Electronic Supplementary Information

Difluoroboron β-diketonate based Thermometer with Temperature-Dependent Emission Wavelength

Jian-Xin Wang,[a] Yi-Shuai Yu,[b] Li-Ya Niu,[a] Bo Zou,[b] Kai Wang*[b] and Qing-Zheng Yang*[a]

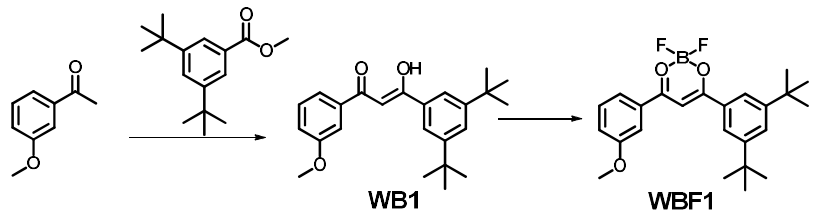
[a]Key Laboratory of Radiopharmaceuticals Ministry of Education, College of Chemistry Beijing Normal University, Beijing 100875, P.R. China

[b]State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012, P. R. China.

Materials and methods

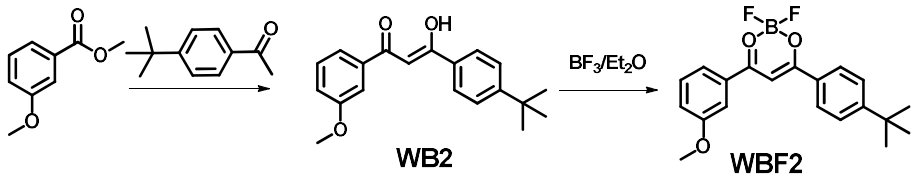
All chemicals were purchased from commercial suppliers and used without further purification. NMR spectra were recorded with a JEOL-400 or JEOL-600 spectrometers. High-resolution mass spectra were measured on a Bruker Solarix XR Fourier Transform Ion Cyclotron Resonance Mass Spectrometer. Powder X-Ray Diffraction spectrum was recorded on X pert pro MPD diffractometer while diffuse reflection absorption spectrum was recorded with Hitachi UV-3600 plus. The emission (temperature-dependent) spectra and lifetime were recorded on Edinburgh FLS980 spectrometer. The temperature-dependent single crystal structure was measured on the XtaLAB PRO 007HF (Mo) single crystal X-ray diffractometer. The film samples of **WBF1** on the quartz sheet are obtained by the spin coating with 10 mM solution of **WBF1** in chloroform. The crystalline samples for the photophysical measurements are obtained by slow evaporation of a mixed solution of dichloromethane and hexane.

Synthesis and Characterization



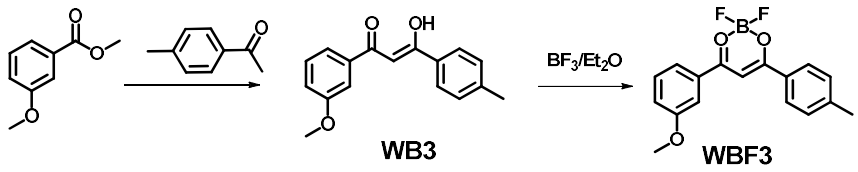
Synthesis of compound **WB1**:[1, 2] 3'-Methoxyacetophenone (1 g, 6.7 mmol) was added to a high-pressure tube in 5 mL anhydrous THF under N_2 atmosphere, then NaH (57-63% oil dispersion, 0.5 g, 12.0 mmol) and methyl 3,5-di-tert-butylbenzoate (1.65 g, 6.7 mmol) were added to the mixture. The reaction mixture was allowed to stir for 20 h at 60 °C under N_2 atmosphere. Upon cooling to room temperature, 200 ml of water was added and the pH was adjusted to 3 with HCl (aq). After extracted with CH_2Cl_2 for three times, the combined organic phase was dried over anhydrous Na_2SO_4, followed by filtration and evaporation of the solvent, purified by column chromatography using CH_2Cl_2/petroleum ether (1:2, v/v) as eluent to afford 2.31 g of compound **WB1** as white solid (yield: 94%). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 16.95(s, 1 H) , 7.80 (d, *J* = 1.8 Hz, 2 H), 7.64 (t, *J* = 1.8 Hz, 1 H), 7.56 (d, *J* = 7.8 Hz, 1 H), 7.55-7.53 (d, 1 H), 7.40 (t, *J* = 7.9 Hz, 1 H), 7.11-7.08 (dd, J = 8.1, 2.3 Hz, 1 H), 6.80 (s, 1 H) , 3.89 (s, 3 H) , 1.39 (s, 18 H). ^{13}C NMR (150 MHz, Chloroform-d) δ 187.4, 185.6, 160.2, 151.6, 137.5, 135.4, 129.9, 127.2, 121.6, 119.8, 118.6, 112.4, 93.8, 55.7, 35.32 , 31.64 (d, J = 19.5 Hz). HRMS: calc. for [M+H$^+$] 367.2266, found 367.2267.

Synthesis of compound **WBF1**: To a solution of compound **WB1** (2.31 g, 6.30 mmol) in 80 mL CH_2Cl_2 was added Et_3N (1.6 mL, 12.0 mmol) and BF_3/Et_2O (3.78 mL, 30 mmol). After stirring at room temperature for 2 h in the dark, 100 mL of water was added, the organic layer was collected, washed with saturated aqueous NH_4Cl and dried over anhydrous Na_2SO_4. Followed by filtration and evaporation of the solvent, purified by column chromatography using CH_2Cl_2/petroleum ether (1:2, v/v) as eluent to afford 2.47 g of **WBF1** as yellow solid (yield: 95%). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 1.7 Hz, 2 H), 7.77 (t, *J* = 1.7 Hz, 1 H), 7.70 (d, *J* = 7.5 Hz, 1 H), 7.68-7.66 (dd, J = 8.3, 2.4 Hz, 1 H), 7.46 (t, *J* = 8.0 Hz, 1 H), 7.22 (dd, *J* = 8.3, 2.6 Hz, 1 H), 7.13 (s, 1 H) , 3.91 (s, 3 H) , 1.38 (s, 18 H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 184.6, 182.4, 160.2, 152.1, 133.6, 131.7, 130.1, 123.2, 121.4, 113.3, 93.8, 55.7, 35.2, 31.4.HRMS: calc. for [M+Na$^+$] 437.2066, found: 437.2070.



Synthesis of compound **WB2**: 4'-tert-Butylacetophenone (1 g, 5.5 mmol) was added to a high-pressure tube in 10 mL anhydrous THF under N_2 atmosphere, then NaH (57-63% oil dispersion, 1 g, 24.0 mmol) and methyl m-anisate (930 mg, 5.5 mmol) were added to the mixture. The reaction mixture was allowed to stir for 24 h at 60 °C under N_2 atmosphere. Upon cooling to room temperature, 100 ml of water was added and the pH was adjusted to 3 with HCl (aq). After extracted with CH_2Cl_2 for three times, the combined organic phase was collected and dried over anhydrous Na_2SO_4. Followed by filtration and evaporation of the solvent, purified by column chromatography using CH_2Cl_2/petroleum ether (1:2, v/v) as eluent to afford 1.56 g of compound **WB2** as white solid (yield: 96%). ^{1}H NMR (400 MHz, Chloroform-d) δ 16.94 (s, 1 H), 7.93 (d, J = 8.7 Hz, 2 H), 7.58-7.52 (m, 2 H), 7.52-7.48 (m, 2 H), 7.38 (t, J = 7.9 Hz, 1 H), 7.08 (dd, J = 8.1, 2.3 Hz, 1 H), 6.83 (s, 1H) , 3.87 (s, 3 H) , 1.36 (s, 9 H). ^{13}C NMR (100 MHz, Chloroform-d) δ 185.6, 159.9, 156.4, 137.3, 132.8, 129.7, 127.2, 125.8, 119.7, 118.6, 112.1, 93.2, 55.5, 35.2, 31.2. HRMS: calc. for [M+H$^+$] 311.1641, found 311.1646.

Synthesis of compound **WBF2**: To a solution of compound **WB2** (1.56 g, 5.28 mmol) in 50 mL CH_2Cl_2 was added Et_3N (840 µL, 6.0 mmol) and BF_3/Et_2O (3.78 mL, 30 mmol). After stirring at room temperature for 1 h in the dark, 100 mL of water was added, the organic layer was collected, washed with saturated aqueous NH_4Cl and dried over anhydrous Na_2SO_4. Followed by filtration and evaporation of the solvent, purified by column chromatography using CH_2Cl_2/petroleum ether (1:2, v/v) as eluent to afford 1.80 g of **WBF2** as white solid (yield: 95%). ^{1}H NMR (600 MHz, Chloroform-d) δ 8.08 (d, J = 8.1 Hz, 2 H), 7.69 (d, J = 7.8 Hz, 1 H), 7.65 (d, J = 1.9 Hz, 1 H), 7.56 (d, J = 8.6 Hz, 2 H), 7.45 (d, J = 8.0 Hz, 1 H), 7.21 (dd, J = 8.3, 2.4 Hz, 1 H), 7.14 (s, 1 H), 3.90 (s, 3 H), 1.36 (s, 9 H). ^{13}C NMR (100 MHz, Chloroform-d) δ 183.1, 182.4, 160.2, 160.0, 133.5, 130.1, 129.1, 126.3, 121.7, 121.4, 113.0, 93.5, 55.7, 35.6, 31.0.HRMS: calc. for [M+NH_4^+] 376.1891, found: 376.1891.



Synthesis of compound **WBF3**: 4'-methylacetophenone (1 g, 7.5 mmol) was added to a high-pressure tube in 10 mL anhydrous THF under N_2 atmosphere, then NaH (57-63% oil dispersion, 1 g, 24.0 mmol) and methyl m-Anisate (1.25 g, 7.5 mmol) were added to the mixture. The reaction mixture was allowed to stir for 24 h at 60 °C under N_2 atmosphere. Upon cooling to room temperature, 100 ml of water was added and the pH was adjusted to 3 with HCl (aq). After extracted with CH_2Cl_2 for three times, the combined organic phase was dried over anhydrous Na_2SO_4, followed by filtration and evaporation of the solvent to afford **WB3** and used without further purification. 20 mL of CH_2Cl_2 was added to **WB3,** then Et_3N (1.6 mL, 12.0 mmol) and BF_3/Et_2O (3.78 mL, 30 mmol) was added. After stirring at room temperature for 1 h in the dark, 100 mL of water was added. The organic layer was collected, washed with saturated aqueous NH_4Cl and dried over anhydrous Na_2SO_4. Followed by filtration and evaporation of the solvent, purified by column chromatography using CH_2Cl_2/petroleum ether (1:2, v/v) as eluent to afford 1.65 g of **WBF3** as yellow solid (yield: 72%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 8.3 Hz, 2 H), 7.68 (d, *J* = 8.0 Hz, 1 H), 7.66-7.61 (m, 1 H), 7.44 (t, *J* = 8.0 Hz, 1 H), 7.35 (d, *J* = 8.2 Hz, 2 H), 7.21 (dd, *J* = 8.3, 2.2 Hz, 1 H), 7.13 (s, 1 H), 3.89 (s, 3 H), 2.47 (s, 3 H). ^{13}C NMR (100 MHz, Chloroform-d) δ 183.2, 182.5, 160.2, 147.1, 133.6, 130.1, 130.1, 129.3, 129.2, 121.7, 121.4, 113.1, 93.4, 55.8, 22.1. HRMS: calc. for [M+NH_4^+] 334.1420, found: 334.1420.

Supplementary Figures and Tables

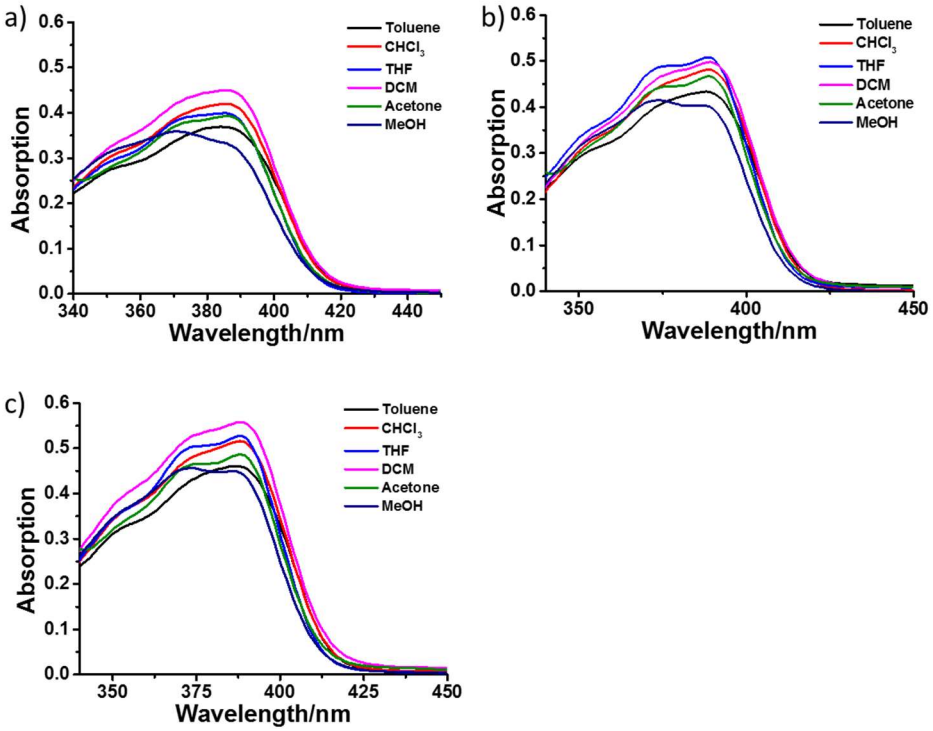


Fig. S1. a)-c) The absorption spectrum of complexes **WBF1-3** in different solvents, respectively.

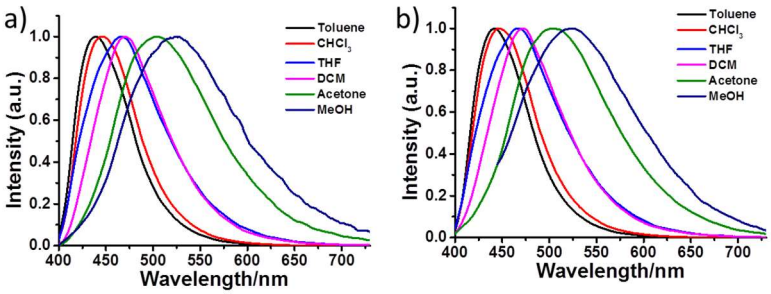


Fig. S2. a)-c) The fluorescence spectrum of complexes **WBF2-3** in different solvents, respectively.

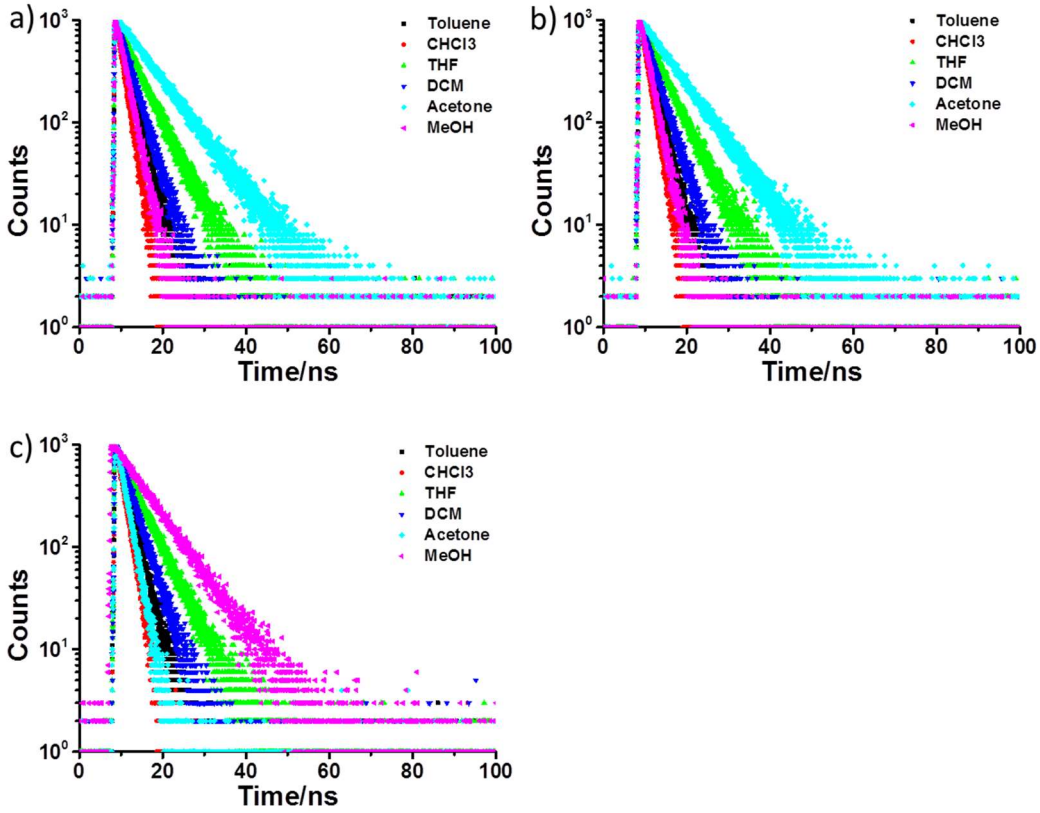


Fig. S3. a)-c) The time-resolved emission at the maximal emission wavelength of complexes **WBF1-3** in different solvents, respectively.

Table S1. The collected photophysical data of complexes **WBF1-3** in different solvents.

	Solvents	[a] λ_{abs} (nm)	[b] $\varepsilon*10^4$ ($cm^{-1}M^{-1}$)	[c] λ_{em} (nm)	[d] Φ_f	[e] τ_f/ns
WBF1	**Toluene**	388	3.71	440	0.34	2.55
	$CHCl_3$	389	4.26	445	0.21	1.70
	THF	388	4.05	465	0.11	4.91
	DCM	388	4.56	470	0.28	3.20
	Acetone	388	3.98	500	0.29	7.96
	CH_3OH	370	3.69	520	0.01	2.06
WBF2	**Toluene**	388	4.36	441	0.38	2.53
	$CHCl_3$	388	4.81	445	0.23	1.77
	THF	389	5.09	464	0.12	5.09
	DCM	388	4.99	472	0.28	3.32
	Acetone	387	4.66	502	0.09	7.74
	CH_3OH	373	4.18	521	0.01	2.07
WBF3	**Toluene**	388	4.61	440	0.37	2.52
	$CHCl_3$	388	5.16	446	0.24	1.83
	THF	387	5.27	465	0.11	4.99
	DCM	387	5.61	471	0.28	3.35
	Acetone	387	4.87	500	0.24	7.53
	CH_3OH	372	4.57	519	0.01	1.91

[a]Absorption maximum. [b]Extinction coefficients calculated at the absorption maxima. [c]Fluorescence emission maxima. [d]The absolute fluorescence quantum yields. [e]Fluorescence lifetime were measured with a 375 nm EPLEDs (picosecond pulsed LEDs) light source and monitored at the emission maximum. All fluorescence lifetimes are fitted with single-exponential decays unless indicated.

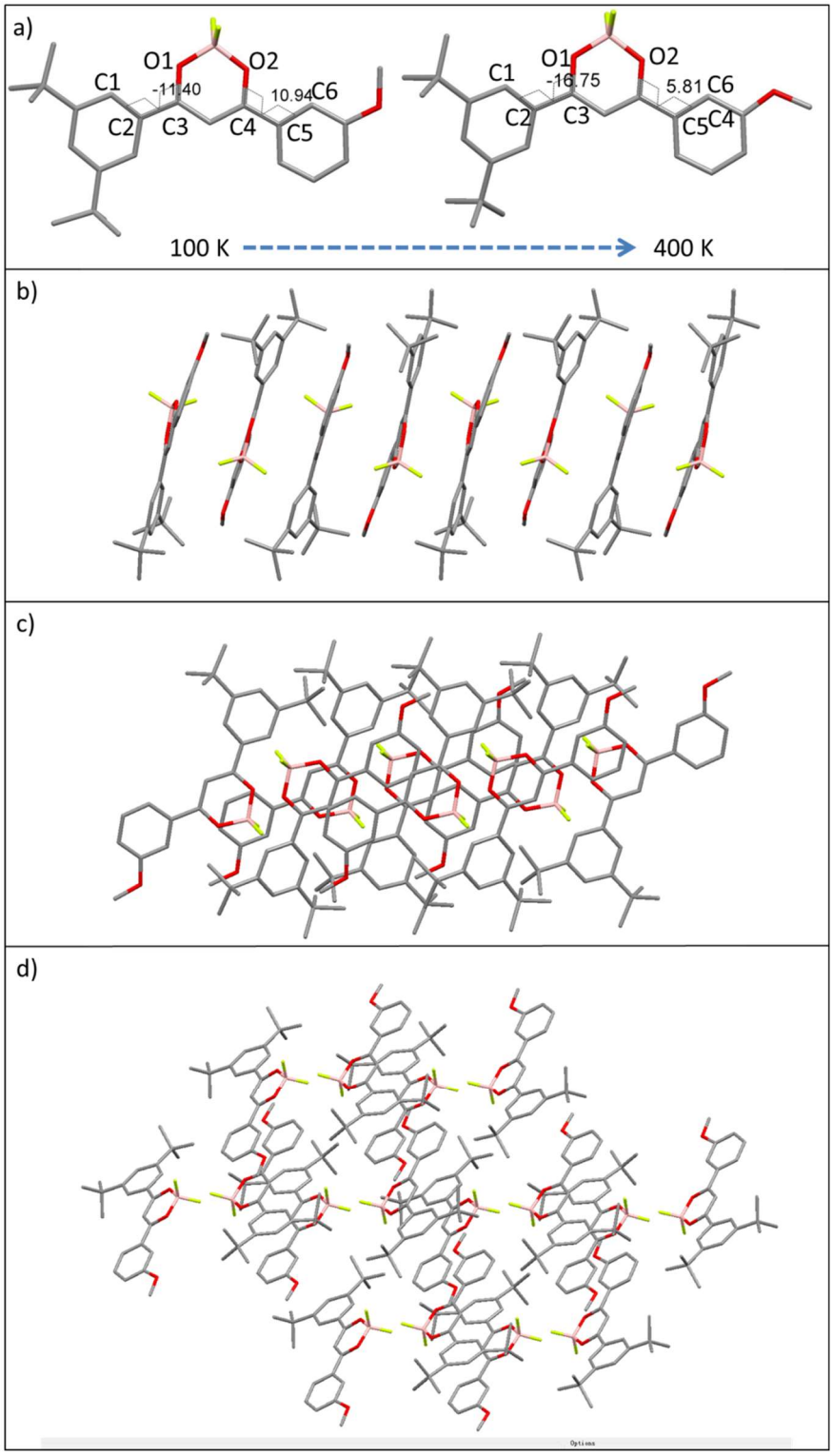


Fig. S4. a) The intramolecular torsion at different temperatures. Molecular stacking structures of complex **WBF1** along the b) a-axis, c) b-axis and d) c-axis directions, hydrogen atoms are omitted for clarity.

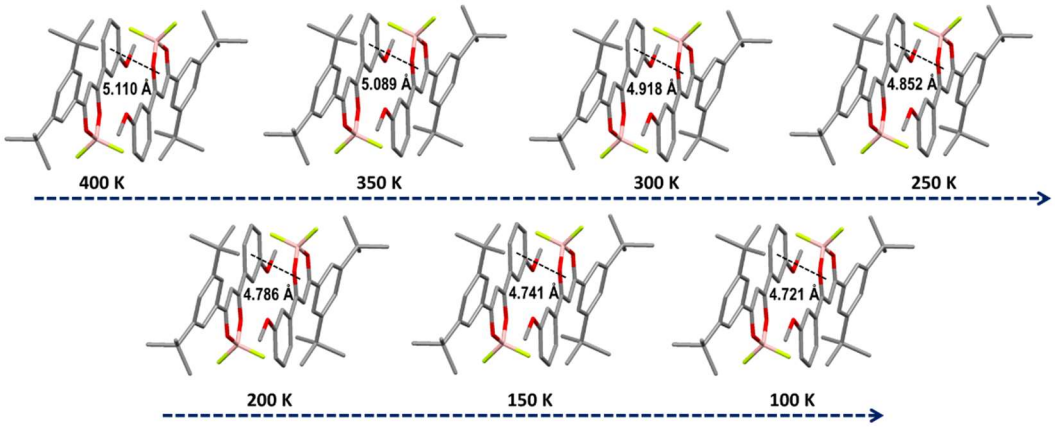


Fig. S5. Single-crystal structure of **WBF1**: Temperature-dependent partial packing modes, hydrogen atoms are omitted for clarity.

Table S2. Collected single crystal data of **WBF1** at different temperature.

CCDC number	1943072	1943071	1943070	1943069
Temperature	400 K	350 K	300 K	250 K
Empirical formula	$C_{24}H_{29}BF_2O_3$	$C_{24}H_{29}BF_2O_3$	$C_{24}H_{29}BF_2O_3$	$C_{24}H_{29}BF_2O_3$
Formula weight	414.28	414.28	414.28	414.28
Color of crystal	Green	green	green	yellow
Crystal system	triclinic	triclinic	triclinic	triclinic
Unit cell dimensions	a = 8.5049(7) Å b = 9.9575(9) Å c=15.6872(12) Å α= 74.405(7)° β= 86.917(7)° γ= 66.543(8)°	a = 8.4132(7) Å b = 9.9177(8) Å c= 15.6851(11) Å α= 74.475(7)° β= 86.897(6)° γ= 66.845(8)°	a = 10.1611(6) Å b= 15.2065(9) Å c = 16.1543(9) Å α= 70.258(5)° β= 78.911(5)° γ=79.039(5)°	a = 10.1447(6) Å b= 15.1024(8) Å c = 16.1256(8) Å α= 70.107(5)° β= 78.921(4)° γ=78.570(5)°
Volume ($Å^3$)	1171.72(19)	1157.49(17)	1142.10(2)	1128.05(2)
Z	2	2	4	4
ρ_{calc} g/cm^3	1.174	1.189	1.205	1.220

CCDC number	1943068	1943067	1943066
Temperature	200 K	150 K	100 K
Empirical formula	$C_{24}H_{29}BF_2O_3$	$C_{24}H_{29}BF_2O_3$	$C_{24}H_{29}BF_2O_3$
Formula weight	414.28	414.28	414.28
Color of crystal	yellow	orange	orange
Crystal system	triclinic	triclinic	triclinic
Unit cell dimensions	a = 10.1293(6) Å b = 14.9169(7) Å c = 16.0997(7) Å α= 70.326(4)° β= 79.384(4) ° γ= 77.847(4)°	a = 10.1217(5) Å b = 14.7660(7) Å c = 16.0705(7) Å α= 70.555(4)° β= 79.713(4) ° γ= 77.319(4)°	a = 10.1095(5) Å b= 14.6951(6) Å c = 16.0516(6) Å α= 70.598(4)° β= 79.739(4)° γ= 77.184(4)°
Volume ($Å^3$)	1111.10(2)	1097.52(19)	1089.49(17)
Z	4	4	4
ρ_{calc} g/cm^3	1.238	1.254	1.263

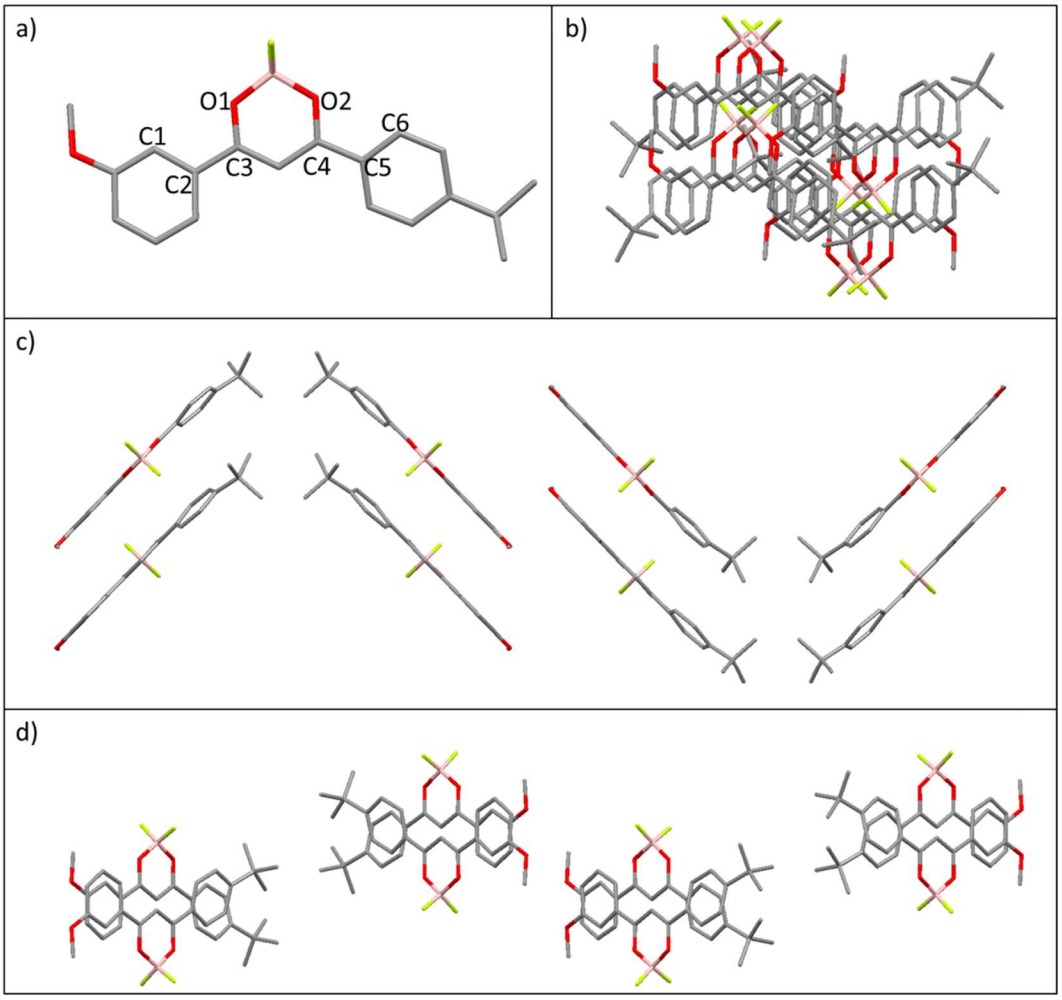


Fig. S6. a) The intramolecular torsion at different temperatures. Molecular stacking structures of complex **WBF2** along the b) a-axis, c) b-axis and d) c-axis directions, hydrogen atoms are omitted for clarity.

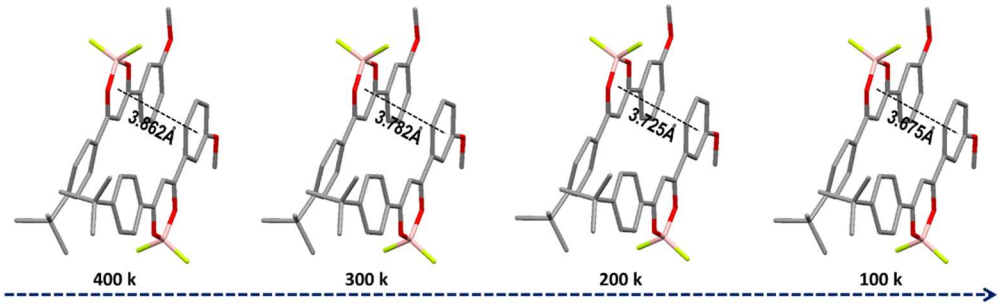


Fig. S7. Single-crystal structure of **WBF2**: Temperature-dependent partial packing modes, hydrogen atoms are omitted for clarity.

Table S3. The intermolecular distance and the molecular torsion of **WBF2** at different temperature.

Temperature	400 K	300 K	200 K	100 K
d(intermolecular) /Å	3.862	3.782	3.725	3.675
Torsion (C1-C2-C3-O1)/°	0.88	2.20	1.87	1.46
Torsion (O2-C4-C5-C6)/°	7.49	6.90	7.00	7.27

Table S4. Collected single crystal data of **WBF2** at different temperature.

CCDC number	**1977233**	**1977234**	**1977249**	**1977245**
Temperature	**400 K**	**300 K**	**200 K**	**100 K**
Empirical formula	$C_{20}H_{21}BF_2O_3$	$C_{20}H_{21}BF_2O_3$	$C_{20}H_{21}BF_2O_3$	$C_{20}H_{21}BF_2O_3$
Formula weight	**358.18**	**358.18**	**358.18**	**358.18**
Color of crystal	**yellow**	**yellow**	**yellow**	**yellow**
Crystal system	**orthorhombic**	**orthorhombic**	**orthorhombic**	**orthorhombic**
Unit cell dimensions	**a = 7.1936(15) Å b = 10.205(3) Å c=50.76 (4) Å α= 90° β= 90° γ= 90°**	**a = 7.2099(10) Å b = 10.1738(9) Å c= 49.415(6) Å α= 90° β= 90° γ= 90°**	**a = 7.1750(2) Å b= 10.0917(3) Å c = 49.0041(13) Å α= 90° β= 90° γ= 90°**	**a = 7.1609(2) Å b= 10.0337(3) Å c = 48.7164(15) Å α= 90° β= 90° γ= 90°**
Volume ($Å^3$)	**3727(3)**	**3624.7(7)**	**3548.29(17)**	**3500.29(18)**
Z	**8**	**8**	**8**	**8**
ρ_{calc} g/cm^3	**1.277**	**1.313**	**1.341**	**1.359**

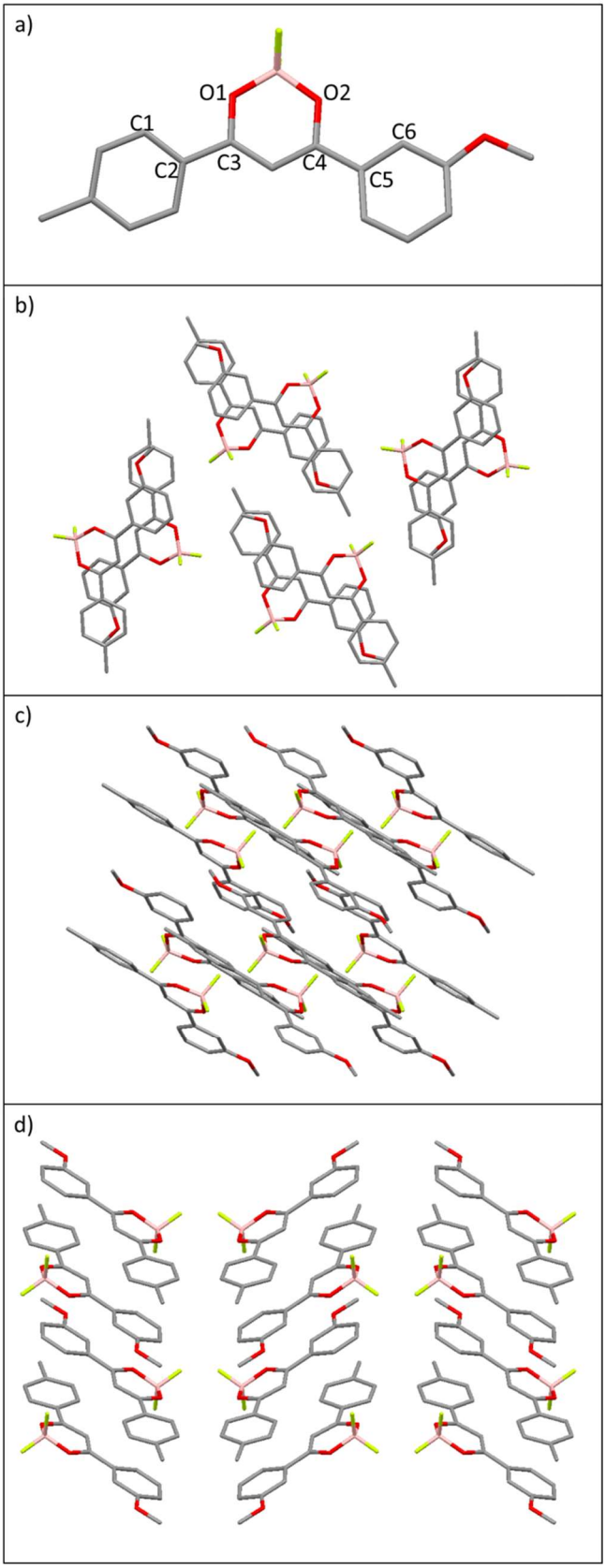


Fig. S8. a) The intramolecular torsion at different temperatures. Molecular stacking structures of complex **WBF3** along the b) a-axis, c) b-axis and d) c-axis directions, hydrogen atoms are omitted for clarity.

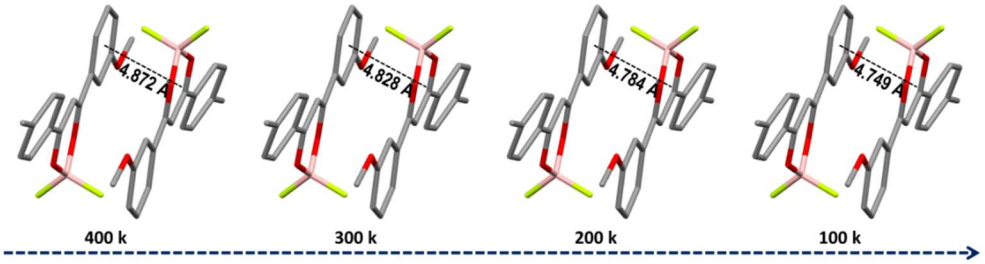


Fig. S9. Single-crystal structure of **WBF3**: Temperature-dependent partial packing modes, hydrogen atoms are omitted for clarity.

Table S5. The intermolecular distance and the molecular torsion of **WBF3** at different temperature.

Temperature	**400 K**	**300 K**	**200 K**	**100 KV**
d(intermolecular) /Å	**4.872**	**4.828**	**4.784**	**4.749**
Torsion (C1-C2-C3-O1)/°	**13.31**	**12.21**	**10.82**	**9.52**
Torsion (O2-C4-C5-C6)/°	**3.75**	**4.67**	**5.20**	**6.26**

Table S6. Collected single crystal data of **WBF3** at different temperature.

CCDC number	**1977246**	**1977247**	**1977250**	**1977251**
Temperature	**400 K**	**300 K**	**200 K**	**100 K**
Empirical formula	$C_{17}H_{15}BF_2O_3$	$C_{17}H_{15}BF_2O_3$	$C_{17}H_{15}BF_2O_3$	$C_{17}H_{15}BF_2O_3$
Formula weight	**316.10**	**316.10**	**316.10**	**316.10**
Color of crystal	**yellow**	**yellow**	**yellow**	**yellow**
Crystal system	**monoclinic**	**monoclinic**	**monoclinic**	**monoclinic**
Unit cell dimensions	**a = 7.9445(7) Å b = 19.2382(16) Å c=10.3606 (11) Å α= 90° β= 104.183(10)° γ= 90°**	**a = 7.8494(4) Å b = 19.1910(10) Å c= 10.3146(5) Å α= 90° β= 103.760(5)° γ= 90°**	**a = 7.7481(4) Å b= 19.1442(7) Å c = 10.2334(4) Å α= 90° β= 103.133(4)° γ=90°**	**a = 7.6754(4) Å b= 19.1327(9) Å c = 10.1490(5) Å α= 90° β= 102.782(5)° γ=90°**
Volume ($Å^3$)	**1535.2(3)**	**1509.18(14)**	**1478.23(11)**	**1453.46(13)**
Z	**4**	**4**	**4**	**4**
ρ_{calc} g/cm^3	**1.368**	**1.391**	**1.420**	**1.445**

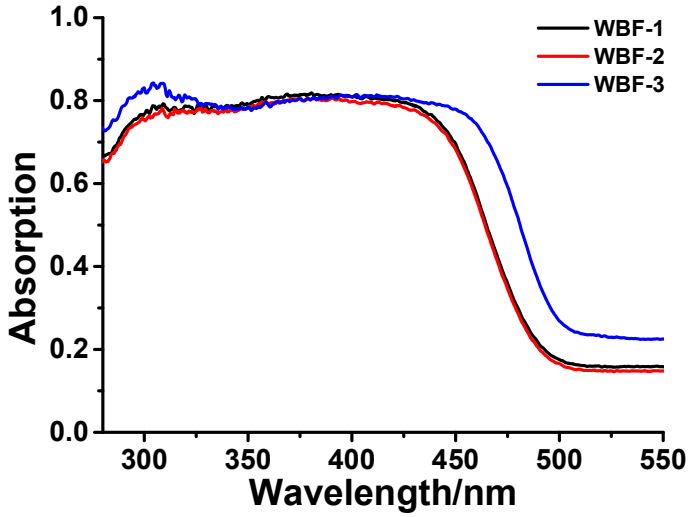


Fig. S10. The diffuse reflection absorption spectrum of complex **WBF1-3** crystals.

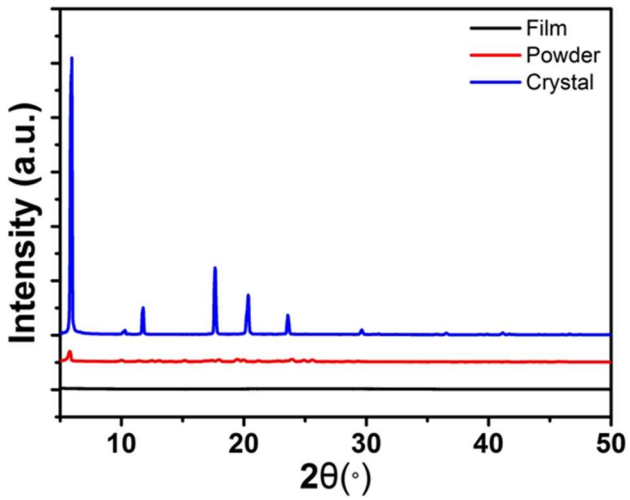


Fig. S11. Powder X-Ray diffraction spectrum of **WBF1**.

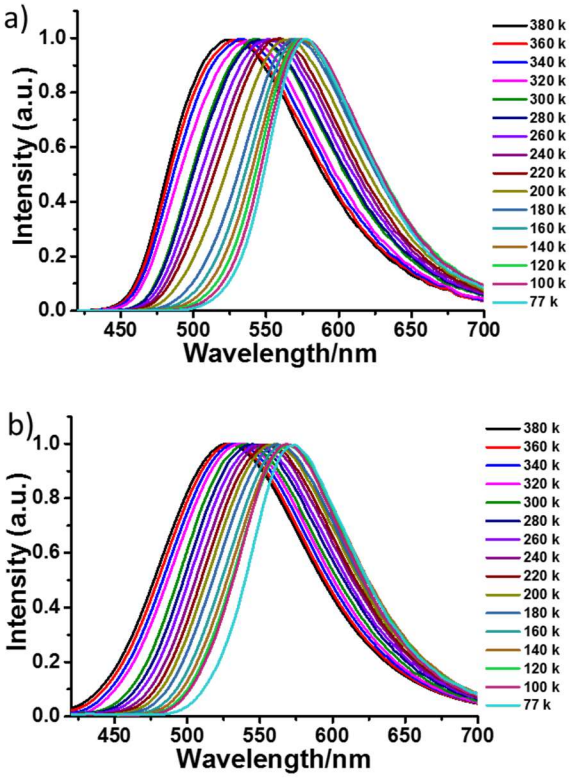


Fig. S12. The temperature-dependent emission spectra of **WBF1** a) powder and b) film samples.

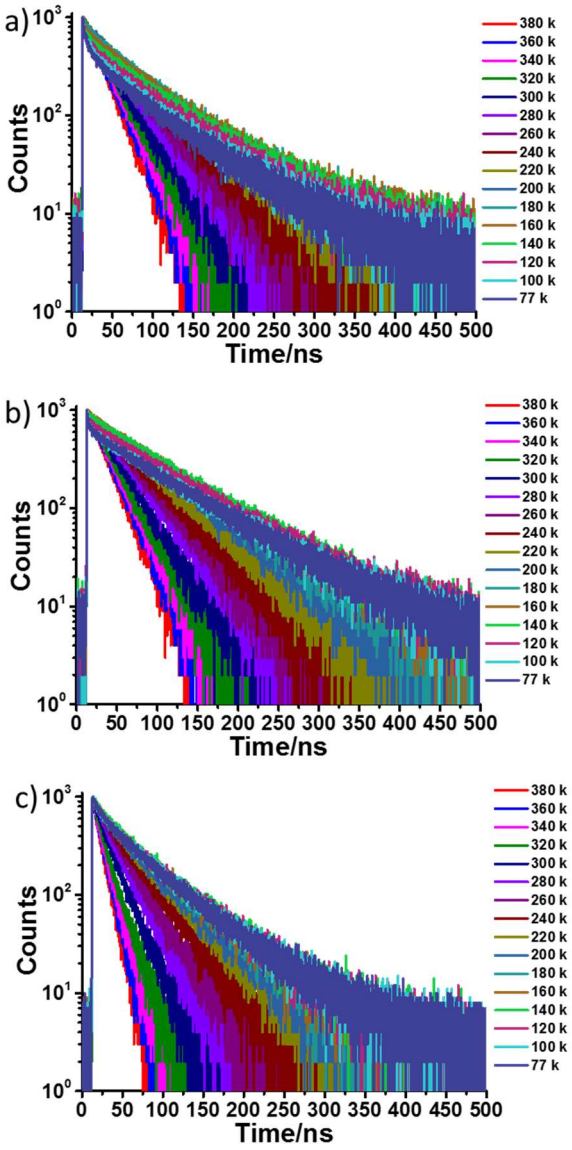


Fig. S13. Temperature-dependent time-resolved emission at the maximal emission wavelength of **WBF1** a) crystals, b) powder and c) film samples.

Table S7: The fluorescence lifetime of **WBF1** crystals, powder and film samples at different temperature.

Temperature/K	Crystals Lifetime/ns	Powder Lifetime/ns	Film Lifetime/ns
380	21.49	21.48	10.71
360	23.21	23.21	11.57
340	25.07	25.05	13.03
320	27.53	27.52	15.44
300	31.78	32.04	20.21
280	36.57	39.81	25.71
260	41.94	43.92	30.38
240	47.36	49.48	37.02
220	51.66	58.23	45.66
200	57.39	67.02	50.75
180	τ_1/ns 7.48, 10.3% τ_2/ns 72.19, 89.7% $\tau_{average}$/ns 65.52	74.34	τ_1/ns 18.15, 12.2% τ_2/ns 62.26, 87.8% $\tau_{average}$/ns 56.88
160	τ_1/ns 16.18, 6.2% τ_2/ns 72.12, 93.8% $\tau_{average}$/ns 68.65	79.77	τ_1/ns 19.03, 13.4% τ_2/ns 66.23, 86.6% $\tau_{average}$/ns 59.91
140	τ_1/ns 17.55, 8.2% τ_2/ns 77.48, 91.8% $\tau_{average}$/ns 72.56	83.81	τ_1/ns 22.28, 16.5% τ_2/ns 69.12, 83.5% $\tau_{average}$/ns 61.39
120	τ_1/ns 15.09, 7.1% τ_2/ns 77.88, 92.9% $\tau_{average}$/ns 73.42	84.17	τ_1/ns 20.15, 13.4% τ_2/ns 67.48, 86.6% $\tau_{average}$/ns 61.14
100	τ_1/ns 8.96, 6.9% τ_2/ns 75.51, 93.1% $\tau_{average}$/ns 70.92	τ_1/ns 3.46, 2.1% τ_2/ns 87.22, 97.9% $\tau_{average}$/ns 85.46	τ_1/ns 20.31, 14.7% τ_2/ns 67.92, 85.3% $\tau_{average}$/ns 60.92
77	τ_1/ns 7.73, 9.0% τ_2/ns 72.75, 91.0% $\tau_{average}$/ns 66.89	τ_1/ns 3.26, 1.9% τ_2/ns 87.38, 98.1% $\tau_{average}$/ns 85.78	τ_1/ns 18.59, 14.2% τ_2/ns 67.06, 85.8% $\tau_{average}$/ns 60.18

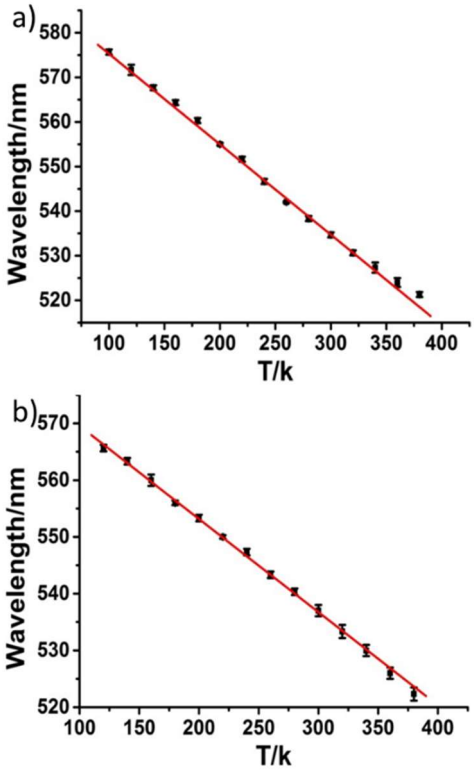


Fig. S14. The linear relationship between the maximal emission wavelength and temperature of **WBF1** a) powder and b) film samples.

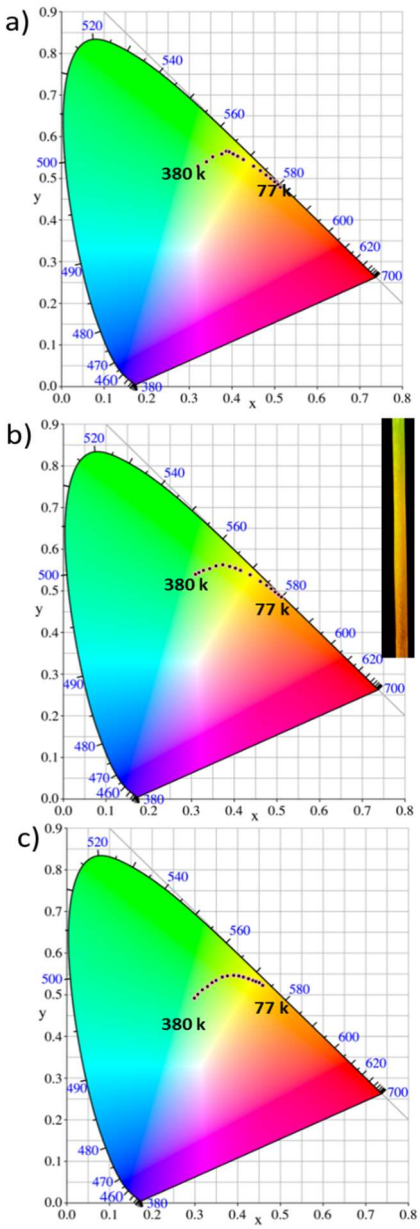


Fig. S15. The CIE chromaticity diagram showing the temperature dependence of the (x,y) color coordinates of **WBF1** a) crystals, b) powder (inset: The photographs of gradient fluorescence of **WBF1** film in a quartz tube) and c) film samples, respectively.

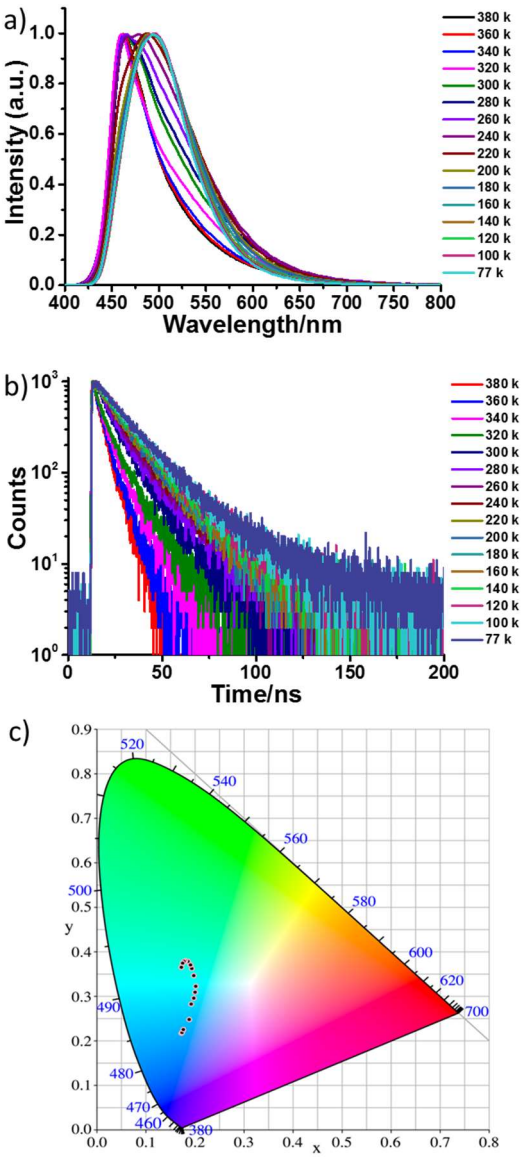


Fig. S16. Temperature-dependent a) emission spectrum and b) time-resolved emission at the maximal emission wavelength. c) CIE chromaticity diagram showing the temperature dependence of the (x,y) color coordinates of **WBF2** crystals.

Table S8: The fluorescence lifetime of **WBF2** crystals at different temperature**.**

Temperature/K	Lifetime/ns
380	5.51
360	6.29
340	7.97
320	9.93
300	12.41
280	15.15
260	16.63
240	τ_1/ns 13.59, 75.2% τ_2/ns 31.24, 24.8 % $\tau_{average}$/ns 17.97
220	τ_1/ns 14.26, 75.8% τ_2/ns 30.22, 24.2 % $\tau_{average}$/ns 18.12
200	τ_1/ns 13.58, 63.7% τ_2/ns 26.26, 36.3 % $\tau_{average}$/ns 18.18
180	τ_1/ns 13.17, 74.7% τ_2/ns 33.11, 25.3 % $\tau_{average}$/ns 18.21
160	τ_1/ns 11.56, 67.9% τ_2/ns 32.51, 32.1 % $\tau_{average}$/ns 18.28
140	τ_1/ns 14.43, 72.1% τ_2/ns 31.70, 27.9 % $\tau_{average}$/ns 19.25
120	τ_1/ns 15.34, 75.2% τ_2/ns 35.55, 23.4 % $\tau_{average}$/ns 20.07
100	τ_1/ns 15.79, 75.7% τ_2/ns 35.91, 24.3 % $\tau_{average}$/ns 20.68
77	τ_1/ns 16.10, 75.5% τ_2/ns 36.52, 24.5% $\tau_{average}$/ns 21.10

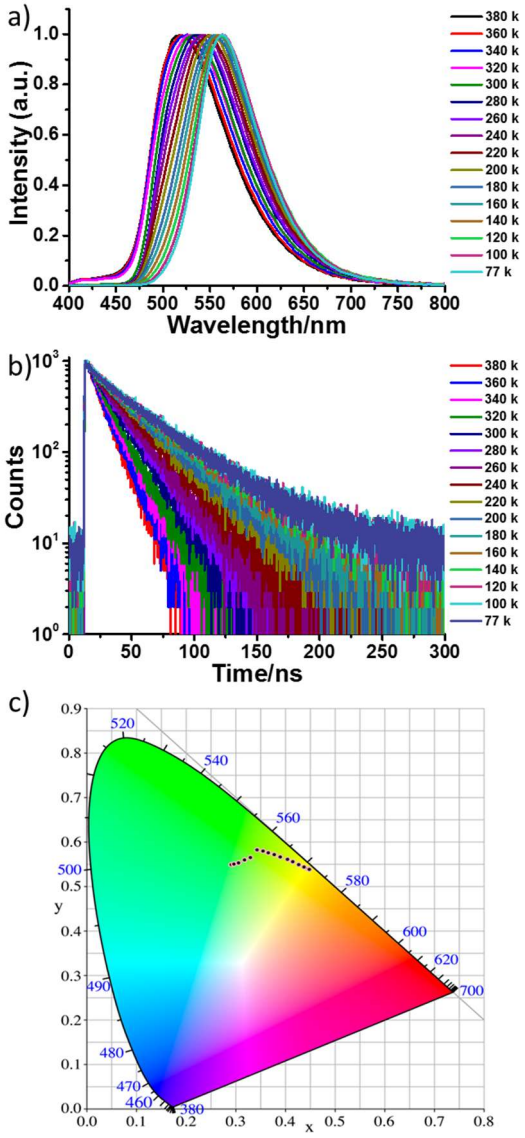


Fig. S17: Temperature-dependent a) emission spectrum and b) time-resolved emission at the maximal emission wavelength. c) CIE chromaticity diagram showing the temperature dependence of the (x,y) color coordinates of **WBF3** crystals.

Table S9: The fluorescence lifetime of **WBF3** crystals at different temperature.

Temperature/K	Lifetime/ns
380	**12.55**
360	**13.28**
340	**14.87**
320	**16.28**
300	**19.99**
280	**21.81**
260	**23.95**
240	**27.36**
220	**τ_1/ns 16.76, 15.9%** **τ_2/ns 34.11, 84.1%** **$\tau_{average}$/ns 31.35**
200	**τ_1/ns 12.59, 7.1%** **τ_2/ns 35.68, 92.9%** **$\tau_{average}$/ns 34.04**
180	**τ_1/ns 15.02, 9.9%** **τ_2/ns 40.05, 90.1%** **$\tau_{average}$/ns 37.57**
160	**τ_1/ns 17.24, 13.7%** **τ_2/ns 44.26, 86.3%** **$\tau_{average}$/ns 40.55**
140	**τ_1/ns 19.47, 15.9%** **τ_2/ns 47.01, 84.1%** **$\tau_{average}$/ns 42.63**
120	**τ_1/ns 18.45, 14.9%** **τ_2/ns 47.13, 85.1%** **$\tau_{average}$/ns 42.85**
100	**τ_1/ns 15.77, 11.1%** **τ_2/ns 46.75, 88.9%** **$\tau_{average}$/ns 43.31**
77	**τ_1/ns 17.26, 12.7%** **τ_2/ns 46.76, 87.3%** **$\tau_{average}$/ns 43.01**

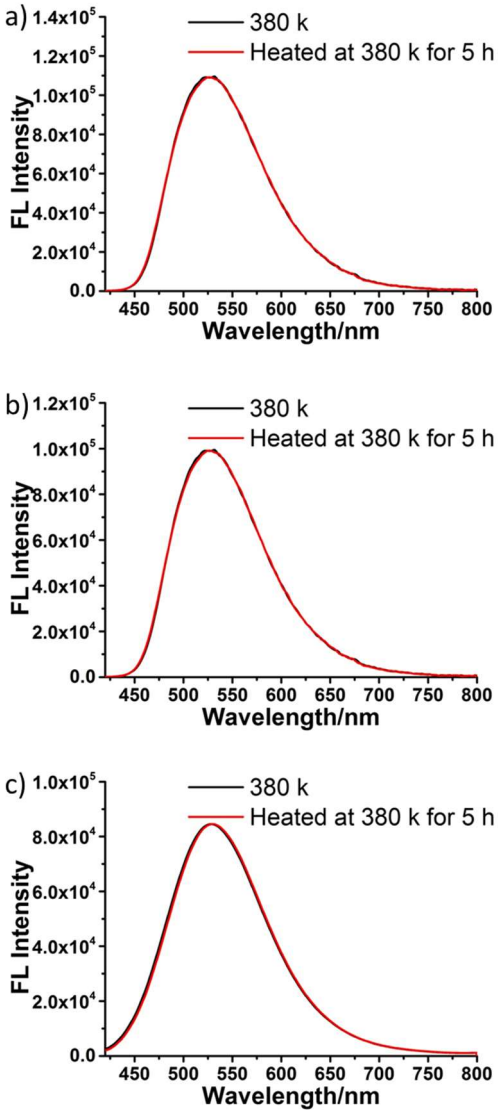


Fig. S18. a) The emission spectra measured at 380 K before and after 5 hours heating of the a) crystal, b) powder and c) film samples of **WBF1**.

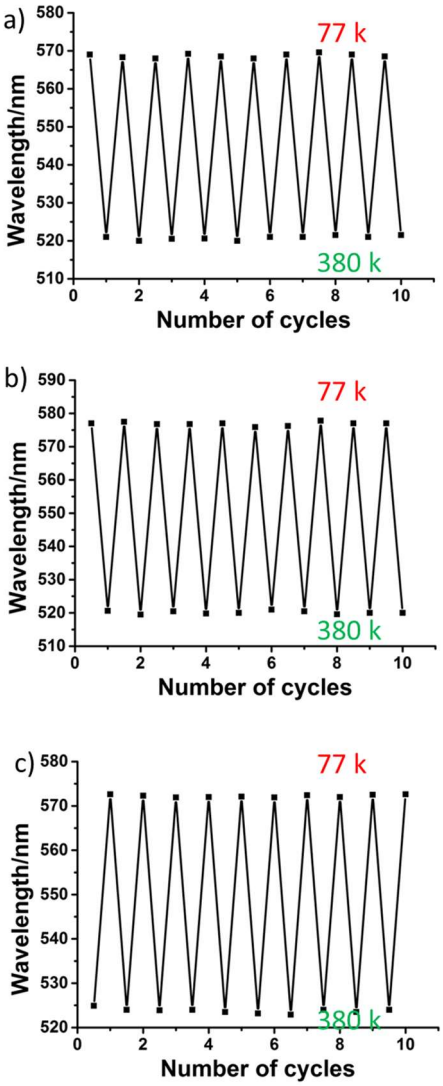


Fig. S19. The wavelength of maximum emission peak measured at 77 K and 380 K of a) crystal b) powder and c) film samples of **WBF1**.

HRMS

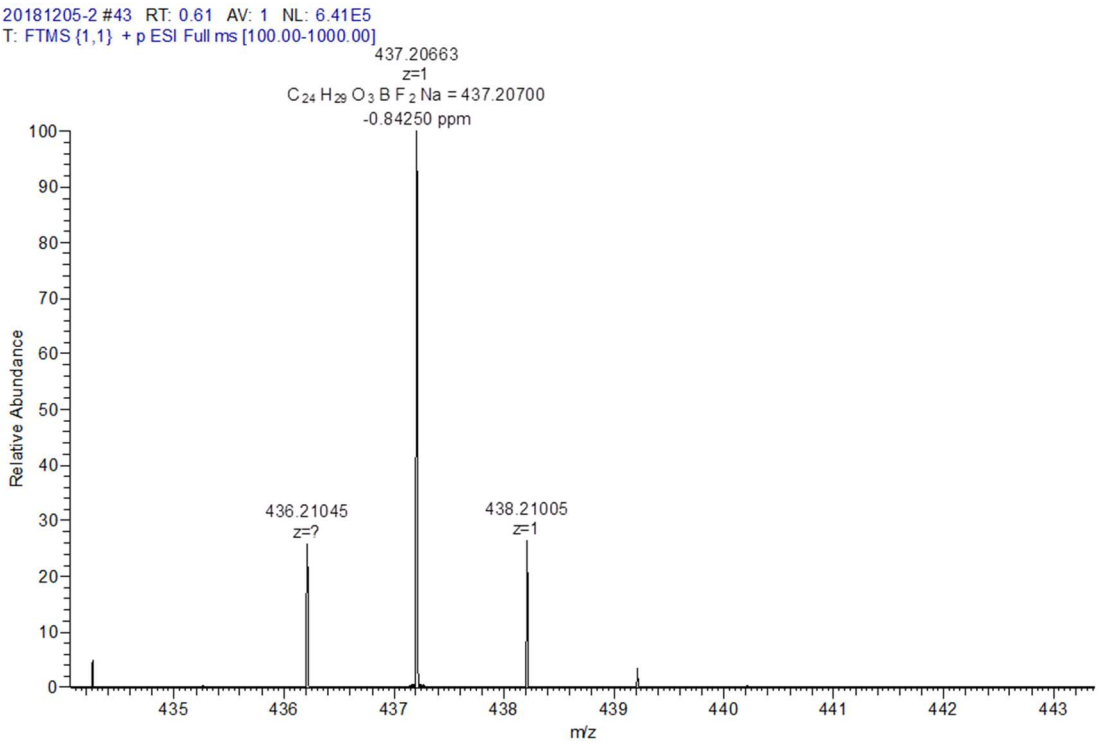


Fig. S20. High-resolution mass spectrum of **WBF1**.

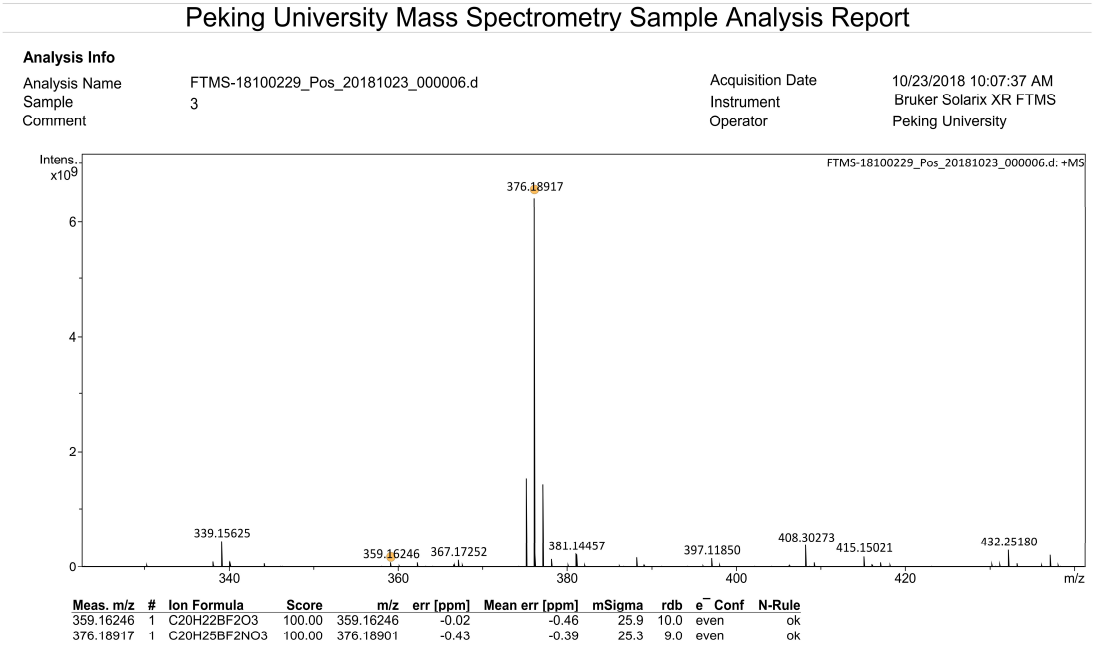


Fig. S21. High-resolution mass spectrum of **WBF2.**

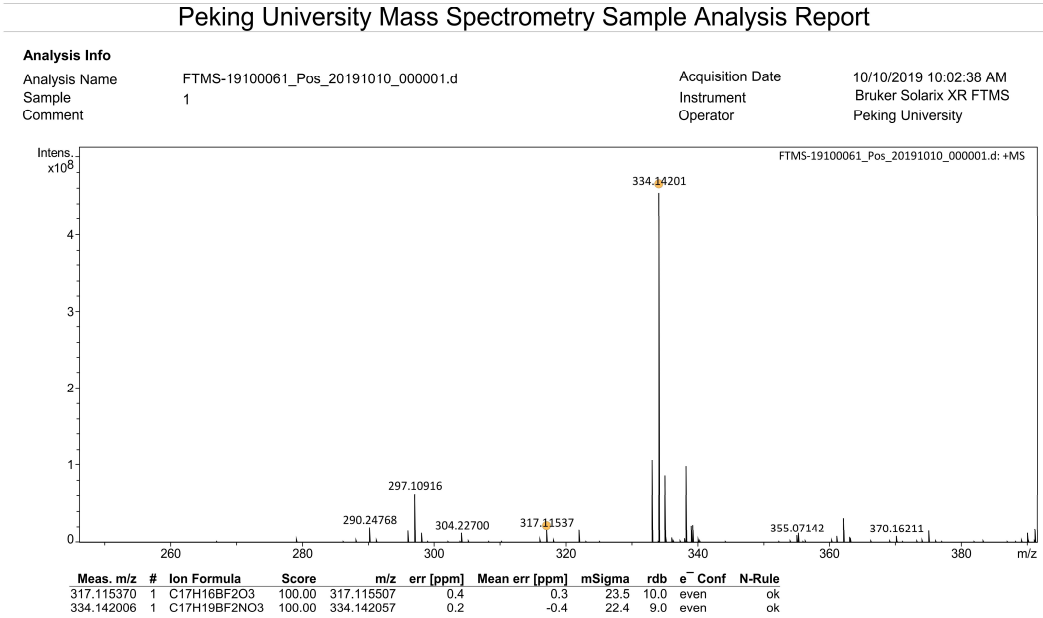


Fig. S22. High-resolution mass spectrum of **WBF3.**

NMR Spectra

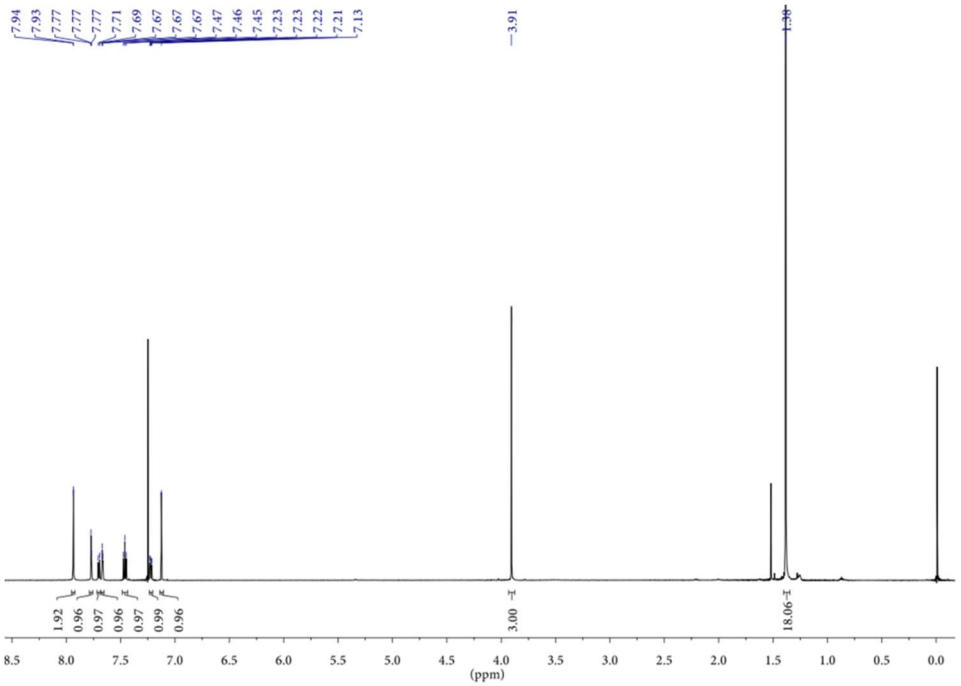


Fig. S23. ^{1}H NMR spectrum of **WBF1** in $CDCl_3$ (500µL).

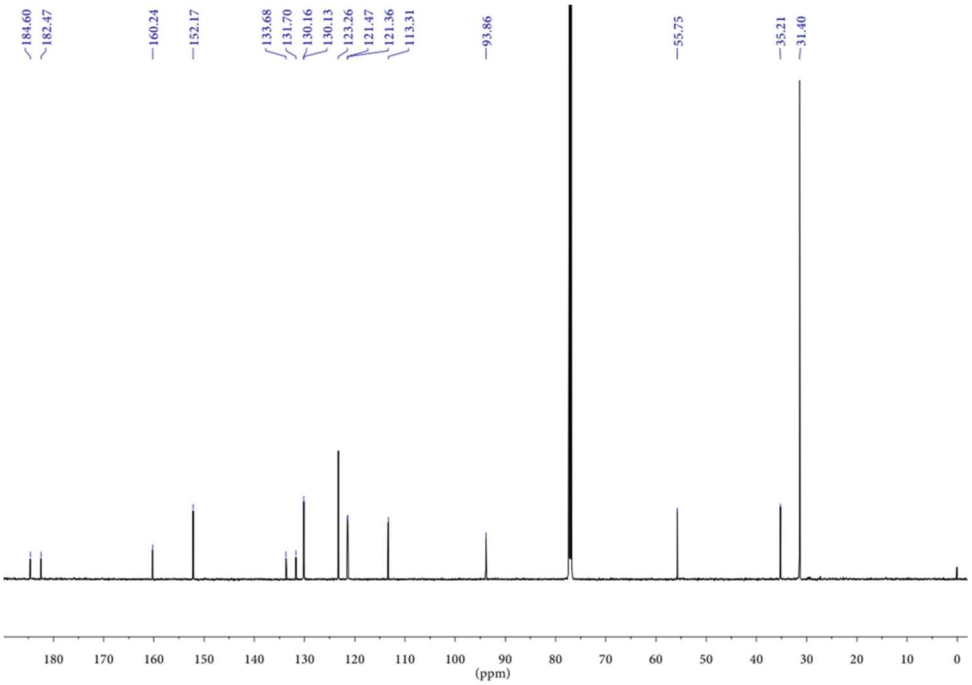


Fig. S24. ^{13}C NMR spectrum of **WBF1** in $CDCl_3$ (500µL).

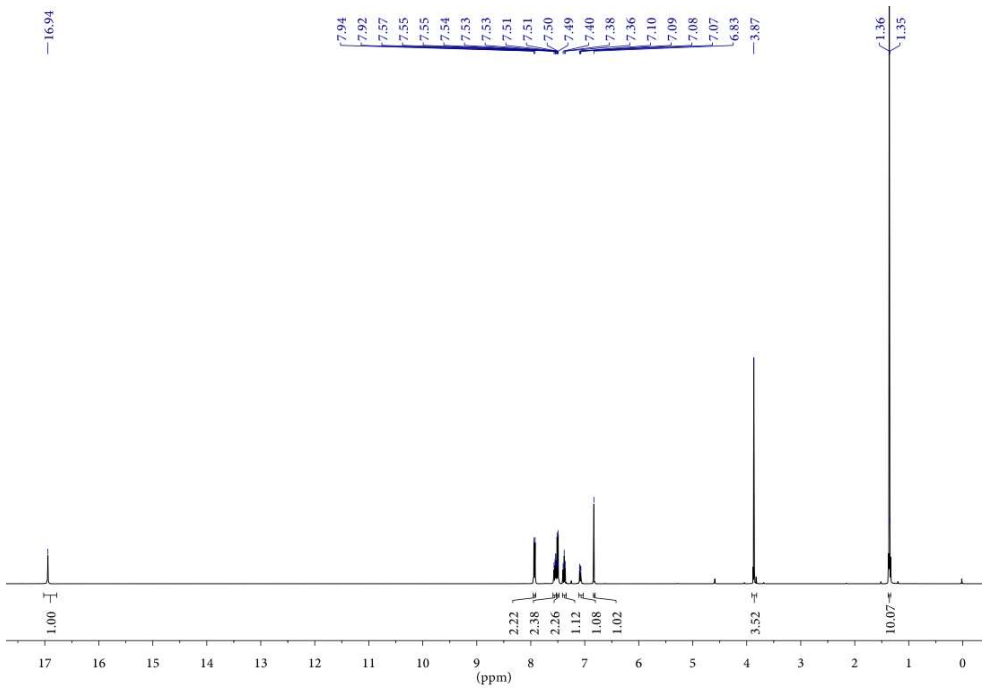


Fig. S25. ^{1}H NMR spectrum of **WBF2** in $CDCl_3$ (500µL).

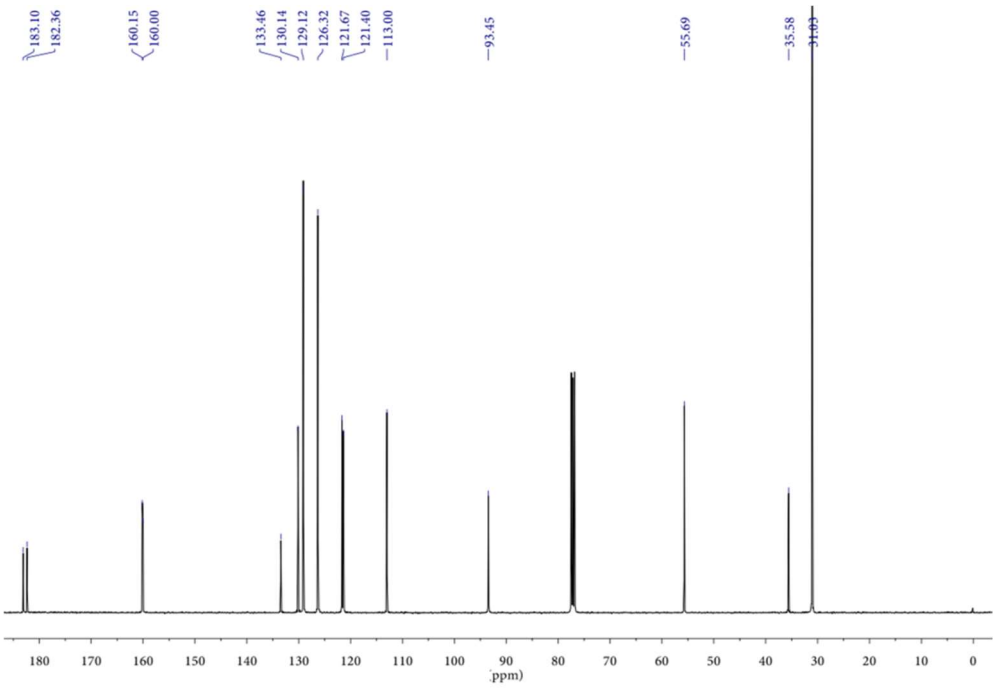


Fig. S26. ^{13}C NMR spectrum of **WBF2** in $CDCl_3$ (500µL).

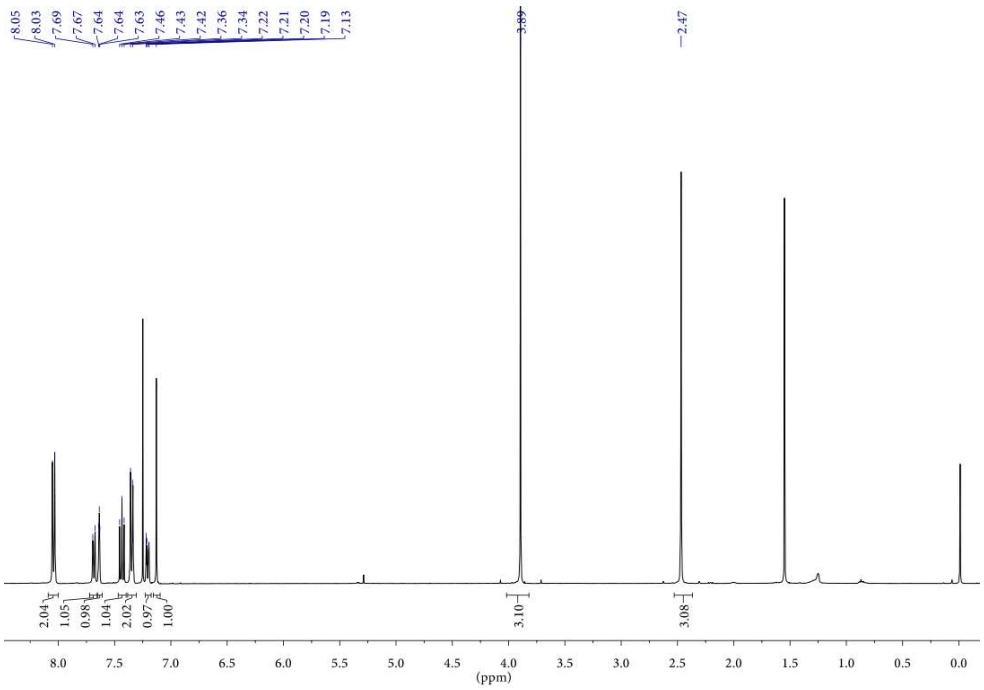


Fig. S27. ^{1}H NMR spectrum of **WBF3** in CDCl3 (500µL).

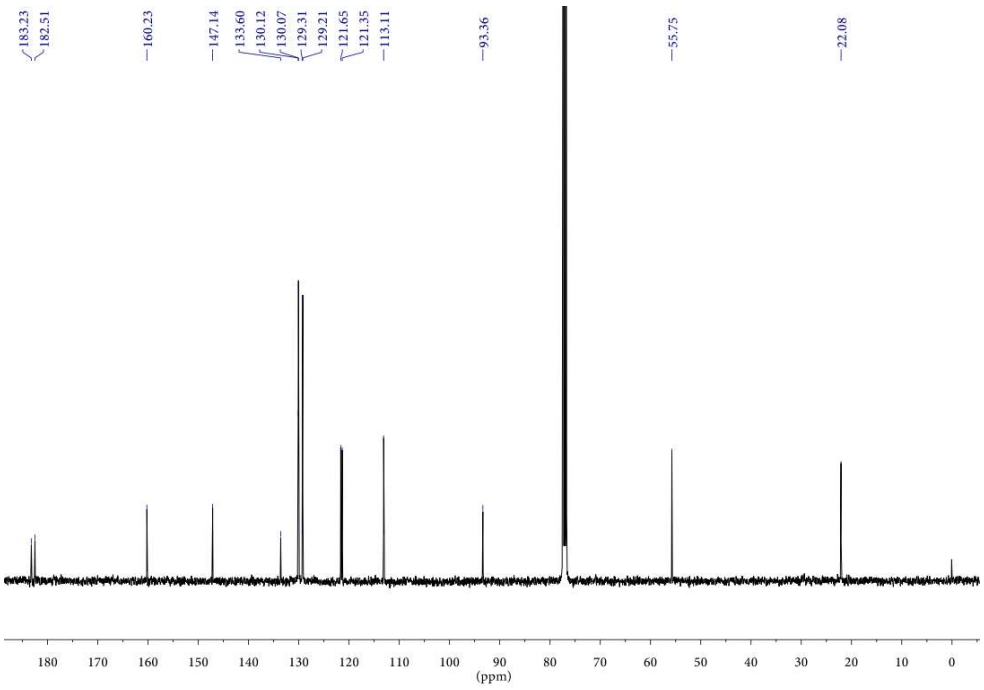


Fig. S28. ^{13}C NMR spectrum of **WBF3** in $CDCl_3$ (500µL).

References

1. J. X. Wang, L. Y. Niu, P. Z. Chen, Y. Z. Chen, Q. Z. Yang and R. Boulatov, *Chem. Commun.*, 2019, **55**, 7017-7020.
2. P. Z. Chen, H. Zhang, L. Y. Niu, Y. Zhang, Y. Z. Chen, H. B. Fu and Q. Z. Yang, *Adv. Funct. Mater.*, 2017, **27**, 1700332.