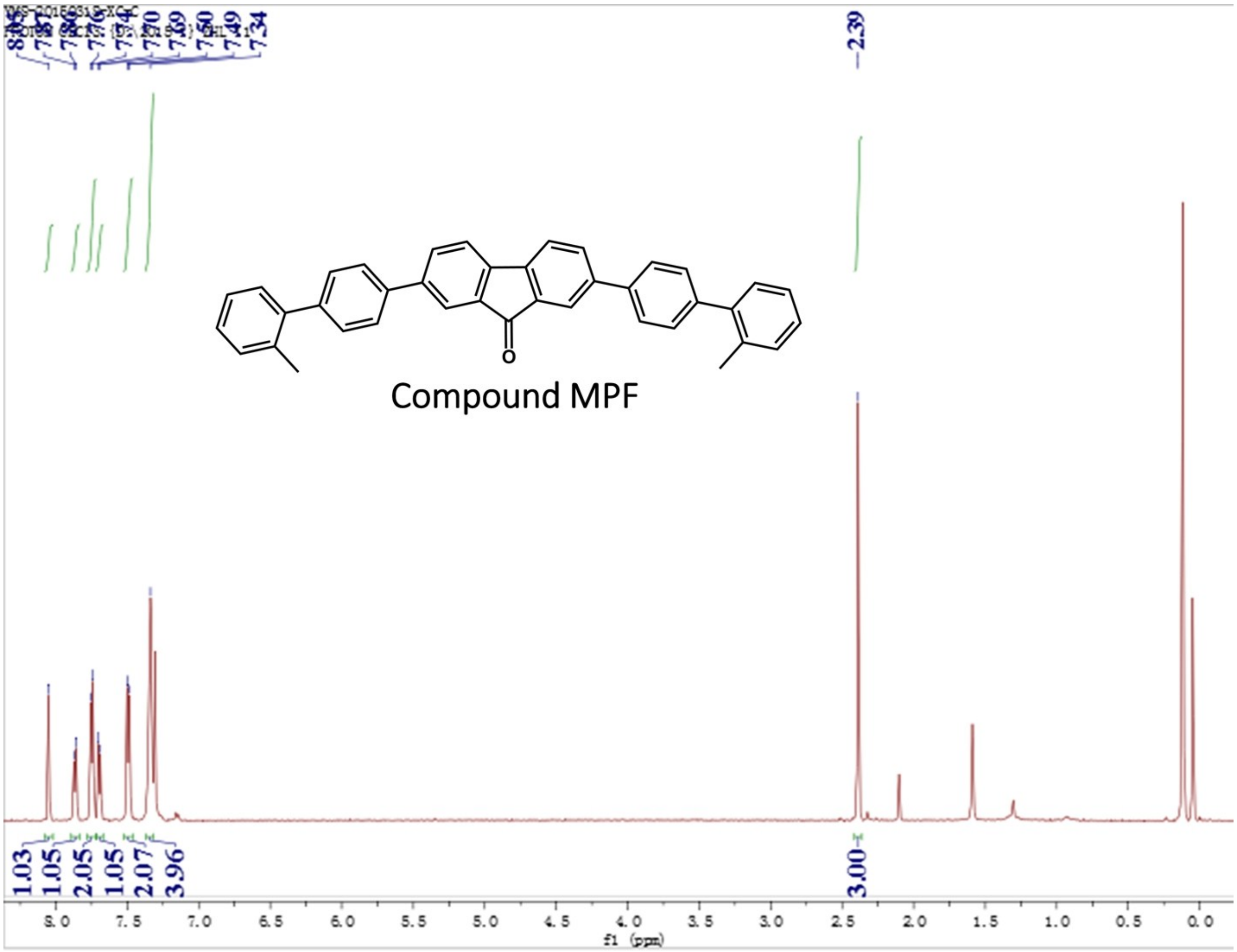


Fig. S6 ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **MPF**.

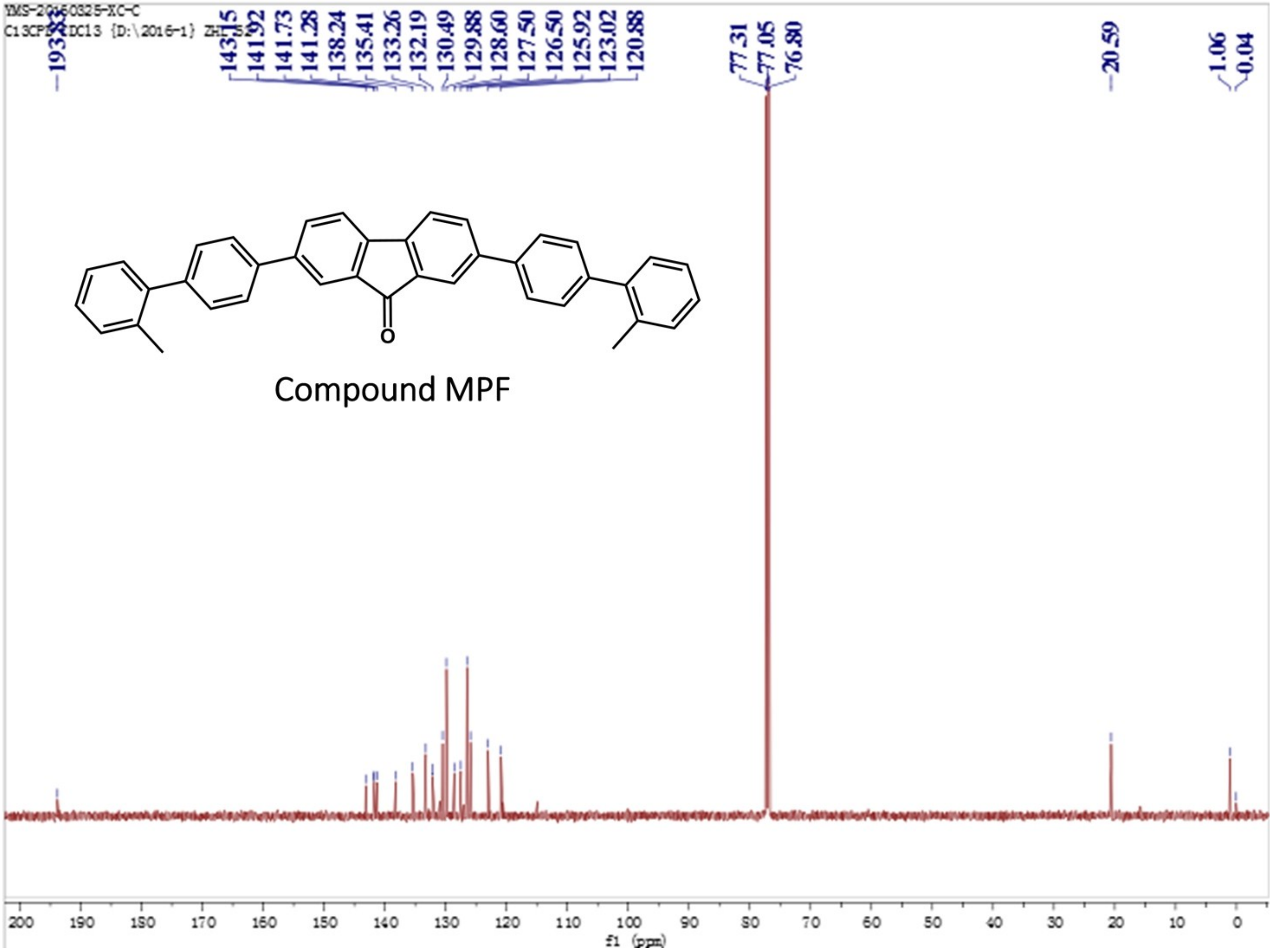


Fig. S7 ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **MPF**.

9. ESI movie

Movie S1. The crystal-color change and phase transformation upon heating the green-yellow crystal for several sec at 225 °C using a microscopic melting-point apparatus.