Electronic Supplementary Information

A Mechanistic Investigation of Mechanochromic Luminescent Organoboron Materials

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Part I. Methods, Materials, and Synthesis

Methods. ^{1}H NMR (300 MHz) spectra were recorded on a Bruker AV300 NMR spectrometer operated in the Fourier transform mode. $CDCl_3$ was used as the solvent ^{1}H and NMR spectra were referenced to the signal for residual protio chloroform at 7.26 ppm. High-resolution mass spectra were recorded on a LTQ ORBITRAP XL mass spectrometer (Thermo Scientific). Single crystals of **1-3** were recrystallized from CH_2Cl_2/n-hexane mounted in inert oil and transferred to the cold gas stream of the diffractometer. Fluorescence microscopy images of the solid samples were obtained from an Olympus DP72 color camera mounted on a BX51 microscope excited by a mercury lamp for wide-band UV excitation. Photographs were taken by a Cannon 500D digital camera. All images are shown as raw data and are not processed in any software excluding cutting and cropping edits. Dynamic laser light scattering (LLS) measurements were conducted on a commercial spectrometer (ALV/DLS/SLS-5022F) equipped with a multitau digital time correlator (ALV5000) and a cylindrical 22 mW UNIPHASE He-Ne laser (λ_0 = 632 nm) as the light source. Scattered light was collected at a fixed angle of 90° for duration of ~5 min. Distribution averages and particle size distributions were computed using cumulants analysis and CONTIN routines. UV/vis absorption spectra were recorded on a Beijing Persee TU-1901 UV-Vis spectrometer. Fluorescence quantum yields, Φ_F, were 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, $n_D^{20}CH_2Cl_2$ = 1.424. Solution excitation and steady-state fluorescence emission spectra were recorded on a FluoroMax-4 spectrofluorometer (Horiba Scientific) and analyzed with an Origin (v8.0) integrated software FluoroEssence (v2.2). Mechanochromic fluorescence spectra in the solid state were recorded on an Ocean Optics USB4000-VIS-NIR Spectrometer equipped with an optical fiber with an integrated LED excitation module (λ_{ex} = 385 nm). The spectra were analyzed in SpectraSuite (Ocean Optics, v2008). 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). Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) equipped with Waters 1515 pump and Waters 2414 differential refractive index detector (set at 30 °C). The detection components used a series of two linear Styragel columns (HR2 and HR4) at an oven temperature of 45 °C. The eluent was THF at a flow rate of 1.0 mL/min. Melting point was recorded on a SGW-X4 (Shanghai Precision and Scientific Instrument Co., Ltd.) illuminated microscope melting point apparatus.

Experimental details regarding mechanochromic luminescence: solid samples (~ 10 mg) of BF_2dbm derivatives (**1-3**, **D1** and **P1**) were gently sprinkled on top of a microscope glass slide and a cover slide was placed on top of the solid samples. The initial emission spectra were then recorded at this stage. Shear/dragging force was applied on the cover slide so that the solid samples were sheared against the two layers of glass. The entire procedure was monitored under a hand-held UV lamp (λ_{ex} = 365 nm). Bright yellow fluorescence streaks/tracks could be immediately observed and recorded. The normalized spectra obtained from the array spectrometer are quite reproducible before and after mechanical stimuli for each individual solid sample.

Materials. Solvents: CH_3CN and CH_2Cl_2 were dried refluxing over CaH_2 for at least 6 h prior to use. THF was dried by KOH for overnight first and then refluxing over sodium using benzophenone as an indicator. Toluene and alcohols were purified by distillation at reduced pressure. DMF, methyl THF and n-hexane were used as received without further purification (Aladdin). Reagents: allyl bromide (*ReagentPlus*®, 99%, contains ≤1000 ppm propylene oxide as stabilizer), NaH (95%), 4-hydroxy acetophenone (99%), methyl 4-hydroxy benzoate (≥99%, *ReagentPlus*®), 4-methoxyacetopheneone (99%), boron trifluoride dietherate (purified by redistillation, ≥46.5% BF_3 basis), chloroplatinic acid (99.995% trace metals basis) and 1,1,3,3-tetramethyldisiloxane (≥98%,) were purchased from Sigma-Aldrich and were used as received.

Difluoroboron 4,′4-di(allyloxybenzoyl)methane (1) 4,4′-di(allyloxybenzoyl)methane (5.00 g, 14.8 mmol) and boron trifluoride dietherate (2.00 mL, 16.0 mmol) were added to 100 mL CH_2Cl_2 and stirred under N_2 at room temperature for 12 h. The solution was then purged with N_2 to remove excess boron trifluoride (absorbed with NaOH aq. solution). The complex (**1**) was obtained by silica gel chromatography with CH_2Cl_2/hexanes as bright yellow needles (4.17g, 73%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (d, *J* = 9.0 Hz, 4H, 2′,6′, 2″, 6″ -Ar*H*), 7.02 (d, *J* = 9.0 Hz, 4H, 3′, 5′, 3″, 5″ -Ar*H*), 7.00 (s, 1H, COC*H*CO), 6.05 (m, 2H, $ArOCH_2CH$=CH_2), 5.45 (d, *J* = 17.0 Hz, 2H, cis-OCH_2CH=C*H*H), 5.35 (d, *J* = 10.5 Hz, 2H, trans-OCH_2CH=CH*H*), 4.65 (d, 4H, *J* = 5.5 Hz, ArOCH_2CH=CH_2). M.P.: 197-198 °C. MS (HRMS): m/z calcd for $C_{21}H_{20}O_4BF_2$ $[M+H]^+$ 385.14172, found 385.14081 (Relative Abundance: 100). UV/vis (CH_2Cl_2): λ_{max} = 412 nm, ε = 79,000 $M^{-1}cm^{-1}$.

Difluoroboron 4 -allyoxybenzoyl-4′ -methoxybenzoyl methane (2) was synthesized similarly as **1**. 4 -allyoxybenzoyl-4′ -methoxybenzoyl methane. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, *J* = 9.0 Hz, 4H, 2′,6′, 2″, 6″ -Ar*H*), 7.03 (d, *J* = 9.0 Hz, 4H, 3′, 5′, 3″, 5″ -Ar*H*), 7.01 (s, 1H, COC*H*CO), 6.06 (m, 1H, $ArOCH_2CH$=CH_2), 5.45 (d, *J* = 18.0 Hz, 1H, cis-OCH_2CH=C*H*H), 5.35 (d, *J* = 10.5 Hz, 1H, trans-OCH_2CH=CH*H*), 4.66 (d, 2H, *J* = 5.5 Hz, ArOCH_2CH=CH_2),3.93(s,3H,ArOCH_3). M.P.: 185-186 °C.MS (HRMS): m/z calcd for $C_{19}H_{18}O_4BF_2$ $[M+H]^+$ 359.12607, found 359.12628.UV/vis (CH_2Cl_2): λ_{max} = 412 nm, ε =85,000 $M^{-1}cm^{-1}$.

Difluoroboron 4,4′-di(methoxybenzoyl)methane (3) is a known compound. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (d, *J* = 9.0 Hz, 4H, 2′,6′, 2″, 6″-Ar*H*), 7.02 (d, *J* = 9.0 Hz, 4H, 3′, 5′, 3″, 5″ -Ar*H*), 6.99 (s, 1H, COC*H*CO), 3.92(s,6H,ArOCH_3). M.P.: 235-236 °C.UV/vis (CH_2Cl_2): λ_{max} = 412 nm, ε = 83,000 $M^{-1}cm^{-1}$

1,1-Bis(difluoroboron 4′ -allyoxybenzoyl-4″ -methoxybenzoyl methane)-1,1,3,3- tetramethyldisiloxane BF_2dbm Dimer (D1) was prepared according to a published procedure.[1] Difluoroboron 4-allyoxybenzoyl-4′-methoxybenzoyl methane (200 mg, 0.558 µmol), 1,1,3,3-tetramethyldisiloxane (37.5 mg, 0.279 µmol), and chloroplatinic acid (0.05% in isopropanol) were sequentially added to a round-bottom flask containing 100 mL dry toluene. The reaction was refluxed under N_2 at 105 °C for 24 hours. The crude product was purified by silica gel column chromatography (first 1-1 n-hexane-dichromethane, and then dichromethane). The product was dried at 45 °C under vacuum for overnight to give yellow powders (96 mg, 40.0%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, J = 9.0 Hz, 8H, 2′,6′, 2″, 6″ -ArH), 6.96 (d, J = 9.0 Hz, 8H, 3′, 5′, 3″, 5″-ArH), 6.91 (s, 2H, COCHCO), 3.97 (t, J = 9 Hz, 4H, ArOCH_2), 3.91 (s, , 6H, ArOCH_3), 1.82 (m, 4H, ArOCH$_2$ CH_2), 0.65 (t, 4H, J = 6 Hz, ArOCH$_2$ CH$_2$ CH_2Si), 0.12 (s,12H,Si CH_3). M.P.: 202-203 °C. MS (HRMS): m/z calcd for $C_{42}H_{48}O_9B_2F_3Si_2$ $[M-F]^+$ 831.29696, found 831.29688.

BF_2dbm Polymer (P1) was prepared according to a published procedure with limited modifications. Difluoroboron 4,4′-di(allyloxybenzoyl)methane (**1**) (1.00 g, 2.96 mmol), 1,1,3,3-tetramethyldisiloxane (0.398g, 0.52 mL), and chloroplatinic acid (0.05% in isopropanol) were sequentially added to a round-bottom flask containing 100 mL dry toluene. The reaction was refluxed under N_2 at 105 °C for 48 hours. The crude reaction mixture was concentrated in vacuuo, redissolved in CH_2Cl_2 and then precipitated in dry methanol. The precipitates were collected by filtration and dried at 45 °C under vacuum for overnight to give strongly fluorescent yellow powders

(0.835g, 84%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13-7.80 (broad, 4H, 2,6-Ar*H*), 7.04-6.69 (broad, 5H, 3, 5-Ar*H* and COC*H*CO), 4.10-3.79 (broad, 4H, $ArOCH_2$), 1.97-1.69 (broad, 4H, $ArOCH_2CH_2$), 0.78-0.51 (broad, 4H, $ArOCH_2CH_2CH_2$), 0.25-0.02 (broad, 12H, Si-CH_3). GPC: M_n = 11900, PDI = 3.80.

Part II: Supporting Tables for Crystal Data

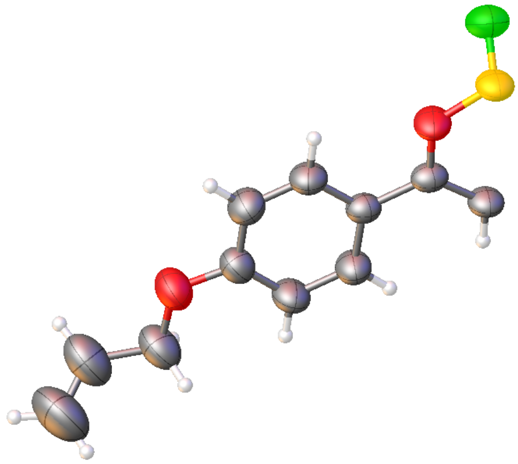


Table S1 Crystal data and structure refinement for 1

Identification code	**1**
Empirical formula	$C_{11}H_{10}BFO_2$
Formula weight	384.17
Temperature	291(2)
Crystal system	Monoclinic
Space group	C2/c
a/Å, b/Å, c/Å	26.2572(17), 7.2012(3), 10.3231(5)
α/°, β/°, γ/°,	90.00, 98.870(5), 90.00
Volume/$Å^3$	1928.58(18)
Z	4
ρ_{calc} mg/mm^3	1.323
m/mm^{-1}	0.102
F(000)	800
Crystal size	0.36 × 0.32 × 0.24
Theta range for data collection	2.94 to 26.37°
Index ranges	$-32 \leq h \leq 32, -8 \leq k \leq 8, -12 \leq l \leq 12$
Reflections collected	8854
Independent reflections	1966[R(int) = 0.0356]
Data/restraints/parameters	1966/1/128
Goodness-of-fit on F^2	1.050
Final R indexes [I>2σ (I)]	$R_1 = 0.0541, wR_2 = 0.1318$
Final R indexes [all data]	$R_1 = 0.0942, wR_2 = 0.1550$
Largest diff. peak/hole	0.178/-0.173

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

Atom	*x*	*y*	*z*	U(eq)
F1	10320.1(5)	5432(18)	1900.6(12)	77.8(5)
O2	9679.3(6)	3185.4(18)	1504.4(14)	64.4(5)
O1	8366.4(7)	-1915(2)	-2625.2(16)	77.3(5)
C11	10000	446(4)	2500	52.7(7)
C1	9343.4(7)	469(2)	459.3(18)	48.5(5)
C10	9686.8(8)	1375(3)	1523.7(19)	48.4(5)
C4	8692.9(8)	-1227(3)	-1583(2)	58.8(6)
C3	8975.6(10)	-2293(3)	-624(2)	65.3(6)
C5	8733.9(9)	690(3)	-1525(2)	65.5(6)
C2	9296.9(9)	-1450(3)	384(2)	60.7(6)
C6	9054.7(9)	1520(3)	-521(2)	58.6(6)
B1	10000	4342(4)	2500	56.6(9)
C7	8336.1(11)	-3888(4)	-2800(3)	84.1(8)
C8	7968.1(13)	-4230(5)	-4010(3)	110.4(11)
C9	7595.1(15)	-5315(6)	-4141(4)	148.8(16)

Table S3 Anisotropic Displacement Parameters (Å^2×10^3) for sxx-3. 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	86.6(10)	61.2(9)	85.4(10)	13.4(6)	12.5(8)	-15.7(7)
O2	86.8(11)	32.4(8)	68.9(10)	1.8(6)	-4.1(9)	1.3(7)
O1	81.2(12)	67.8(11)	76.6(11)	-10(8)	-7.5(9)	-5.5(8)
C11	63.6(18)	31.2(15)	61.8(18)	0	5.2(15)	0
C1	55.2(12)	38(12)	53.3(12)	1.2(9)	11.7(10)	0(9)
C10	56.9(12)	34.1(11)	56.6(12)	0.6(9)	16.8(10)	2(9)
C4	59.5(14)	55.5(14)	60.2(13)	-6.5(11)	5.3(11)	-4.2(10)
C3	79.2(16)	41.6(12)	71.6(15)	-3.3(11)	0.3(13)	-4.9(11)
C5	71.6(15)	54.3(14)	67.3(14)	6.6(11)	0.6(12)	4.8(11)
C2	73.2(15)	41.2(12)	63.7(14)	2.6(10)	-1.8(12)	1.7(10)
C6	71.3(15)	37.7(12)	65.8(14)	2.2(10)	7.2(12)	1.2(10)
B1	69(2)	32(17)	68(2)	0	7.3(19)	0
C7	81(18)	71.6(18)	95(19)	-21.4(15)	-1.7(16)	-7.6(14)
C8	101(2)	106(3)	119(2)	-35(2)	1(2)	-17(2)
C9	119(3)	137(3)	180(4)	-30(3)	-9(3)	-41(3)

Table S4 Bond Lengths for 1.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F1	B1	1.366(2)	C1	C10	1.463(3)
O2	C10	1.304(2)	C4	C3	1.376(3)
O2	B1	1.481(2)	C4	C5	1.385(3)
O1	C4	1.361(2)	C3	C2	1.376(3)
O1	C7	1.433(3)	C5	C6	1.368(3)
C11	C10[1]	1.372(2)	B1	F1	1.366(2)
C11	C10	1.372(2)	B1	O2	1.481(2)
C1	C2	1.389(3)	C7	C8	1.477(4)
C1	C6	1.391(3)	C8	C9[1]	1.243(4)

[1]2-X,+Y,0.5-Z

Table S5 Bond Angles for 1.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C10	O2	B1	123.11(17)	C2	C3	C4	119.8(2)
C4	O1	C7	118.45(18)	C6	C5	C4	120.2(2)
C10[1]	C11	C10	121.7(2)	C3	C2	C1	121.3(2)
C2	C1	C6	117.85(19)	C5	C6	C1	121.11(19)
C2	C1	C10	121.63(18)	F1	B1	F1	109.9(2)
C6	C1	C10	120.52(17)	F1	B1	O2	108.30(8)
O2	C10	C11	120.28(19)	F1	B1	O2	109.42(8)
O2	C10	C1	115.34(17)	F1	B1	O2	109.42(8)
C11	C10	C1	124.38(17)	F1	B1	O2	108.30(8)
O1	C4	C3	124.7(2)	O2	B1	O2	111.5(2)
O1	C4	C5	115.6(2)	O1	C7	C8	106.8(2)
C3	C4	C5	119.7(2)	C9	C8	C7	126.7(4)

[1]2-X,+Y,0.5-Z

Table S6 Torsion Angles for sxx-3.

A	B	C	D	Angle/°
B1	O2	C10	C11	0.3(2)
B1	O2	C10	C1	179.97(13)
C10[1]	C11	C10	O2	-0.13(12)
C10[1]	C11	C10	C1	-179.8(2)
C2	C1	C10	O2	-177.54(18)
C6	C1	C10	O2	3.0(3)
C2	C1	C10	C11	2.2(3)
C6	C1	C10	C1	-177.32(16)

C7	O1	C4	C3	-4.4(3)
C7	O1	C4	C5	175.2(2)
O1	C4	C3	C2	179.6(2)
C5	C4	C3	C2	-0.1(3)
O1	C4	C5	C6	-179.6(2)
C3	C4	C5	C6	0.1(4)
C4	C3	C2	C1	0.0(3)
C6	C1	C2	C3	-0.1(3)
C10	C1	C2	C3	-179.61(19)
C4	C5	C6	C1	-0.2(3)
C2	C1	C6	C5	0.2(3)
C10	C1	C6	C5	179.71(19)
C10	O2	B1	F1[1]	-120.6(2)
C10	O2	B1	F1	119.7(2)
C10	O2	B1	O2[1]	-0.14(13)
C4	O1	C7	C8	-178.5(2)
O1	C7	C8	C9	-129.8(4)

[1]2-X,+Y,0.5-Z

Table S7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 1.

Atom	*x*	*y*	*z*	U(eq)
H11	10000	-845	2500	63
H3	8949	-3581	-657	78
H5	8543	1415	-2170	79
H2	9487	-2180	1028	73
H6	9080	2808	-493	70
H7A	8216	-4472	-2056	101
H7B	8672	-4392	-2884	101
H8	8021	-3566	-4751	132
H9A	7526	-6012	-3429	179
H9B	7385	-5429	-4949	179

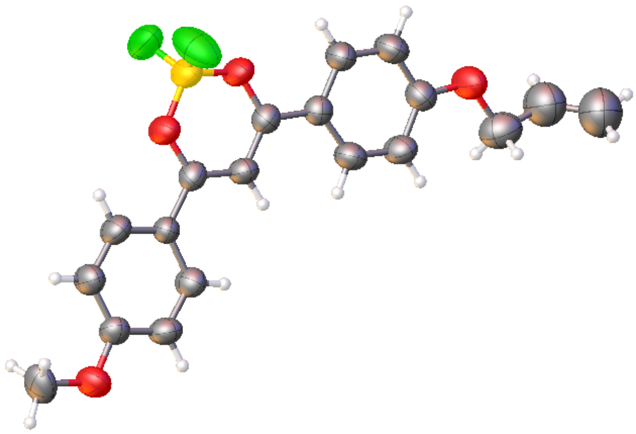


Table S8 Crystal data and structure refinement for Complex 2

Identification code	**2**
Empirical formula	$C_{19}H_{17}BF_2O_4$
Formula weight	358.14
Temperature	291(2)
Crystal system	Monoclinic
Space group	Pc
a/Å, b/Å, c/Å	10.6842(7), 7.2837(4), 12.8423(7)
α/°, β/°, γ/°,	90.00, 120.355(7), 90.00
Volume/Å^3	862.39(9)
Z	2
ρ_{calc} mg/mm^3	1.379
m/mm^{-1}	0.921
F(000)	372
Crystal size	0.36 × 0.30 × 0.20
Theta range for data collection	4.80 to 62.78°
Index ranges	$-12 \le h \le 12$, $-7 \le k \le 8$, $-14 \le l \le 9$
Reflections collected	3520
Independent reflections	1740[R(int) = 0.0465]
Data/restraints/parameters	1740/25/236
Goodness-of-fit on F^2	1.009
Final R indexes [I>2σ (I)]	R_1 = 0.0727, wR_2 = 0.1812
Final R indexes [all data]	R_1 = 0.0807, wR_2 = 0.1899
Largest diff. peak/hole	0.550/-0.324

Table S9 Atomic Coordinates (Å×10^4) and Equivalent Isotropic Displacement

Parameters ($Å^2×10^3$) for sxx-1. U_{eq} is defined as 1/3 of of the trace of the orthogonalized U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F1	5710(7)	10544(8)	1680(5)	118(2)
F2	3678(6)	10907(6)	1767(4)	101.8(16)
O1	5243(6)	8563(6)	2846(4)	74.1(14)
O2	3815(6)	8530(5)	650(4)	73.4(14)
O3	776(7)	3343(7)	-3845(5)	88.7(18)
O4	8245(6)	3502(7)	7405(4)	78.6(15)
C1	5991(7)	5908(9)	4037(5)	52.5(14)
C2	6724(8)	7002(9)	5067(7)	68(2)
C3	7465(9)	6255(9)	6207(6)	69.7(19)
C4	7537(7)	4386(8)	6342(6)	58.3(15)
C5	6809(8)	3289(10)	5312(7)	66.4(19)
C6	6053(8)	4018(10)	4193(6)	62.2(17)
C7	5252(7)	6784(9)	2854(6)	55.6(15)
C8	4523(9)	5822(7)	1775(7)	58.3(13)
C9	3829(7)	6718(8)	681(6)	55.8(15)
C10	3035(7)	5818(10)	-477(6)	56.9(16)
C11	2430(8)	6807(10)	-1560(6)	67.1(19)
C12	1687(10)	5929(11)	-2667(7)	78(2)
C13	1508(8)	4036(11)	-2726(6)	66.3(18)
C14	2129(8)	3025(9)	-1668(6)	69.3(19)
C15	2878(8)	3920(10)	-581(6)	65.3(18)
C16	8972(9)	4580(12)	8490(6)	83(2)
C17	529(10)	1372(11)	-3948(9)	97(2)
C18	-466(15)	1055(15)	-5220(10)	130(3)
B1	4635(13)	9642(9)	1738(9)	70.6(19)
C19	-187(17)	-27(18)	-5914(12)	148(4)

Table S10 Anisotropic Displacement Parameters ($Å^2×10^3$) for sxx-1. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka×b×U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F1	130(4)	130(5)	79(3)	8(3)	42(3)	-57(4)
F2	137(4)	67(2)	75(3)	-4(2)	34(3)	27(3)
O1	105(4)	47(3)	53(3)	-3(2)	28(3)	-1(3)
O2	106(4)	42(2)	57(3)	-2(2)	30(3)	2(3)
O3	121(5)	65(3)	53(3)	-5(3)	24(3)	-7(3)
O4	97(4)	69(3)	51(3)	6(2)	23(3)	4(3)

C1	70(4)	43(3)	45(3)	0(3)	29(3)	3(3)
C2	90(5)	43(3)	64(5)	-4(3)	34(4)	0(3)
C3	88(5)	57(4)	49(4)	-3(3)	23(4)	1(4)
C4	63(4)	52(3)	53(3)	4(3)	23(3)	8(3)
C5	80(5)	47(3)	63(4)	8(3)	30(4)	3(3)
C6	73(4)	50(3)	55(4)	-4(3)	26(3)	-7(3)
C7	67(4)	45(3)	57(4)	-6(3)	33(3)	-5(3)
C8	74(3)	43(2)	52(3)	4(4)	27(3)	4(4)
C9	64(3)	48(3)	57(4)	-3(3)	31(3)	-1(3)
C10	65(4)	53(3)	53(4)	-2(3)	30(3)	-1(3)
C11	91(5)	53(4)	54(4)	2(3)	34(4)	0(4)
C12	104(6)	67(4)	55(4)	11(4)	34(4)	4(4)
C13	80(4)	62(4)	54(4)	1(3)	33(4)	-2(4)
C14	86(5)	48(3)	63(5)	2(3)	30(4)	-5(3)
C15	81(5)	56(4)	54(4)	9(3)	30(4)	3(3)
C16	81(5)	100(6)	47(4)	-11(4)	17(3)	2(4)
C17	99(4)	77(4)	103(3)	6(3)	42(3)	-2(3)
C18	154(6)	115(5)	104(4)	-7(4)	54(3)	-1(4)
B1	98(5)	47(3)	58(4)	-3(4)	32(4)	-3(5)
C19	179(7)	138(6)	126(5)	-11(4)	77(5)	7(5)

Table S11 Bond Lengths for 2.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F1	B1	1.358(12)	C3	C4	1.370(9)
F2	B1	1.391(11)	C4	C5	1.398(10)
O1	C7	1.296(8)	C5	C6	1.351(10)
O1	B1	1.459(10)	C7	C8	1.389(9)
O2	C9	1.320(7)	C8	C9	1.377(9)
O2	B1	1.463(10)	C9	C10	1.444(9)
O3	C13	1.339(9)	C10	C15	1.391(9)
O3	C17	1.453(9)	C10	C11	1.401(10)
O4	C4	1.344(8)	C11	C12	1.385(11)
O4	C16	1.438(8)	C12	C13	1.389(10)
C1	C6	1.388(9)	C13	C14	1.385(10)
C1	C2	1.397(9)	C14	C15	1.372(10)
C1	C7	1.459(9)	C17	C18	1.448(12)
C2	C3	1.376(10)	C18	C19	1.332(9)

Table S12 Bond Angles for 2.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C7	O1	B1	123.0(6)	C8	C9	C10	124.7(6)
C9	O2	B1	122.2(6)	C15	C10	C11	116.2(6)
C13	O3	C17	116.8(7)	C15	C10	C9	122.0(6)
C4	O4	C16	118.3(5)	C11	C10	C9	121.7(6)
C6	C1	C2	117.8(6)	C12	C11	C10	121.3(7)
C6	C1	C7	123.0(6)	C11	C12	C13	120.4(7)
C2	C1	C7	119.1(6)	O3	C13	C14	125.6(7)
C3	C2	C1	121.8(6)	O3	C13	C12	115.0(7)
C4	C3	C2	119.6(7)	C14	C13	C12	119.3(7)
O4	C4	C3	124.8(6)	C15	C14	C13	119.3(7)
O4	C4	C5	116.5(6)	C14	C15	C10	123.4(7)
C3	C4	C5	118.6(6)	C18	C17	O3	104.9(8)
C6	C5	C4	122.0(7)	C19	C18	C17	124.4(13)
C5	C6	C1	120.1(7)	F1	B1	F2	109.5(6)
O1	C7	C8	119.9(6)	F1	B1	O1	110.0(8)
O1	C7	C1	116.4(6)	F2	B1	O1	107.6(7)
C8	C7	C1	123.7(6)	F1	B1	O2	109.3(8)
C9	C8	C7	121.4(5)	F2	B1	O2	107.4(8)
O2	C9	C8	119.8(6)	O1	B1	O2	113.0(5)
O2	C9	C10	115.5(6)				

Table S13 Torsion Angles for 2.

A	B	C	D	Angle/°
C6	C1	C2	C3	-1.2(11)
C7	C1	C2	C3	-178.7(7)
C1	C2	C3	C4	2.4(12)
C16	O4	C4	C3	0.8(12)
C16	O4	C4	C5	-178.2(6)
C2	C3	C4	O4	179.0(7)
C2	C3	C4	C5	-2.0(12)
O4	C4	C5	C6	179.7(7)
C3	C4	C5	C6	0.6(11)
C4	C5	C6	C1	0.5(11)
C2	C1	C6	C5	-0.3(11)
C7	C1	C6	C5	177.1(7)
B1	O1	C7	C8	-7.2(11)
B1	O1	C7	C1	175.8(7)
C6	C1	C7	O1	178.0(7)

C2	C1	C7	O1	-4.7(10)
C6	C1	C7	C8	1.0(11)
C2	C1	C7	C8	178.4(6)
O1	C7	C8	C9	2.5(12)
C1	C7	C8	C9	179.3(6)
B1	O2	C9	C8	6.0(11)
B1	O2	C9	C10	-176.4(8)
C7	C8	C9	O2	-1.9(12)
C7	C8	C9	C10	-179.2(6)
O2	C9	C10	C15	-176.0(7)
C8	C9	C10	C15	1.5(11)
O2	C9	C10	C11	6.6(10)
C8	C9	C10	C11	-175.9(7)
C15	C10	C11	C12	1.6(11)
C9	C10	C11	C12	179.1(7)
C10	C11	C12	C13	0.9(12)
C17	O3	C13	C14	4.6(12)
C17	O3	C13	C12	-178.3(8)
C11	C12	C13	O3	-179.8(8)
C11	C12	C13	C14	-2.5(12)
O3	C13	C14	C15	178.5(8)
C12	C13	C14	C15	1.6(11)
C13	C14	C15	C10	1.0(11)
C11	C10	C15	C14	-2.6(11)
C9	C10	C15	C14	179.9(7)
C13	O3	C17	C18	171.0(8)
O3	C17	C18	C19	120.8(13)
C7	O1	B1	F1	-112.0(8)
C7	O1	B1	F2	128.7(7)
C7	O1	B1	O2	10.4(13)
C9	O2	B1	F1	113.1(8)
C9	O2	B1	F2	-128.2(7)
C9	O2	B1	O1	-9.7(12)

Table S14 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2.

Atom	*x*	*y*	*z*	U(eq)
H2	6710	8270	4980	82
H3	7915	7014	6880	84
H5	6846	2019	5399	80
H6	5573	3251	3526	75
H8	4504	4546	1791	70
H11	2529	8077	-1536	80
H12	1305	6612	-3375	94
H14	2040	1754	-1693	83
H15	3303	3221	121	78
H16A	9706	5319	8475	124
H16B	9413	3780	9178	124
H16C	8282	5362	8542	124
H17A	1430	713	-3677	117
H17B	106	980	-3471	117
H18	-1359	1647	-5576	156
H19A	697	-639	-5587	178
H19B	-875	-171	-6727	178

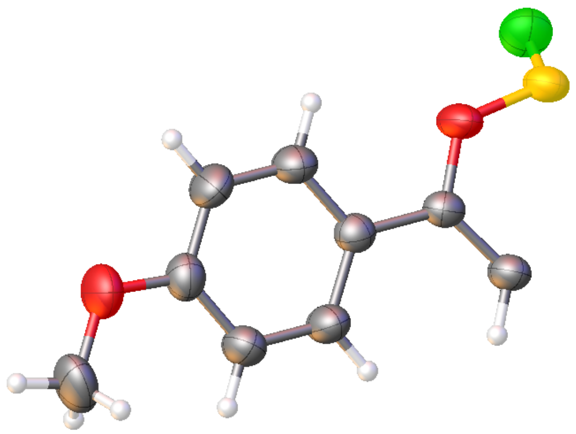


Table S15 Crystal data and structure refinement for 3

Identification code	**3**
Empirical formula	$C_9H_8BFO_2$
Formula weight	332.10
Temperature	291(2)
Crystal system	Monoclinic
Space group	C2/c
a/Å, b/Å, c/Å	21.1856(12), 7.1155(4), 10.3692(6)
α/°, β/°, γ/°,	90.00, 96.363(5), 90.00
Volume/Å^3	1553.49(15)
Z	4
ρ_{calc} mg/mm^3	1.420
m/mm^{-1}	0.114
F(000)	688
Crystal size	0.45 × 0.31 × 0.30
Theta range for data collection	3.02 to 26.35°
Index ranges	$-26 \le h \le 26$, $-8 \le k \le 8$, $-10 \le l \le 12$
Reflections collected	4077
Independent reflections	1579[R(int) = 0.0233]
Data/restraints/parameters	1579/0/111
Goodness-of-fit on F^2	1.047
Final R indexes [I>2σ (I)]	R_1 = 0.0454, wR_2 = 0.1163
Final R indexes [all data]	R_1 = 0.0642, wR_2 = 0.1323
Largest diff. peak/hole	0.143/-0.182

Table S16 Atomic Coordinates (Å×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for sxx02132. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F1	389.1(5)	5456.4(14)	3320.1(9)	61.3(4)
O1	399.4(6)	3178.5(15)	1736.4(10)	52.8(4)
O2	2011.6(6)	-1973.4(18)	-1519.3(12)	67.4(4)
C1	815.5(7)	435(2)	918.7(13)	38.8(4)
C8	0	397(3)	2500	42.3(5)

C5	1262.2(8)	-2360(2)	58.2(16)	49.8(4)
C7	390.6(7)	1346(2)	1745.6(12)	37.3(4)
C4	1614.1(7)	-1276(3)	-697.9(14)	47.2(4)
C6	866.1(8)	-1506(2)	856.3(15)	48.5(4)
C3	1567.4(8)	662(3)	-647.2(17)	56.1(5)
C2	1174.8(8)	1506(2)	146.5(15)	49.1(4)
C9	2030(10)	-3958(3)	-1705(2)	73(6)
B1	0	4344(3)	2500	45.3(6)

Table S17 Anisotropic Displacement Parameters (Å^2×10^3) for sxx02132. 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	64.1(7)	52.7(7)	67.4(7)	-12.4(4)	8.5(5)	-9.3(5)
O1	67.9(8)	28.4(6)	67.3(8)	1.1(5)	29.7(6)	-0.9(5)
O2	66.8(8)	65.8(9)	76.5(9)	-3.8(6)	38.3(6)	7.2(7)
C1	41.4(8)	36.7(9)	38.6(8)	1.8(6)	5.7(6)	-0.2(7)
C8	50.8(13)	30.2(12)	47.6(12)	0	12.8(9)	0
C5	56.4(11)	36.8(9)	58.7(10)	-1.9(7)	17.5(8)	0.7(8)
C7	41.6(8)	30.6(8)	39.3(8)	1.3(6)	3.6(6)	0.1(6)
C4	42.7(9)	52.4(11)	48(9)	-1(7)	12(6)	3.6(8)
C6	57(10)	36.2(9)	55.8(9)	1.3(7)	21.7(7)	-3.3(8)
C3	59.5(11)	50.3(11)	63.3(11)	10.3(8)	28(8)	-1.3(9)
C2	56.8(10)	36.4(9)	56.2(9)	6.3(7)	15.9(7)	0(8)
C9	65.2(12)	68.6(14)	89.6(14)	-22(11)	28.1(10)	11.3(11)
B1	55.2(16)	29.4(13)	52.4(14)	0	11.3(11)	0

Table S18 Bond Lengths for 3.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F1	B1	1.3688(17)	C8	C7	1.3771(17)
O1	C7	1.3038(18)	C8	C7^1	1.3771(17)
O1	B1	1.4762(17)	C5	C4	1.377(2)
O2	C4	1.3565(19)	C5	C6	1.383(2)
O2	C9	1.426(2)	C4	C3	1.384(2)
C1	C6	1.387(2)	C3	C2	1.372(2)
C1	C2	1.391(2)	B1	F1	1.3688(17)
C1	C7	1.462(2)	B1	O1^{11}	1.4762(17)

[1]-X,+Y,0.5-Z

Table S19 Bond Angles for 3.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C7	O1	B1	123.25(12)	O2	C4	C3	116.13(14)
C4	O2	C9	118.38(14)	C5	C4	C3	119.42(15)
C6	C1	C2	117.92(14)	C5	C6	C1	121.36(15)
C6	C1	C7	121.65(13)	C2	C3	C4	120.63(15)
C2	C1	C7	120.42(14)	C3	C2	C1	120.83(15)
C7	C8	C7[1]	121.26(19)	F1	B1	F1	109.35(19)
C4	C5	C6	119.83(16)	F1	B1	O1	109.46(6)
O1	C7	C8	120.30(13)	F1	B1	O1	108.45(6)
O1	C7	C1	115.40(12)	F1	B1	O1	108.45(6)
C8	C7	C1	124.30(14)	F1	B1	O1	109.46(6)
O2	C4	C5	124.45(16)	O1[1]	B1	O1[1]	111.64(17)

[1]-X,+Y,0.5-Z

Table S20 Torsion Angles for 3.

A	B	C	D	Angle/°
B1	O1	C7	C8	-0.57(17)
B1	O1	C7	C1	179.50(10)
C7[1]	C8	C7	O1	0.29(9)
C7[1]	C8	C7	C1	-179.79(14)
C6	C1	C7	O1	178.48(13)
C2	C1	C7	O1	-2.75(19)
C6	C1	C7	C8	-1.4(2)
C2	C1	C7	C8	177.33(11)
C9	O2	C4	C5	5.7(3)
C9	O2	C4	C3	-173.89(15)
C6	C5	C4	O2	-179.42(14)
C6	C5	C4	C3	0.1(2)
C4	C5	C6	C1	-0.2(2)
C2	C1	C6	C5	0.3(2)
C7	C1	C6	C5	179.07(14)
O2	C4	C3	C2	179.55(16)
C5	C4	C3	C2	0.0(3)
C4	C3	C2	C1	0.1(3)
C6	C1	C2	C3	-0.2(2)
C7	C1	C2	C3	-178.99(15)
C7	O1	B1	F1	120.97(15)

C7	O1	B1	F1[1]	-119.80(15)
C7	O1	B1	O1[1]	0.29(9)

[1]-X,+Y,0.5-Z

Table S21 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3.

Atom	*x*	*y*	*z*	U(eq)
H8	0	-910	2500	51
H5	1291	-3663	32	60
H6	629	-2248	1362	58
H3	1804	1400	-1156	67
H2	1148	2810	169	59
H9B	2170	-4559	-895	110
H9C	2319	-4249	-2328	110
H9A	1613	-4402	-2018	110

Part III. Supporting Figures.

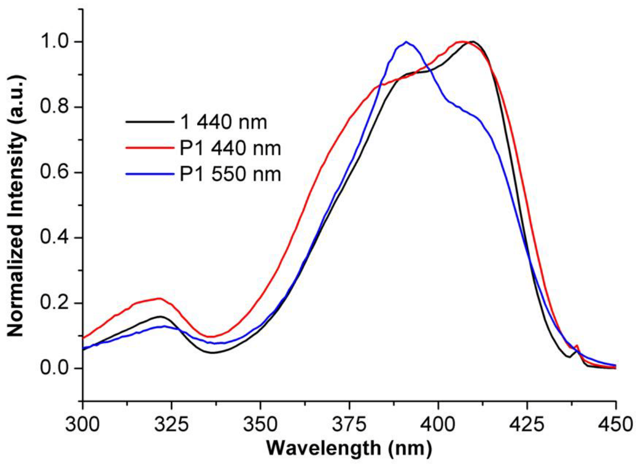


Fig. S1. Excitation spectra of **1** and **P1** monitored at different wavelengths in CH_2Cl_2.

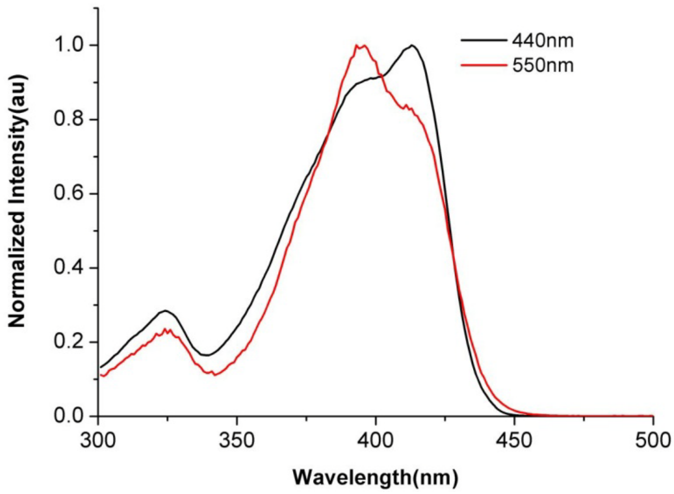


Fig. S2. Excitation spectra of **D1** monitored at different wavelengths in CH_2Cl_2.

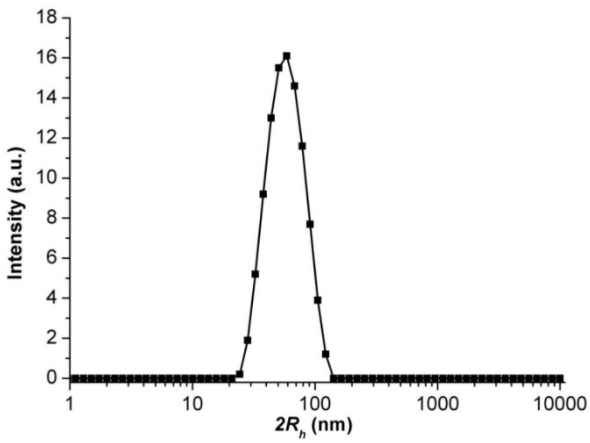
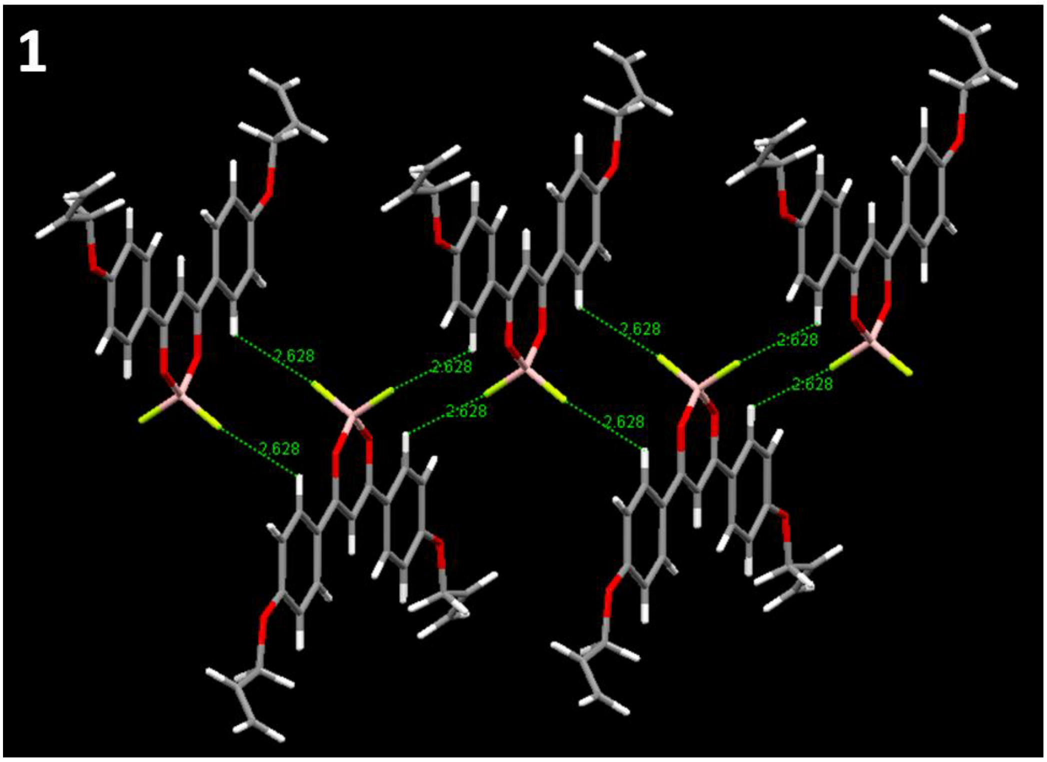


Fig. S3 Dynamic light scattering data of polymer nanoparticles (PNPs) fabricated from polymer **P1** in acetone (1×10^{-3}M) in Milli Q water.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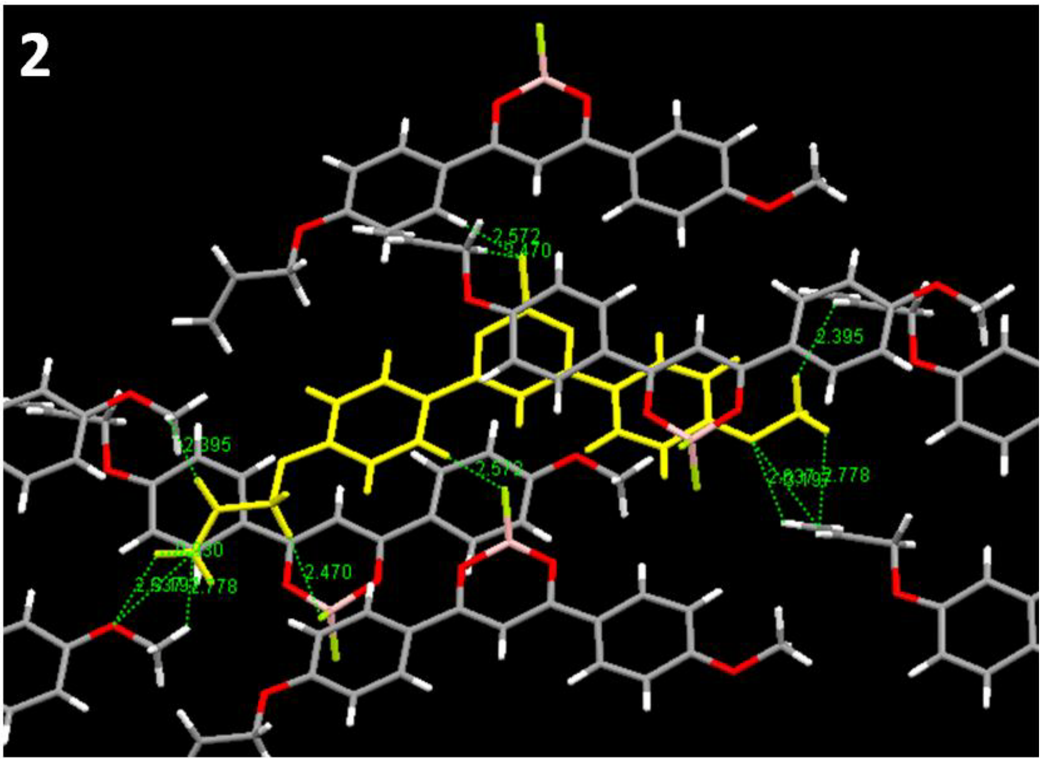
2.628
2.628
2.628
2.628
2.628
2.628
2.628


2
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2.395
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2.778

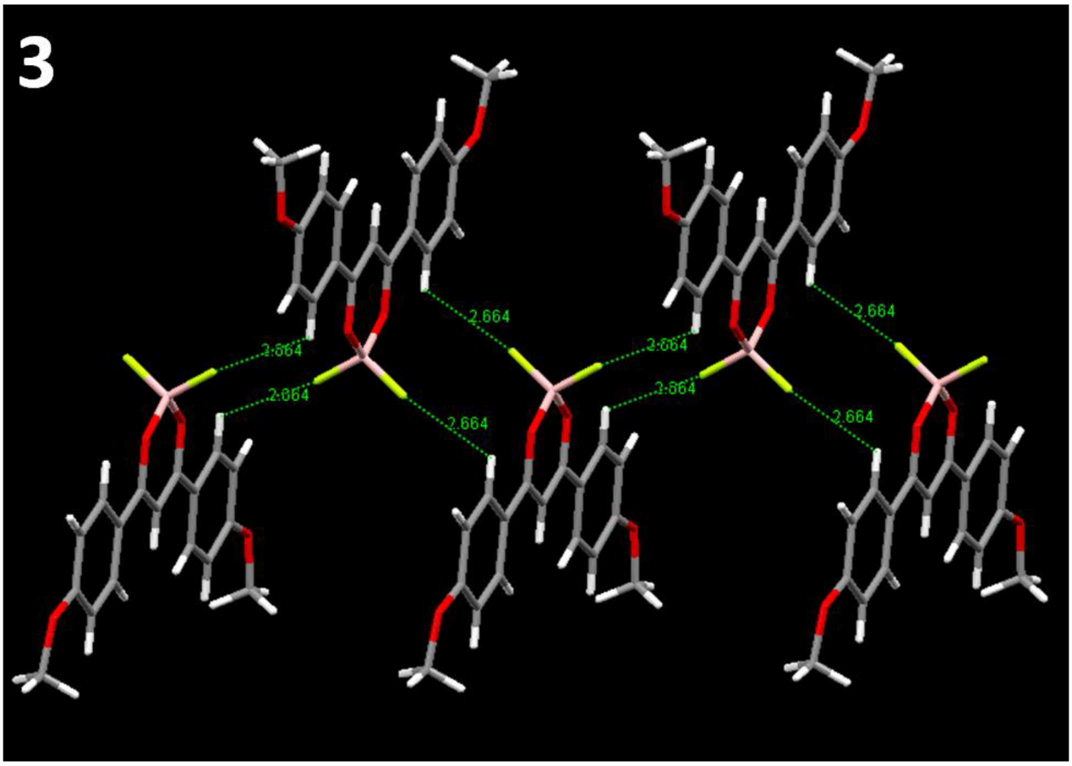
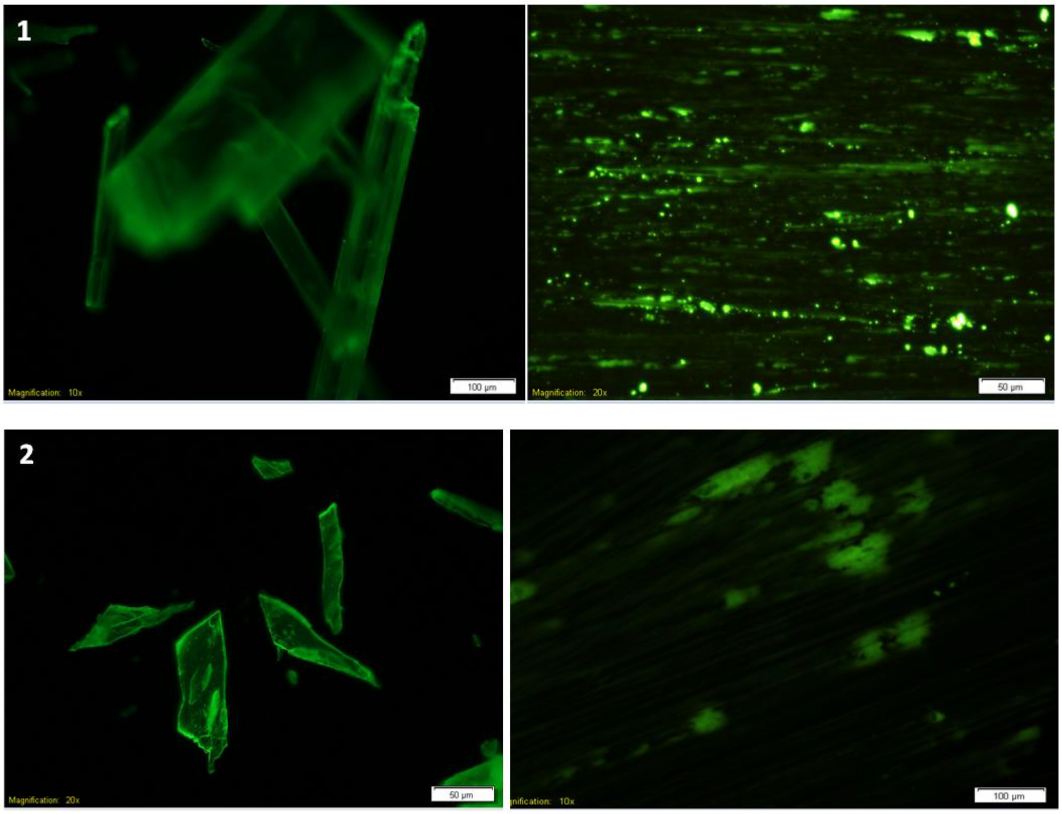


Fig. S4 Weak interactions in crystals of boron complexes **1-3** represented with green dotted lines and measured distances (Å).



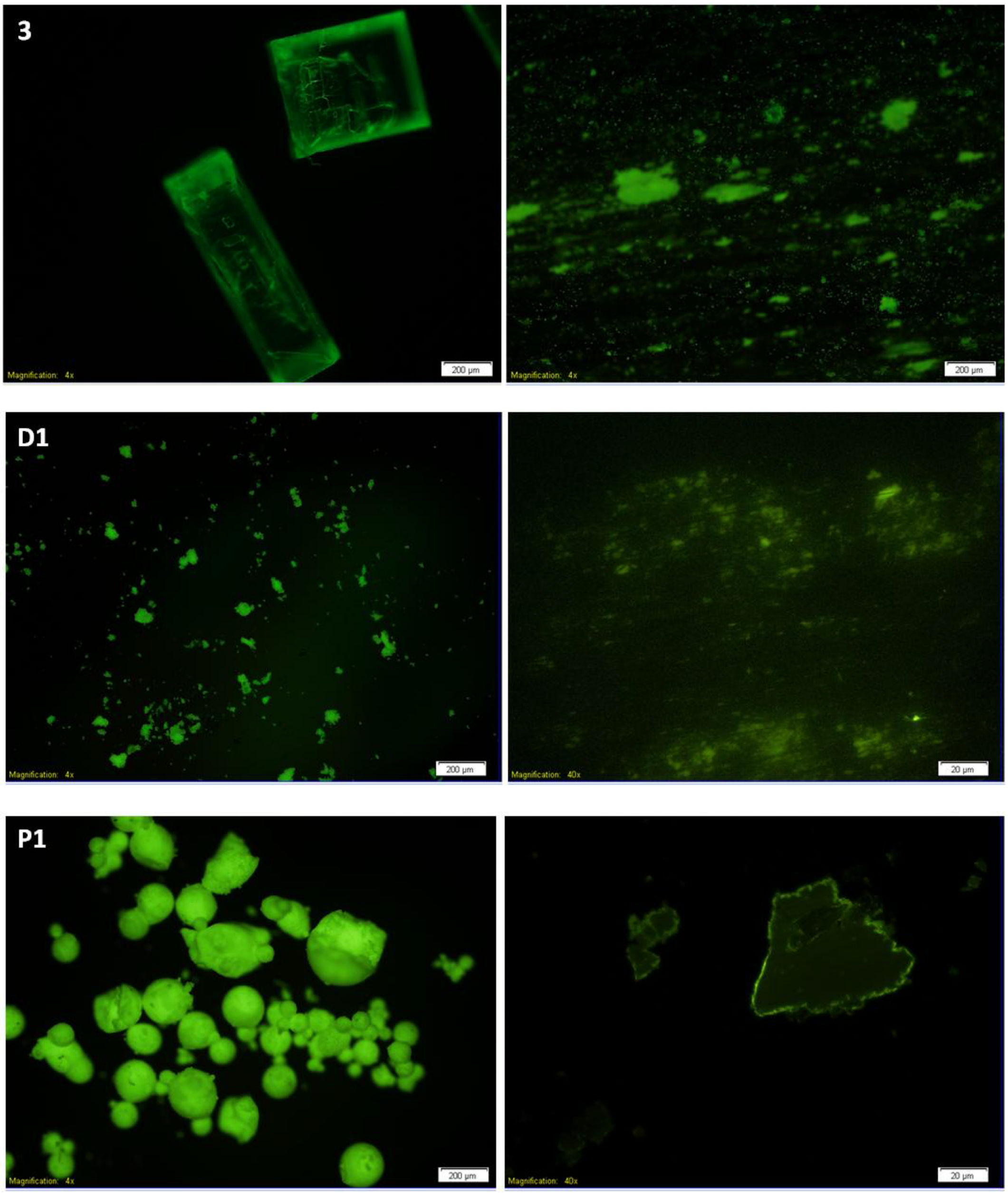
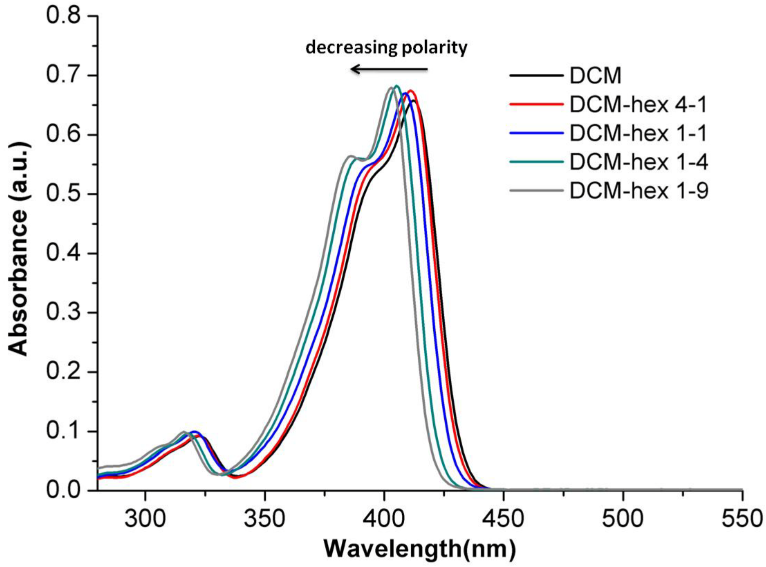


Fig. S5 False-colored fluorescence micrographs of crystals of **1-3**, **D1**, and **P1** solids before (left) and after (right) mechanical shear force (λ_{ex} = 405 nm).



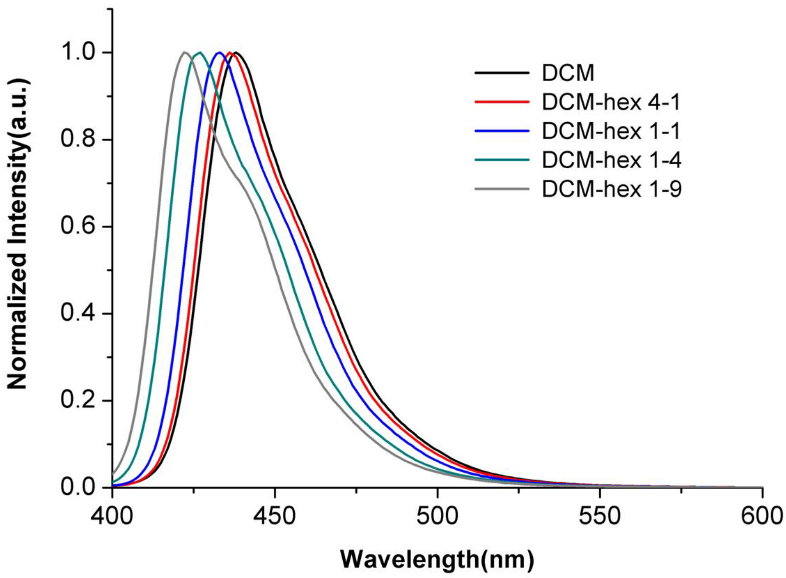
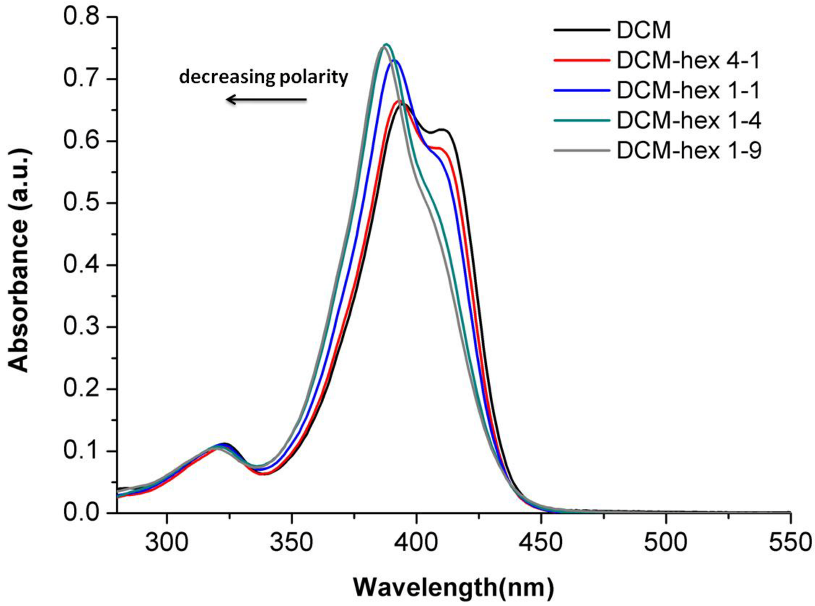


Fig. S6 Absorption (top) and normalized emission (bottom) spectra of **1** in a mixture of CH_2Cl_2 and n-hexane with different CH_2Cl_2 content percentages: 100%, 90%, 80%, 50%, 20%, and 10% at a fixed concentration of 1×10^{-5} M.



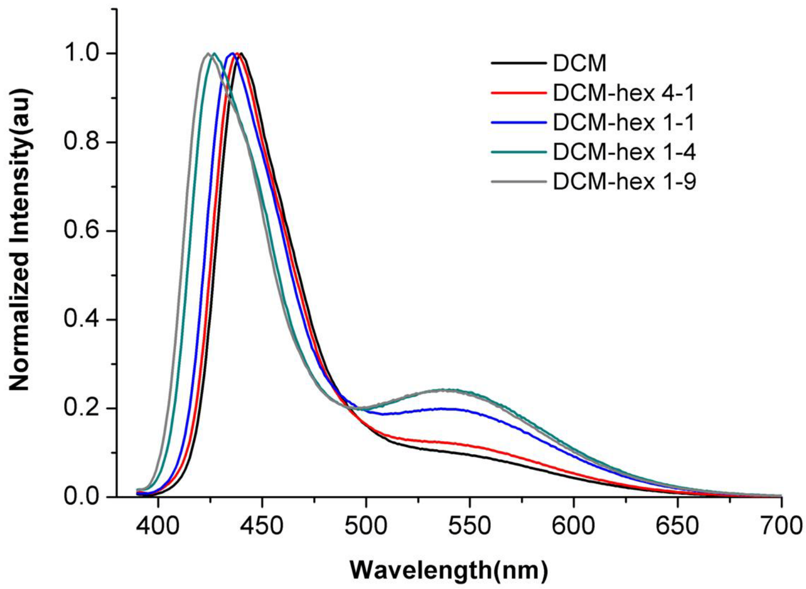
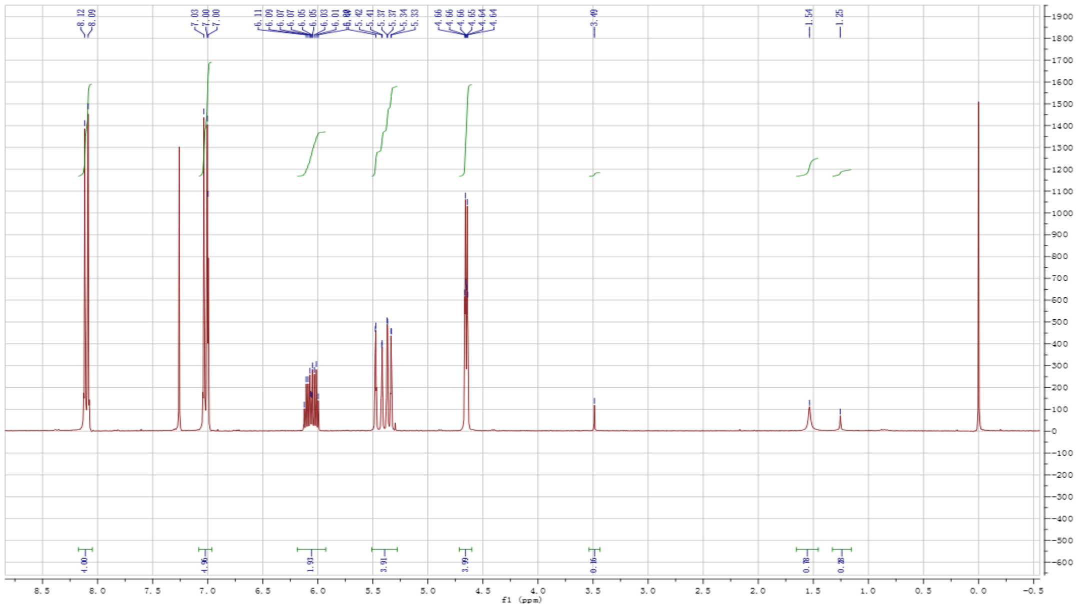
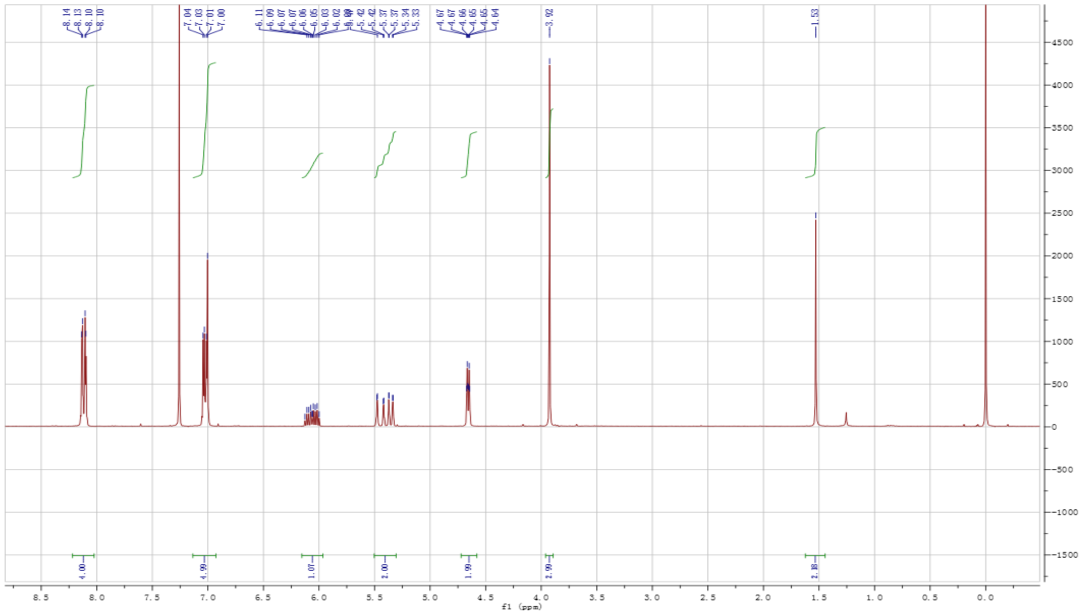


Fig. S7 Absorption (top) and normalized emission (bottom) spectra of **P1** in a mixture of CH_2Cl_2 and n-hexane with different CH_2Cl_2 content percentages: 100%, 90%, 80%, 50%, 20%, and 10% at a fixed BF_2dbm chromophore concentration of 1×10^{-5} M.

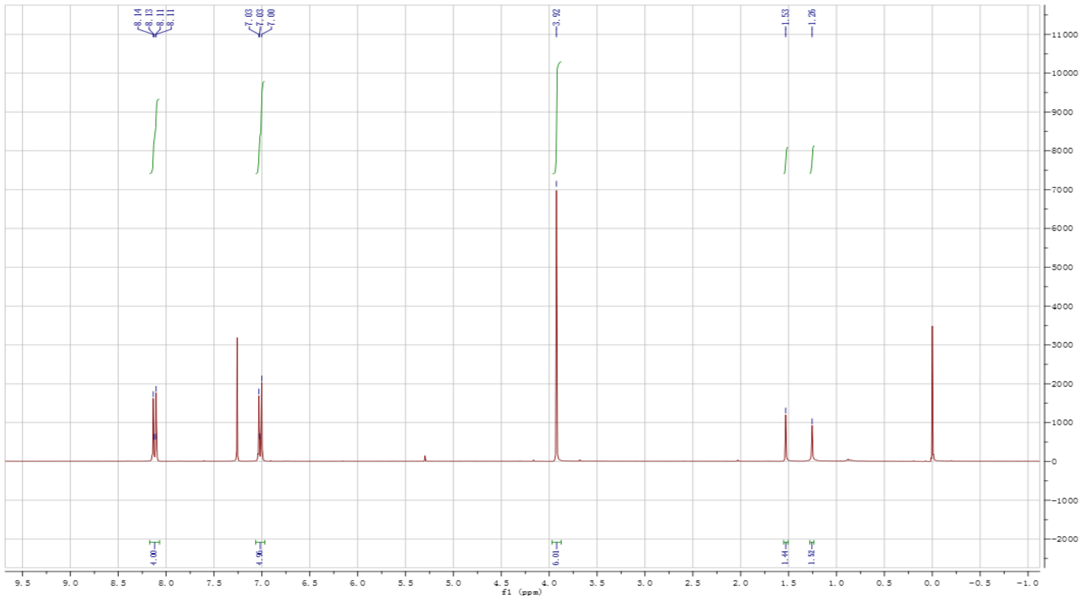
Part IV ^{1}H-NMR and HRMS Spectra for **1-3** and **D1**.



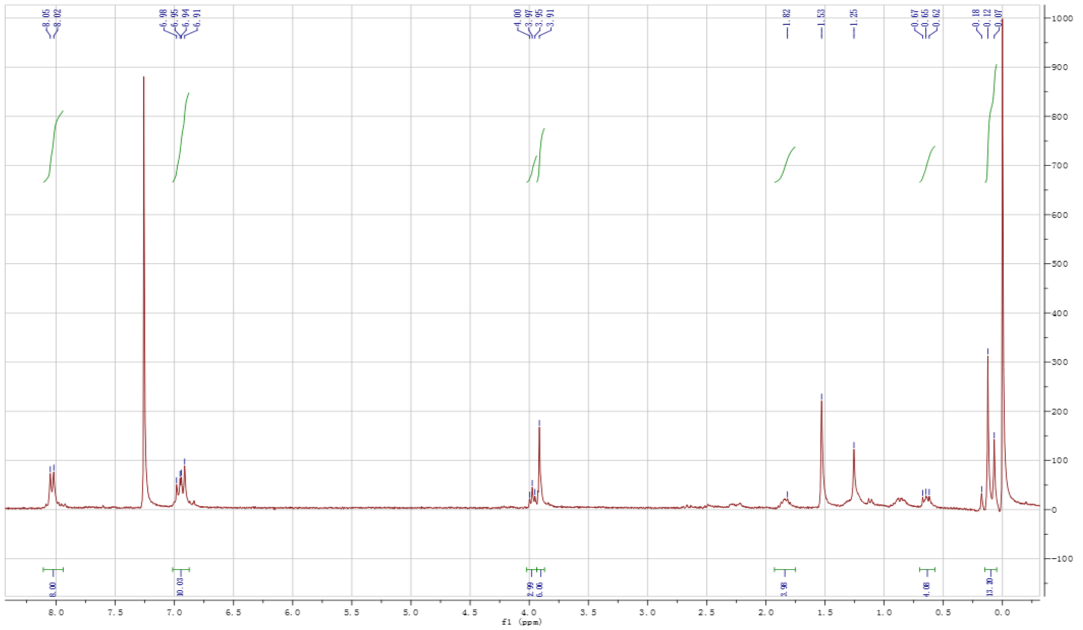
^{1}H-NMR spectrum of **1** in $CDCl_3$



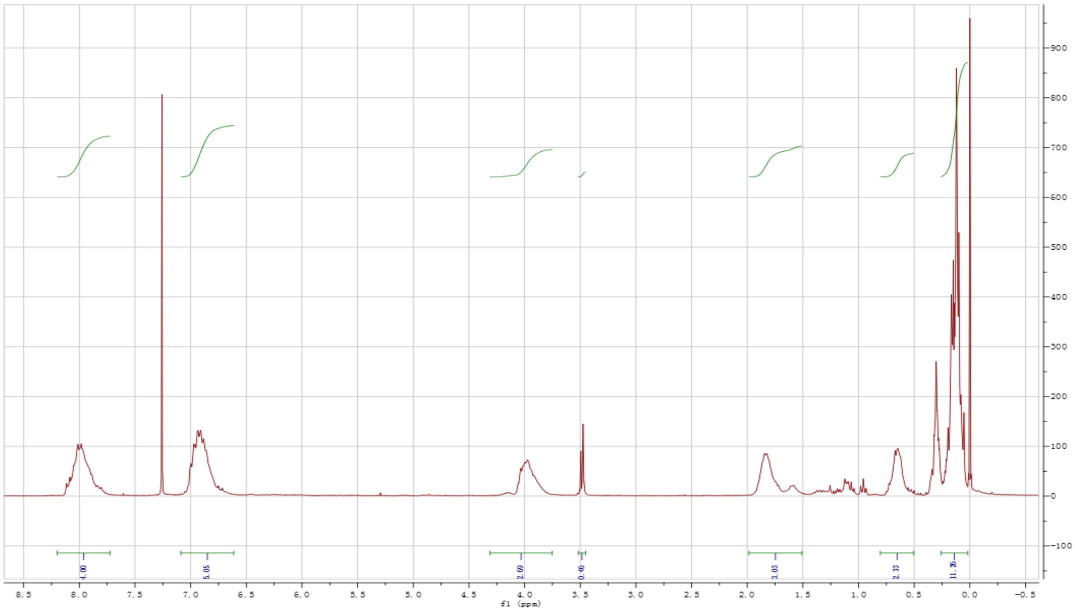
^{1}H-NMR spectrum of **2** in $CDCl_3$



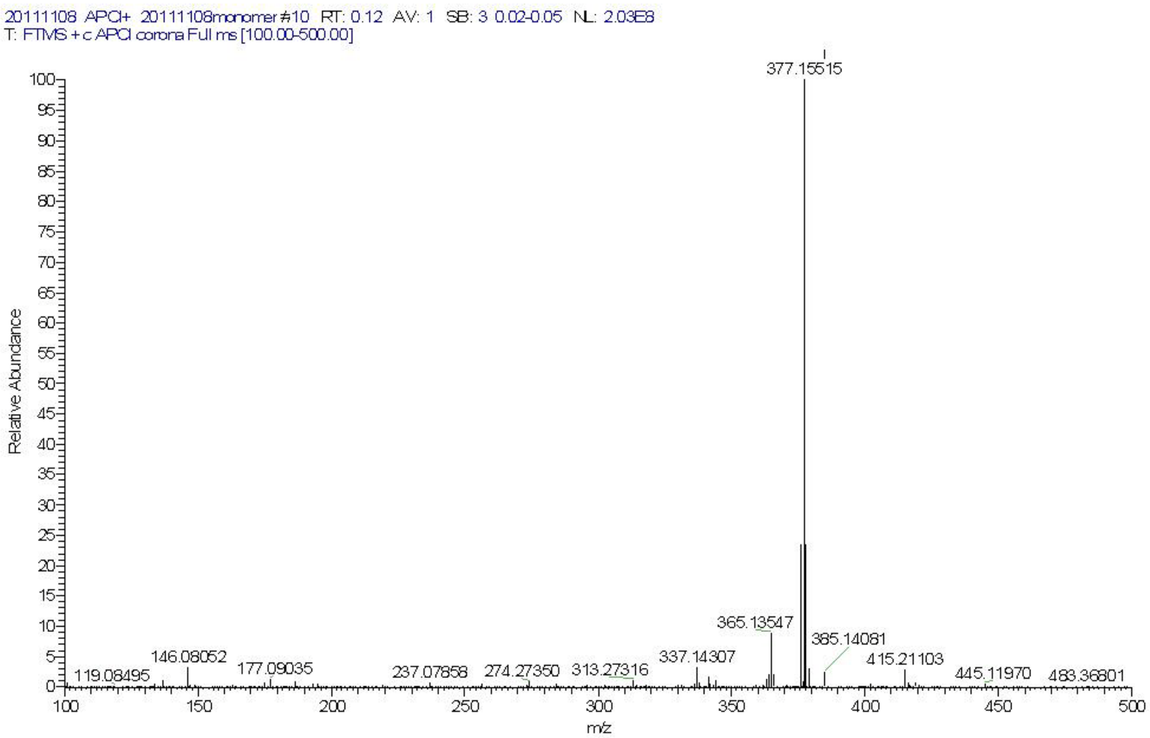
[1]H-NMR spectrum of **3** in $CDCl_3$



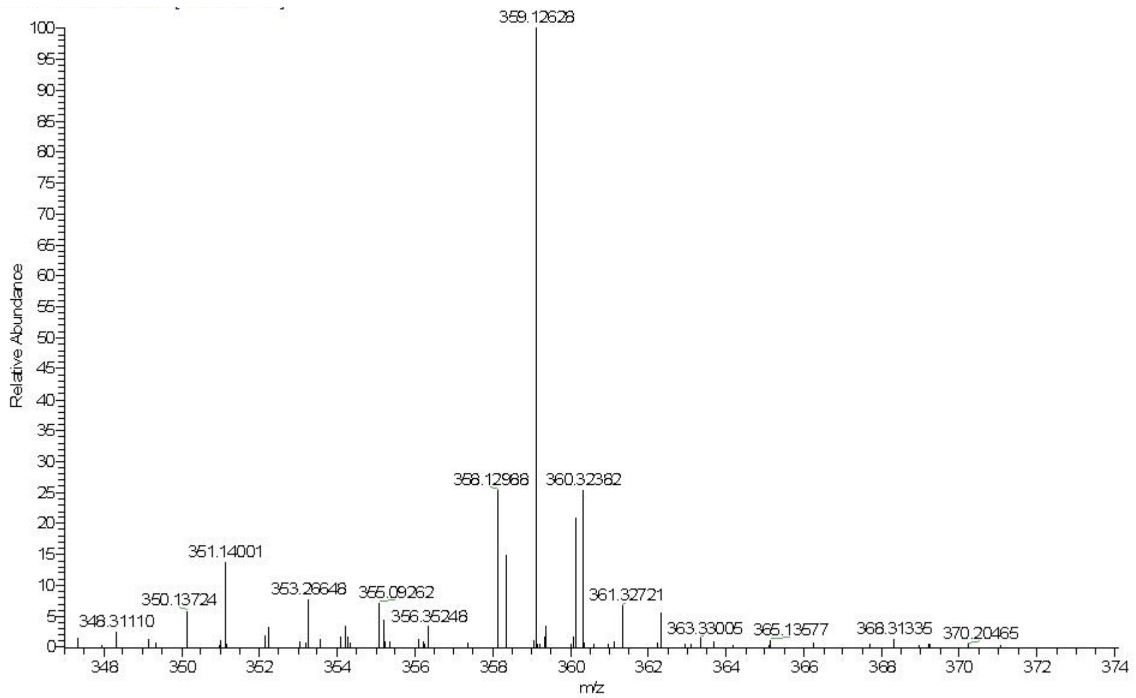
[1]H-NMR spectrum of **D1** in $CDCl_3$



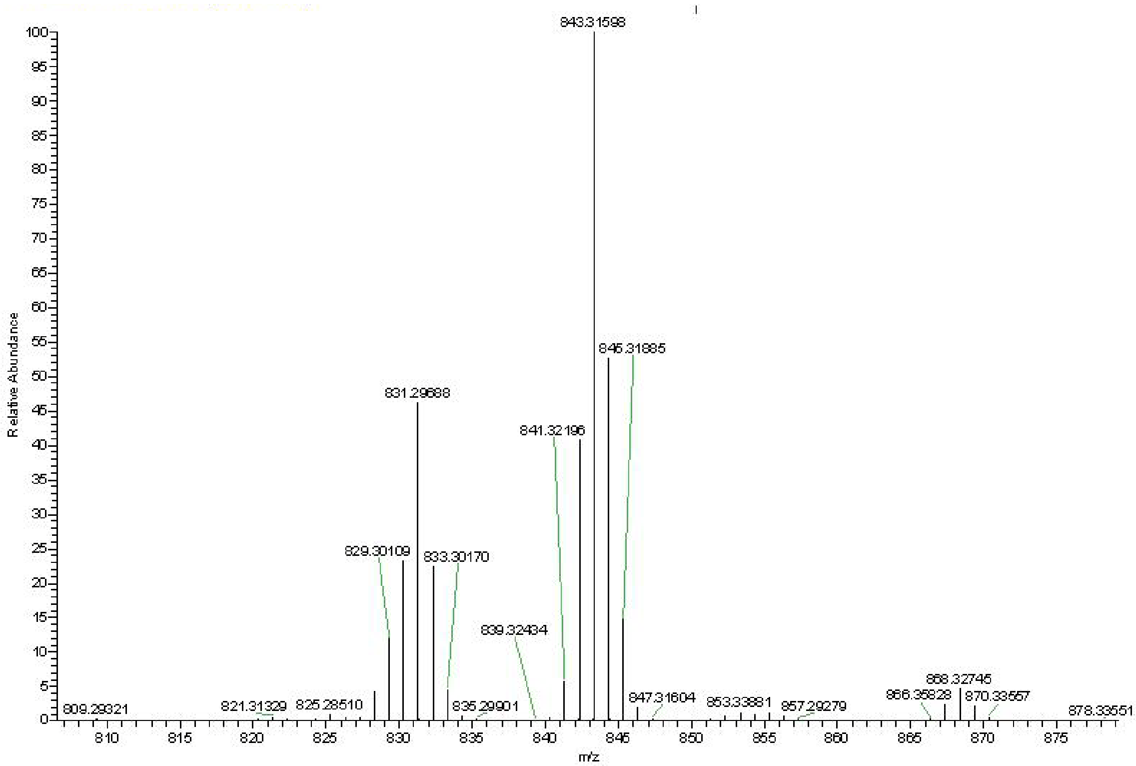
^{1}H-NMR spectrum of **P1** in $CDCl_3$



HRMS spectrum of **1** in CH_3OH.



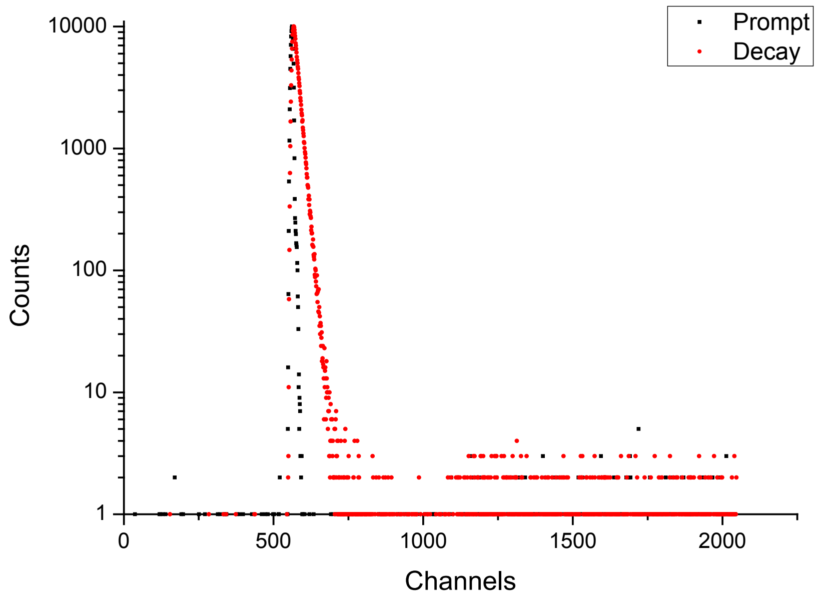
HRMS spectrum of **2** in CH_3OH.



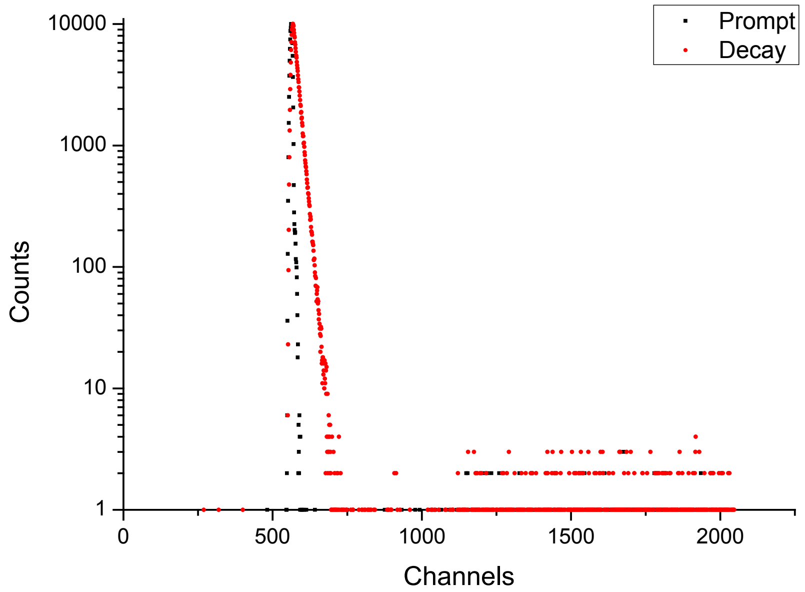
HRMS spectrum of **D1** in CH_3OH.

m/z	Intensity	Relative	Theo. Mass	Delta (mmu)	Composition
829.3011	1522499	11.97	829.3013	-0.21	C42 H49 O10 B2 F2 Si2
830.3004	2957834	23.25	830.3055	-5.18	C43 H48 O7 B2 F4 Si2
831.2969	5883592	46.24	831.297	-0.08	C42 H48 O9 B2 F3 Si2
832.2986	2855155	22.44	832.3028	-4.2	C43 H46 O9 B2 F4 Si
833.3017	584036.1	4.59	833.2966	5.08	C40 H50 O10 B F4 Si2
841.322	721363.3	5.67	841.3217	0.27	C42 H53 O10 B F3 Si2
842.319	5182476	40.73	842.3124	6.58	C43 H53 O10 F3 Si2
843.316	12724130	100	843.3169	-0.97	C43 H51 O10 B2 F2 Si2
844.3178	6705020	52.7	844.3248	-7.02	C43 H52 O10 B2 F2 Si2
845.3189	1857687	14.6	845.3159	2.97	C43 H53 O9 F4 Si2

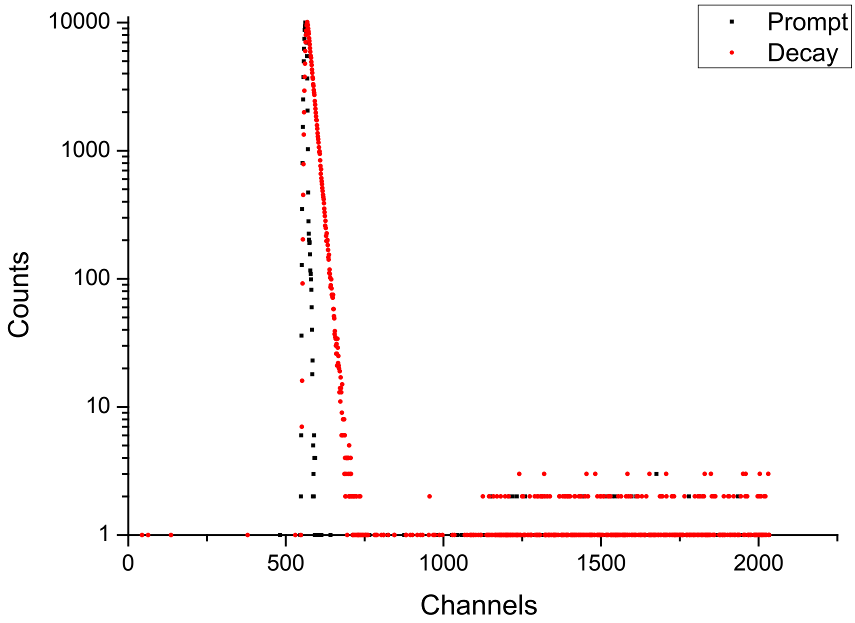
Part V. Fluorescence Lifetime Decay Profiles



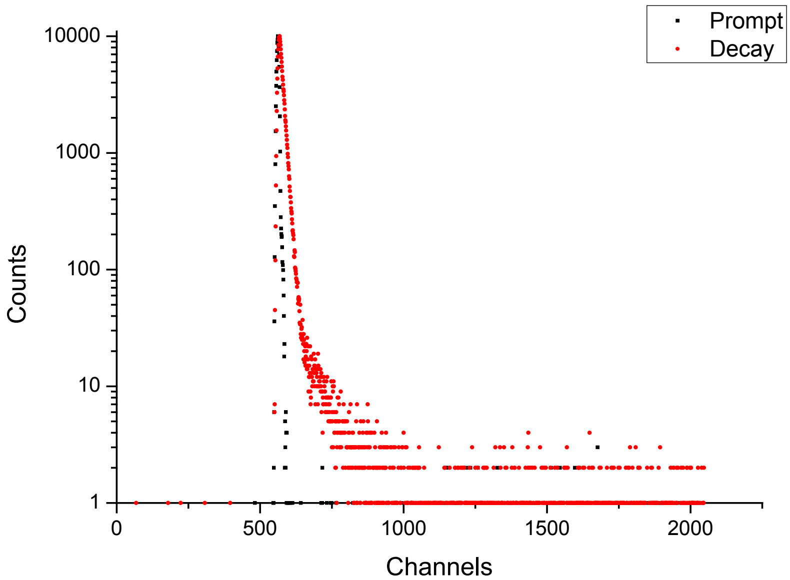
Fluorescence lifetime decay profile for solution of **1** (Time-to-amplitude converter (TAC) range: 200 ns)



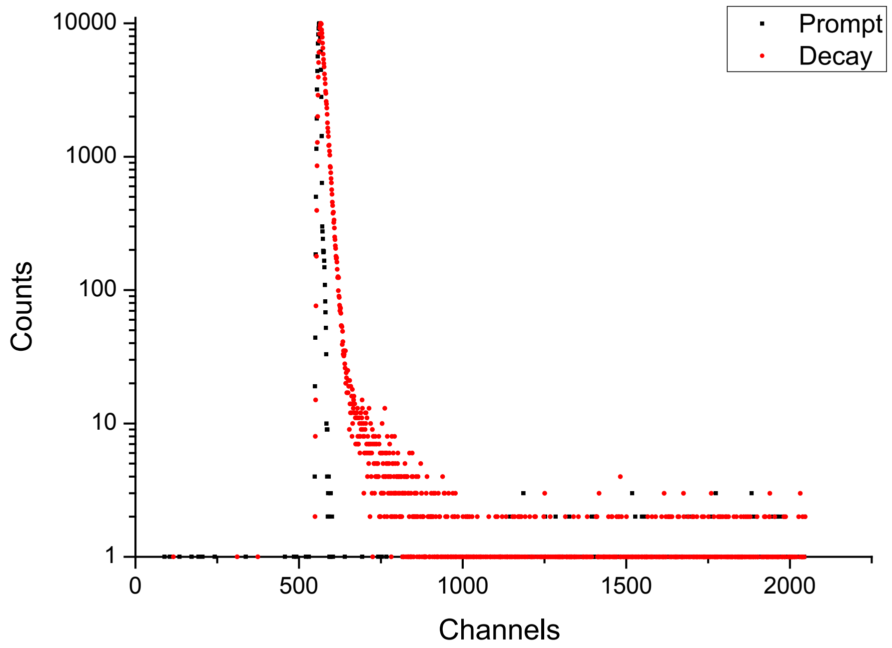
Fluorescence lifetime decay profile for solution of **2** (TAC range: 200 ns)



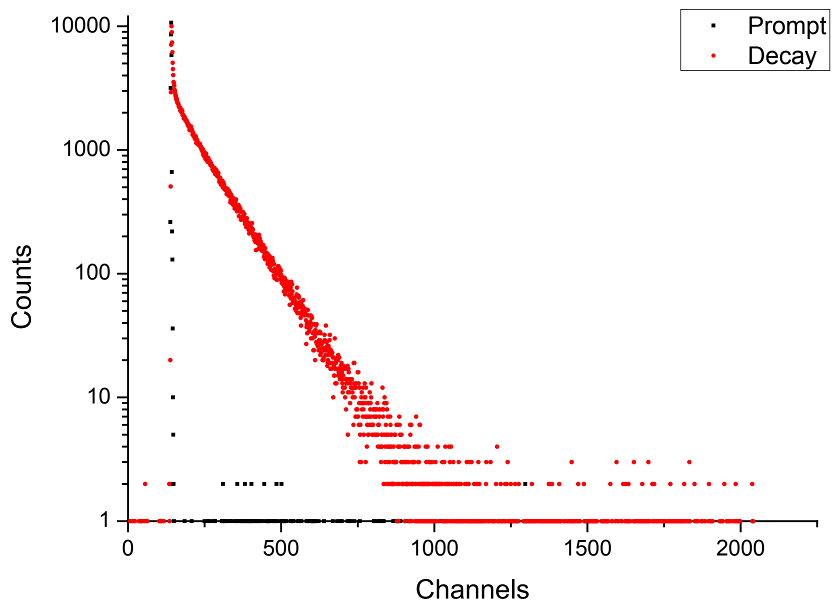
Fluorescence lifetime decay profile for solution of **3** (TAC range: 200 ns)



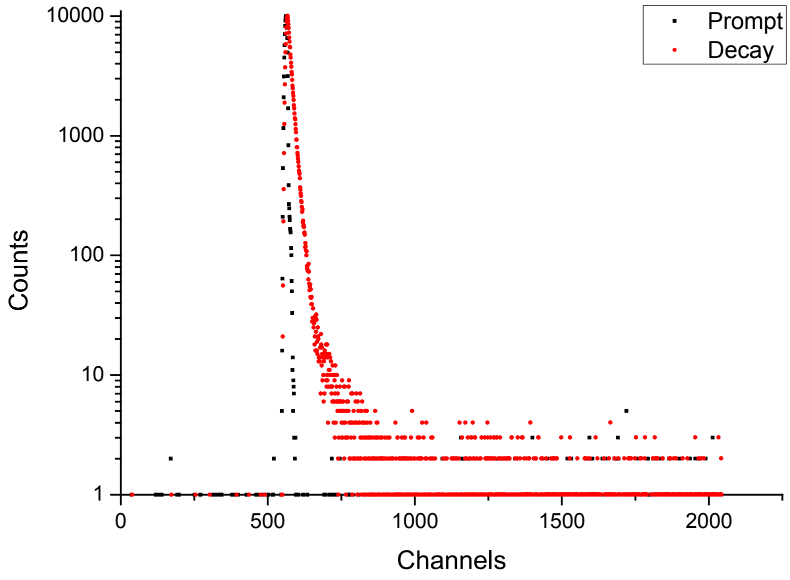
Fluorescence lifetime decay profile for solution of **D1** (TAC range: 200ns)



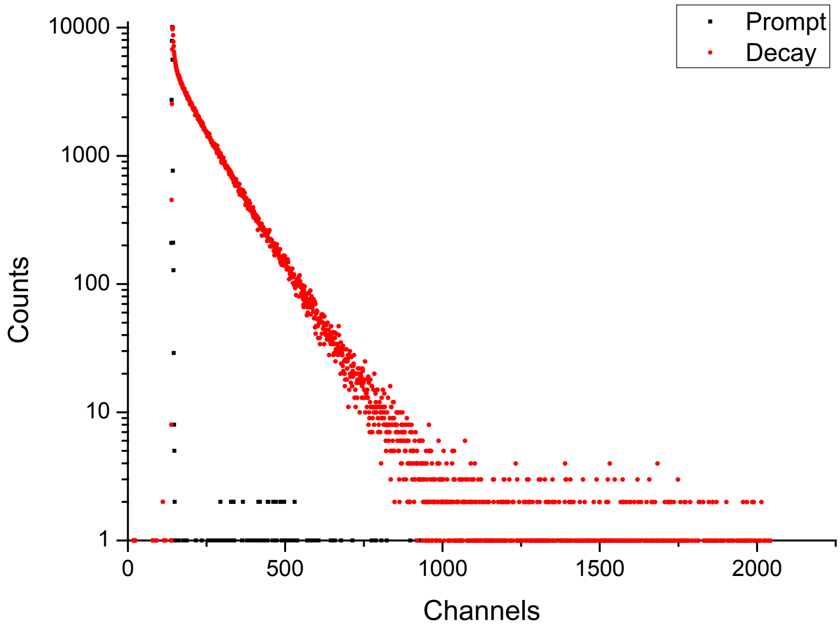
Fluorescence lifetime decay profile for **D1** 1-1 mixed solvent solution measured at 440 nm (TAC range: 200 ns)



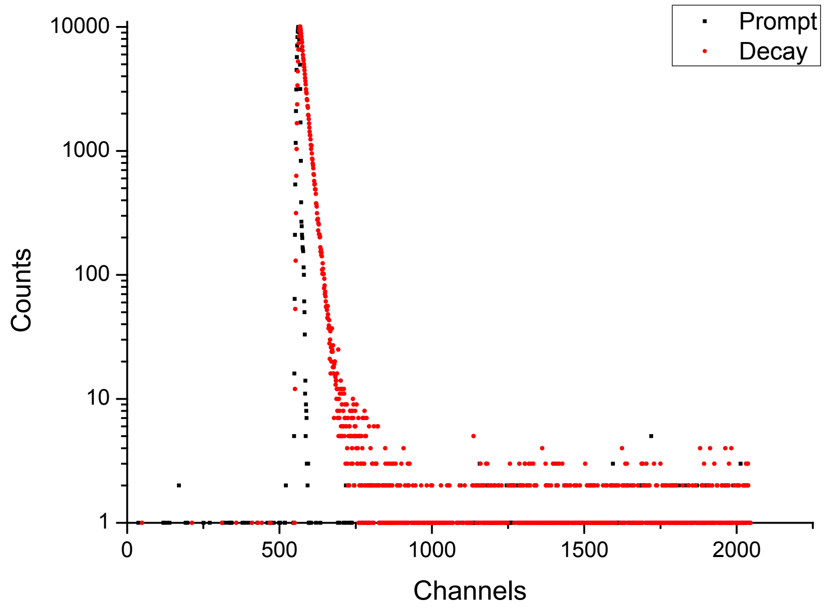
Fluorescence lifetime decay profile for **D1** 1-1 mixed-solvent solution measured at 550 nm (TAC range: 400 ns)



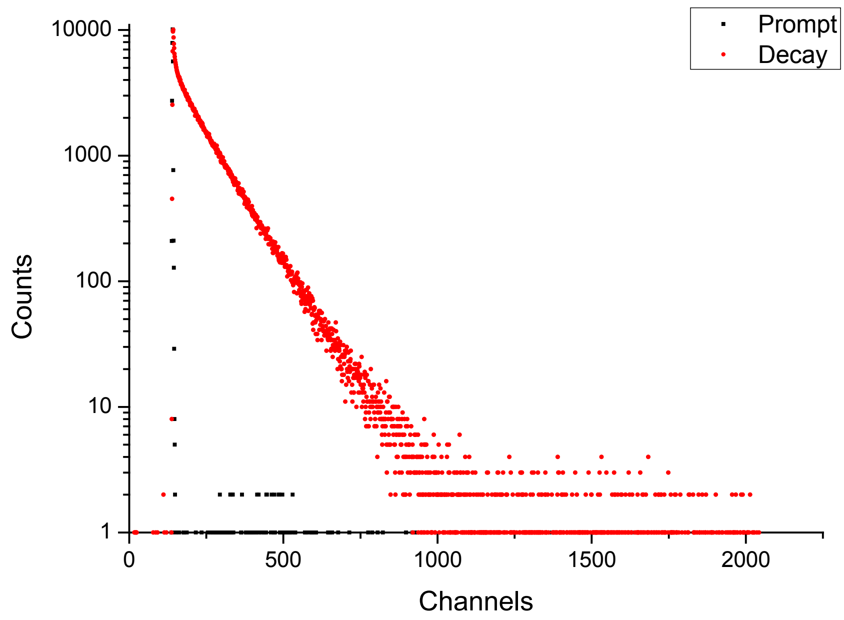
Fluorescence lifetime decay profile for **P1** solution mearuerd at 440 nm (TAC range: 200ns)



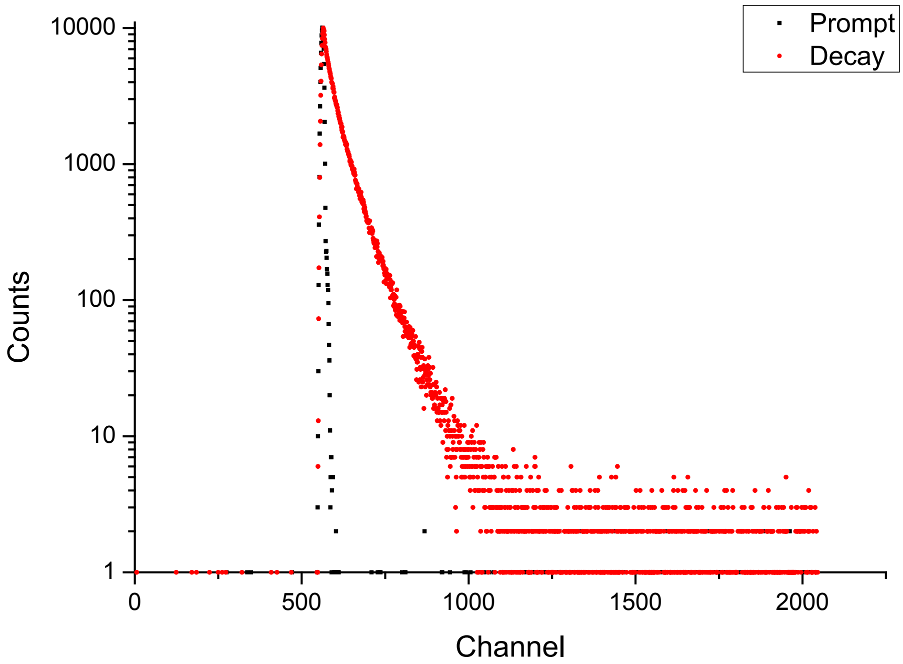
Fluorescence lifetime decay profile for **P1** solution measured at 550nm (TAC range: 400 ns)



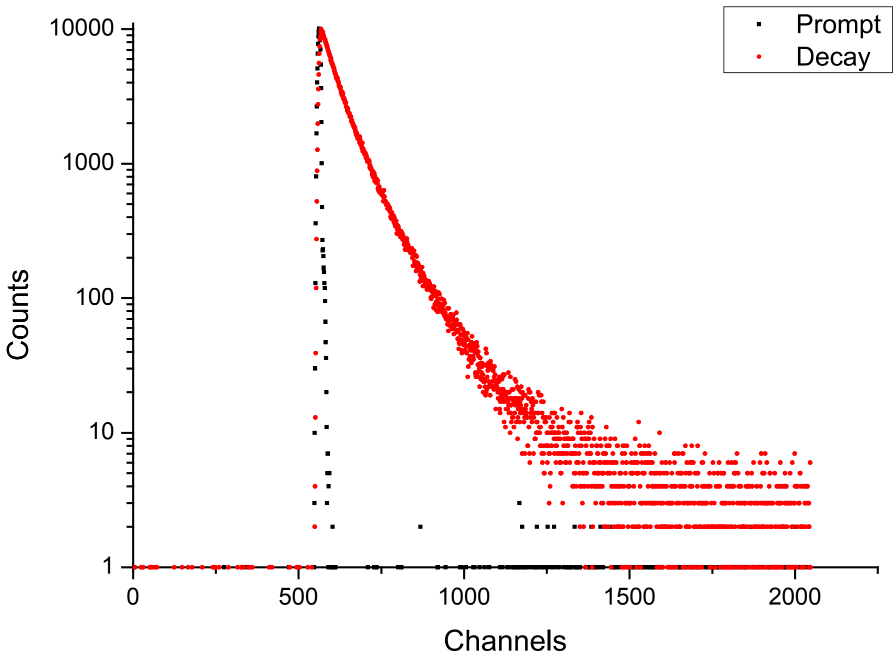
Fluorescence lifetime decay profile for **P1** 1-1 mixed-solvent solution measured at 440 nm (TAC range: 200ns)



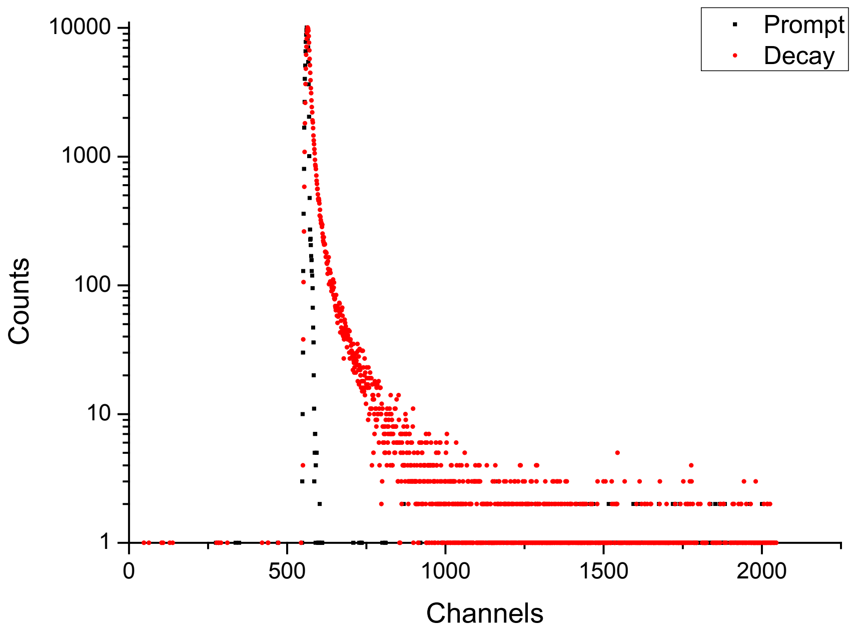
Fluorescence lifetime decay profile for **P1** 1-1 mixed-solvent solution measured at 550nm (TAC range: 400 ns)



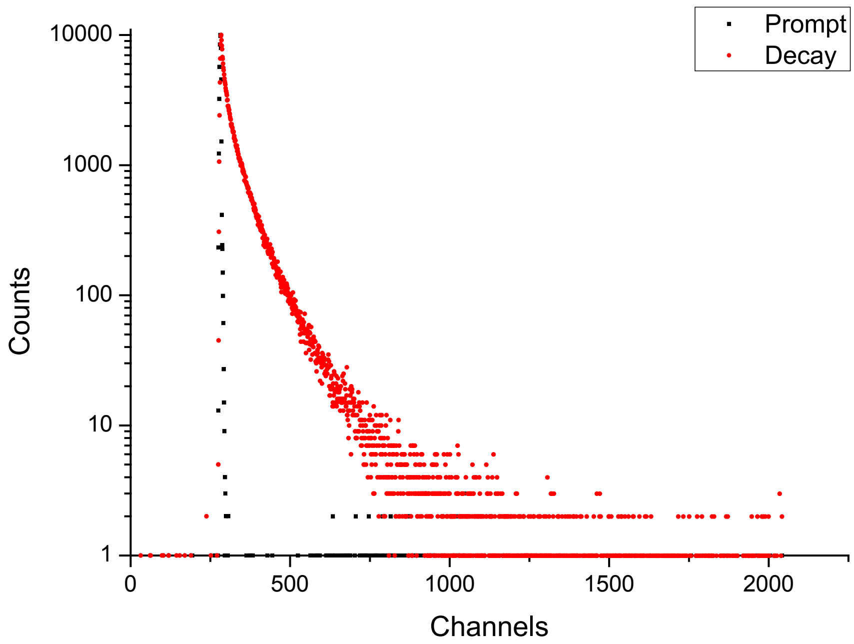
Fluorescence lifetime decay profile for solid of **1** (TAC range: 200 ns)



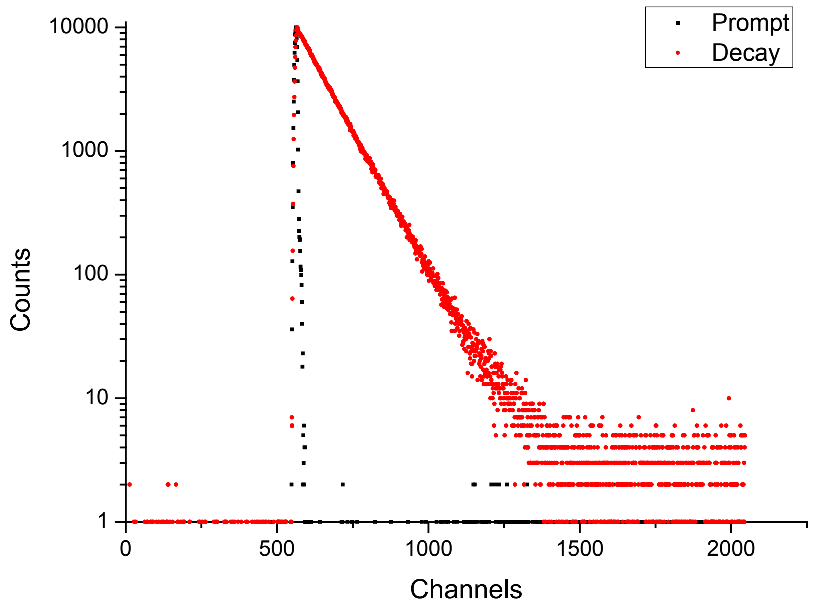
Fluorescence lifetime decay profile for smeared solid of **1** (TAC range: 200 ns)



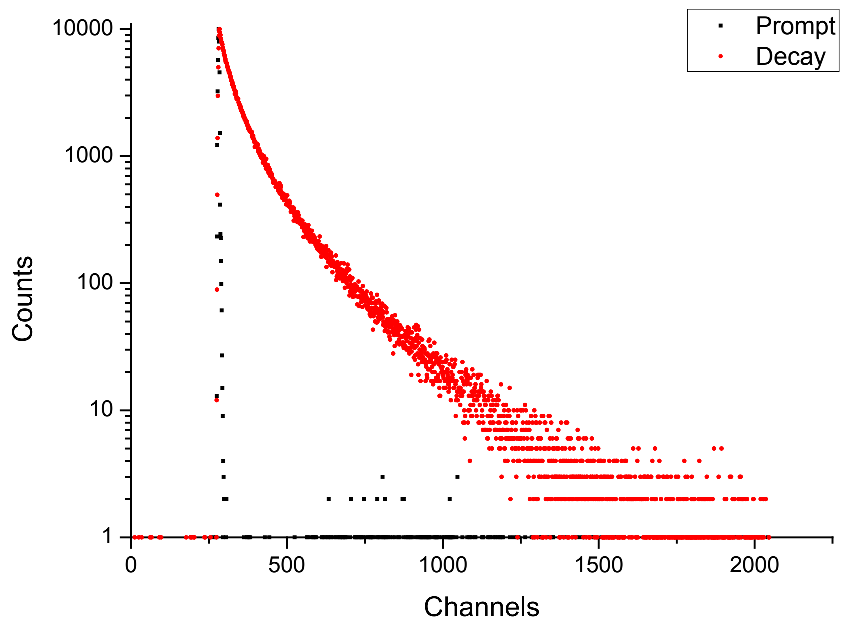
Fluorescence lifetime decay profile for solid of **2** (TAC range 200 ns)



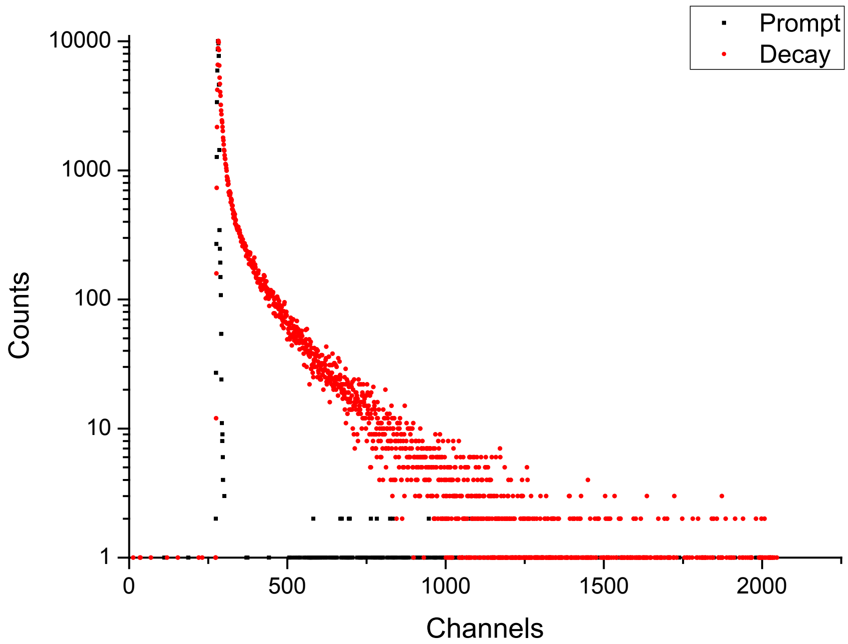
Fluorescence lifetime decay profile for smeared solid of **2** (TAC range: 400 ns)



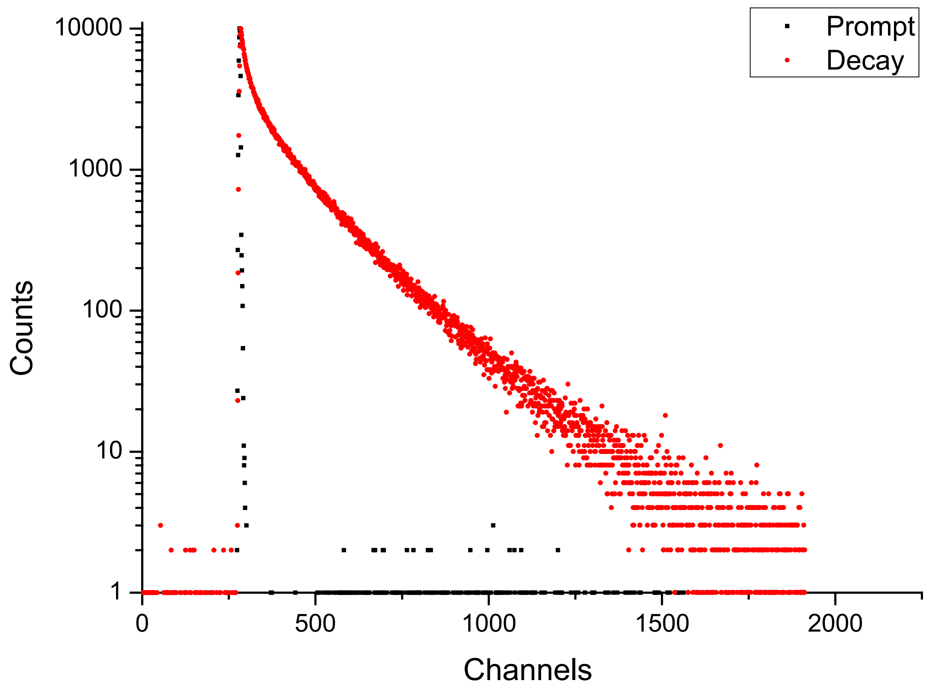
Fluorescence lifetime decay profile for solid of **3** (TAC range: 200 ns)



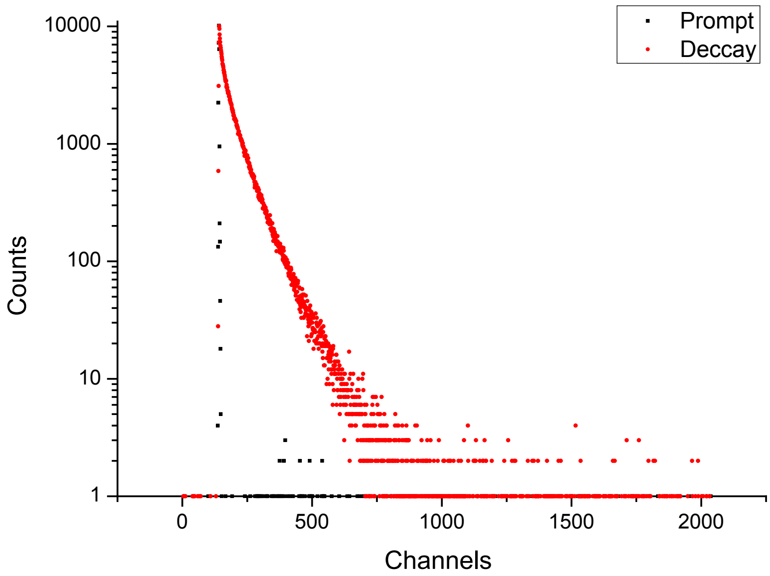
Fluorescence lifetime decay profile for smeared solid of **3** (TAC range: 400 ns)



Fluorescence lifetime decay profile for solid of **D1** (TAC range: 400 ns)



Fluorescence lifetime decay profile for smeared solid of **D1** (TAC range: 400 ns)



Fluorescence lifetime decay profile for solid of **P1** (TAC range: 400 ns)

1 P. Xie, Z. Shen, Y. Liu, B. Kong, C. Liu, R. Zhang, Z. Fan, R. Bai, T.-S. Chung, C. He, *Liq. Crys.* **2001**, *28*, 477.