SUPPORTING INFORMATION

A General Design Strategy for Aromatic Ketone-Based Single-Component Dual-Emissive Materials

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Part I. Materials, methods, and synthesis

Materials. Dichloromethane was dried over calcium hydride for ~ 3 h before use. Sodium hydride (95%), boron trichloride solution (1.0 M in methylene chloride) and boron trifluoride diethyl etherate (purified by redistillation) were purchased from Sigma-Aldrich and all other reagents and solvents were obtained from Aladdin Reagent (Shanghai) and were used as received.

Methods. ^{1}H NMR (300 MHz) spectra were recorded on a Bruker AV300 NMR spectrometer operated in the Fourier transform mode. ^{1}H NMR (400 MHz) spectra were recorded on a Bruker AV400 NMR spectrometer operated in the Fourier transform mode. ^{1}H NMR spectra were referenced to the signal for residual protio chloroform at 7.26 ppm and coupling constants are given in hertz. HRMS (ESI) spectra were recorded on a LTQ ORBITRAP XL mass spectrometer (Thermo Scientific, USA). HRMS (MALDI-TOF MS) spectrum was recorded on an Autoflex Speed MALDI-TOF MS (Bruker Daltonics, Germany). HRMS (EI) spectrum was recorded on a GCT EI-mass spectrometer (Micromass, Britain) with ionizing voltage of 70 eV. HRMS (APCI) spectra were recorded on an Obitrap mass spectrometer (Thermo Scientific, USA). Elemental analysis for C and H was performed by a vario EL cube elemental analyzer. The temperatures of the combustion tube and the reduction tube were 950□ and 550 □, respectively. UV-Vis absorption spectra were recorded on a Beijing Persee TU-1901 UV-Vis spectrometer. Photographs were taken by a Cannon 500D digital camera. Micrograph of $Gd(dbm)_3{\cdot}H_2O$ was taken on an Olympus DP72 color camera mounted on a BX51 microscope. Fluorescence quantum yield, Φ_F, for MB**1** in water was measured vs. quinine sulfate in H_2SO_4 (aq, 0.1M) as a standard, using the following values: Φ_F quinine sulfate = 0.54, n_D^{20} H_2O = 1.333. Steady-state fluorescence spectra and phosphorescence spectra were recorded on an F-4600 Fluorescence Spectrofluorometer (quantum yield measurements were recorded on a Horiba Fluorolog-3 Spectrofluorometer). Fluorescence lifetime data were acquired with a 1MHz LED laser with the excitation peak at 369 nm (NanoLED-370). Lifetime data were analyzed with DataStation v6.6 (Horiba Scientific). Single crystal data of BF_2EMO were acquired with a Gemini S Ultra Single Crystal Diffractometer. The crystal was kept at 291 K during data collection. Using Olex2, the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimisation. Calculations were performed using the Gaussian 09 suite of programs[1] employing density functional theory and B3LYP/6-31G for geometry optimization.

Preparation of monoketone-BCl_3 complexes 1a-1c in CH_2Cl_2. Monoketones were dissolved in CH_2Cl_2 for UV-vis absorption spectra measurements. Absorbance of each monoketone solution was kept between 0.2 ~ 0.8. Then 50 μL of boron trichloride solution (1.0 M in CH_2Cl_2) was added to the above monoketone solutions and the

resulted mixtures were used for UV-vis absorption, fluorescence emission, and fluorescence excitation spectra measurements.

MB1. Diethylamine hydrochloride (1.31 g, 12.0 mmol), 1-(6-methoxynaphthalen-2-yl) ethanone (3.00 g, 15.0 mmol), paraformaldehyde (0.40 g) and ethonal (4 ml) were introduced to a round-bottom flask successively and three drops of concentrated hydrochloric acid (36% ~ 38%) were added to the flask subsequently under stirring. The flask was then immersed in an oil bath set at 120 °C for refluxing for ~ 10 h. Ethyl acetate (20ml) was added dropwise to the flask under stirring and then the flask was cooled to room temperature gradually and stood overnight at room temperature. The crystals thus formed were filtered out, washed with ethyl acetate and dried *in vacuo* (4.25 g, 88%). ^{1}H NMR (300 MHz, $CDCl_3$, δ) 8.57 (s, 1H, 2-Ar*H*), 8.01 (dd, *J* = 8.7, 1.6 Hz, 1H, 4-Ar*H*), 7.93 (d, *J* = 9.0 Hz, 1H, 10-Ar*H*), 7.78 (d, *J* = 8.7 Hz, 1H, 9-Ar*H*), 7.22 (dd, *J* = 8.9, 2.5 Hz, 1H, 7-Ar*H*), 7.16 (d, *J* = 2.3 Hz, 1H, 5-Ar*H*), 3.96 (s, 3H, OCH_3), 3.90 (t, *J* = 7.3 Hz, 2H, CO$CH_2$$CH_2$), 3.54 (dd, *J* = 12.6, 7.1 Hz, 2H, $COCH_2CH_2$), 3.36 – 3.11 (m, 4H, N($CH_2$$CH_3$)$_2$), 1.47 (td, *J* = 7.3, 4.6 Hz, 13H, N(CH_2CH_3)$_2$). HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{24}NO_2$ 286.18070, found 286.17975. Anal. Calcd for $C_{18}H_{24}ClNO_2$: C, 67.17, H, 7.52; found: C, 67.12, H, 7.50.

Al(AVB)$_3$. Avobenzone (3.00 g, 9.67 mmol), dichloromethane (50 ml) , anhydrous aluminum trichloride (0.43 g, 3.22 mmol), and sodium hydride (0.23 g, 9.67 mmol) were introduced to a round-bottom flask successively. The mixture was stirred under N_2 at room temperature for ~ 24 h. Then the insolubles in the reaction mixture were removed by filtration, and n-hexane was added dropwise to the filtrate under stirring until precipitation commenced. The precipitate was collected by centrifugation, washed with n-hexane and then recrystallized in CH_2Cl_2/n-hexane to obtain white powder (3.3 g, 36%). ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.96 (m, 12H, 2′,6′,2″,6″-Ar*H*), 7.37 (dd, *J* = 8.5, 2.7 Hz, 6H, 3′,5′-Ar*H*), 6.86 (m, 9H, 3″,5″-Ar*H*, COC*H*CO), 3.82 (d, *J* = 1.1 Hz, 9H, OCH_3), 1.28 (m, 27H, C(CH_3)$_3$). HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{60}H_{63}AlO_9$ 955.43657, found 955.43579. Anal. Calcd for $C_{60}H_{63}AlO_9$: C, 75.45, H, 6.65; found: C, 75.39, H, 6.50.

Al(OBZ)$_3$. Oxybenzone (2.00 g, 8.76 mmol), dichloromethane (20 ml), and anhydrous aluminum isopropoxide (0.60 g, 2.92 mmol) were introduced to a round-bottom flask successively. The mixture was refluxed for ~ 24 h under N_2. Then the insolubles in the reaction mixture were removed by filtration, and hexane was added dropwise to the filtrate under stirring until precipitation commenced. The precipitate was collected by centrifugation, washed with n-hexane and then recrystallized in CH_2Cl_2/n-hexane twice to obtain yellow powder (1.6 g, 62%). ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.50, 6.38 (m, 8H, -Ar*H*), 3.76 (s, 3H, -OCH_3). MALDI-TOF MS: m/z calcd for $C_{42}H_{33}AlO_9$ 708.1940, found 708.1319. HRMS (EI): m/z $[M+H]^+$ calcd for $C_{42}H_{33}AlO_9$ 708.19400, found 708.19430. Anal. Calcd for $C_{42}H_{33}AlO_9$: C, 71.18, H, 4.69; found: C, 71.12, H, 4.61.

$Gd(dbm)_3 \cdot H_2O$. Dibenzoylmethane (510 mg, 2.28 mmol), NaOH (91 mg, 2.28 mmol) and ethanol (60 ml) were added to a round-bottom flask and the mixture was stirred at room temperature for 30 min. Then $GdCl_3$ (200 mg, 0.76 mmol) was introduced to the above solution and the mixture was stirred for another 6 h and then standed for 3 h. The precipitate thus obtained was collected by centrifugation and then dissolved in CH_2Cl_2. The insolubles were removed by filtration and n-hexane was added to the solution for crystallization. Pale green crystals (Figure s9) were thus obtained and dried *in vacuo* (300 mg, 59%). HRMS (MALDI-TOF MASS): m/z $[M+Na]^+$ calcd for $C_{45}H_{33}GdNaO_6$ 850.1416, found 850.1337. Anal. Calcd for $C_{45}H_{35}GdO_7$: C, 63.96, H, 4.17; found: C, 63.82, H, 4.27.

BF_2IK1. Synthesized according to literature method.[1] ^1H NMR (400 MHz, $CDCl_3$, δ) 8.05~7.15 (m, 15H, -ArH), 6.41 (s, 1H, -OCC*H*-). HRMS (APCI): m/z M^+ calcd for $C_{21}H_{17}BF_2NO$ 348.13713, found 348.13666. Anal. Calcd for $C_{21}H_{17}BF_2NO$: C, 72.44, H, 4.92; found: C, 72.60, H, 4.72.

BF_2IK2. Synthesized according to literature method.[2] ^1H NMR (400 MHz, $CDCl_3$, δ) 8.75 (s, 1H, 3-ArH on pyrazine ring), 8.10 (s, 1H, 6-ArH on pyrazine ring), 7.96 (dd, 2H, 2,6-ArH on benzene ring), 7.48 (m, 3H, 3,4,5-ArH on benzene ring), 6.47 (s, 1H, -OCC*H*-), 2.65 (s, 3H, -CH_3). HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{13}H_{11}BF_2N_2O$ 261.09325, found 261.10056. Anal. Calcd for $C_{13}H_{11}BF_2N_2O$: C, 60.04, H, 4.26; found: C, 60.16, H, 4.19.

BF_2EMO. Synthesized according to literature method.[3] ^1H NMR (400 MHz, $CDCl_3$, δ) 7.92 (d, 2H, 2,6-ArH), 6.96 (d, 2H, 3,5-ArH), 5.92 (s, 1H, OCC*H*CO), 4.55 (q, 2H, CH_2CH$_3$), 1.44 (t, 3H, CH$_2$CH_3). HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{12}H_{14}BF_2O_4$ 271.09532, found 271.09407. Anal. Calcd for $C_{12}H_{13}BF_2O_4$: C,53.37, H, 4.85; found: C, 53.32, H, 4.91.

Part II. Supplementary Figures

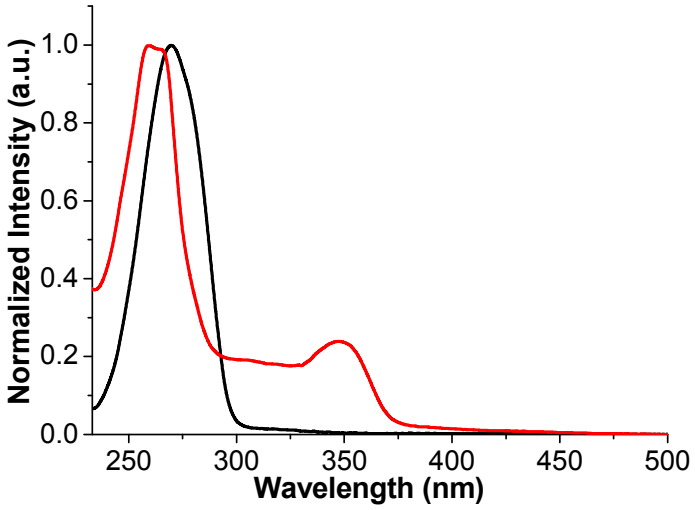

Figure S1. Normalized absorption spectra of 1-(4-methoxyphenyl) ethanone (**mka**) in CH_2Cl_2 before (black line) and after (red line) adding BCl_3.

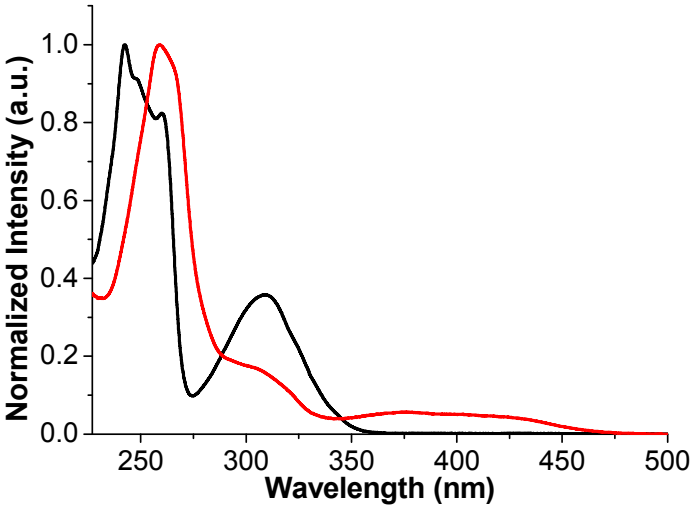

Figure S2. Normalized absorption spectra of 1-(6-methoxynaphthalen-2-yl) ethanone (**mkb**) in CH_2Cl_2 before (black line) and after (red line) adding BCl_3.

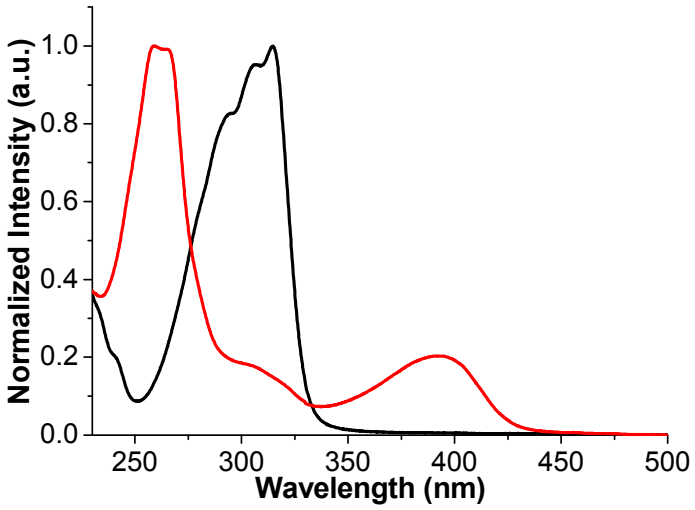

Figure S3. Normalized absorption spectra of 1-(4aH-fluoren-3-yl) ethanone (**mkc**) in CH_2Cl_2 before (black line) and after (red line) adding BCl_3.

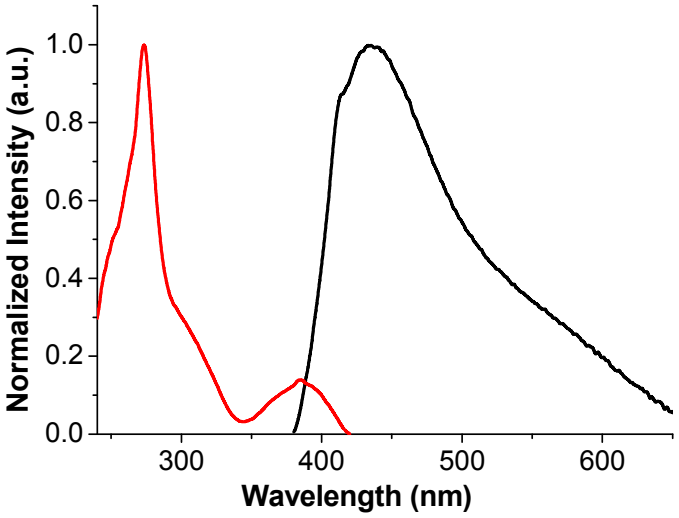

Figure S4. Normalized steady-state emission spectrum (black line) and excitation spectrum (red line) of **1a** in CH_2Cl_2.

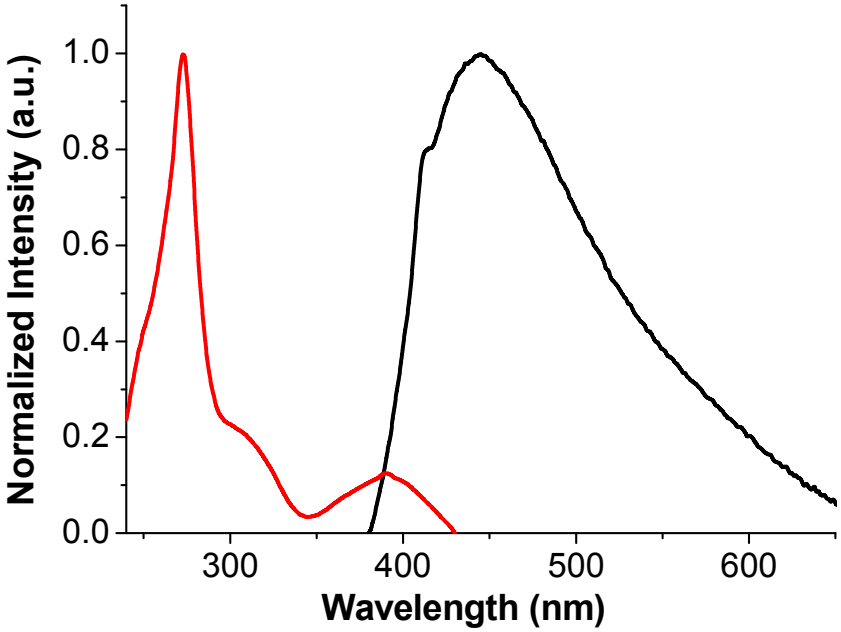

Figure S5. Normalized steady-state emission spectrum (black line) and excitation spectrum (red line) of **1b** in CH_2Cl_2.

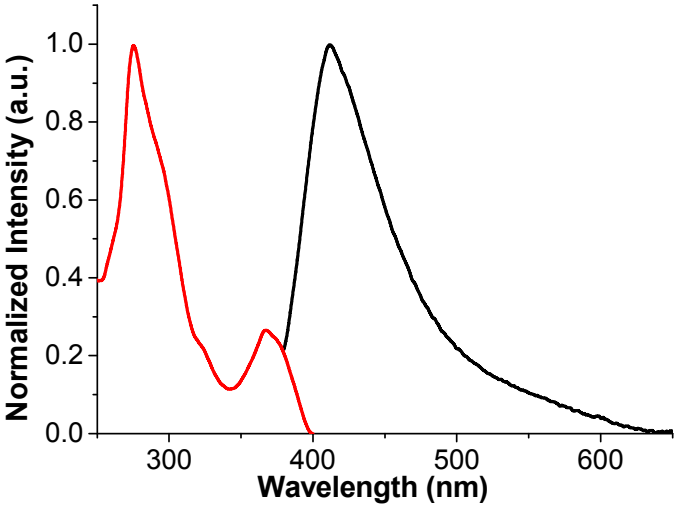

Figure S6. Normalized steady-state emission spectrum (black line) and excitation spectrum (red line) of **1c** in CH_2Cl_2.

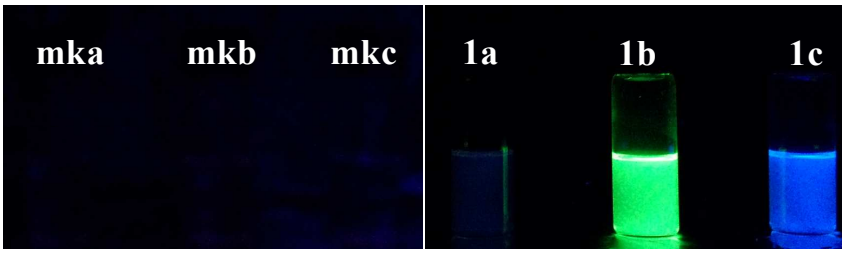

Figure S7. Photos of monketones (**mka-mkc**, left) in CH_2Cl_2 and monketone-BCl_3 complexes (**1a-1c**, right) in CH_2Cl_2 under UV excitation (λ_{ex} = 365 nm).

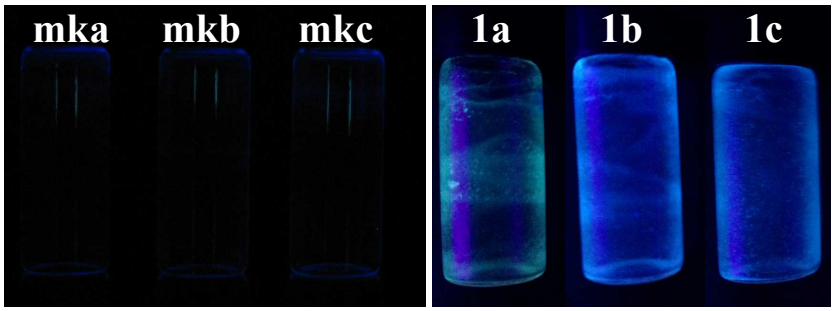

Figure S8. Photos of monketones (**mka-mkc**, left) in PLA and monketone-BCl_3 complexes (**1a-1c**, right) in PLA under UV excitation (λ_{ex} = 365 nm).

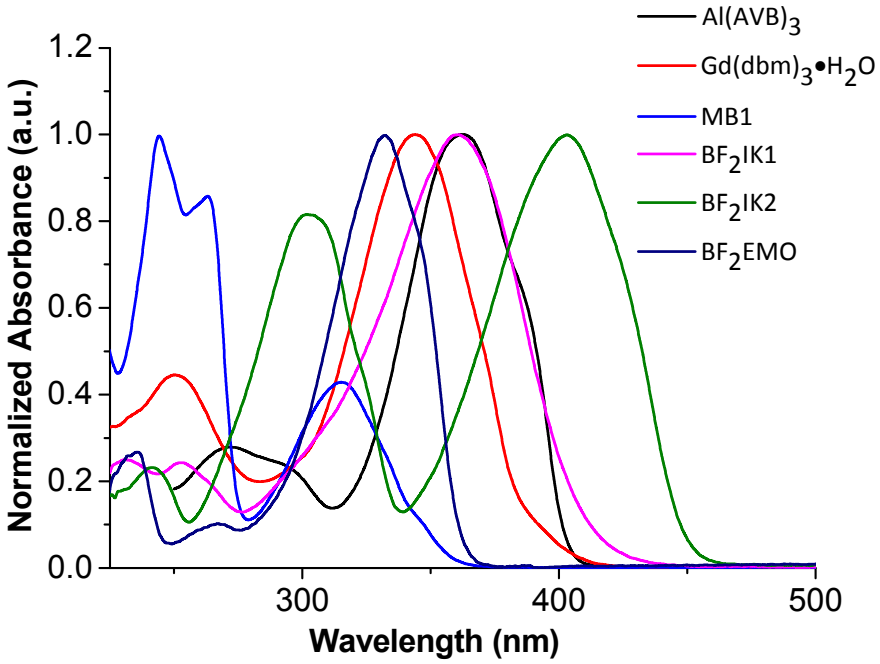

Figure S9. Normalized absorption spectra of $Al(AVB)_3$ (black line), $Gd(dbm)_3 \cdot H_2O$ (red line), MB1 (blue line), BF_2IK1 (pink line), BF_2IK2 (green line) and BF_2EMO (violet line) in CH_2Cl_2 at 25 ℃.

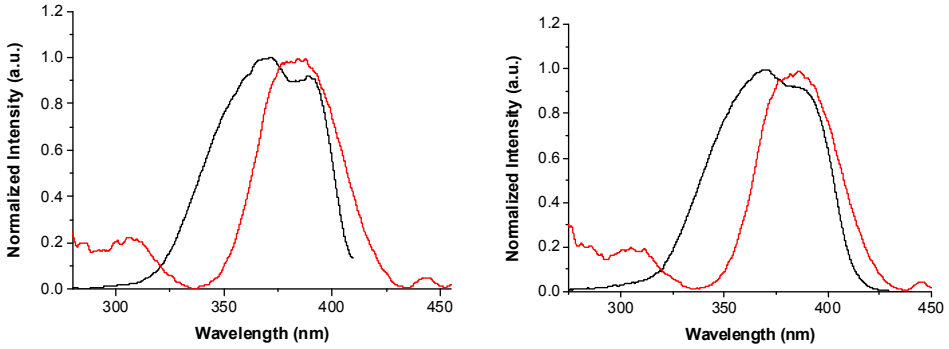

Figure S10. Fluorescence (left) and RTP (right) excitation spectra of $Al(AVB)_3$ (black line) and $Al(OBZ)_3$ (red line) in PLA.

Figure S11. Micrographs of $Gd(dbm)_3{\cdot}H_2O$ crystals under bright field. Scale bar = 100µm.

Part III. NMR and HRMS Spectra

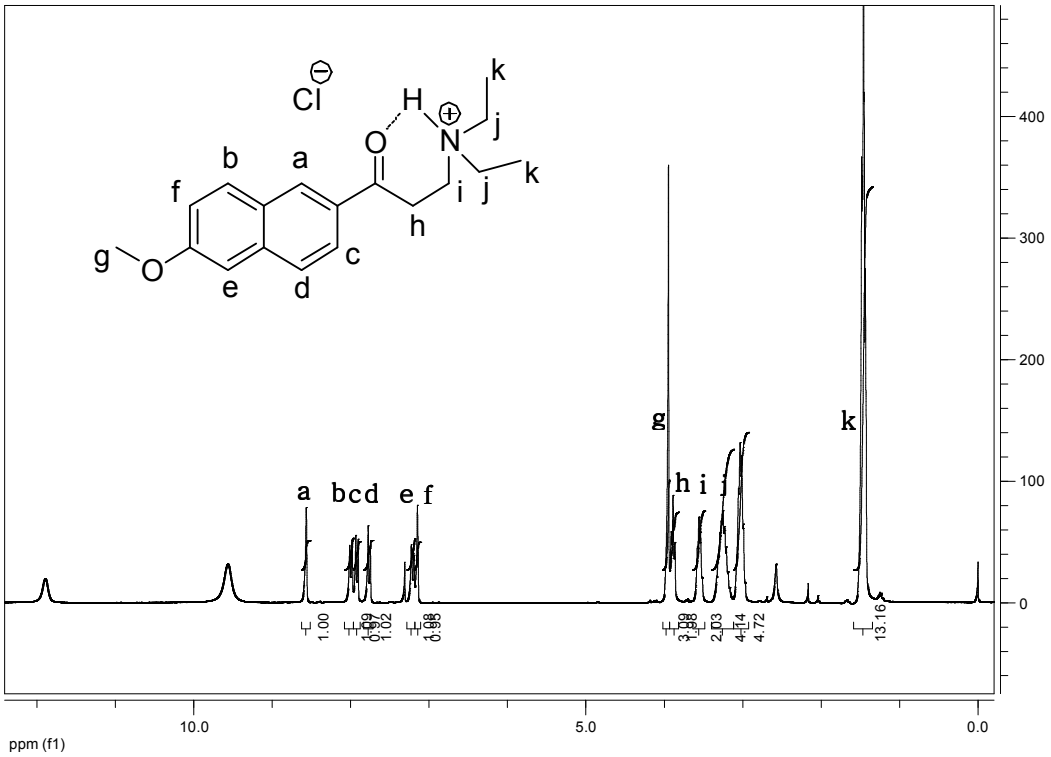

Figure SA. ^{1}H NMR spectrum of **MB1** in $CDCl_3$.

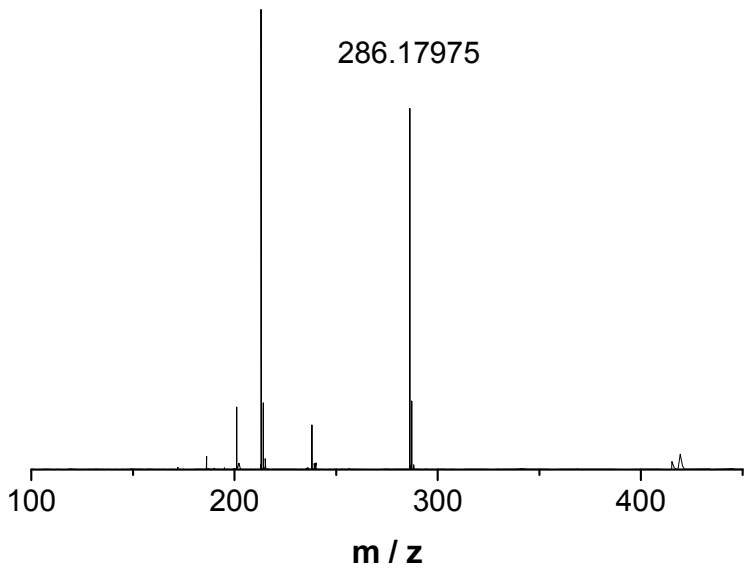

Figure SB. HRMS (ESI) spectrum of **MB1**.

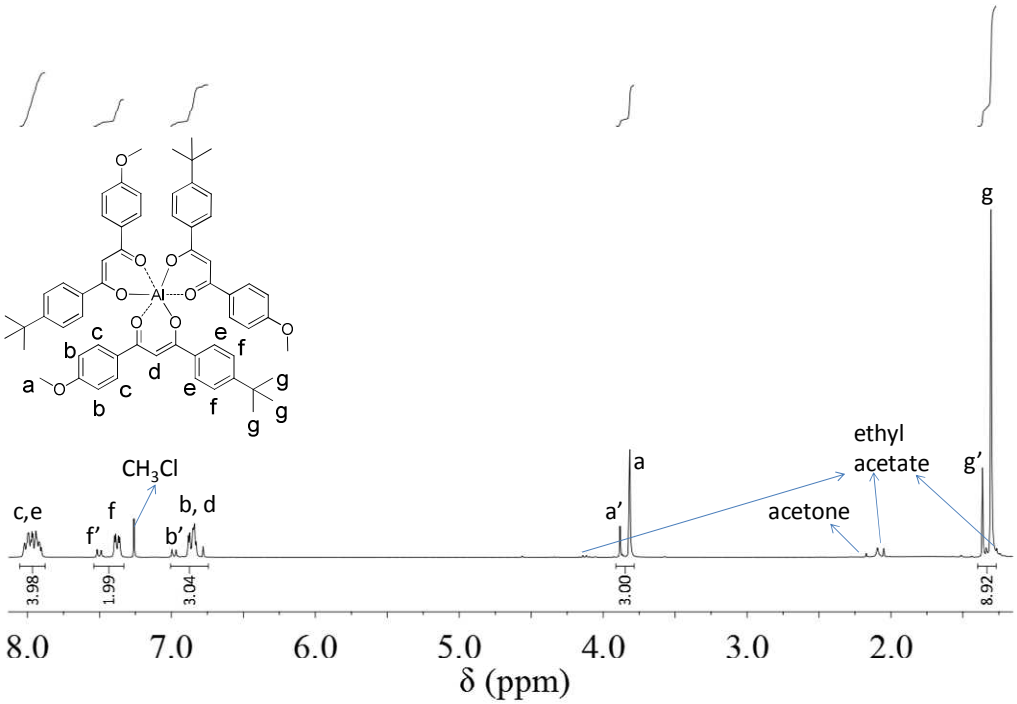

Figure SC. ^{1}H NMR spectrum of $Al(AVB)_3$ in $CDCl_3$.

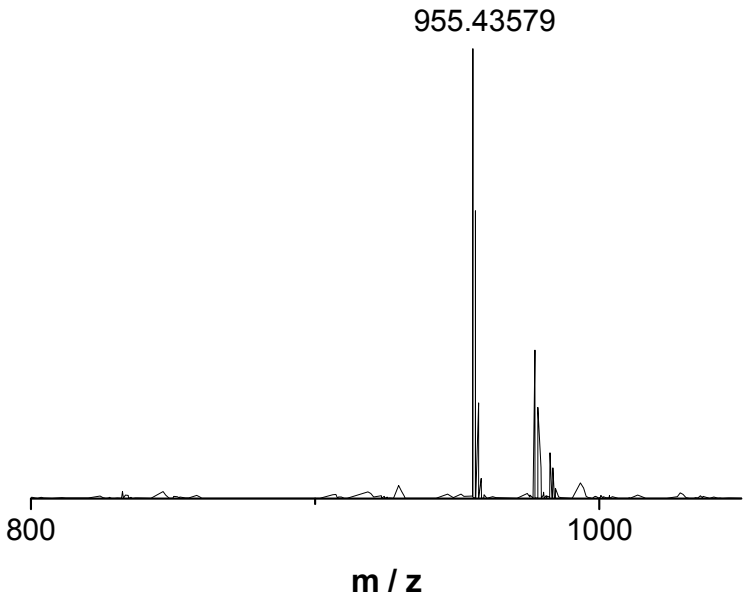

Figure SD. HRMS (ESI) spectrum of $Al(AVB)_3$.

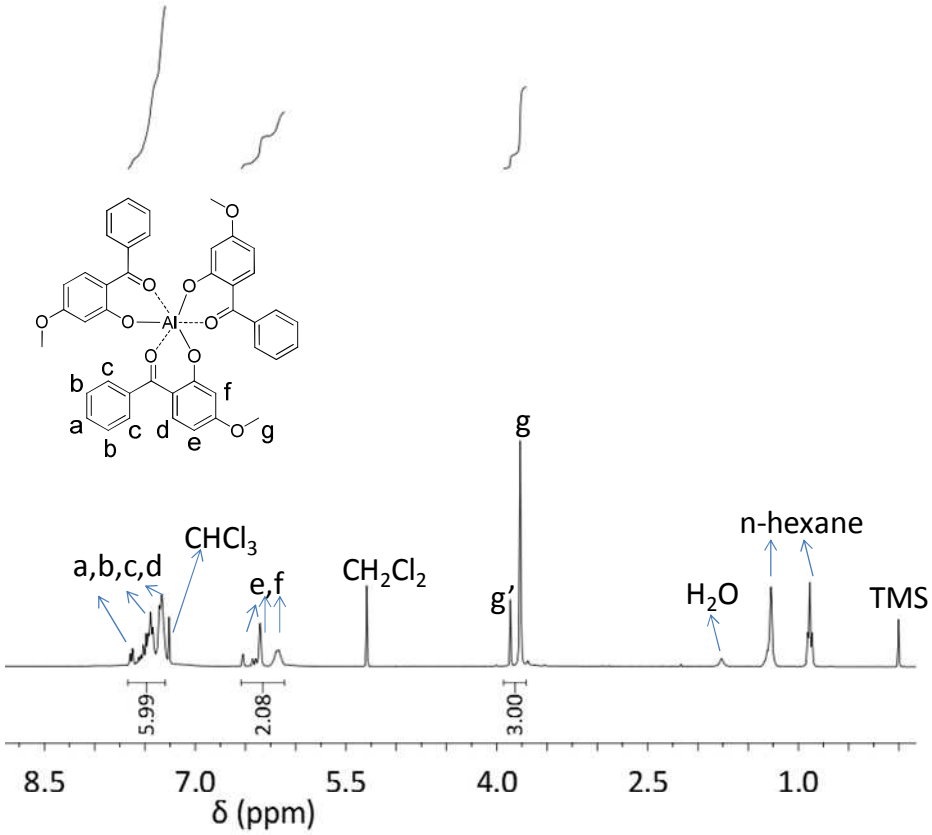

Figure SE. ^{1}H NMR spectrum of $Al(OBZ)_3$ in $CDCl_3$.

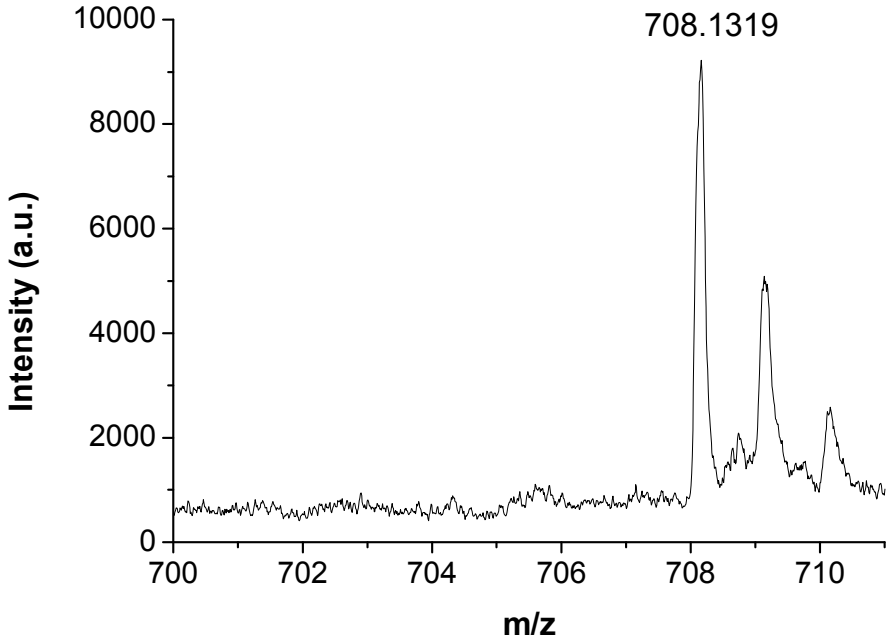

Figure SF. MALDI-TOF mass spectrum of $Al(OBZ)_3$.

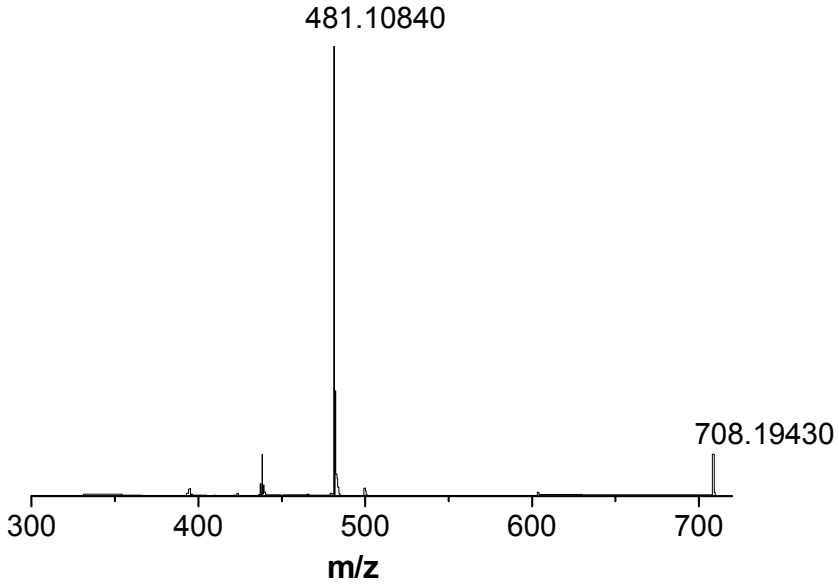

Figure SG. HRMS (EI-TOF) spectrum of $Al(OBZ)_3$.

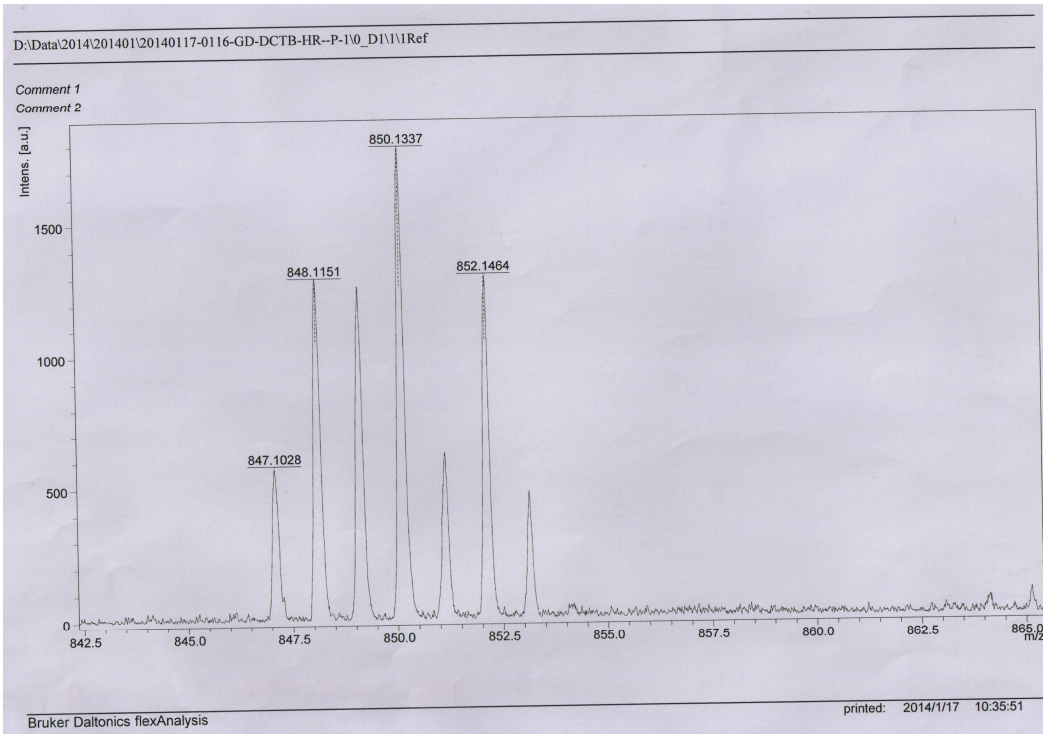

Figure SH. HRMS (MALDI-TOF) spectrum of $Gd(dbm)_3 \cdot H_2O$.

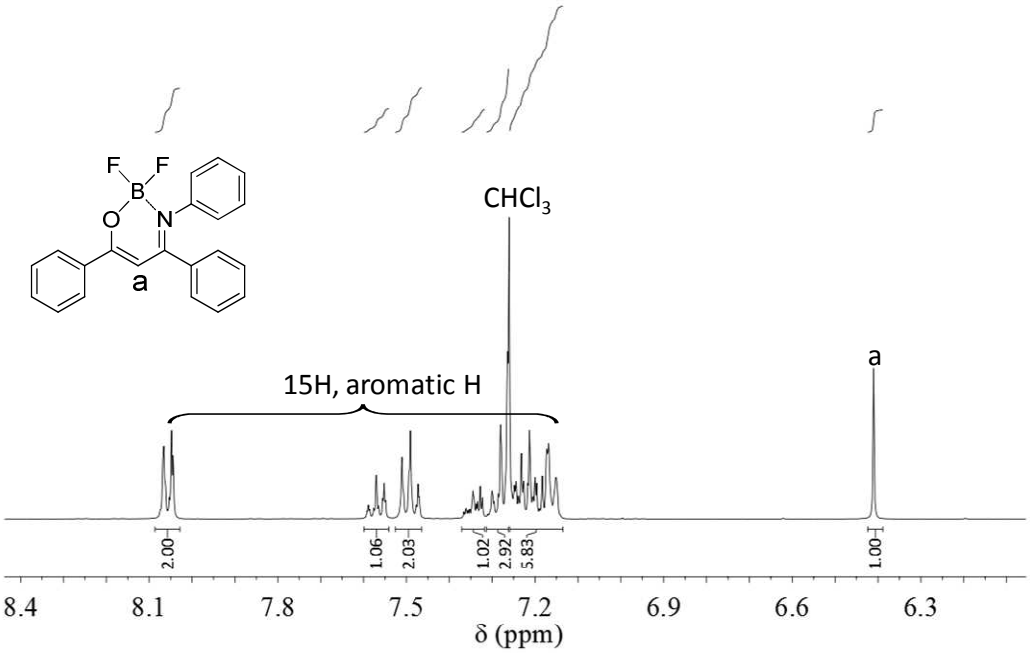

Figure SI. ^1H NMR spectrum of BF_2IK1 in $CDCl_3$.

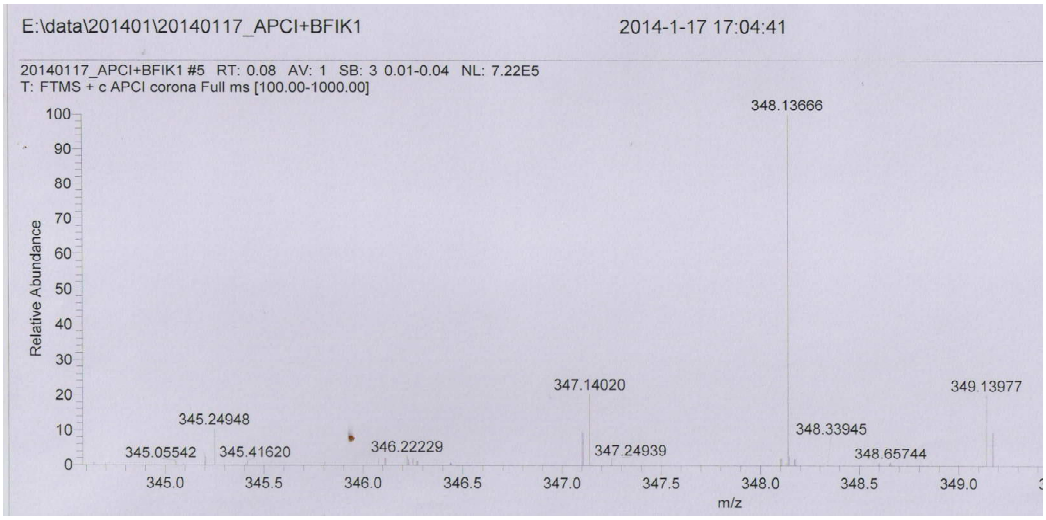

Figure SJ. HRMS (APCI) spectrum of BF_2IK1.

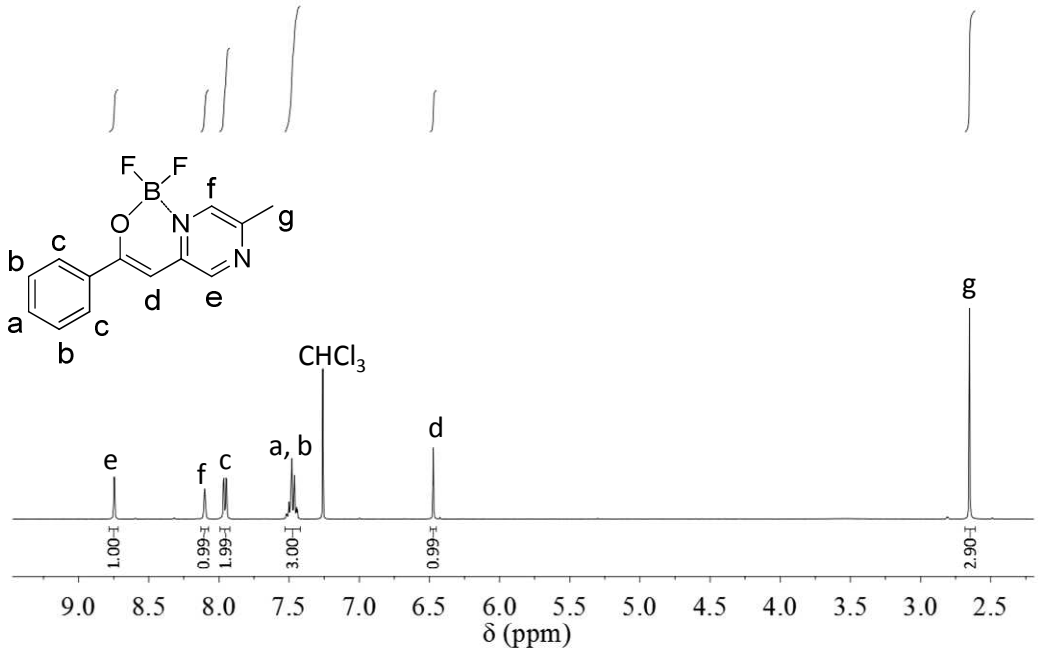

Figure SK. ^1H NMR spectrum of BF_2IK2 in $CDCl_3$.

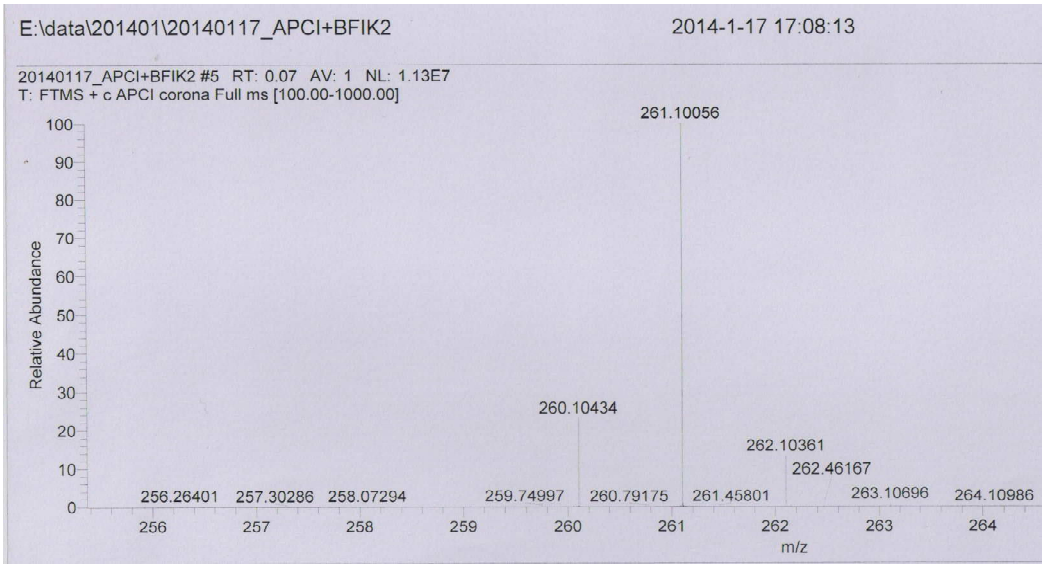

Figure SL. HRMS (APCI) spectrum of BF_2IK2.

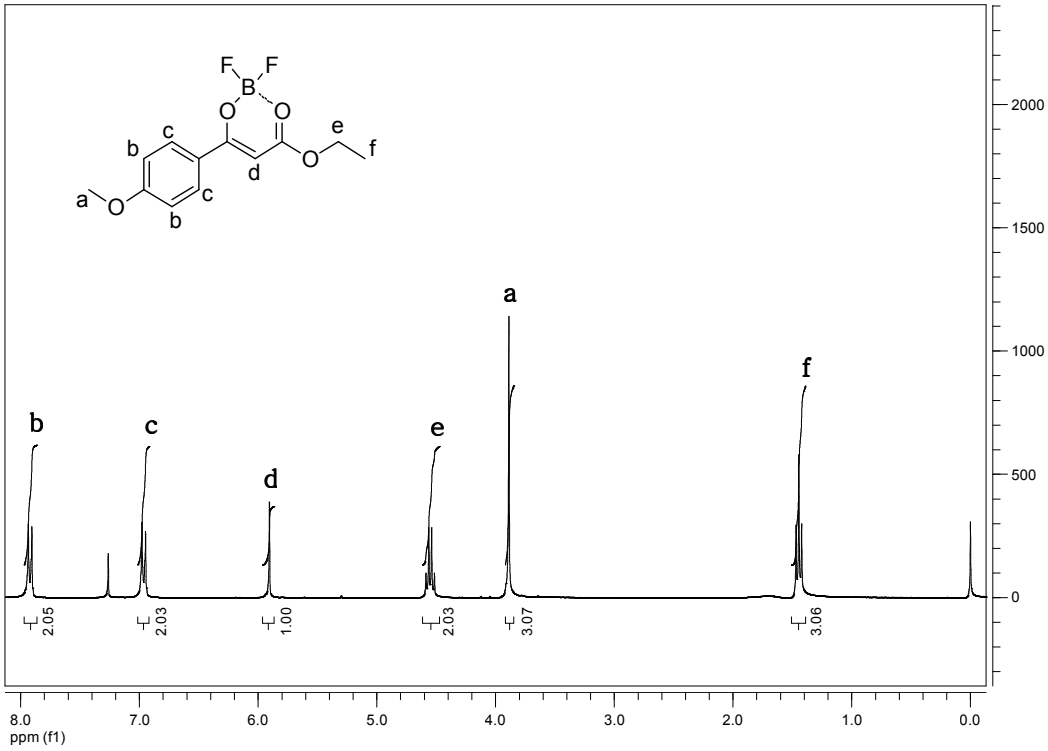

Figure SM. ^{1}H NMR spectrum of BF_2EMO in $CDCl_3$.

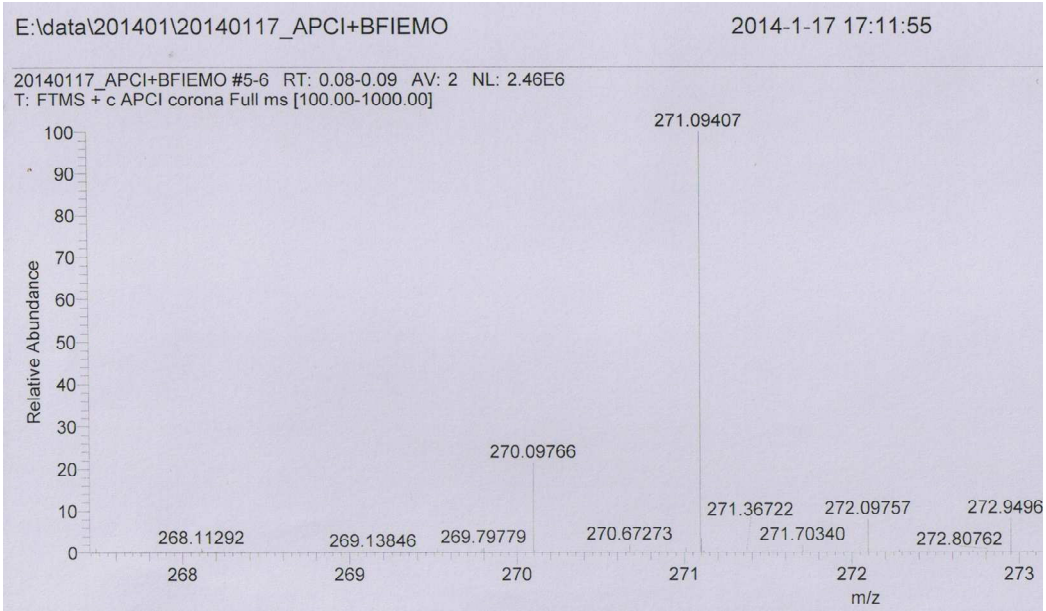

Figure SN. HRMS (APCI) spectrum of BF_2EMO.

Part IV. Supporting Tables for Single Crystal Data

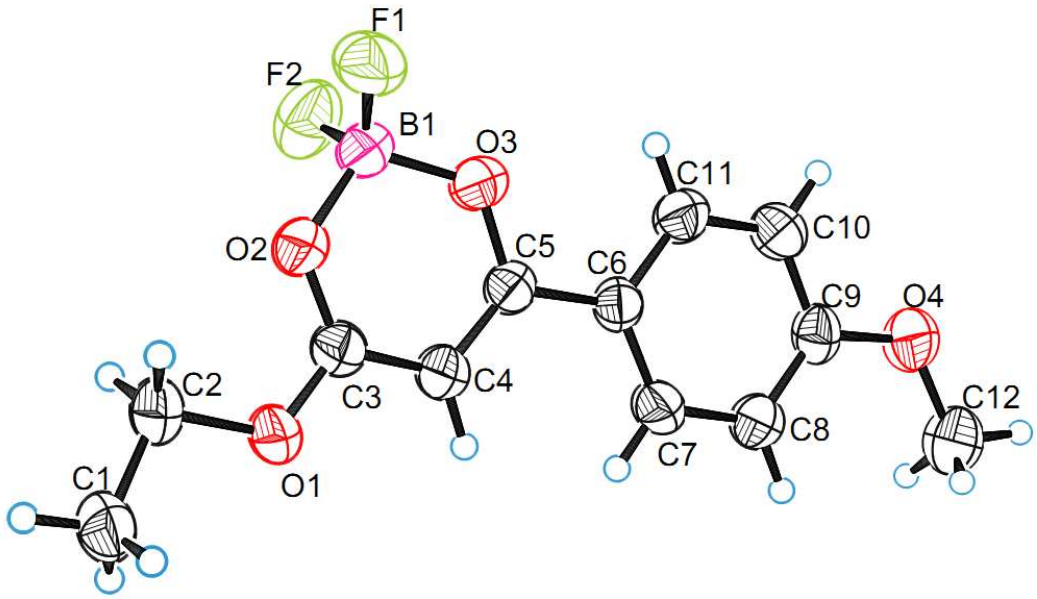

Table S1 Crystal data and structure refinement for BF_2EMO.

Identification code	BF_2EMO
Empirical formula	$C_{12}H_{13}BF_2O_4$
Formula weight	269.93
Temperature/K	291(2)
Crystal system	triclinic
Space group	P-1
a/Å	6.9547(11)
b/Å	8.5168(14)
c/Å	11.8751(18)
α/°	82.715(13)
β/°	78.561(13)
γ/°	67.088(16)
Volume/$Å^3$	634.06(17)
Z	2
ρ_{calc}mg/mm^3	1.414
m/mm^{-1}	0.122
F(000)	280.0
Crystal size/mm^3	0.36 × 0.32 × 0.31
2Θ range for data collection	6.44 to 52.74°

Index ranges	$-8 \leq h \leq 7$, $-8 \leq k \leq 10$, $-14 \leq l \leq 14$
Reflections collected	4354
Independent reflections	2555[R(int) = 0.0263]
Data/restraints/parameters	2555/0/174
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0538, wR_2 = 0.1280
Final R indexes [all data]	R_1 = 0.0811, wR_2 = 0.1520
Largest diff. peak/hole / e $Å^{-3}$	0.18/-0.19

Table S2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for BF_2EMO. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F1	-4989(2)	3843.6(18)	7487.7(12)	83.8(5)
F2	-2617(2)	1844.8(15)	8470.9(12)	88.2(5)
O1	-1188(2)	6212.5(17)	8715.8(11)	58.8(4)
O4	5874(3)	882.4(19)	2465.7(13)	72.3(5)
O3	-1459(2)	2897.8(18)	6685.5(13)	66.6(5)
O2	-2891(2)	4648.8(18)	8368.7(12)	59.3(4)
C6	1687(3)	2739(2)	5436.8(15)	45.9(5)
C4	282(3)	4483(2)	7167.5(17)	55.0(5)
C3	-1304(3)	5101(2)	8094.6(16)	48.6(5)
C8	4908(3)	2537(3)	4142.9(18)	59.2(6)
C11	1384(4)	1696(2)	4732.4(18)	57.2(5)
C9	4578(3)	1511(2)	3454.6(17)	53.4(5)
C10	2799(4)	1094(3)	3758.1(19)	62.4(6)
C2	-2821(4)	6832(3)	9727.9(18)	62.1(6)
C7	3472(3)	3129(3)	5121.4(18)	57.6(5)
C1	-2344(4)	8154(3)	10197.4(18)	66.4(6)
C12	7680(4)	1319(3)	2100(2)	83.5(8)
C5	146(3)	3396(2)	6466.4(16)	45.4(5)
B1	-3007(4)	3265(3)	7746(2)	57.3(6)

Table S3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for BF_2EMO. The Anisotropic displacement factor exponent takes the form:

$-2\pi^2[h^2a^{*2}U_{11}+...+2hka\times b\times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F1	59.4(9)	116.7(11)	84.5(10)	-31.7(8)	-7.4(7)	-36.9(8)
F2	103.3(12)	71.3(8)	82.2(10)	0.2(7)	10.7(8)	-37.9(8)
O1	58.3(9)	76.5(9)	48.5(9)	-24.5(7)	5.1(7)	-33.0(7)
O4	75.1(11)	81.2(10)	59.6(10)	-29.4(7)	14.7(8)	-32.7(8)
O3	68.1(10)	82.4(10)	62.9(10)	-25.5(7)	11.5(8)	-46.9(8)
O2	55.3(9)	74.4(9)	53.7(9)	-17.9(6)	7.7(7)	-33.7(7)
C6	49.2(12)	47.5(10)	40.6(11)	-3.8(7)	-4.9(9)	-18.3(8)
C4	48.8(12)	69.7(12)	50.4(12)	-16.2(9)	1.4(10)	-27(1)
C3	46.5(11)	55.0(11)	46.3(12)	-4.4(8)	-8.4(9)	-20.4(9)
C8	51.7(13)	75.3(13)	54.0(13)	-16.9(10)	3.5(10)	-29.1(10)
C11	62.0(14)	58.7(12)	56.3(13)	-10.3(9)	2.1(10)	-31.9(10)
C9	57.3(13)	52.0(11)	44.0(12)	-10.2(8)	0.9(9)	-15.2(9)
C10	75.5(16)	61.4(12)	57.5(14)	-22.9(10)	1.2(12)	-33.2(11)
C2	60.6(14)	76.6(13)	48.2(13)	-18.9(10)	5.7(10)	-26.9(11)
C7	55.7(13)	73.3(13)	50.9(13)	-20.4(9)	-1(1)	-30.4(10)
C1	78.7(17)	67.6(13)	52.8(14)	-15.9(10)	-0.3(12)	-28.7(12)
C12	68.5(17)	105.1(19)	70.4(17)	-31.7(13)	19.3(13)	-32.1(14)
C5	43.7(11)	47.6(10)	44.4(11)	-1.2(7)	-5.5(8)	-17.8(8)
B1	55.0(15)	66.2(14)	56.3(15)	-12.1(11)	2.4(12)	-31.5(11)

Table S4 Bond Lengths for BF_2EMO.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F1	B1	1.356(3)	C6	C11	1.392(3)
F2	B1	1.360(3)	C6	C7	1.378(3)
O1	C3	1.306(2)	C6	C5	1.464(3)
O1	C2	1.472(2)	C4	C3	1.385(3)
O4	C9	1.357(2)	C4	C5	1.362(3)
O4	C12	1.419(3)	C8	C9	1.377(3)
O3	C5	1.311(2)	C8	C7	1.378(3)
O3	B1	1.464(3)	C11	C10	1.370(3)
O2	C3	1.276(2)	C9	C10	1.385(3)
O2	B1	1.504(3)	C2	C1	1.488(3)

Table S5 Bond Angles for BF_2EMO.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C3	O1	C2	119.24(17)	O4	C9	C10	116.34(19)
C9	O4	C12	118.42(18)	C8	C9	C10	119.29(19)
C5	O3	B1	123.06(16)	C11	C10	C9	120.36(19)
C3	O2	B1	120.18(16)	O1	C2	C1	106.44(18)
C11	C6	C5	120.69(19)	C8	C7	C6	122.08(19)
C7	C6	C11	117.43(19)	O3	C5	C6	115.85(17)
C7	C6	C5	121.89(18)	O3	C5	C4	120.04(18)
C5	C4	C3	120.0(2)	C4	C5	C6	124.10(19)
O1	C3	C4	118.69(19)	F1	B1	F2	111.8(2)
O2	C3	O1	118.10(17)	F1	B1	O3	109.61(19)
O2	C3	C4	123.21(18)	F1	B1	O2	106.54(18)
C9	C8	C7	119.7(2)	F2	B1	O3	109.94(18)
C10	C11	C6	121.2(2)	F2	B1	O2	107.38(19)
O4	C9	C8	124.4(2)	O3	B1	O2	111.55(18)

Table S6 Torsion Angles for BF_2EMO.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O4	C9	C10	C11	-178.92(17)	C7	C6	C5	C4	2.7(3)
C6	C11	C10	C9	0.2(3)	C7	C8	C9	O4	178.96(17)
C3	O1	C2	C1	-176.10(17)	C7	C8	C9	C10	0.2(3)
C3	O2	B1	F1	-133.8(2)	C12	O4	C9	C8	-0.8(3)
C3	O2	B1	F2	106.3(2)	C12	O4	C9	C10	178.0(2)
C3	O2	B1	O3	-14.2(3)	C5	O3	B1	F1	133.6(2)
C3	C4	C5	O3	-1.8(3)	C5	O3	B1	F2	-103.2(2)
C3	C4	C5	C6	177.01(16)	C5	O3	B1	O2	15.8(3)
C8	C9	C10	C11	0.0(3)	C5	C6	C11	C10	179.04(17)
C11	C6	C7	C8	0.7(3)	C5	C6	C7	C8	-178.89(17)
C11	C6	C5	O3	1.9(3)	C5	C4	C3	O1	-176.37(17)
C11	C6	C5	C4	-176.91(18)	C5	C4	C3	O2	3.0(3)
C9	C8	C7	C6	-0.5(3)	B1	O3	C5	C6	172.57(17)
C2	O1	C3	O2	2.8(3)	B1	O3	C5	C4	-8.5(3)
C2	O1	C3	C4	-177.80(16)	B1	O2	C3	O1	-174.78(17)
C7	C6	C11	C10	-0.6(3)	B1	O2	C3	C4	5.8(3)

C7 C6 C5 O3 -178.44(17)

Table S7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for BF_2EMO.

Atom	*x*	*y*	*z*	U(eq)
H4	1441	4811	7024	66
H8	6094	2829	3948	71
H11	200	1402	4927	69
H10	2564	402	3298	75
H2A	-2778	5902	10299	75
H2B	-4217	7320	9509	75
H7	3716	3813	5584	69
H1A	-3319	8546	10891	100
H1B	-2478	9097	9641	100
H1C	-925	7672	10363	100
H12A	8622	858	2654	125
H12B	7248	2539	2030	125
H12C	8393	857	1367	125

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