Supporting Information

Terpyridine–Triarylborane Conjugates for the Dual Complexation of Zn(II) Cation and Fluoride Anion

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Table S1. Crystallographic data and parameters for **3** and **1**·$ZnCl_2$–**3**·$ZnCl_2$.

Compound	**3**	[**1**·$ZnCl_2$]·CH_3CN	**2**·$ZnCl_2$	**3**·$ZnCl_2$
formula	$C_{41}H_{36}BN_3$	$C_{43}H_{39}BCl_2N_4Zn$	$C_{41}H_{36}BCl_2N_3Zn$	$C_{41}H_{36}BCl_2N_3Zn$
formula weight	581.54	758.86	717.81	717.81
crystal system	triclinic	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a (Å)	7.1041(2)	8.2360(16)	16.101(3)	8.4974(3)
b (Å)	13.5525(3)	12.962(3)	13.544(3)	8.5062(3)
c (Å)	17.0666(4)	18.207(4)	15.993(3)	24.2990(9)
α (°)	81.6980(10)	84.03(3)	90.00	89.841(2)
β (°)	85.4660(10)	85.26(3)	93.91(3)	83.333(2)
γ (°)	83.3450(10)	83.31(3)	90.00	84.430(2)
V (Å^3)	1611.72(7)	1915.1(7)	3479.5(12)	1736.17(11)
Z	2	2	4	2
ρ_{calc} (g cm^{-3})	1.198	1.316	1.370	1.373
μ (mm^{-1})	0.069	0.817	0.644	0.896
λ (Å^3)	0.71073	0.79998	0.630	0.71073
F(000)	616	788	1488	744
T (K)	100(2)	100(2)	100(2)	100(2)
scan mode	ϕ and ω	ω	ω	ϕ and ω
hkl range	$-8 \rightarrow 8$, $-16 \rightarrow +16$, $-20 \rightarrow +20$	$0 \rightarrow 8$, $-12 \rightarrow +12$, $-18 \rightarrow +19$	$-25 \rightarrow +20$, $-20 \rightarrow +20$, $-22 \rightarrow +24$	$10 \rightarrow +10$, $-10 \rightarrow +8$, $-29 \rightarrow +28$
measd reflns	24518	4396	49278	15749
unique reflns [R_{int}]	5675 [0.0614]	4396 [0.0472]	13732 [0.0534]	6372 [0.0124]
reflns used for refinement	3995	3613	10890	6057
refined parameters	412	467	440	439
R1[a] ($I > 2\sigma(I)$)	0.0650	0.0545	0.0409	0.0232
wR2[b] all data	0.1926	0.1406	0.1111	0.0702
GOF on F^2	1.078	0.992	1.085	1.049
ρ_{fin} (max/min) (e Å^{-3})	0.409, –0.445	0.084, –0.685	0.597, –1.399	0.351, –0.367

[a] $R1 = \sum||Fo| - |Fc||/\sum|Fo|$. [b] $wR2 = \{[\sum w(Fo^2 - Fc^2)^2]/[\sum w(Fo^2)^2]\}^{1/2}$.

Table S2. Selected bond lengths (Å) and angles (deg) for **1**·$ZnCl_2$– **3**·$ZnCl_2$ and **3**.

Compound	**1**·$ZnCl_2$	**2**·$ZnCl_2$	**3**·$ZnCl_2$	**3**
		Lengths		
B(1)–C(1)	1.565(8)	1.5681(19)	1.577(2)	1.579(4)
B(1)–C(10)	1.571(8)	1.569(2)	1.579(2)	1.568(4)
B(1)–C(19)	1.567(8)	1.5769(19)	1.575(2)	1.574(4)
Zn(1)–N(1)	2.096(4)	2.1118(11)	2.0957(13)	–
Zn(1)–N(2)	2.216(4)	2.2200(12)	2.1897(13)	–
Zn(1)–N(3)	2.190(4)	2.2105(12)	2.1874(13)	–
Zn(1)–Cl(1)	2.2664(14)	2.2610(5)	2.2622(4)	–
Zn(1)–Cl(2)	2.2672(14)	2.2576(6)	2.2767(4)	–
		Angles		
C(1)–B(1)–C(10)	123.3(5)	125.28(11)	121.50(15)	121.1(2)
C(1)–B(1)–C(19)	118.6(5)	119.40(11)	115.70(14)	115.6(2)
C(10)–B(1)–C(19)	118.1(5)	115.28(11)	122.77(15)	123.3(2)
N(1)–Zn(1)–N(2)	74.11(15)	73.89(4)	74.24(5)	–
N(1)–Zn(1)–N(3)	74.39(15)	74.31(4)	74.55(5)	–
N(2)–Zn(1)–N(3)	144.92(14)	146.55(4)	145.14(5)	–
N(1)–Zn(1)–Cl(1)	104.28(10)	110.72(3)	144.15(4)	–
N(1)–Zn(1)–Cl(2)	142.34(10)	136.53(3)	102.89(4)	–
Cl(1)–Zn(1)–Cl(2)	113.37(5)	112.748(14)	112.882(16)	–
C(25)–C(26)–C(27)	177.6(6)	176.26(15)	170.65(18)	177.0(3)

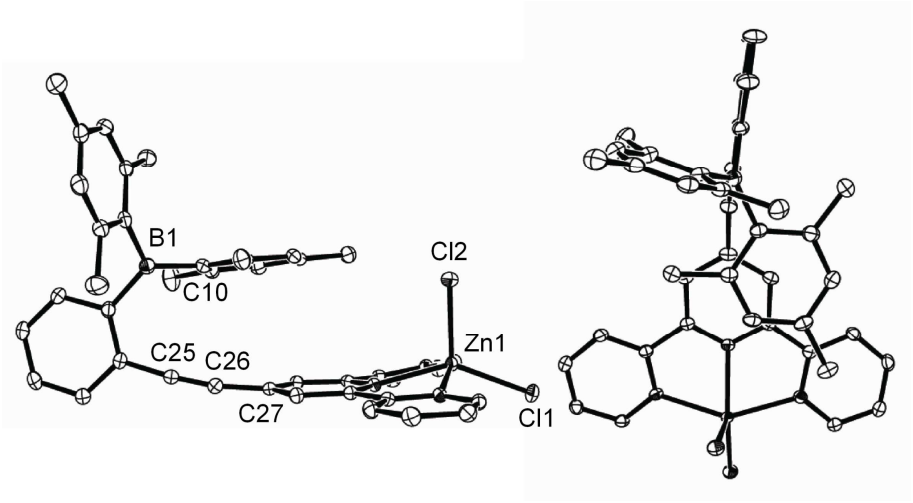

Figure S1. Side (left) and top (right) views of crystal structure of **3**·$ZnCl_2$.

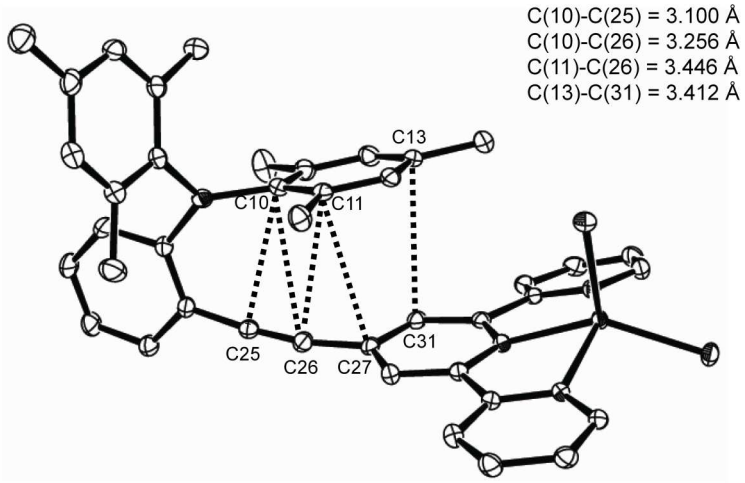

Figure S2. Interatomic distances between the mesityl carbon atoms and ethynylene-pyridine carbon atoms in **3**·$ZnCl_2$.

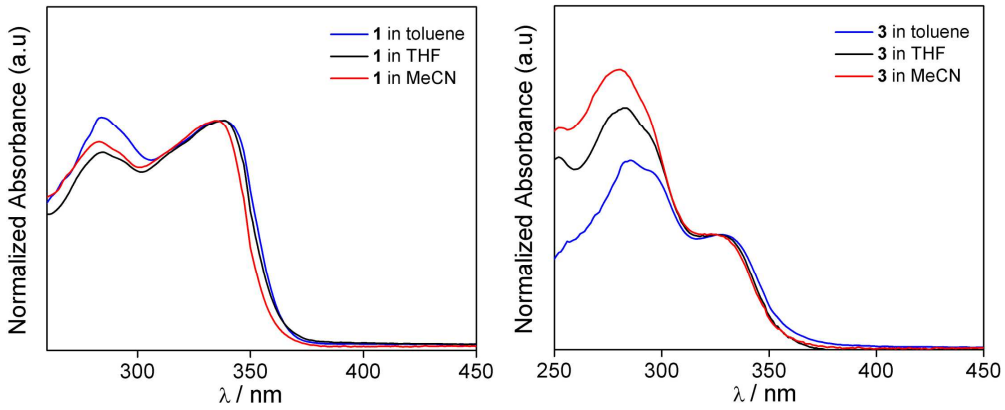

Figure S3. Normailzed absorption spectra of **1** (left) and **3** (right) in solvents with differenct polarities.

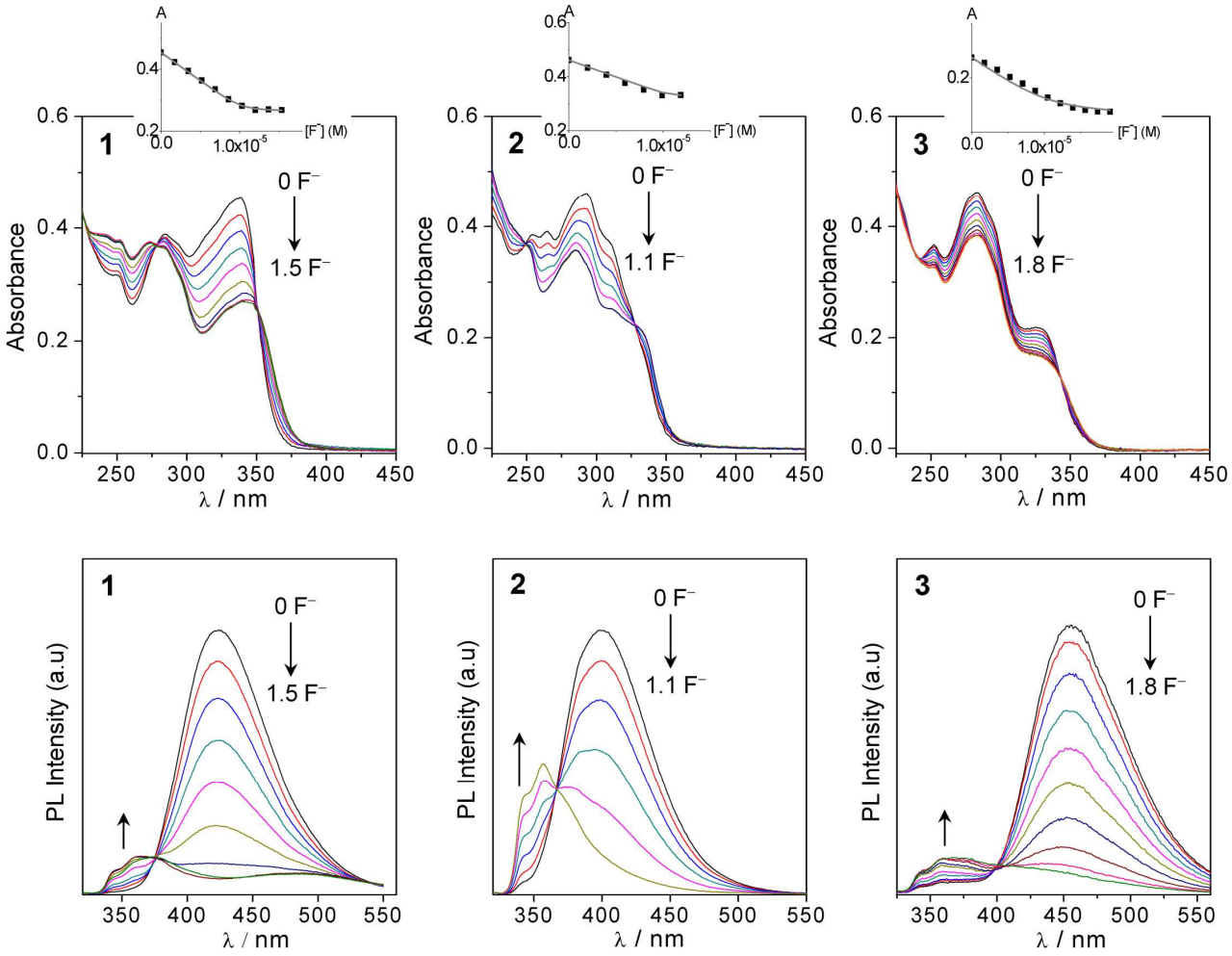

Figure S4. Spectral changes in UV/vis absorption (top) and fluorescence (bottom) of **1**–**3** (1.0×10^{-5} M in THF) upon addition of TBAF. The insets show the absorbance of the solution at 338, 293, and 325 nm, respectively, as a function of [F^-]. The thin line corresponds to the binding isotherm calculated with $K = 1.0 \times 10^7\ M^{-1}$ for **1**, $3.0 \times 10^7\ M^{-1}$ for **2**, and $1.0 \times 10^6\ M^{-1}$ for **3**.

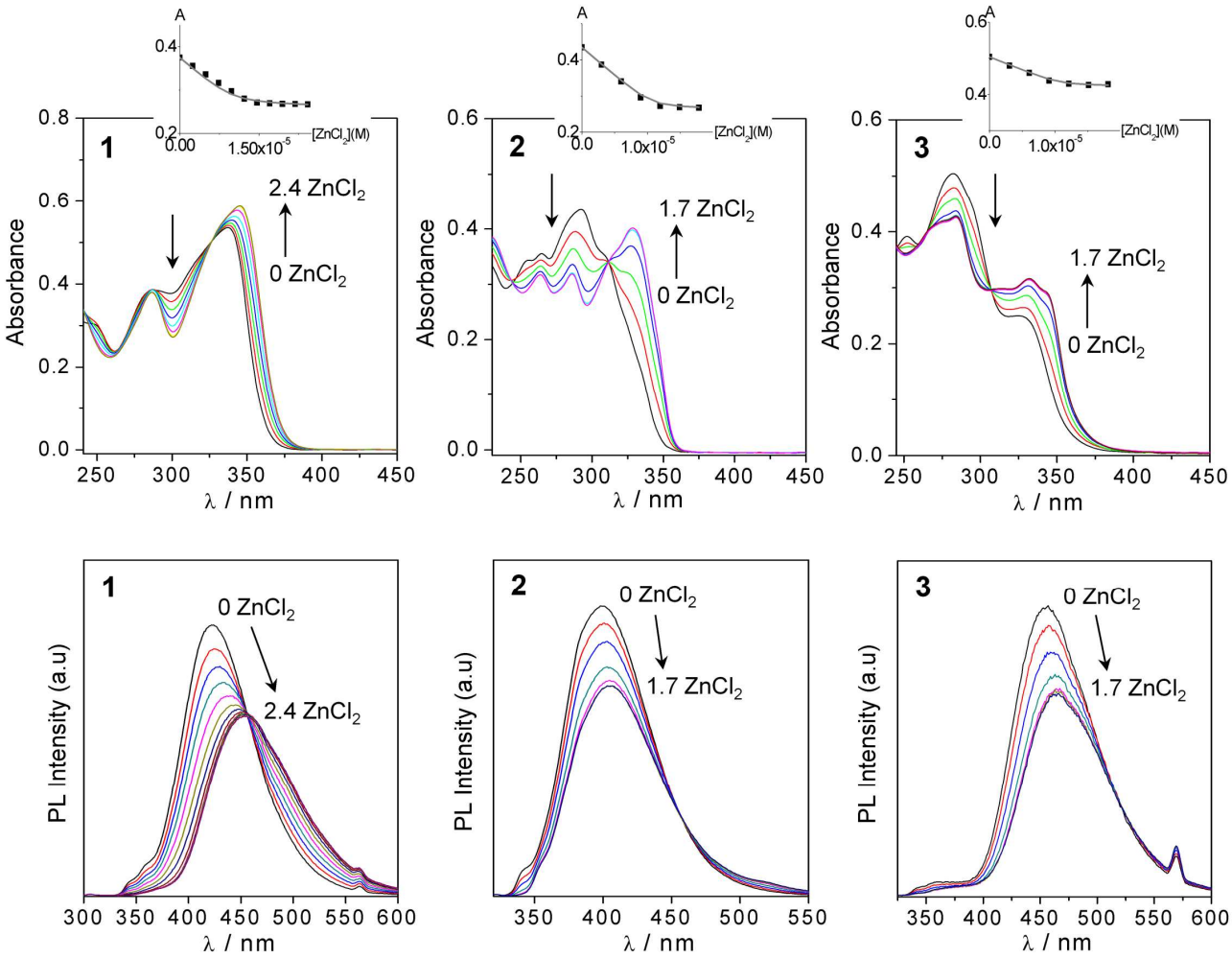

Figure S5. Spectral changes in UV/vis absorption (top) and fluorescence (bottom) of **1**–**3** (1.0×10^{-5} M in THF) upon addition of $ZnCl_2$. The insets show the absorbance of the solution at 300, 293, and 284 nm, respectively, as a function of [$ZnCl_2$]. The thin line corresponds to the binding isotherm calculated with $K = 1.5 \times 10^6\ M^{-1}$ for **1**, $5.0 \times 10^6\ M^{-1}$ for **2**, and $5.0 \times 10^6\ M^{-1}$ for **3**.

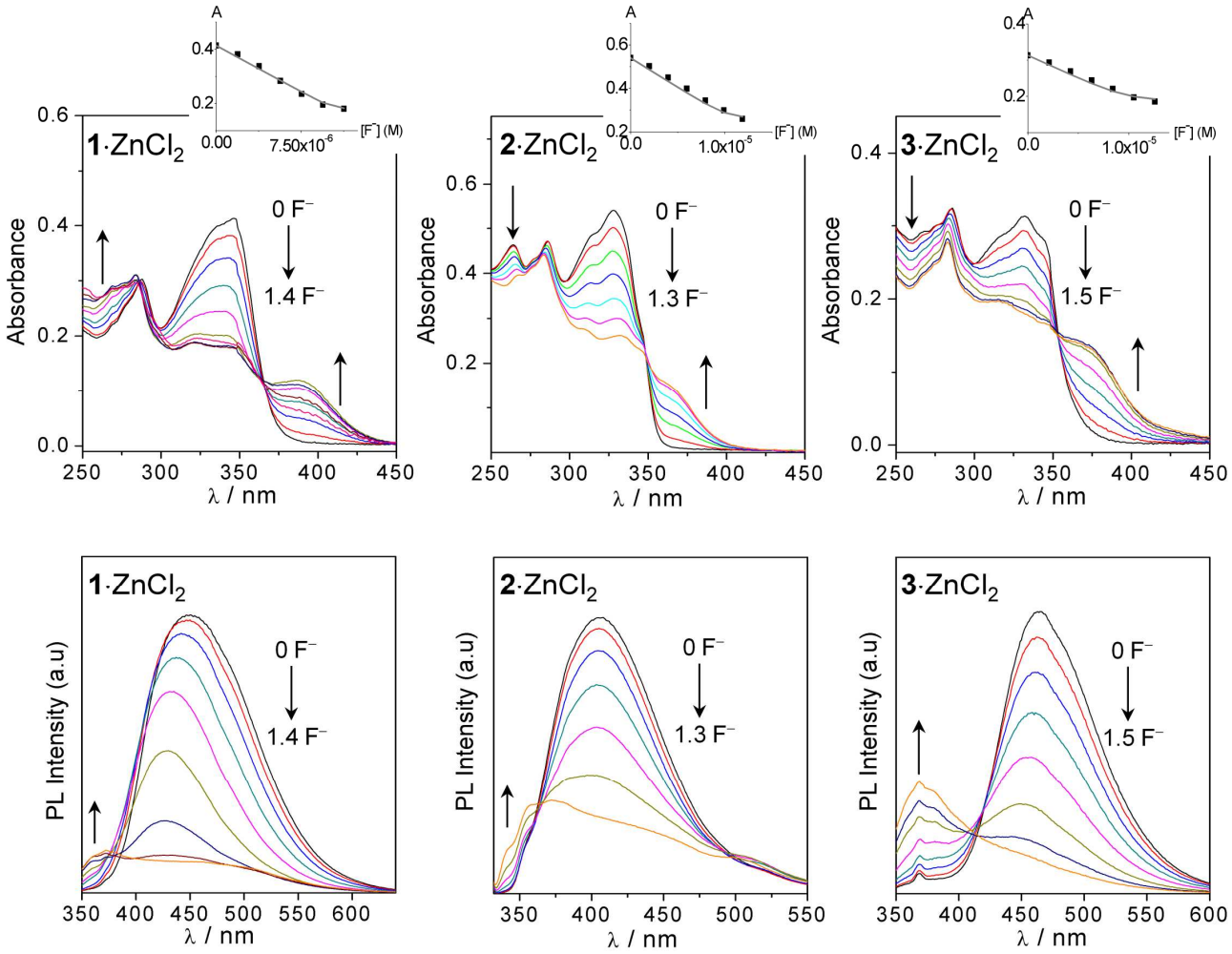

Figure S6. Spectral changes in UV/vis absorption (top) and fluorescence (bottom) of **1**·$ZnCl_2$–**3**·$ZnCl_2$ (1.0×10^{-5} M in THF) upon addition of TBAF. The insets show the absorbance of the solution at 346, 328, and 332 nm, respectively, as a function of [F^-]. The thin line corresponds to the binding isotherm calculated with $K = 5.0 \times 10^7\ M^{-1}$ for **1**·$ZnCl_2$, $1.0 \times 10^7\ M^{-1}$ for **2**·$ZnCl_2$, and $4.0 \times 10^6\ M^{-1}$ for **3**·$ZnCl_2$.

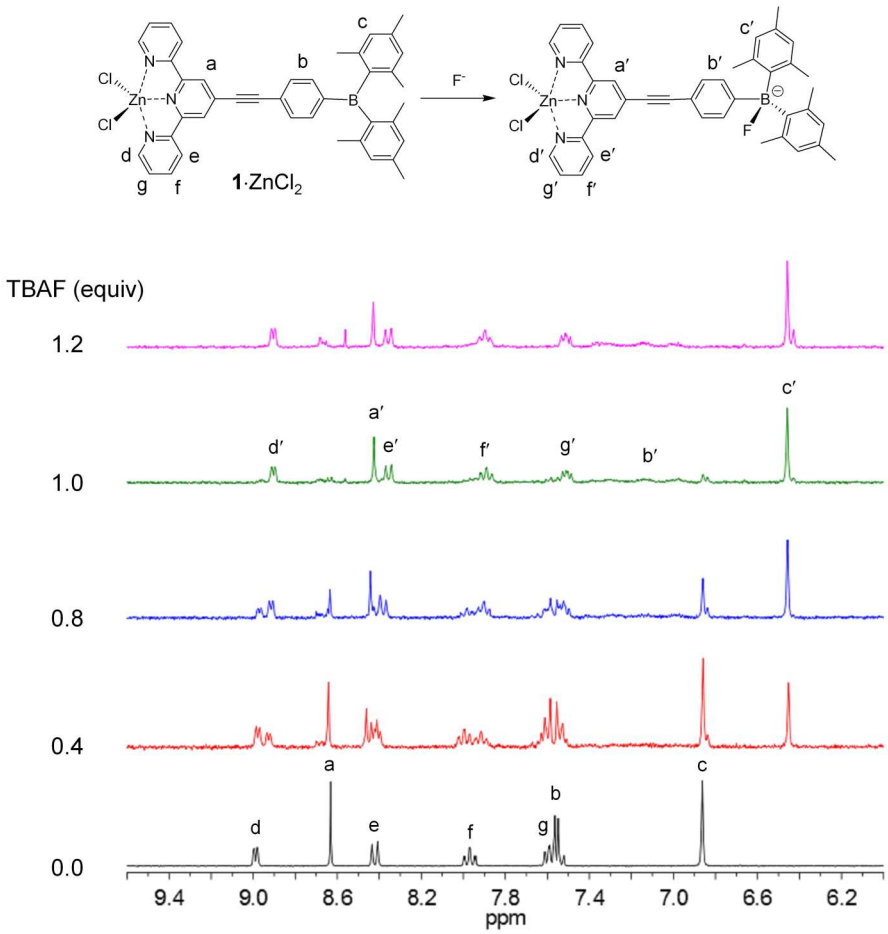

Figure S7. ^{1}H NMR spectral changes of **1**·$ZnCl_2$ upon addition of TBAF in THF-d_8.

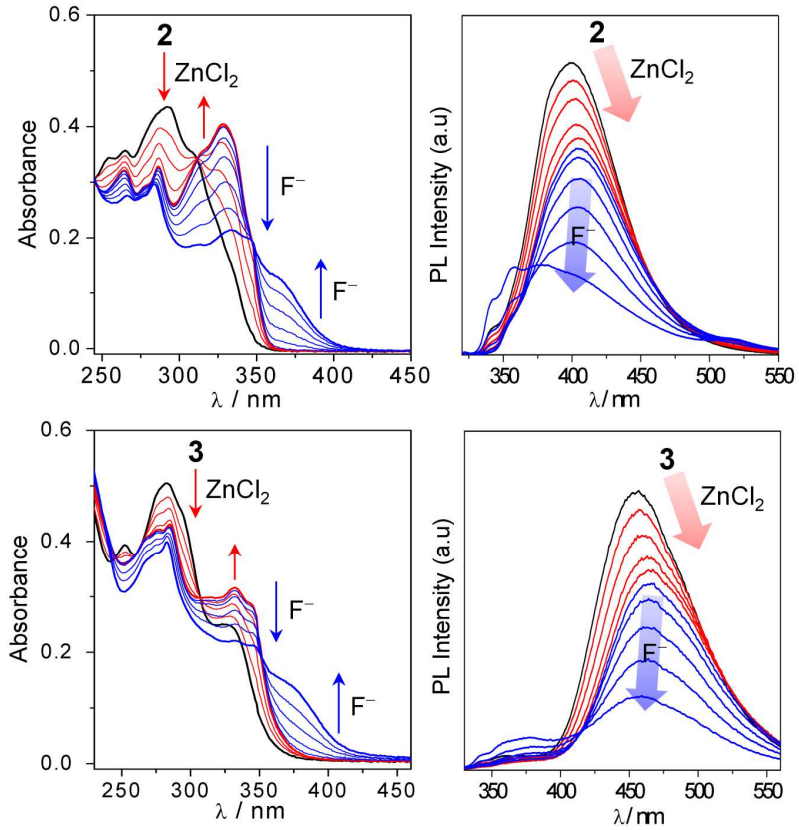

Figure S8. Spectral changes in UV/vis absorption and fluorescence of **2** (top) and **3** (bottom) (1.0×10^{-5} M in THF) upon sequential addition of 1 equiv of $ZnCl_2$ (red curves) and TBAF (blue curves).