Electronic Supplementary Material (ESI) for Chemical Communications

Ion pair receptors based on anion-π interaction

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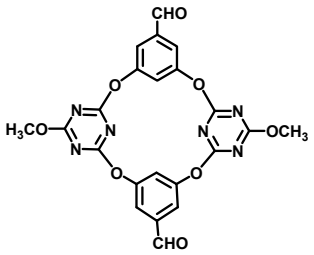
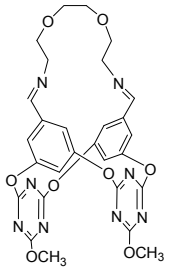
1. General Information

^{1}H and ^{13}C NMR spectra were recorded on a 300MHz NMR spectrometer. Chemical shifts are reported in ppm versus tetramethylsilane with either tetramethylsilane or the residual solvent resonance used as an internal standard. Melting points are uncorrected. All solvents were dried according to standard procedures prior to use. All other major chemicals were obtained from commercial sources and used without further purification.

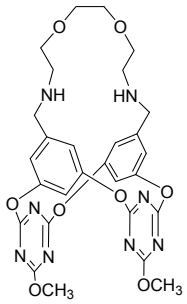
2. Experimental details and characterization of products.



Synthesis of 3: To a solution of 2,4-chloride-6-methoxytriazine **1** (1.8 g, 10 mmol), 3,5-dihydroxybenzaldehyde **2** (0.69 g, 5 mmol) in acetone (50 mL) and grinded potassium carbonate (1.4 g, 10 mmol) were added. After the resulting mixture was stirred at room temperature for 0.5 h, another portion of **2** (0.69 g, 5 mmol) and grinded potassium carbonate (1.4 g, 10 mmol) and acetone (350 mL) were added. The mixture was refluxed for 1.5 h. The solid was removed by filtration, and the filtrate was concentrated to about 30 mL. Product **3** (1.9 g, 74%) as white solid was then precipitated from the solution. **3:** mp 282-283 ^{o}C; ^{1}H NMR (300MHz, $CDCl_3$, TMS, 298K) 9.77 (s, 2H), 7.31 (d, J = 2.2 Hz, 4H), 6.90 (t, J = 2.2 Hz, 2H), 4.08 (s, 6H); ^{13}C NMR (75MHz, $CDCl_3$, TMS) 189.3, 174.9, 173.1, 152.5, 138.7, 122.5, 120.3, 56.2; IR (KBr) 3080, 2879, 1710, 1693, 1566 cm^{-1}; MS (MALDI-TOF) m/z (%) 491.0 [$M+H^{+}$] (100), 492.0 (24). Anal. Calcd. for $C_{22}H_{14}N_6O_8$: C, 53.88; H, 2.88; N, 17.14. Found: C, 53.51; H, 2.96; N, 16.77.

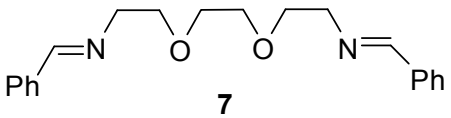


Synthesis of 5: To a solution of **3** (248 mg, 5 mmol) in acetonitrile (50 ml), 2,2'-(ethane-1,2-diylbis(oxy))diethanamine (69 mg, 5 mmol) was added. The mixture was stirred at room temperature for 2 h. After removing impurities by a short silicon gel column, the resulting solution was concentrated. Dichloromethane was used to dissolve the residue, then hexane was added. After slowly evaporating of the solvent and filtration, colorless needle-like product of **5** was obtained (280mg, 94%). **5**: mp >270 ^{o}C (decomp.); ^{1}H NMR (300MHz, $CDCl_3$, TMS, 298K) 8.12 (s, 2H), 7.26 (d, J = 2.2 Hz, 4H), 6.73(t, J = 2.2 Hz, 2H), 4.16 (s, 6H), 3.78 (m, 4H), 3.76 (m, 4H), 3.53(s, 4H); ^{13}C NMR (75MHz, $CDCl_3$, TMS) 174.8, 173.4, 160.0, 152.0, 138.8, 118.9, 70.9, 70.4, 62.0, 56.0; IR (KBr) 2884, 1651, 1577, 1503 cm^{-1}; MS (MALDI-TOF) m/z (%) 603.4 [M+H^{+}] (100), 625.3 [M+Na^{+}] (81). Anal. Calcd. for $C_{28}H_{26}N_8O_8$·1/2 H_2O: C, 54.99; H, 4.45; N, 18.32. Found: C, 54.65; H, 4.49, N, 18.04.



Synthesis of 6: To a solution of **5** (301 mg, 5 mmol) in dichloromethane (15ml) (*caution: the solution is under vigorously stirring*), $NaHB(CH_3CO_2)_3$ (316 mg, 15 mmol) was added gradually. The mixture was stirred at room temperature for 2 h. Then water (20ml) and sodium carbonate was added. The solution was extracted with dichloromethane (3 × 30 ml), the combined solutions was dried with anhydrous $MgSO_4$ for 24 h. After filtration, the filtrate was concentrated to about 20ml followed

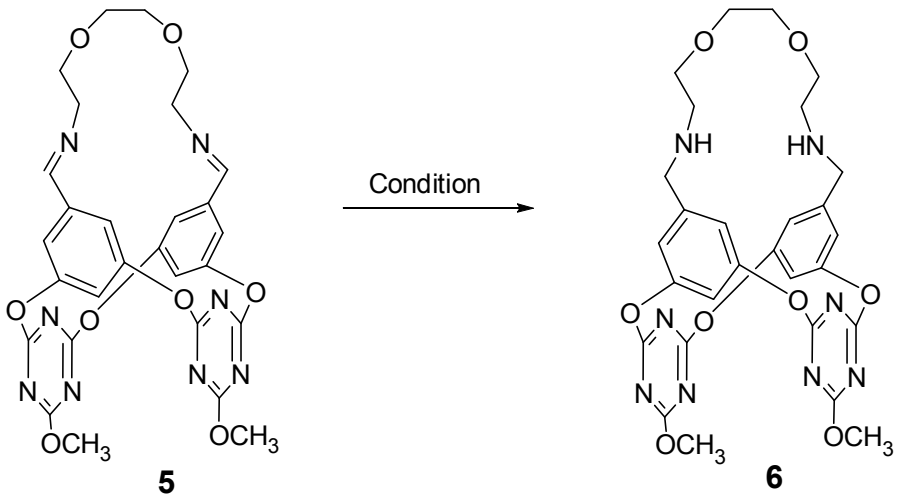
by the addition of hexane (10 ml). By slowly evaporation of the solvent, product **6** (273 mg, 91%) as white powder product was obtained. **6**: mp>270 ^{o}C (decomp.); ^{1}H NMR (300MHz, $CDCl_3$, TMS, 298K) 6.91(d, J =2.2 Hz, 4H), 6.59(t, J =2.2 Hz, 2H), 4.12 (s, 6H), 3.70(s, 4H), 3.59(m, 8H), 2.78 (t, J_1 =4.5Hz, 4H), 1.85 (br. s, 2H); ^{13}C NMR (75MHz, $CDCl_3$, TMS) 174.6, 173.2, 151.6, 143.6, 118.7, 115.0, 55.9, 53.4, 49.3; IR (KBr) 2951, 2875, 1575, 1503 cm^{-1}; MS (MALDI-TOF) m/z (%) 607.4 [M+H^{+}] (100), 629.3 [M+Na^{+}] (72). Anal. Calcd. for $C_{28}H_{30}N_8O_8 \cdot H_2O$: C, 53.84; H, 5.16; N, 17.94. Found: C, 53.98; H, 5.08; N, 18.06.



7

Synthesis of 7: Newly distilled benzaldehyde (531 mg, 50 mmol) 2,2'-(ethane-1,2-diylbis(oxy))diethanamine (345 mg, 25 mmol) and benzene (10ml) were mixed and the resulting mixture was refluxed for 1 h. After removal of the solvent, product **7** (810 mg, 99%) as pale yellow oil was obtained. **7**: ^{1}H NMR (300MHz, $CDCl_3$, TMS, 298K) 8.312(s, 2H), 7.76(t, J_1 = 2.4Hz, 4H), 7.44(m, 6H), 3.80(m, 8H), 3.66 (m,4H). Anal. Calcd. for $C_{20}H_{24}N_2O_2$: C, 74.04; H, 7.46; N, 8.64. Found: C, 73.91; H, 7.38, N, 8.53.

Optimization the synthesis of compound 6:



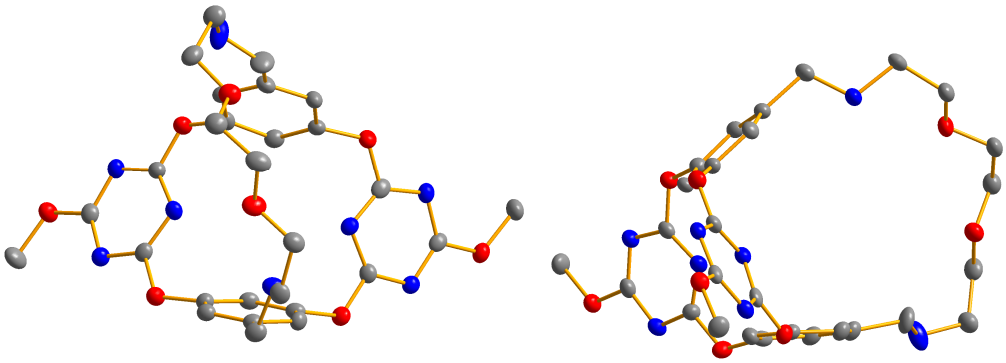
5 **6**

Scheme S1

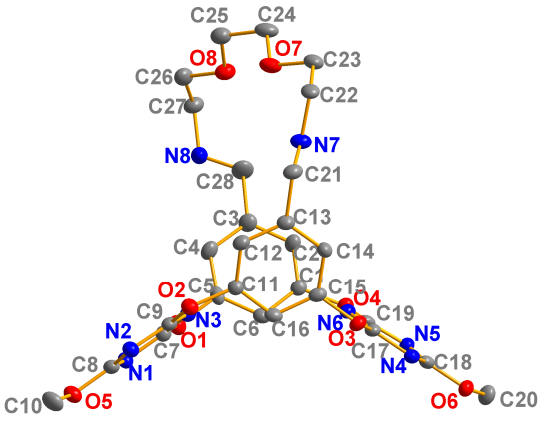
Table S1: Optimization of the conditions for the synthesis of **6**

Entry	Conditions	Yield
1	$NaBH_4$, MeOH, r.t., 2h	Decomp.
2	$NaBH_4$, MeOH, -20°C, 2h	Decomp.
3	Pd/C, MeOH, 1.5atm H_2, r.t., 10h	N.R.
4	Pd/C, MeOH, 1.5atm H_2, 40 °C, 10h	N.R.
5	Pd/C, MeOH, CH_3CO_2H,1.5atm H_2, r.t., 10h	N.R.
6	Pd/C, MeOH, HCO_2H,1.5atm H_2, r.t., 10h	N.R.
7	Pd/C, MeOH, NH_4CO_2H,1.5atm H_2, r.t., 12h	Mixture
8	Zn, CH_3CO_2H,MeOH, r.t., 5h	N.R.
9	PtO_2, MeOH, 1.5atm H_2, r.t, 10h	Mixture
10	$NaHB(CH_3CO_2)_3$, MeOH, r.t, 5h	N.R.
11	$NaHB(CH_3CO_2)_3$, CH_3CO_2H, MeOH, r.t., 5h	N.R.
12	$NaHB(CH_3CO_2)_3$, HCl, MeOH, r.t., 5h	N.R.
13	$NaHB(CH_3CO_2)_3$, CH_2Cl_2 , r.t., 2h	91%

3. Crystal Structure



(a) (b)



(c)

Figure S1: X-Ray crystal structure of **6**. (a) top view, (b) (c) side views. Selected bond lengths [Å]: O(1)-C(7) 1.337, O(1)-C(5) 1.425, O(2)-C(9) 1.348, O(2)-C(11) 1.402, O(3)-C(17) 1.344, O(3)-C(15) 1.417, O(4)-C(19) 1.353, O(4)-C(1) 1.420. Selected distances [Å]: C(8)···C(18) 9.004, N(3)···N(6) 4.554, C(6)···C(16) 4.283, C(3)···C(13) 6.201.

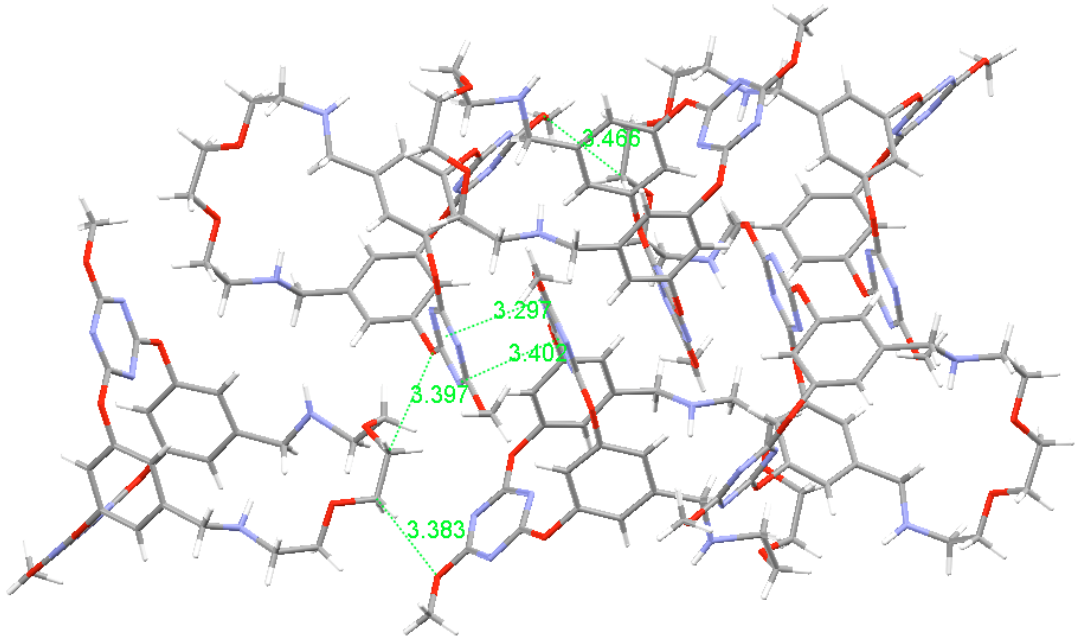
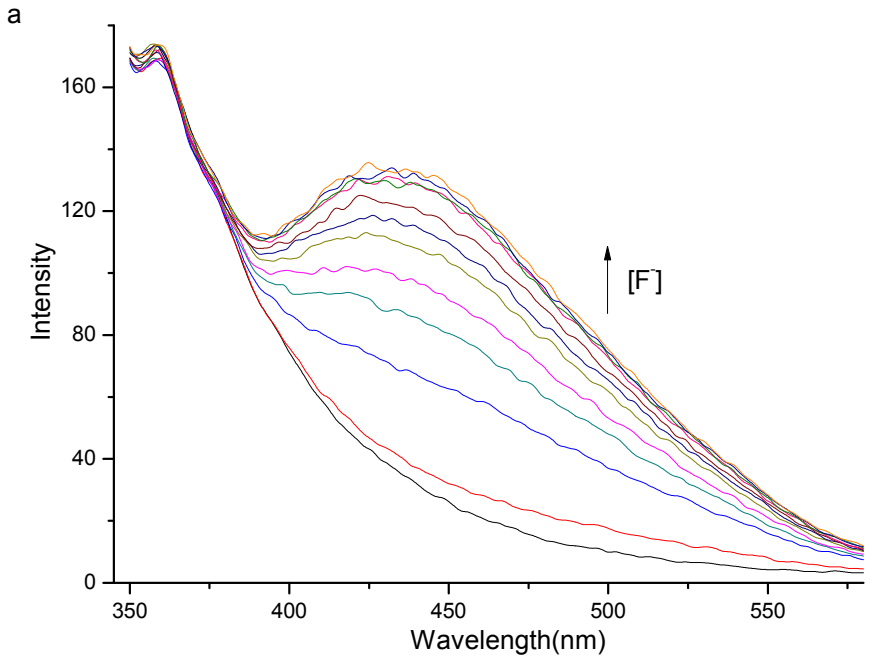
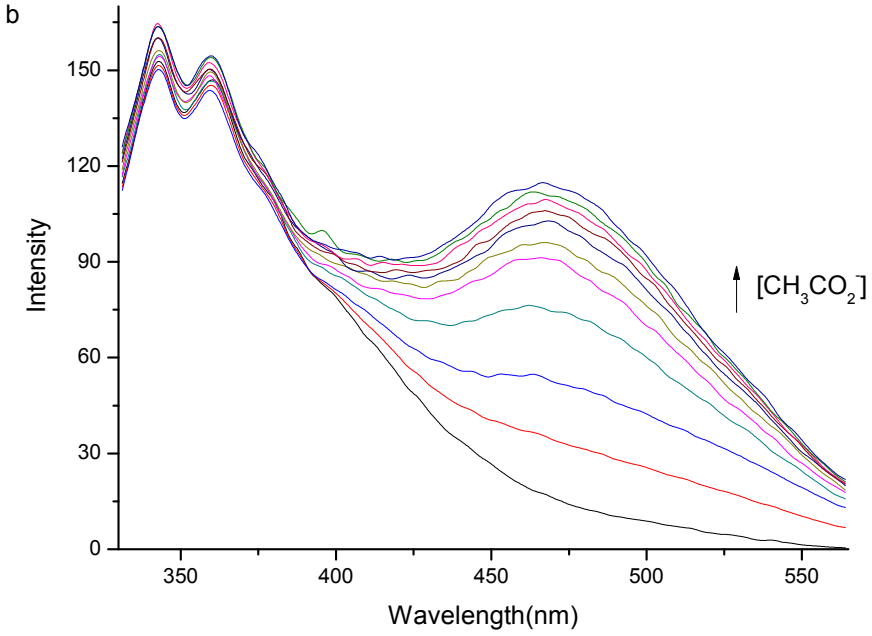


Figure S2: One dimensional self assembly of **6**.

4. Fluorescence titrations





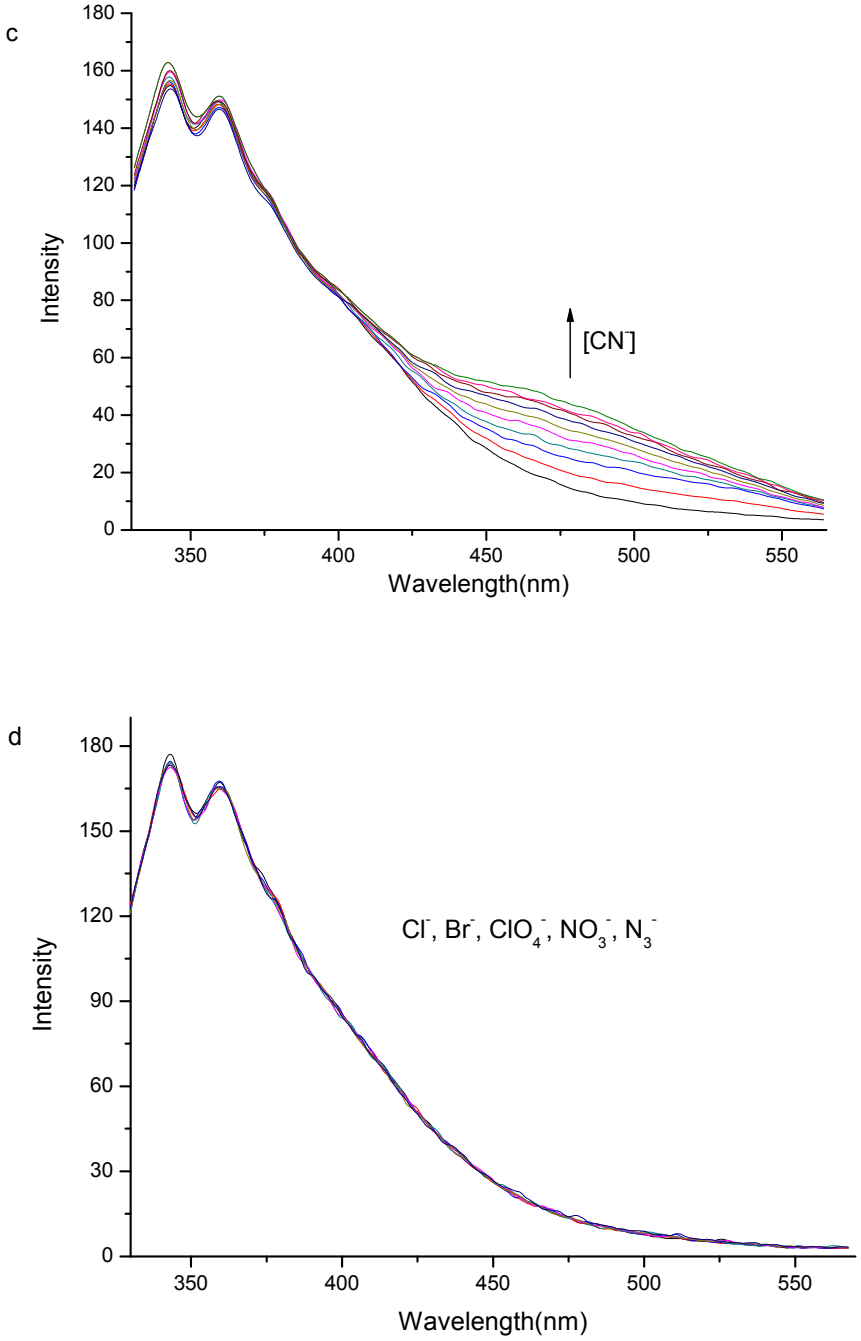
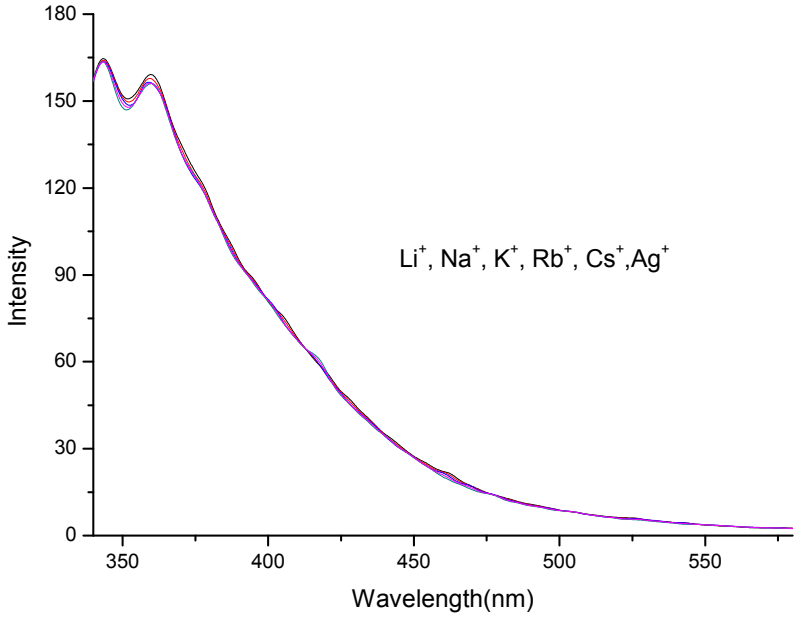
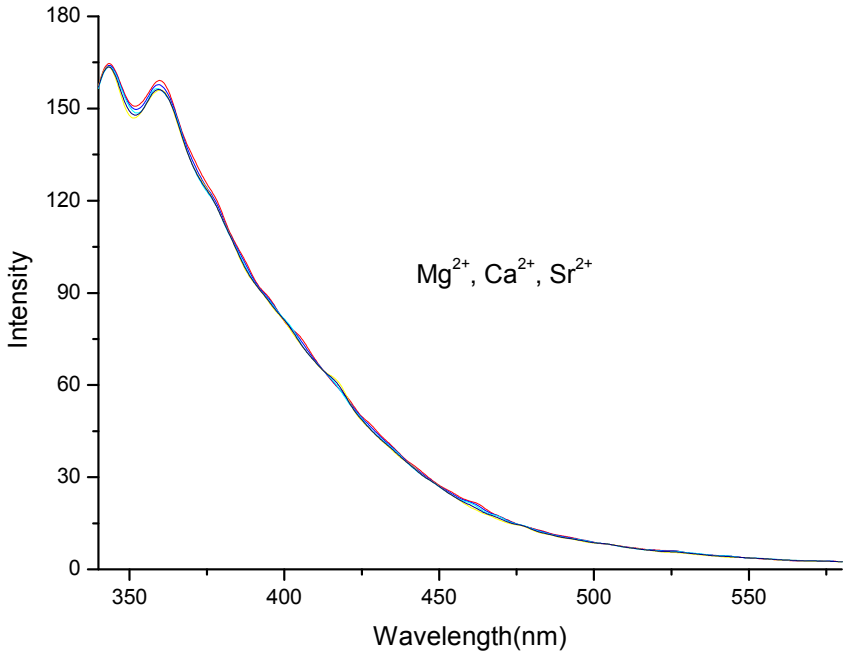


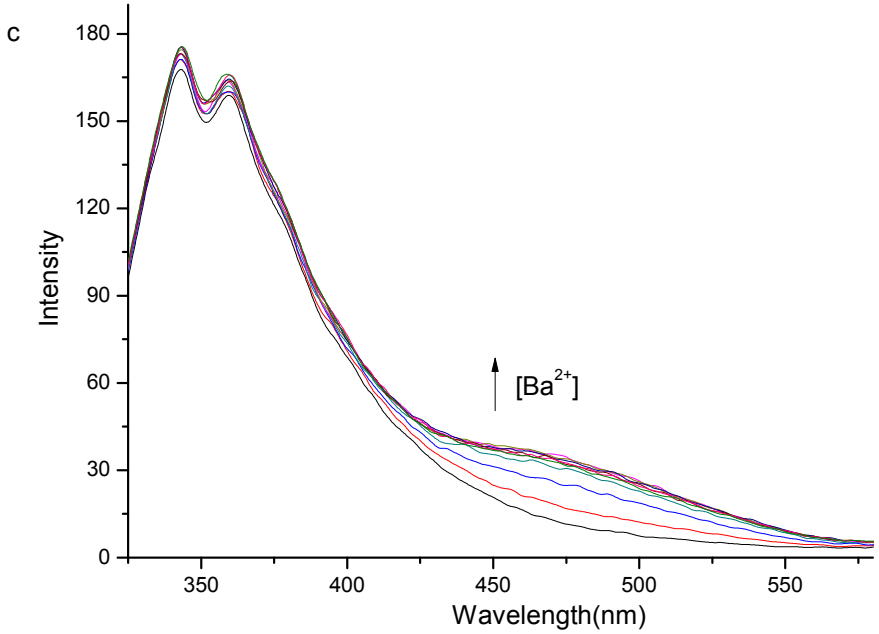
Figure S3: Fluorescence titration curves of **5** (3.984×10^{-4} M) in acetonitrile (2mL) with increasing of (a) $Bu_4N^+F^-$ (0~3.41×10^{-4} M), (b) $Bu_4N^+CH_3CO_2^-$ (0~9.02×10^{-4} M), (c) $Bu_4N^+CN^-$ (0~8.12×10^{-4} M), (d) $Bu_4N^+X^-$ (X^- = Cl^-, Br^-, NO_3^-, ClO_4^-, N_3^-) (0~2.75×10^{-4} M).

a


180
150
120
90
60
30
0
Intensity
350
400
450
500
550
Wavelength(nm)
Li+, Na+, K+, Rb+, Cs+,Ag+

b


180
150
120
90
60
30
0
Intensity
350
400
450
500
550
Wavelength(nm)
Mg2+, Ca2+, Sr2+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Intensity
Wavelength(nm)
[Ba2+]
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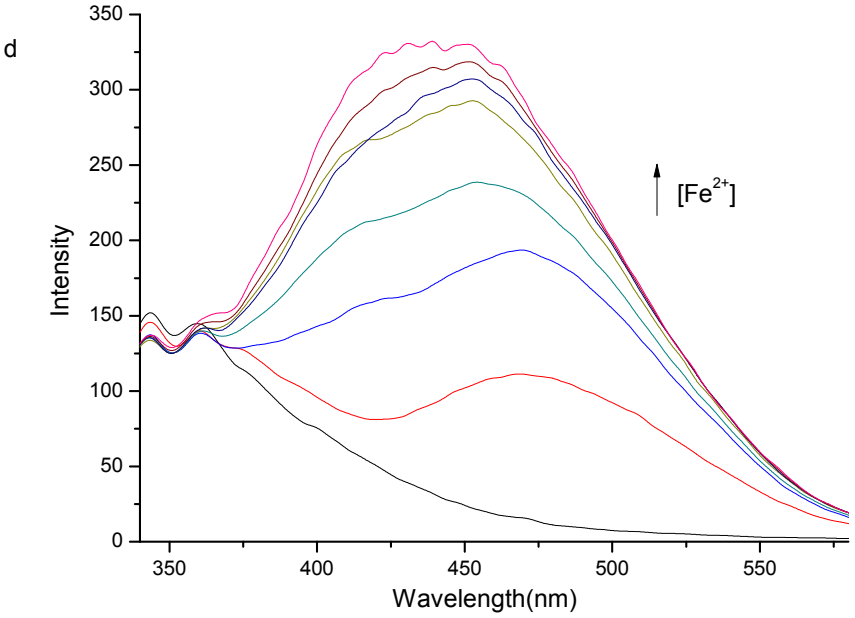
150
180
350
400
450
500
550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Intensity
Wavelength(nm)
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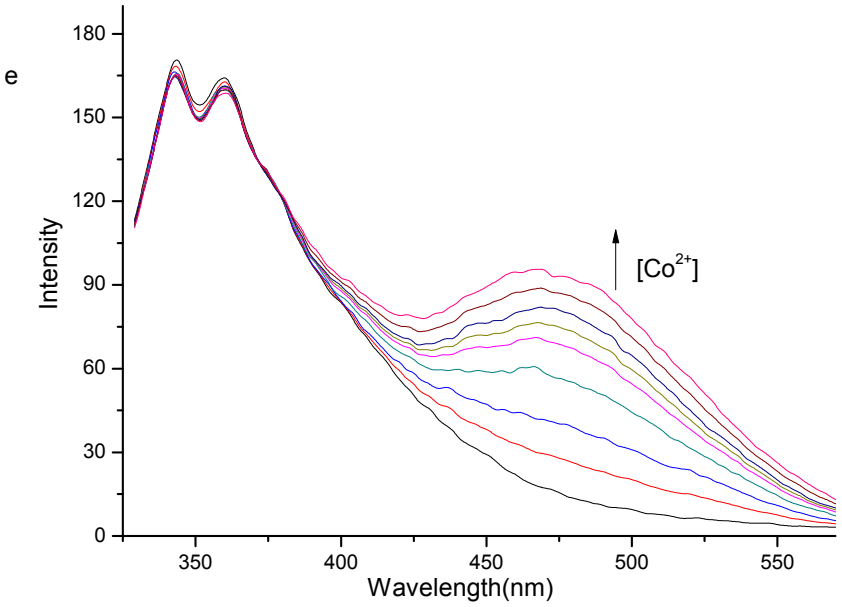
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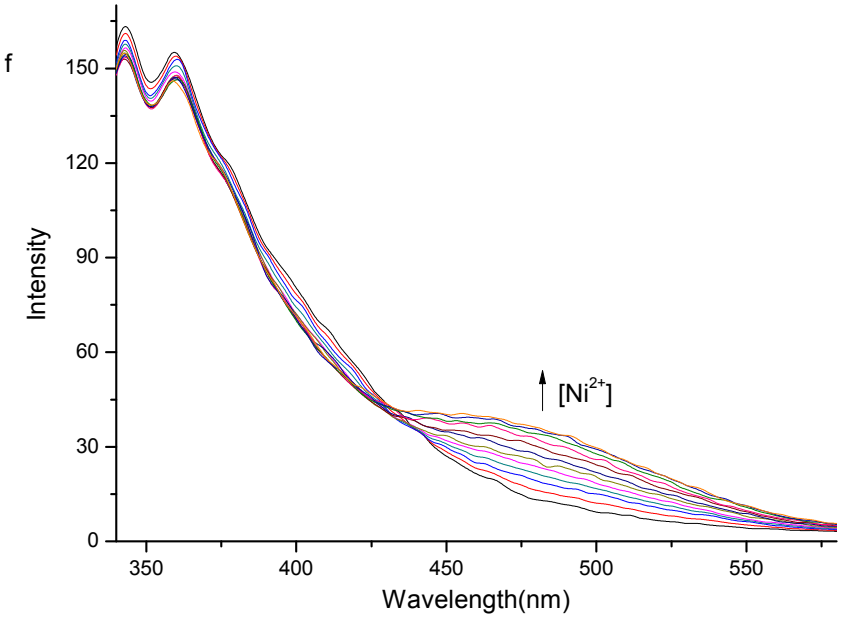
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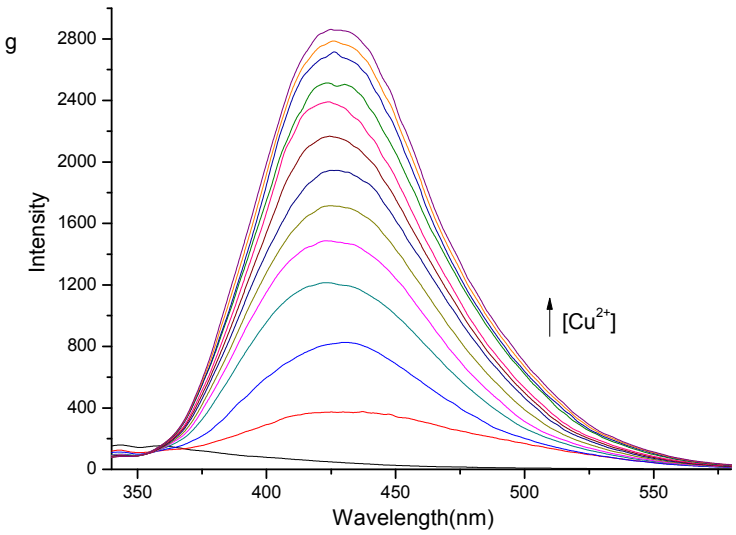
450
500
550

g



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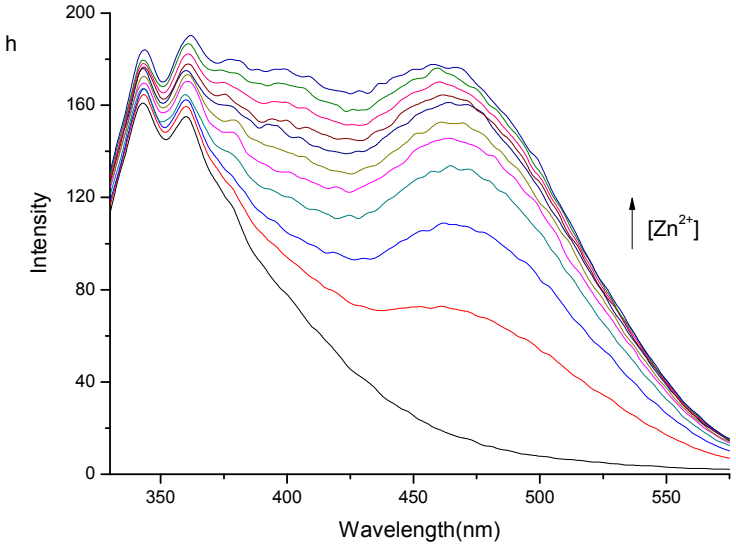


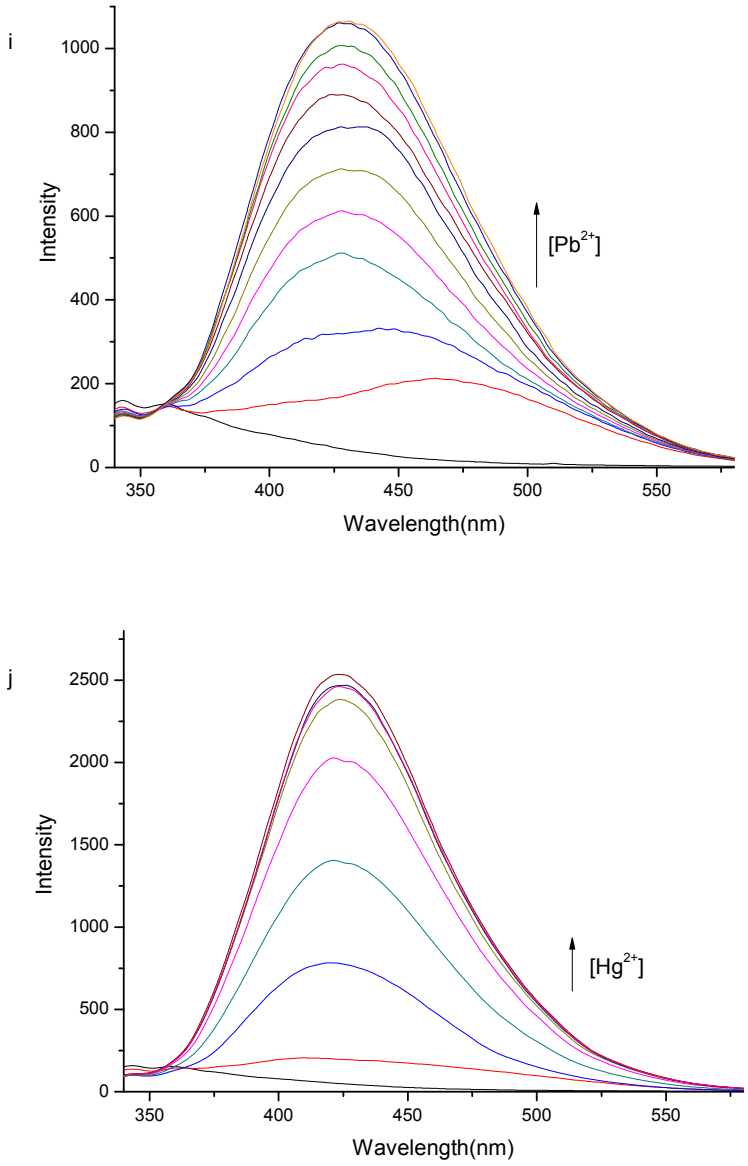
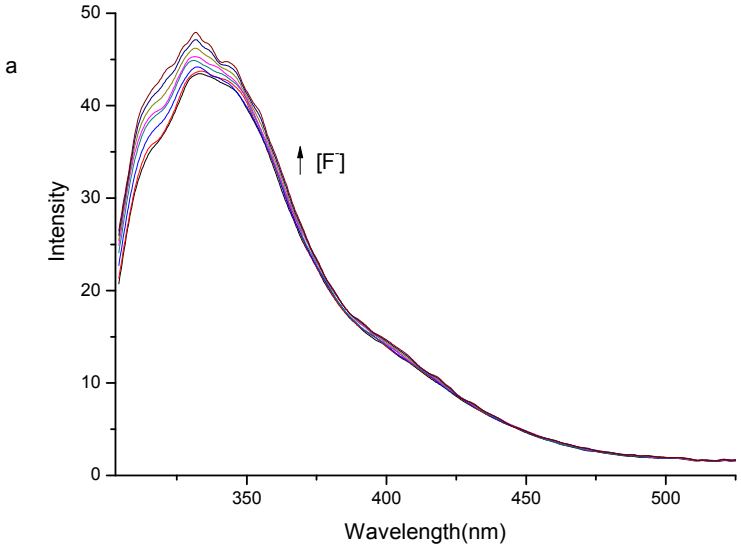


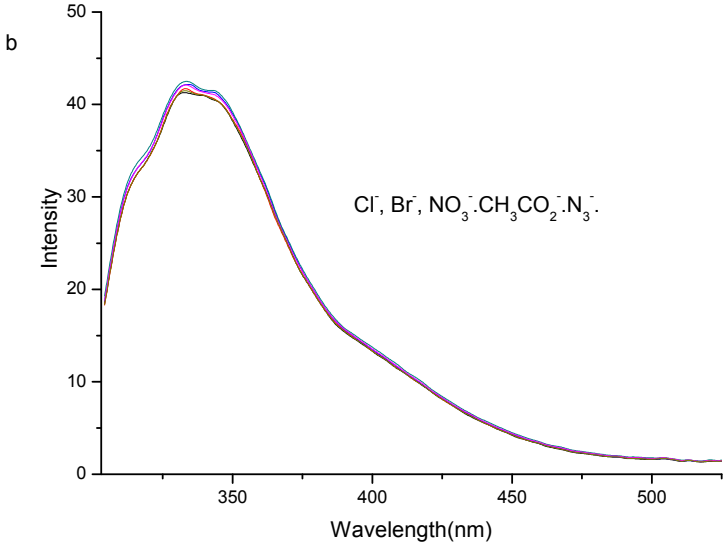
Figure S4: Fluorescence titration curves of **5** (3.99×10^{-4} M) in acetonitrile (2mL) with increasing of (a) (Li^+, Na^+, K^+, Rb^+, Cs^+) (0~4.00×10^{-4} M), Ag^+ (0~3.61×10^{-4} M), (b) Mg^{2+}, Ca^{2+}, Sr^{2+} (0~3.60×10^{-4} M), (c) Ba^{2+} (0~8.11×10^{-4} M), (d) Fe^{2+} (0~6.31×10^{-4} M), (e) Co^{2+} (0~7.20×10^{-4} M), (f) Ni^{2+} (0~9.92×10^{-4} M), (g) Cu^{2+} (0~7.22×10^{-4} M), (h) Zn^{2+} (0~9.65×10^{-4} M), (i) Pb^{2+} (0~9.91×10^{-4} M), (j) Hg^{2+} (0~7.21×10^{-4} M). The counter ion for these cations is ClO_4^-.

Table S2: Association constants $K_a(M^{-1})$ of **5** with ions

F^-	6.591×10^3	Li^+, Na^+, K^+, Rb^+, Cs^+	/
CN^-	4.161×10^3	Mg^{2+}, Ca^{2+}, Sr^{2+}	/

$CH_3CO_2^-$	4.517×10^4	Ba^{2+}	1.846×10^4
Cl^-	/	Fe^{2+}	1.517×10^4
Br^-	/	Co^{2+}	7.651×10^3
NO_3^-	/	Ni^{2+}	7.233×10^2
N_3^-	/	Cu^{2+}	3.715×10^4
		Zn^{2+}	8.125×10^3
		Pb^{2+}	3.281×10^4
		Ag^+	/
		Hg^{2+}	9.213×10^4





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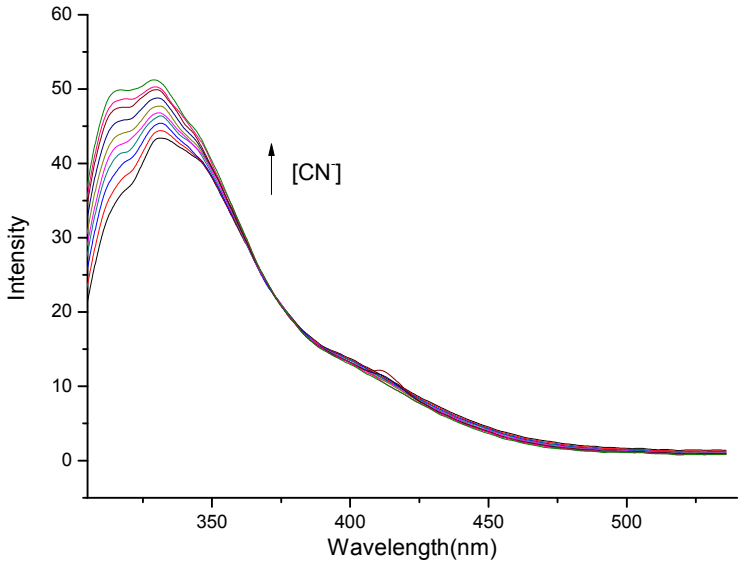

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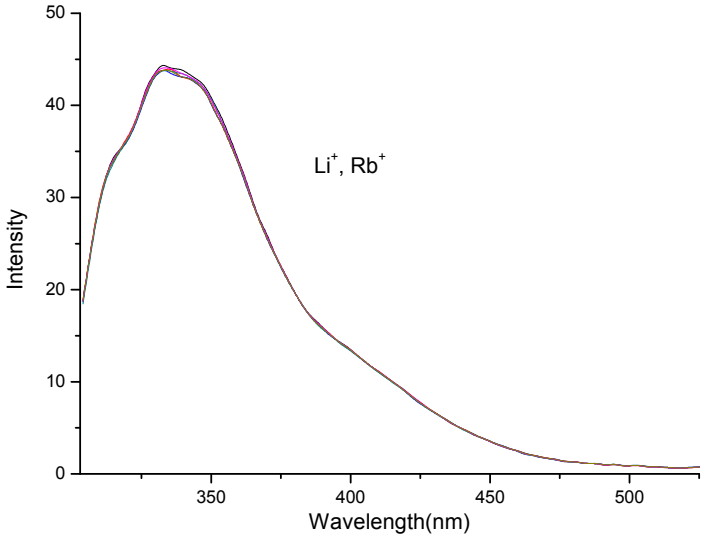

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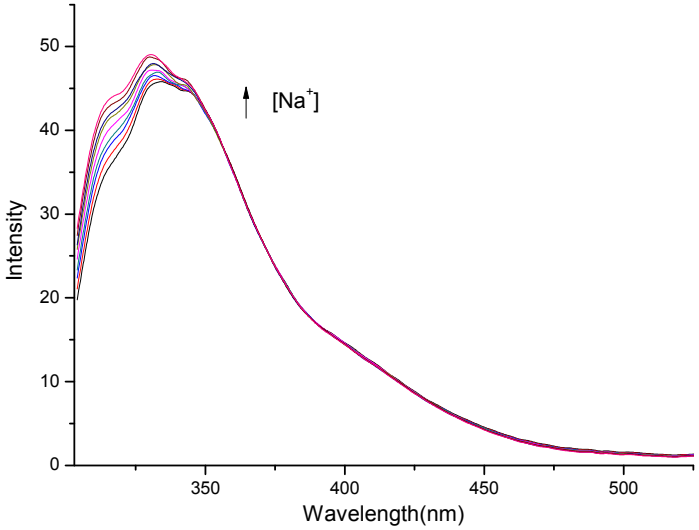
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500

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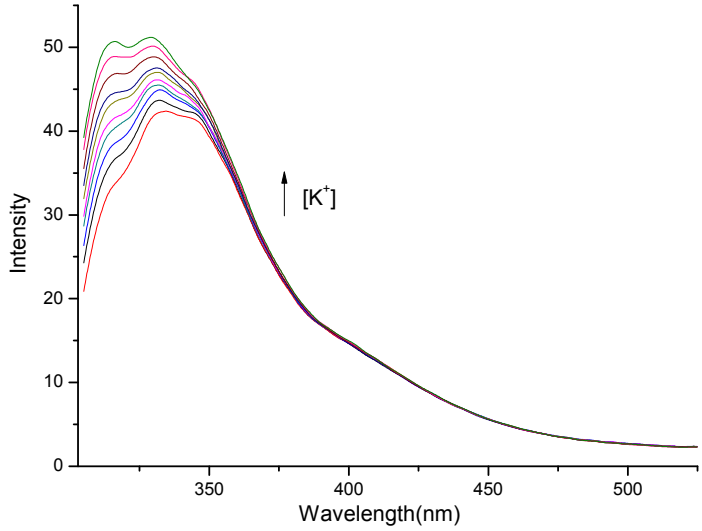
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Wavelength(nm)
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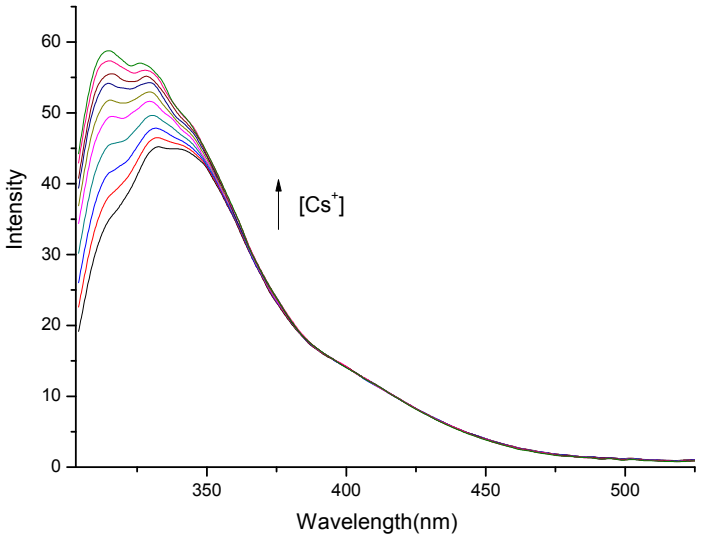
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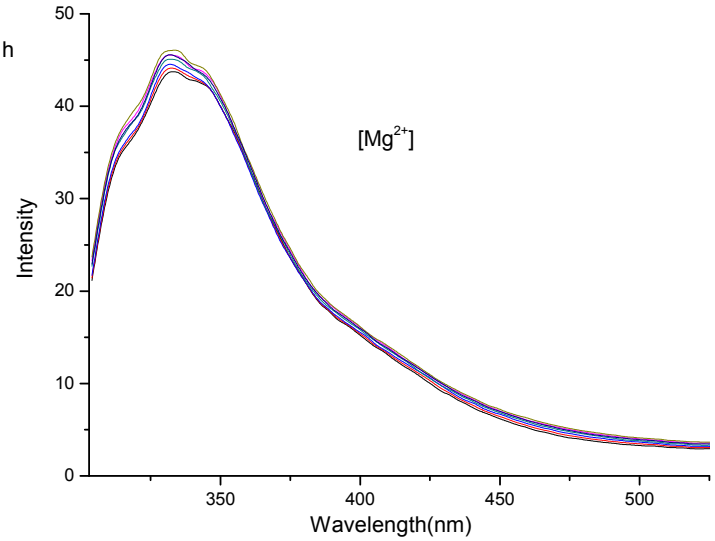
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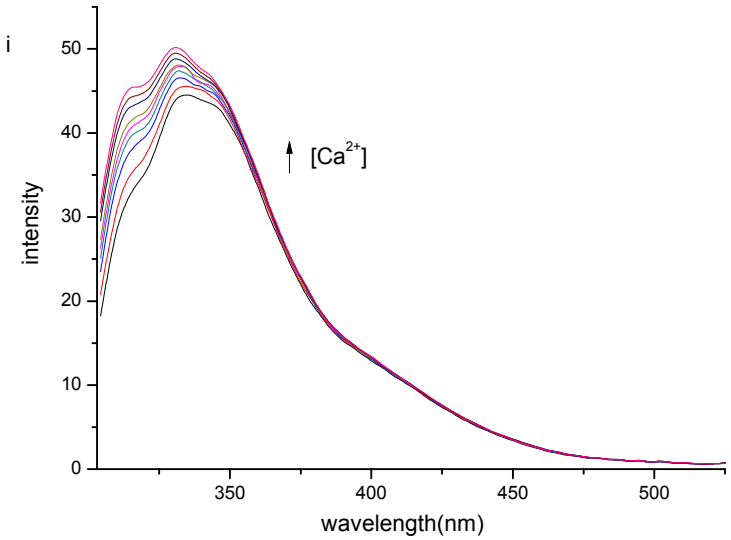
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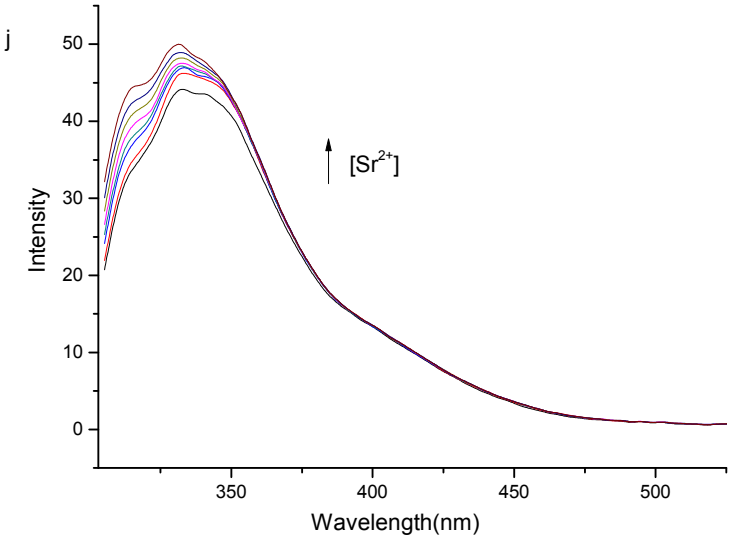
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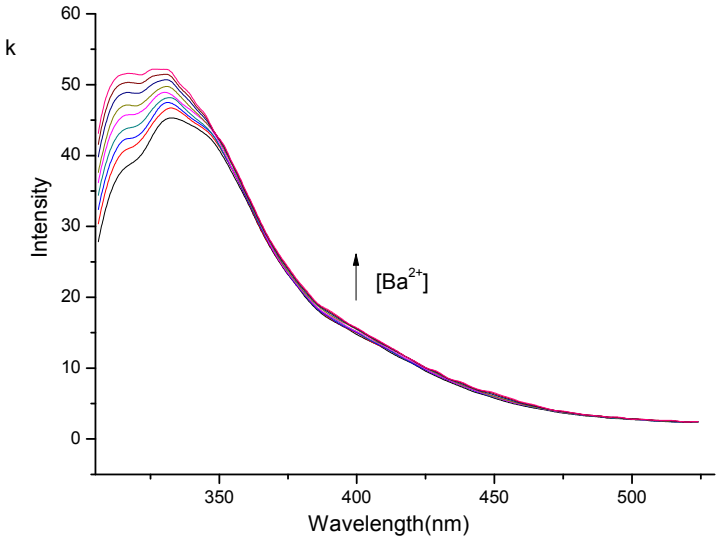

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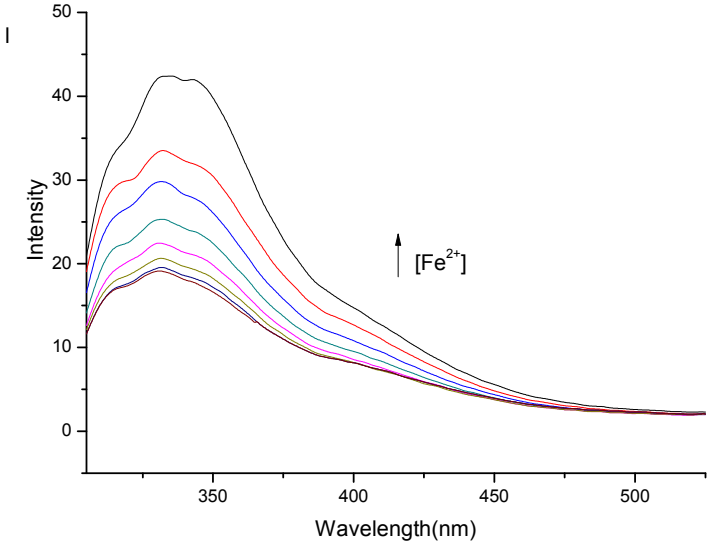

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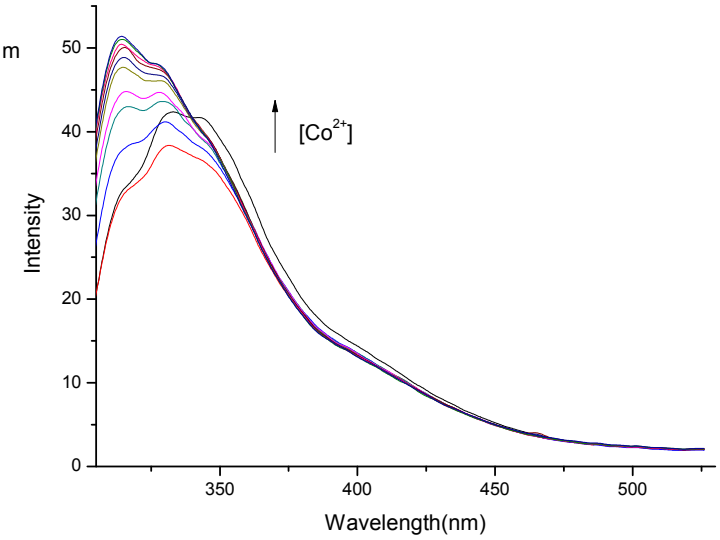
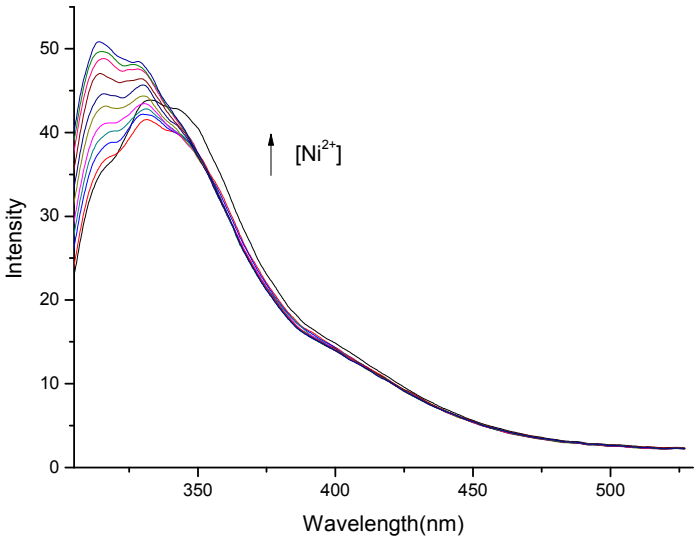
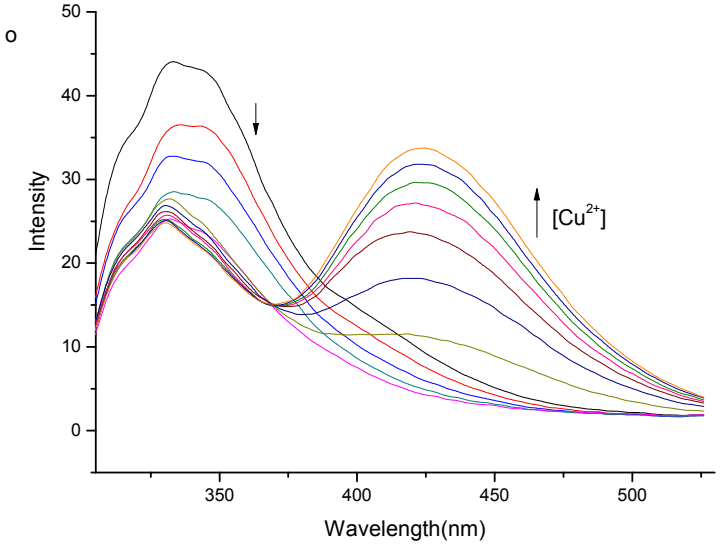


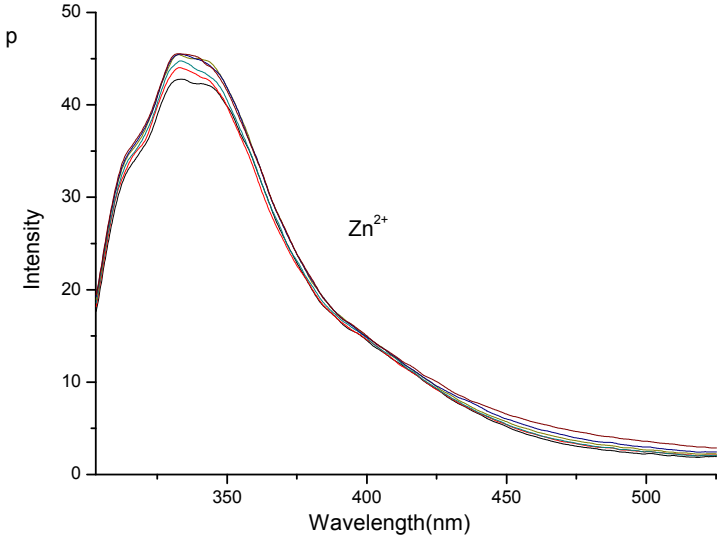
n



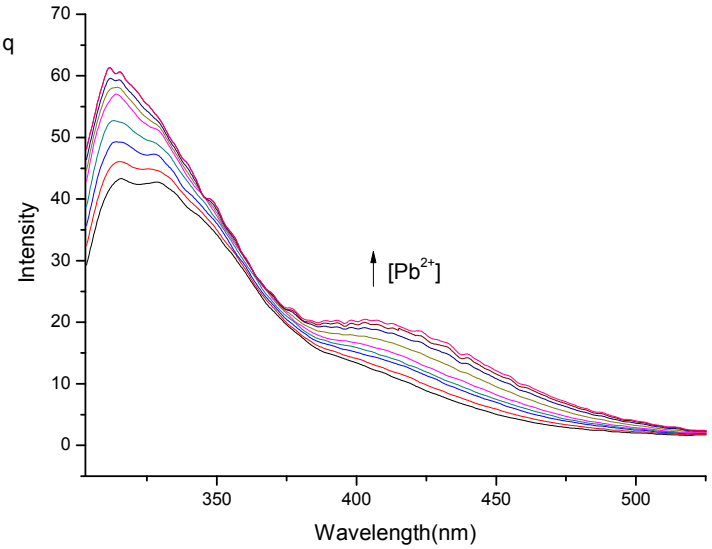
o



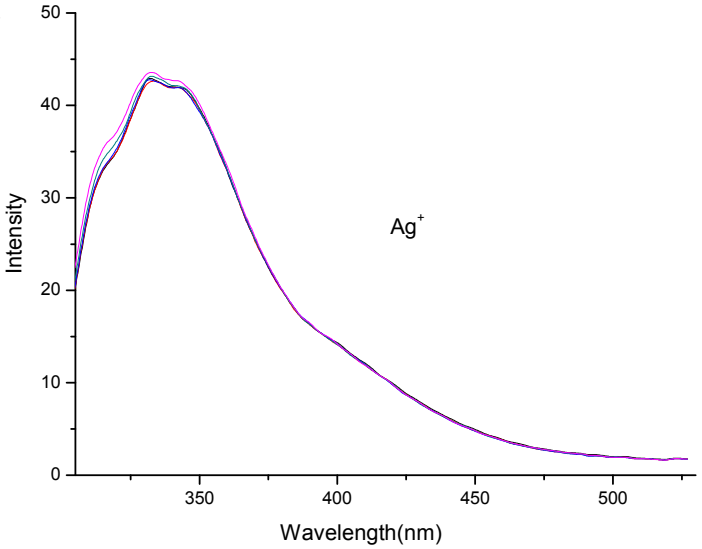
p



q



r



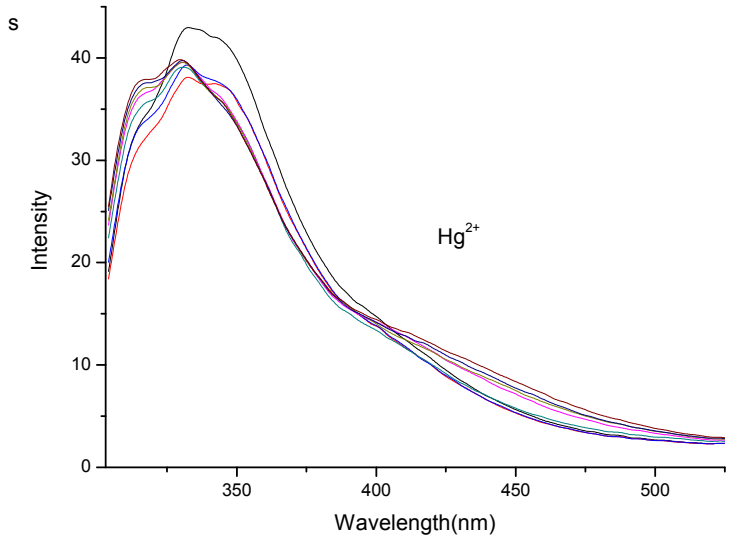


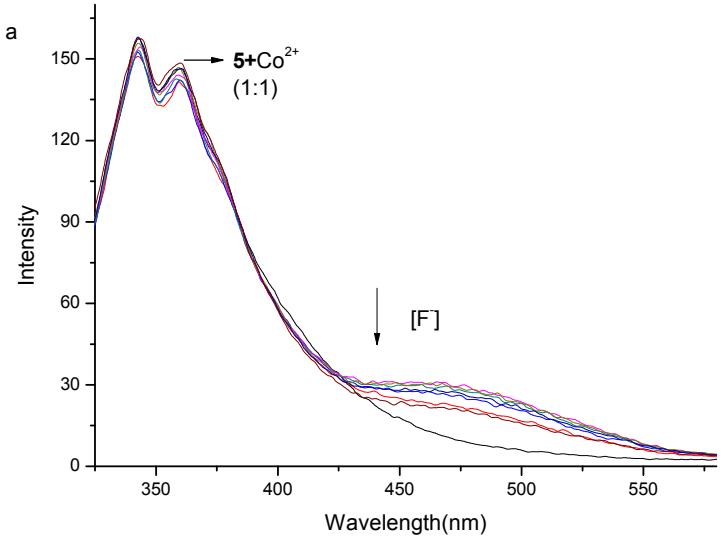
Figure S5: Fluorescence titration curves of **6** (3.18×10^{-4} M) in acetonitrile (2mL) with increasing of (a) $Bu_4N^+F^-$ (0~3.26×10^{-4} M), (b) $Bu_4N^+Br^-$, $Bu_4N^+Cl^-$, $Bu_4N^+NO_3^-$, $Bu_4N^+CH_3CO_2^-$, $Bu_4N^+N_3^-$ (0~2.70×10^{-4} M), (c) $Bu_4N^+CN^-$ (0~3.26×10^{-4} M), (d) K^+ (0~9.00×10^{-4} M), (e) Li^+, Rb(0~9.00×10^{-4} M), (f) K^+ (0~9.00×10^{-4} M), (g) Cs^+ (0~12.00×10^{-4} M), (h) Mg^{2+} (0~5.41×10^{-4} M), (i) Ca^{2+} (0~7.20×10^{-4} M), (j) Sr^{2+} (0~6.31×10^{-4} M), (k)Ba^{2+} (0~7.20×10^{-4} M), (l) Fe^{2+} (0~6.31×10^{-4} M), (m) Co^{2+} (0~9.01×10^{-4} M), (n) Ni^{2+} (0~9.01×10^{-4} M), (o) Cu^{2+} (0~9.90×10^{-4} M), (p) Zn^{2+} (0~6.30×10^{-4} M), (q) Pb^{2+} (0~6.31×10^{-4} M), (r) Ag^+ (0~2.70×10^{-4} M), (s) Hg^{2+} (0~6.31×10^{-4} M). The counter ion for these cations is ClO_4^-.

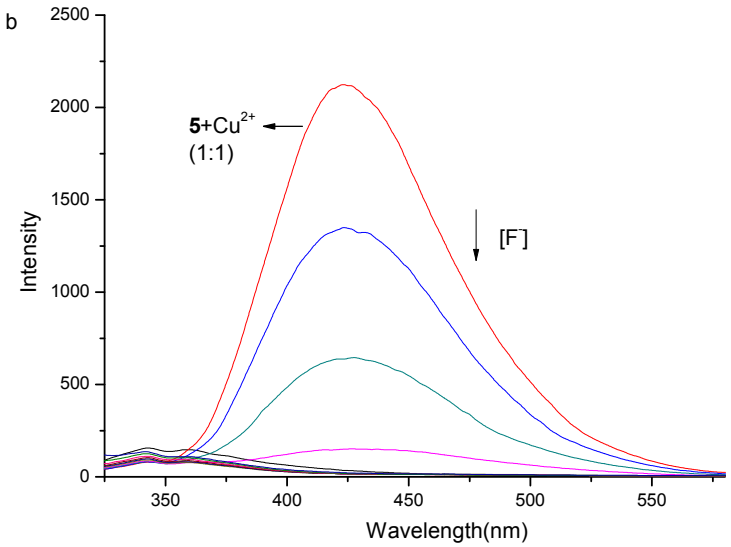
Table S3: Association constants $K_a(M^{-1})$ of **6** with ions

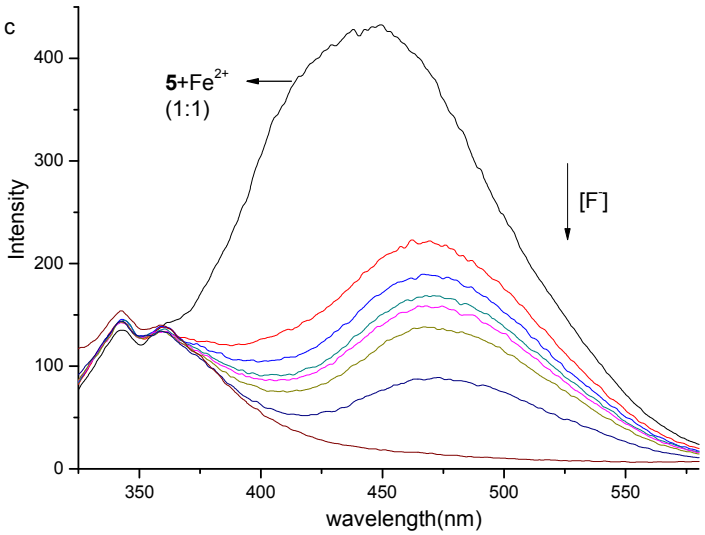
F^-	1.108×10^4	Li^+, Rb^+	/
CN^-	5.871×10^3	Na^+	/
Cl^-	/	K^+	5.903×10^3
Br^-	/	Cs^+	9.855×10^2
N_3^-	/	Mg^{2+}	/
$CH_3CO_2^-$	/	Ca^{2+}	1.864×10^4
NO_3^-	/	Sr^{2+}	3.879×10^4
		Ba^{2+}	9.628×10^3
		Fe^{2+}	1.539×10^5
		Co^{2+}	1.016×10^4
		Ni^{2+}	3.904×10^3
		Cu^{2+}	/[a]
		Zn^{2+}	/[a]
		Pb^{2+}	6.560×10^3

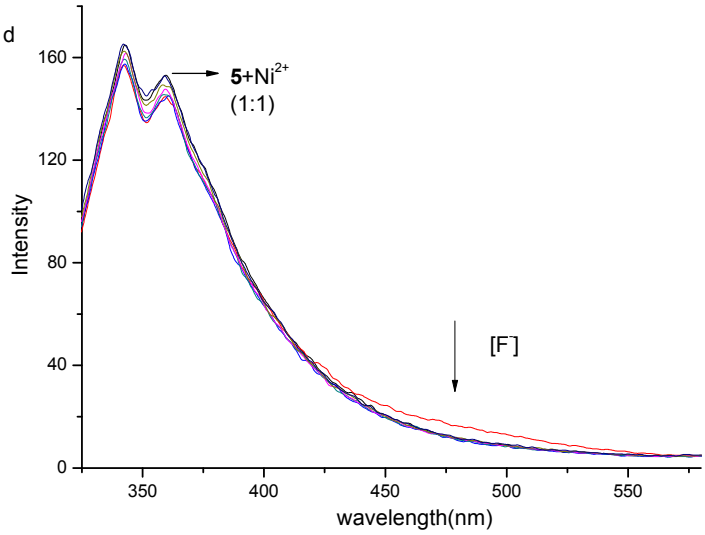
		Ag^{+}	/
		Hg^{2+}	/[a]

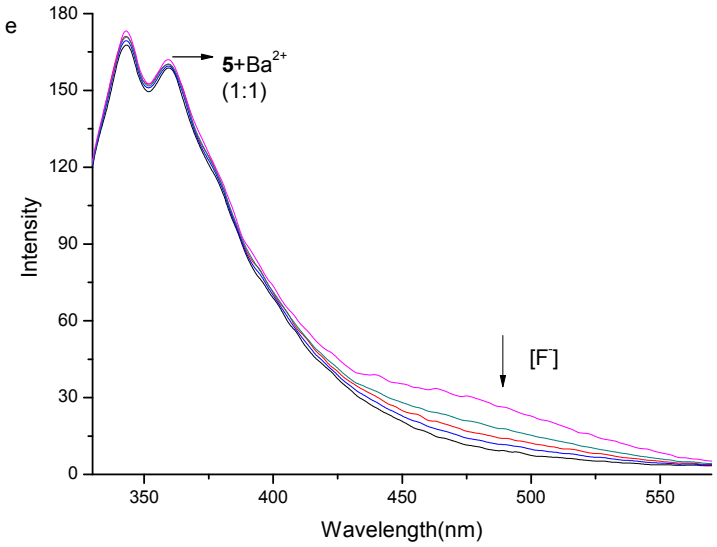
a. Spectral change is observed, but association constant is not available.

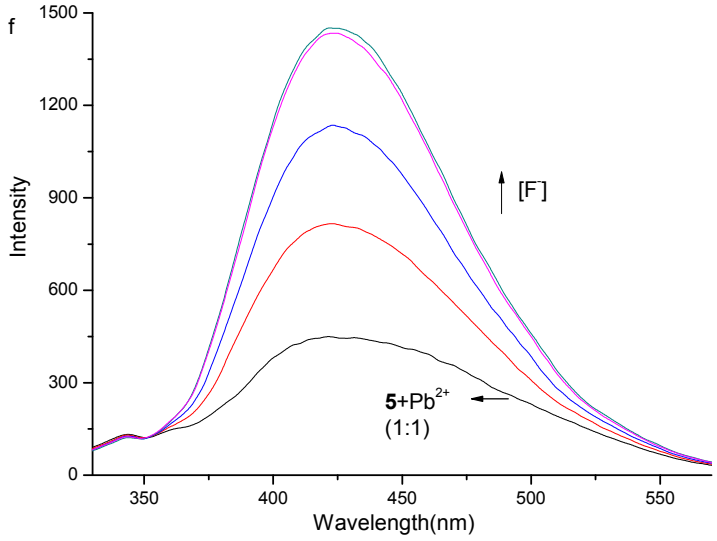





c
400
300
200
100
0
Intensity
5+Fe2+
(1:1)
[F-]
350
400
450
500
550
wavelength(nm)


d
160
120
80
40
0
Intensity
5+Ni2+
(1:1)
[F-]
350
400
450
500
550
wavelength(nm)


e
180
150
120
90
60
30
0
Intensity
350
400
450
500
550
Wavelength(nm)
5+Ba2+
(1:1)
[F-]


f
1500
1200
900
600
300
0
Intensity
350
400
450
500
550
Wavelength(nm)
[F-]
5+Pb2+
(1:1)

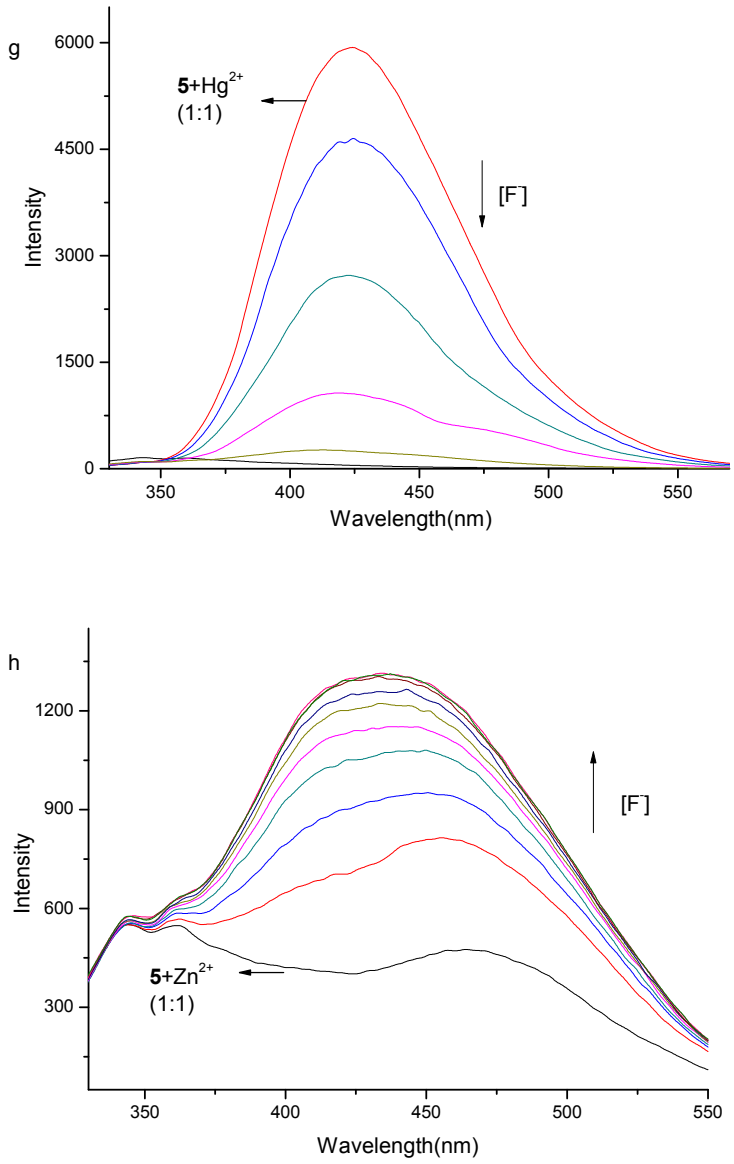
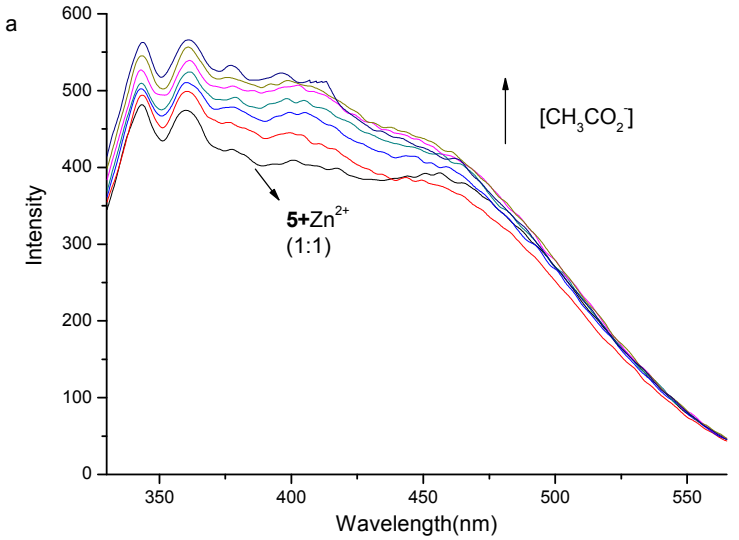
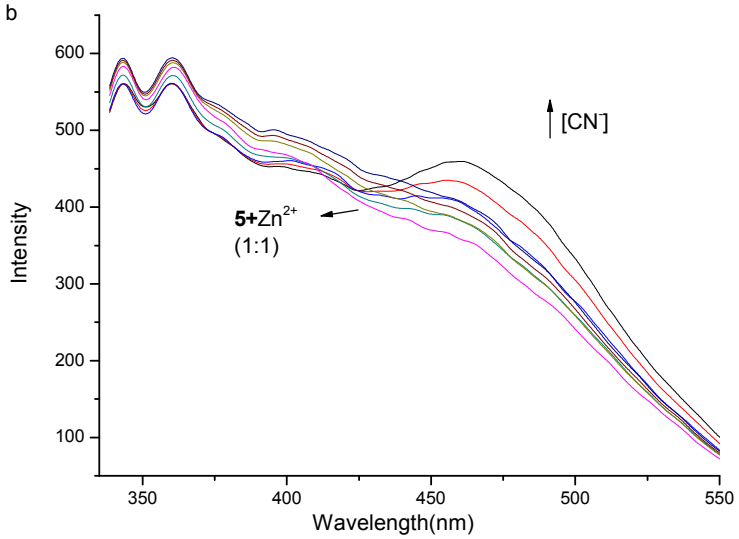
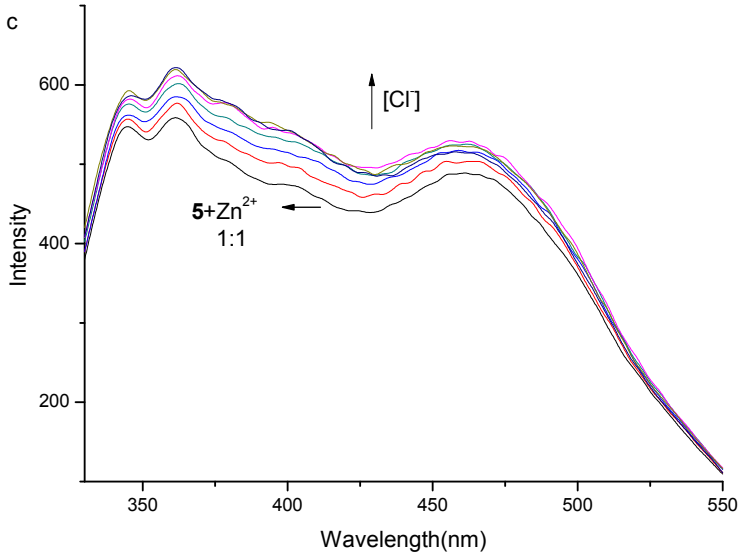
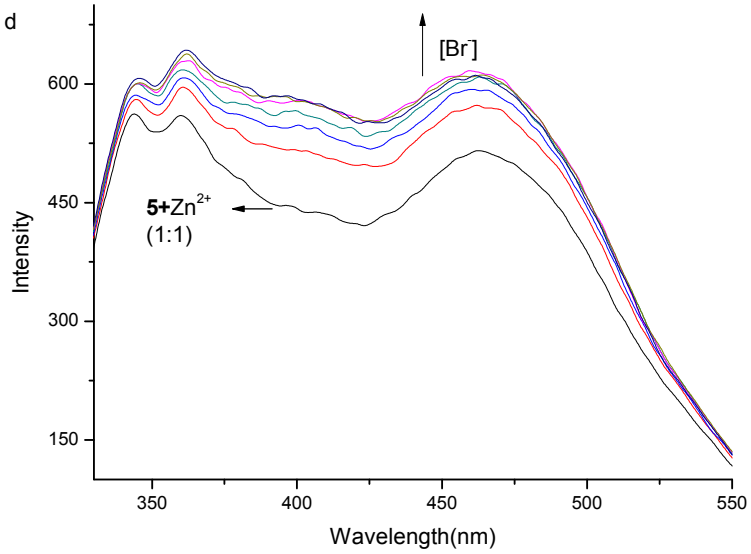


Figure S6: Fluorescence titration curves of **5** (3.984×10^{-4} M) in acetonitrile (2mL) with increasing of $Bu_4N^+F^-$ (0~7.388×10^{-4} M) in the presence of (a) $Co(ClO_4)_2$ (4.003×10^{-4} M), (b) $Cu(ClO_4)_2$(3.992×10^{-4}M), (c) $Fe(ClO_4)_2$ (3.994×10^{-4} M), (d) i $Ni(ClO_4)_2$ (3.996×10^{-4} M), (e) $Ba(ClO_4)_2$ (3.994×10^{-4} M), (f) $Pb(ClO_4)_2$ (4.001×10^{-4} M), (g) $Hg(ClO_4)_2$ (3.996×10^{-4}M) and (h) $Bu_4N^+F^-$ (0.465, 0.920, 1.395, 1.840, 2.325, 2.790, 3.255, 3.720, 4.185×10^{-4} M) in the presence of $Zn(ClO_4)_2$ (3.991×10^{-4} M).


a
600
500
400
300
200
100
0
Intensity
350
400
450
500
550
Wavelength(nm)
[CH3CO2-]
5+Zn2+
(1:1)


b
600
500
400
300
200
100
Intensity
350
400
450
500
550
Wavelength(nm)
[CN-]
5+Zn2+
(1:1)


c
600
400
200
Intensity
[Cl-]
5+Zn2+
1:1
350
400
450
500
550
Wavelength(nm)


d
600
450
300
150
Intensity
[Br-]
5+Zn2+
(1:1)
350
400
450
500
550
Wavelength(nm)

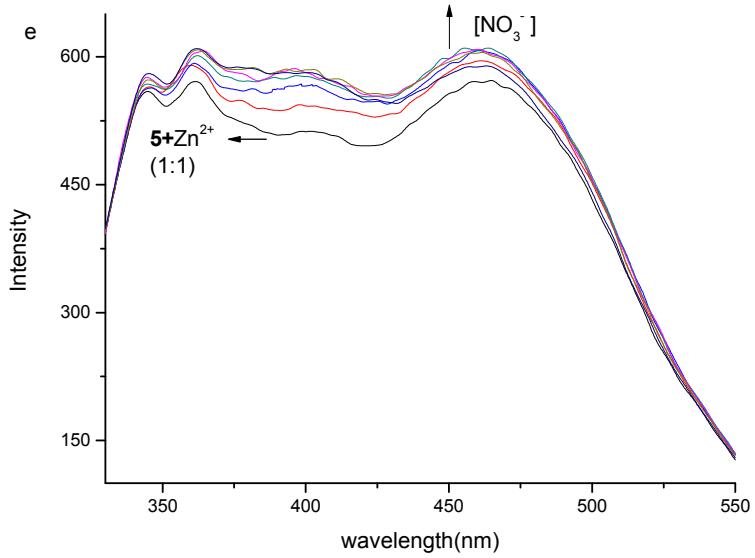
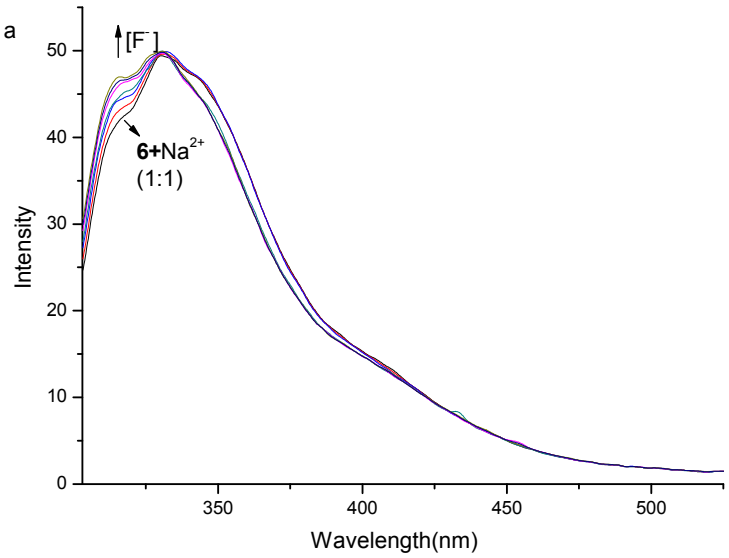


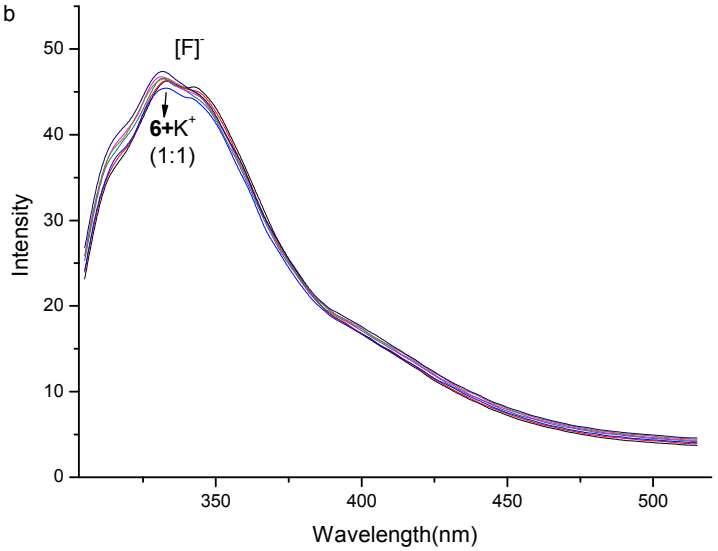
Figure S7: Fluorescence titration curves of the complex of **5** (3.984×10^{-4} M) and zinc ion (4.011×10^{-4} M) in acetonitrile (2ml) with increasing of (a) $Bu_4N^+CH_3CO_2^-$ (0~5.41×10^{-4}M), (b) $Bu_4N^+CN^-$ (0~5.42×10^{-4}M), (c) $Bu_4N^+Cl^-$ (0~9.00×10^{-4}M), (d) $Bu_4N^+Br^-$ (0~10.81×10^{-4} M), (e) $Bu_4N^+NO_3^-$ (0~14.42×10^{-4} M).

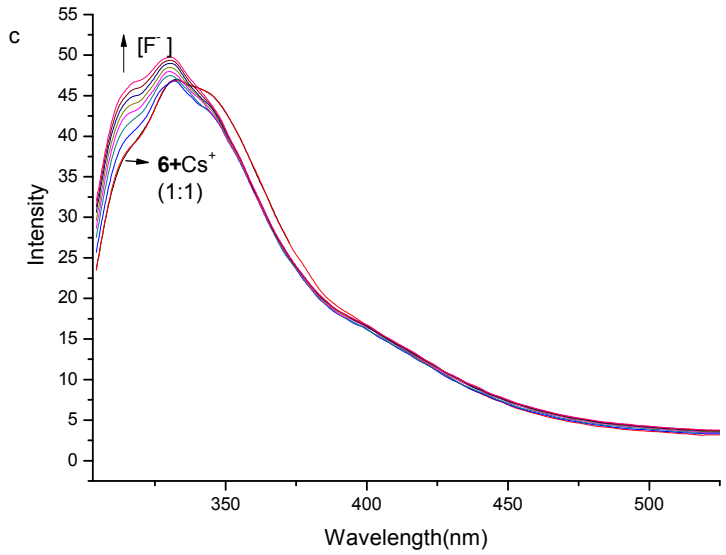
Table S4: Association constants $K_a(M^{-1})$ of compound **5a** and different anions with or without the presence of zinc ion

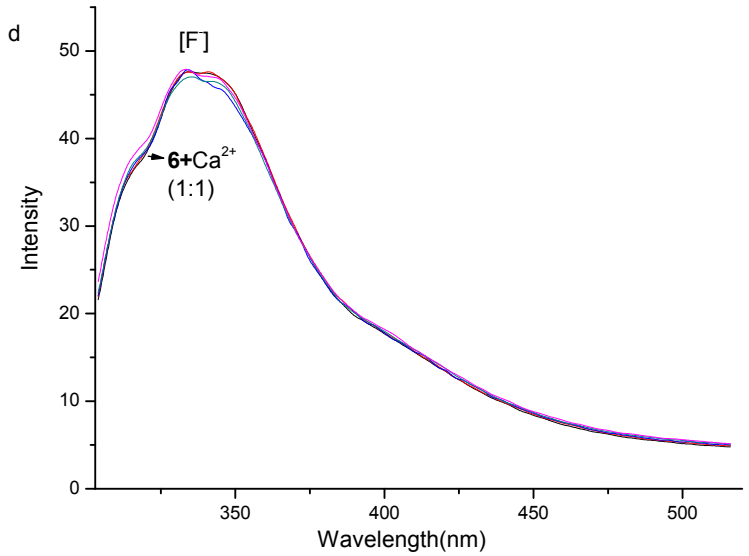
	Ka/M^{-1} [a]	
	free **5**	[**5**·Zn^{2+}]
F^-	6.59×10^3	1.53×10^5
Cl^-	-[c]	7.39×10^3
Br^-	-[c]	1.58×10^3
NO_3^-	-[c]	4.25×10^3
CH_3COO^-	4.52×10^4	3.53×10^4
CN^-	4.16×10^3	-[b]

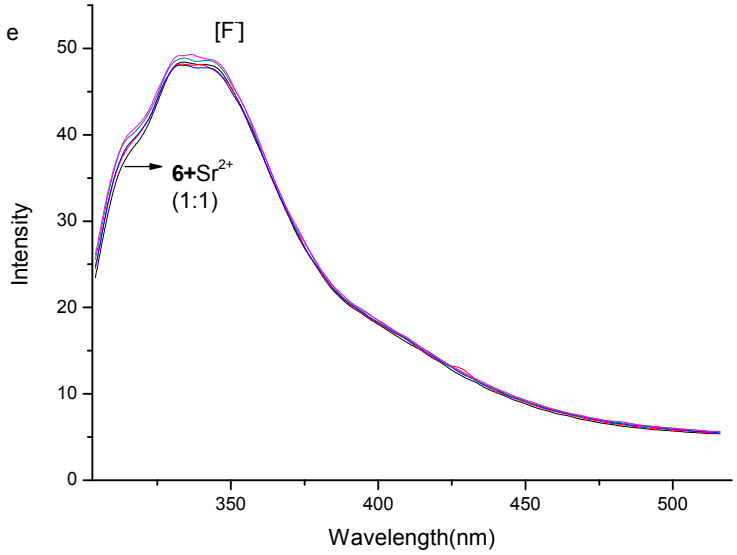
[a] association constants were calculated by using a Hyperquad program. [b] spectral change was observed but failed to calculate the association constant. [c] No spectral change.

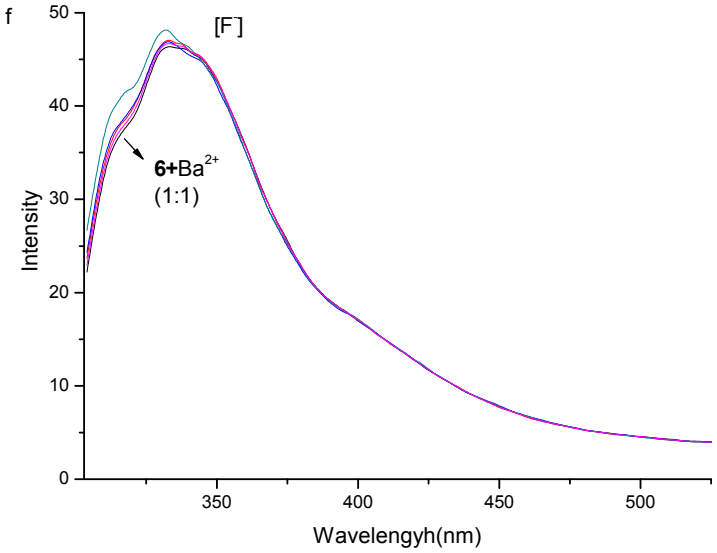

a
[F⁻]
6+Na2+
(1:1)
Intensity
Wavelength(nm)
0
10
20
30
40
50
350
400
450
500

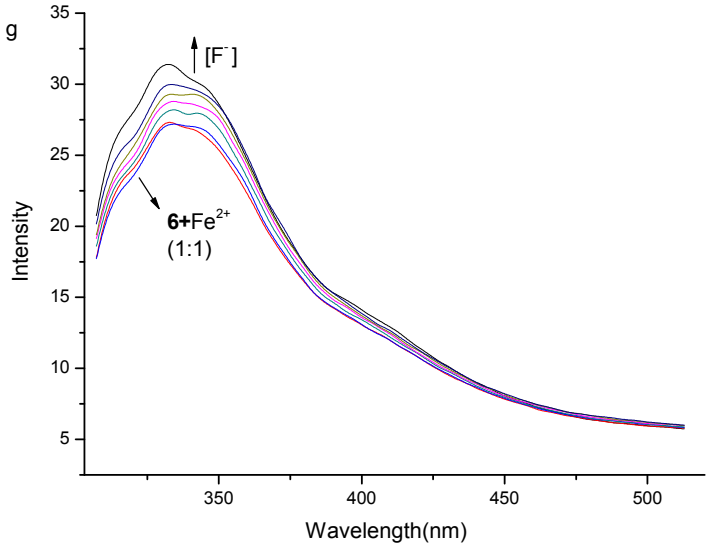

b
[F]-
6+K+
(1:1)
Intensity
Wavelength(nm)
0
10
20
30
40
50
350
400
450
500

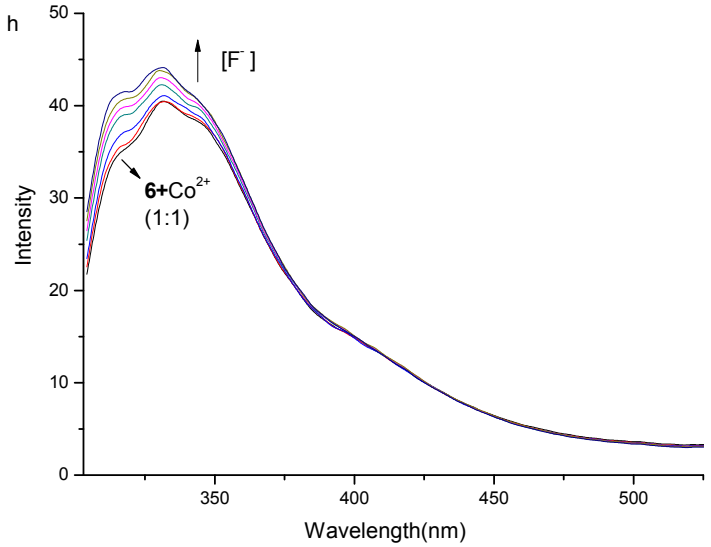


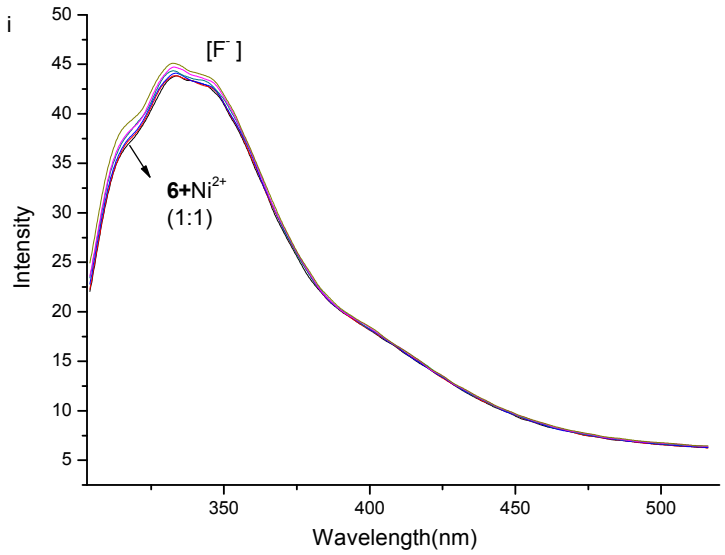


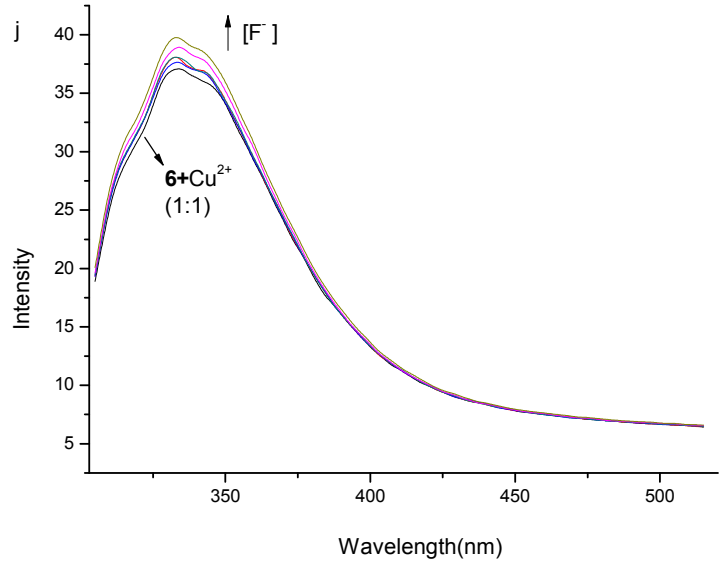


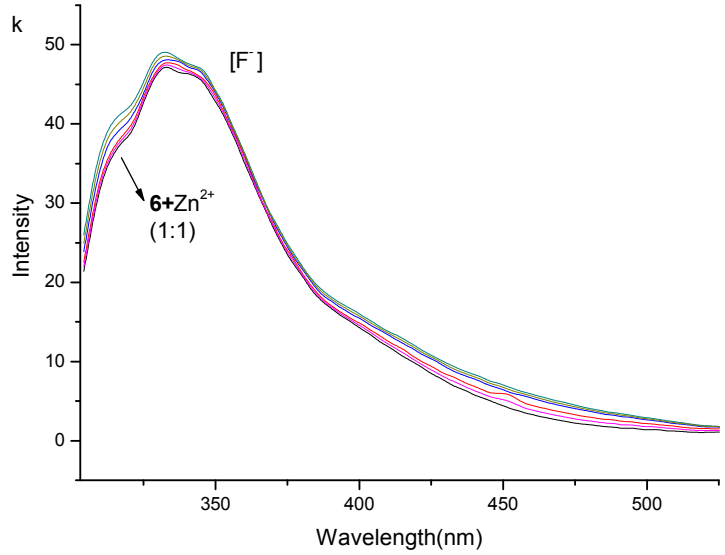


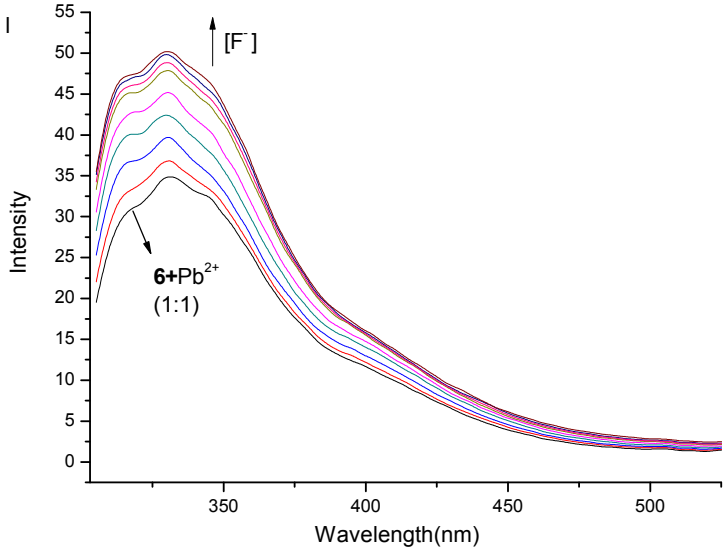

g
[F⁻]
6+Fe2+
(1:1)
Intensity
Wavelength(nm)
35
30
25
20
15
10
5
350
400
450
500


h
[F⁻]
6+Co2+
(1:1)
Intensity
Wavelength(nm)
50
40
30
20
10
0
350
400
450
500


i
[F⁻]
6+Ni2+
(1:1)
Intensity
Wavelength(nm)


j
[F⁻]
6+Cu2+
(1:1)
Intensity
Wavelength(nm)


k
Intensity
Wavelength(nm)
[F-]
6+Zn2+
(1:1)


l
Intensity
Wavelength(nm)
[F-]
6+Pb2+
(1:1)

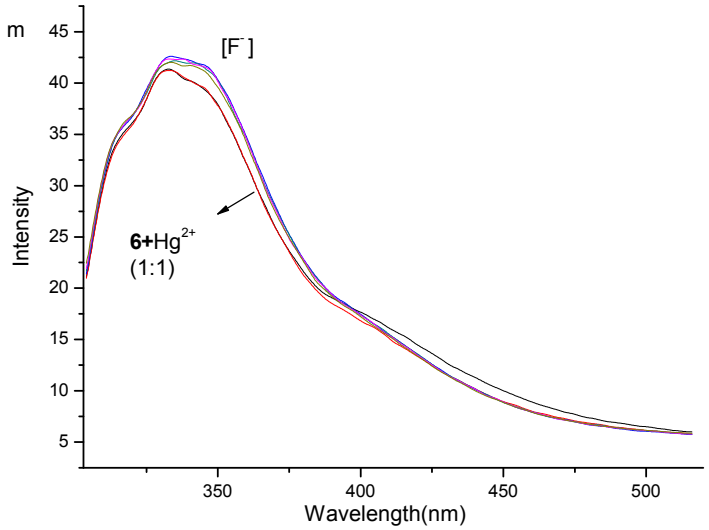
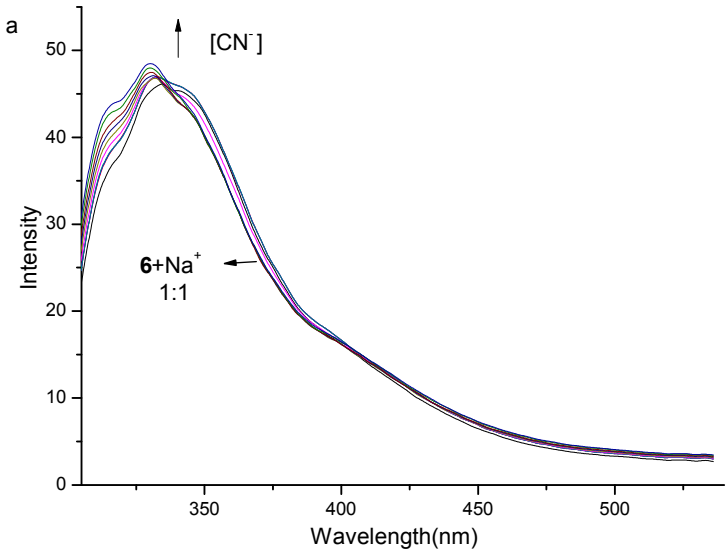
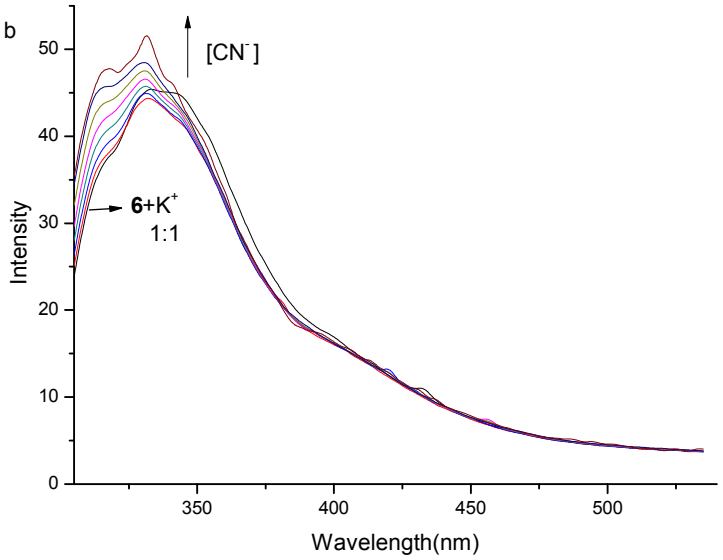
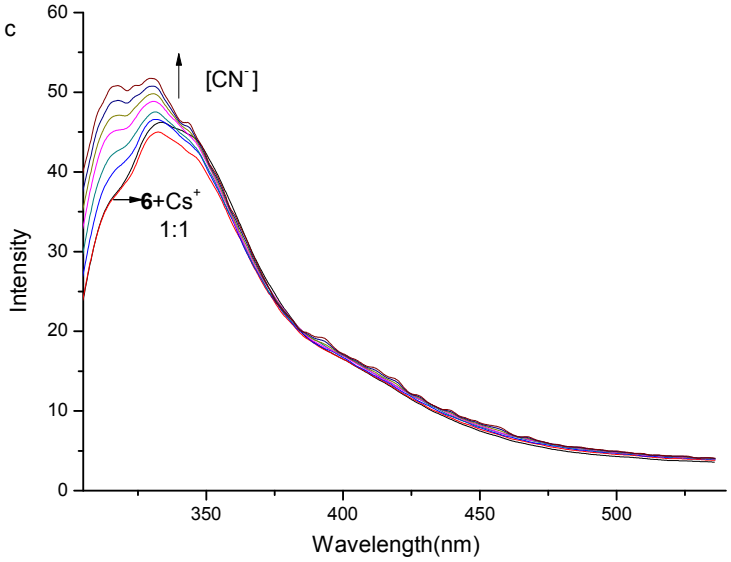
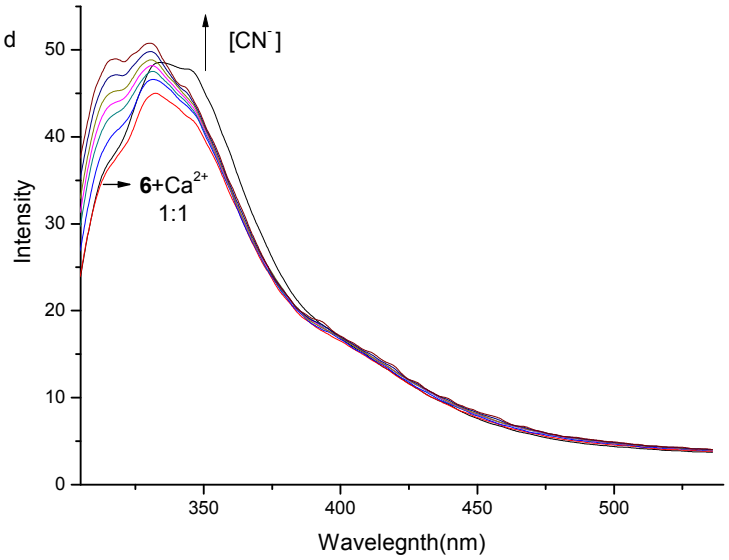


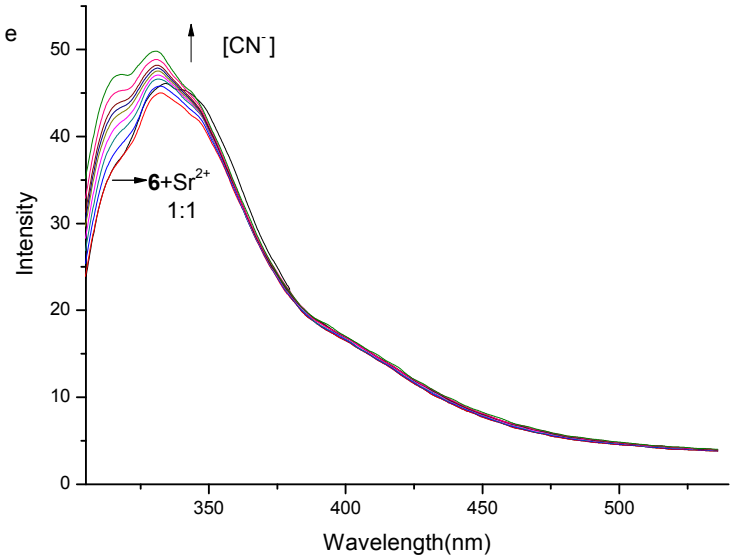
Figure S8: Fluorescence titration curves of **6** (3.18×10^{-4} M) in acetonitrile (2mL) with increasing of $Bu_4N^+F^-$ (0.62, 1.24, 1.86, 2.48, 3.10, 3.72, 4.34, 4.96×10^{-4} M)respectively, in the presence of (a) $NaClO_4$ (3.20×10^{-4} M), (b) $KClO_4$ (3.20×10^{-4} M), (c) $CsClO_4$ (3.20×10^{-4} M), (d) $Ca(ClO_4)_2$ (3.12×10^{-4} M), (e) $Sr(ClO_4)_2$ (3.11×10^{-4} M), (f) $Ba(ClO_4)_2$ (3.10×10^{-4}M), (g) $Fe(ClO_4)_2$ (3.10×10^{-4} M), (h) $Co(ClO_4)_2$ (3.10×10^{-4} M), (i) $Ni(ClO_4)_2$ (3.10×10^{-4} M), (j) $Cu(ClO_4)_2$ (3.10×10^{-4} M), (k) $Zn(ClO_4)_2$ (3.14×10^{-4} M), (l) $Pb(ClO_4)_2$ (3.10×10^{-4} M) and (m) $Hg(ClO_4)_2$ (3.12×10^{-4} M).

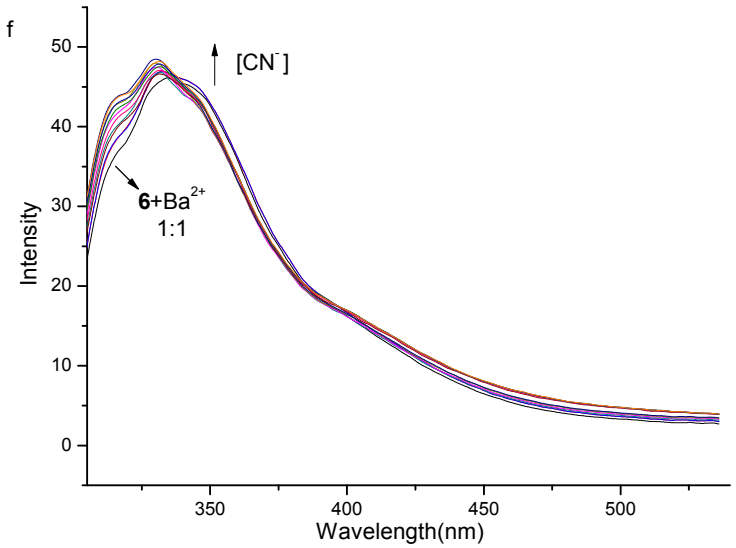


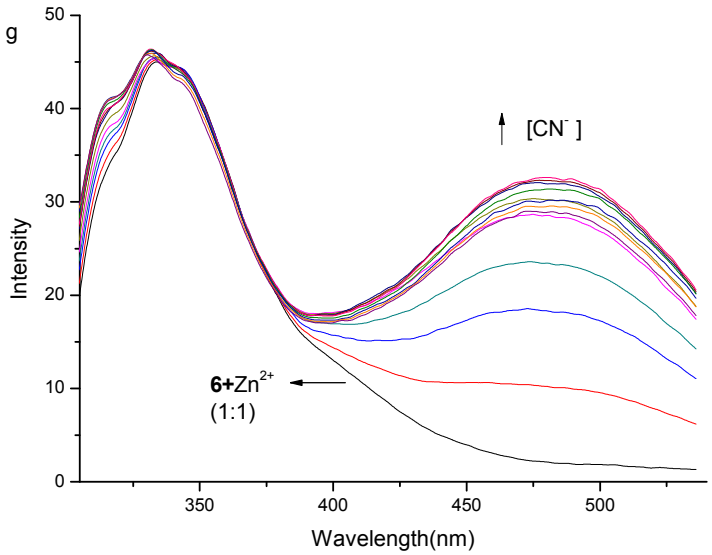





d
[CN-]
6+Ca2+
1:1
Intensity
Wavelegnth(nm)
0
10
20
30
40
50
350
400
450
500


e
[CN-]
6+Sr2+
1:1
Intensity
Wavelength(nm)
0
10
20
30
40
50
350
400
450
500


f
[CN-]
6+Ba2+
1:1
Intensity
Wavelength(nm)


g
[CN-]
6+Zn2+
(1:1)
Intensity
Wavelength(nm)

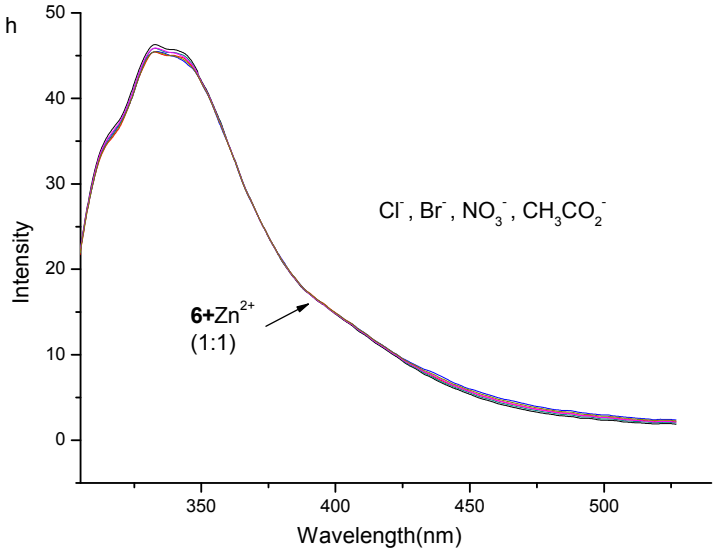


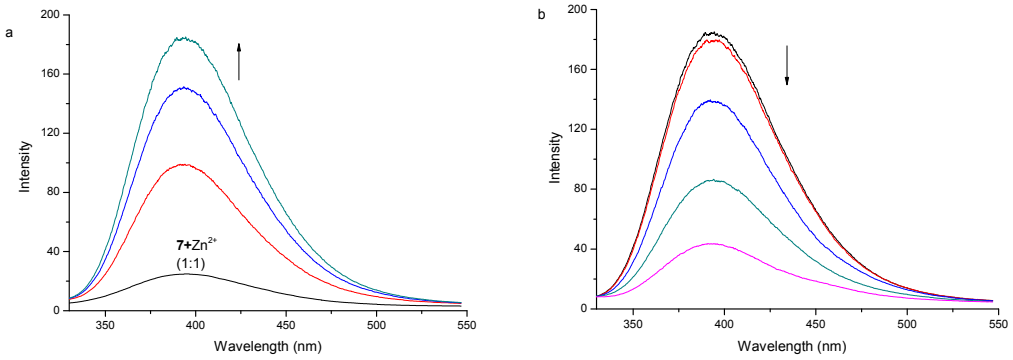
Figure S9: Fluorescence titration curves of **6** (3.18×10^{-4} M in acetonitrile) with increasing of $Bu_4N^+CN^-$(0~ 7.23×10^{-4} M) in the presence of (a) $NaClO_4$ (3.20×10^{-4} M), (b) $KClO_4$ (3.20×10^{-4} M), (c) $CsClO_4$ (3.20×10^{-4} M), (d) $Ca(ClO_4)_2$ (3.12×10^{-4}M), (e) $Sr(ClO_4)_2$ (3.11×10^{-4}M), (f) $Ba(ClO_4)_2$ (3.10×10^{-4}M), (g) $Zn(ClO_4)_2$ (3.20×10^{-4} M). (h) Fluorescence titration curves of **6** (3.18×10^{-4} M in acetonitrile) with increasing of $Bu_4N^+Cl^-$, $Bu_4N^+Br^-$, $Bu_4N^+NO_3^-$, $Bu_4N^+CH_3CO_2^-$ (0~6.01×10^{-4} M) in the presence of $Zn(ClO_4)_2$ (3.20×10^{-4} M).

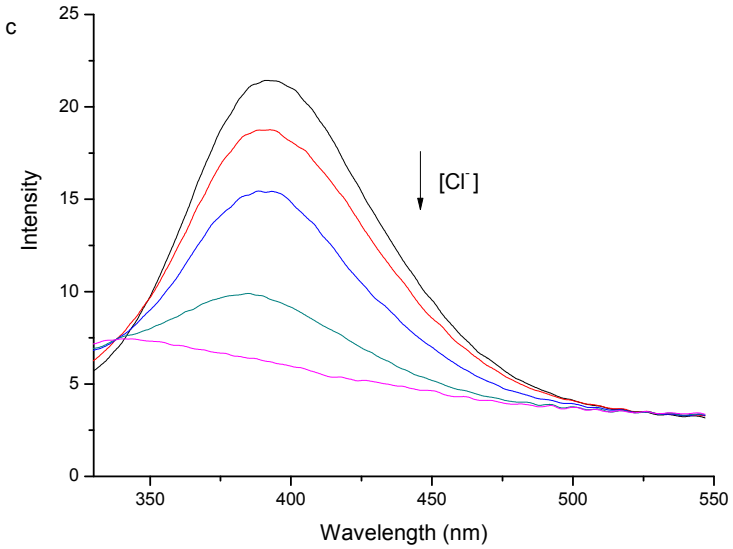
Table S5: Association constants $K_a(M^{-1})$ of compound **6** and CN^- with or without the presence of cations

	Ka/M^{-1} [a]
	[6·M]
free **6**	5.871×10^3
Na^+	/[b]
K^+	4.164×10^3
Cs^+	8.356×10^3
Ca^{2+}	7.682×10^3
Sr^{2+}	3.461×10^3

Ba^{2+}	/[b]
Zn^{2+}	/[b]

[a] association constants were calculated by using a Hyperquad program. [b] spectral change was observed but failed to calculate the association constant.





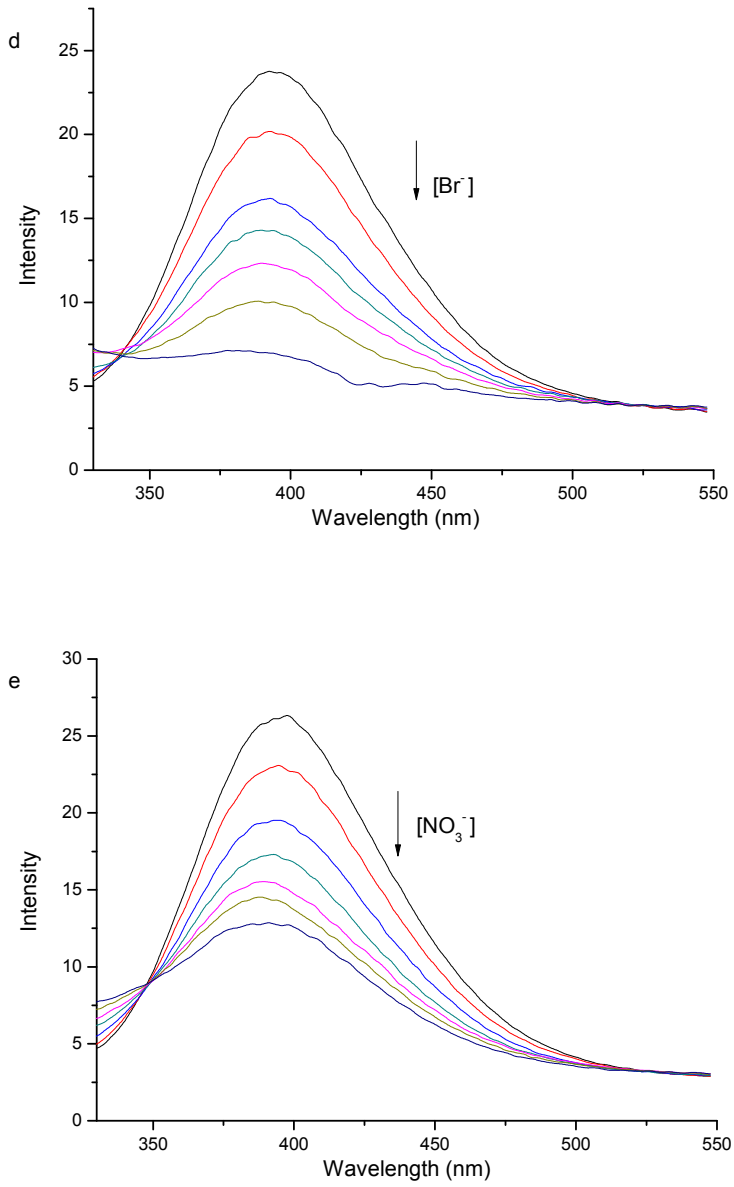


Figure S10: Fluorescence titration curves of **7** (2.812×10^{-4} M) in acetonitrile (2 ml) in the presence of $Zn(ClO_4)_2$ (2.824×10^{-4} M) with increasing of $Bu_4N^+F^-$ (a) (0, 0.465, 0.93 $\times 10^{-4}$ M) and (b) (1.395, 1.86, 2.325, 2.79, 3.348 $\times 10^{-4}$ M), respectively, (c) $Bu_4N^+Cl^-$ (0~2.44×10^{-4} M), (d) $Bu_4N^+Br^-$ (0~2.718×10^{-4} M), (e) $Bu_4N^+NO_3^-$ (0~2.754×10^{-4} M).

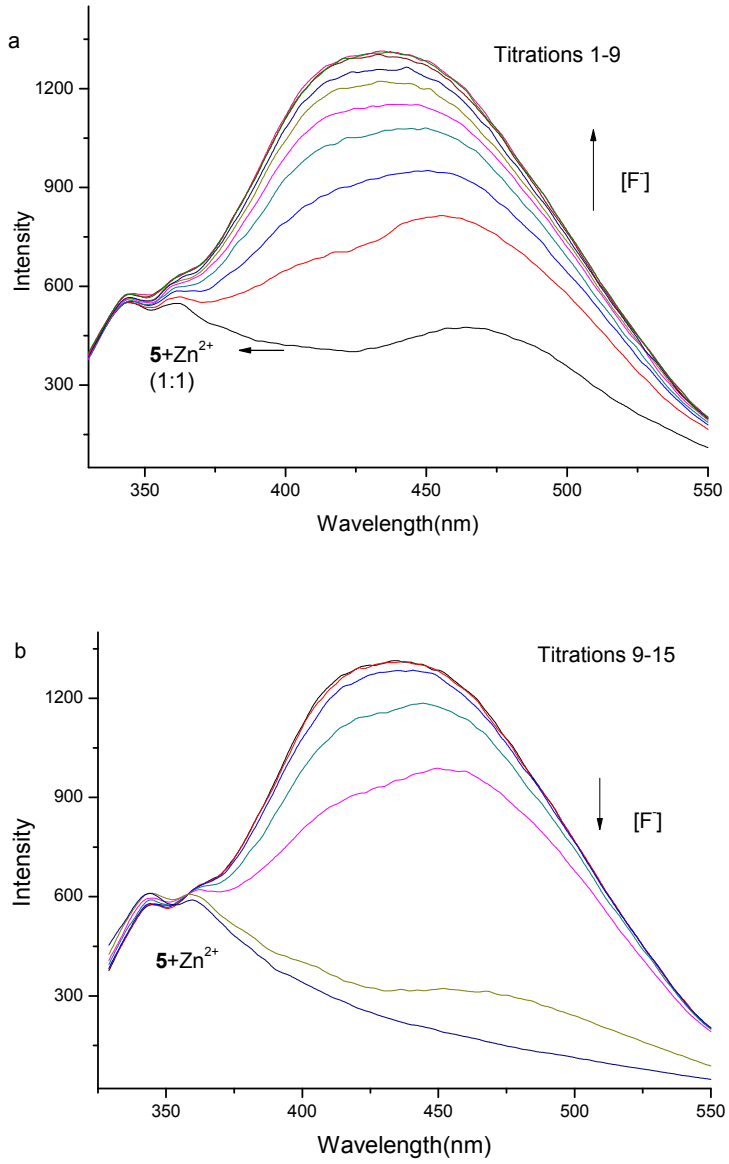


Figure S11: Fluorescence titration curves of the complex of **5** (3.984×10^{-4} M) and zinc ion (4.011×10^{-4} M) in acetonitrile (2ml) with increasing of Bu_4NF (a) 0~4.185×10^{-4} M, (b) 4.185~6.975×10^{-4} M.

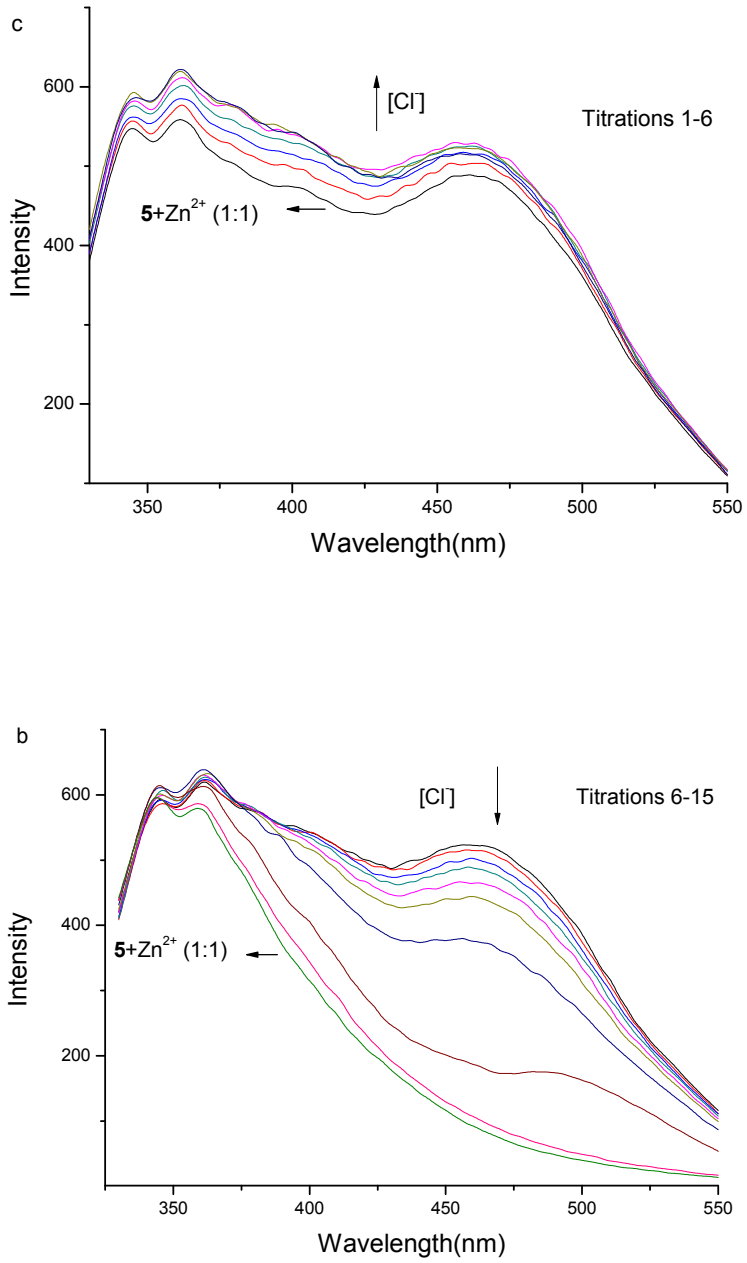


Figure S12: Fluorescence titration curves of the complex of **5** (3.984×10^{-4} M) and zinc ion (4.011×10^{-4} M) in acetonitrile (2ml) with increasing of $Bu_4N^+Cl^-$ (a) ($0\sim3.60\times10^{-4}$M), $Bu_4N^+Cl^-$ ($3.60\sim9.00\times10^{-4}$M),

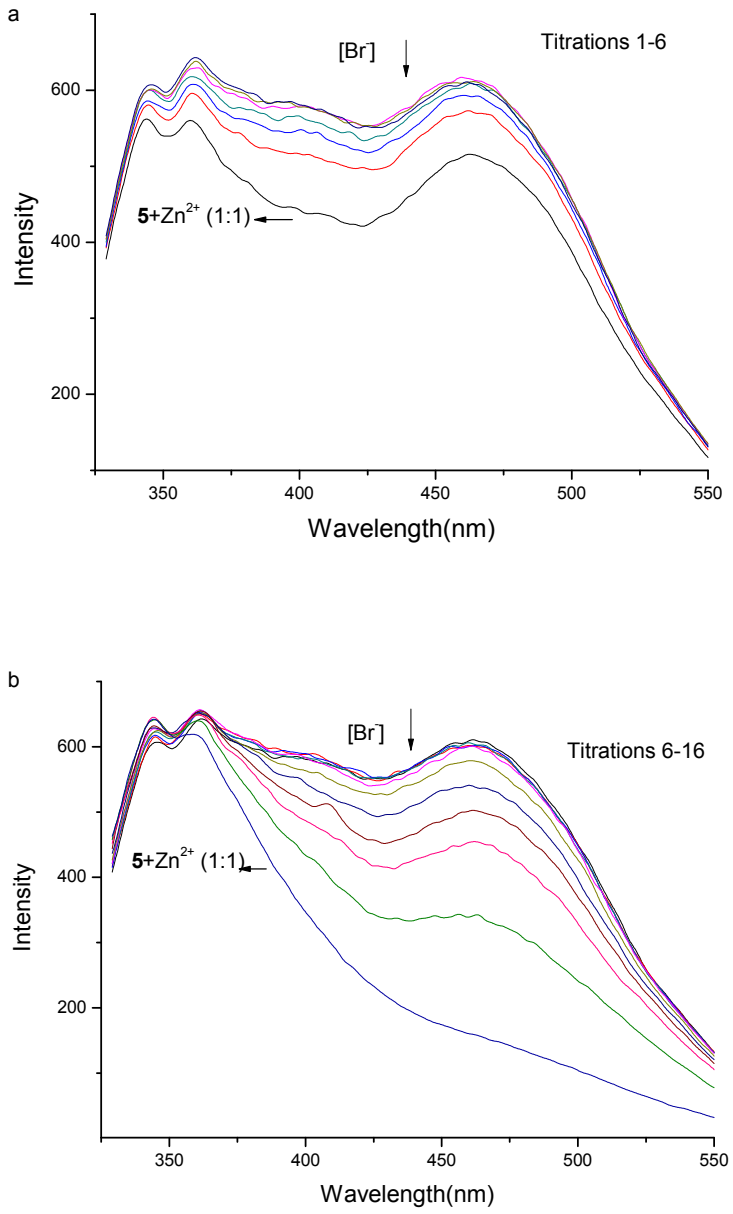


Figure S13: Fluorescence titration curves of the complex of **5** (3.984×10^{-4} M) and zinc ion (4.011×10^{-4} M) in acetonitrile (2ml) with increasing of Bu_4NBr (a) 0~4.050×10^{-4} M, (b) 4.050~10.81×10^{-4} M.

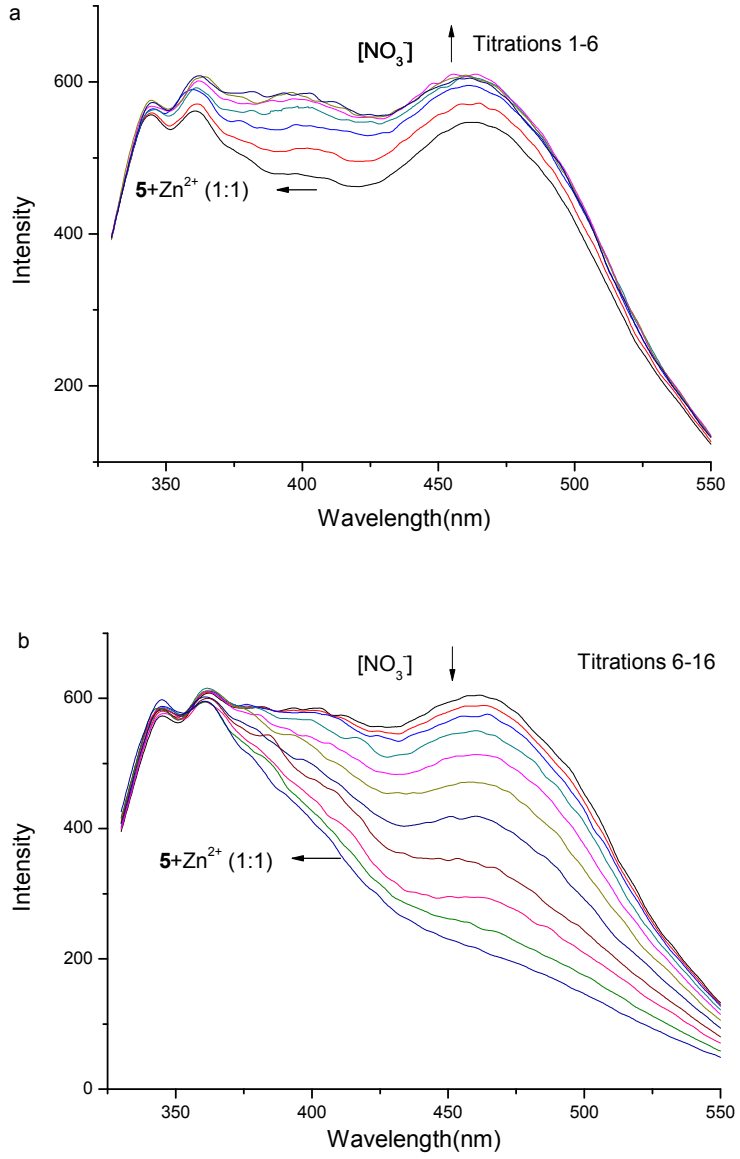
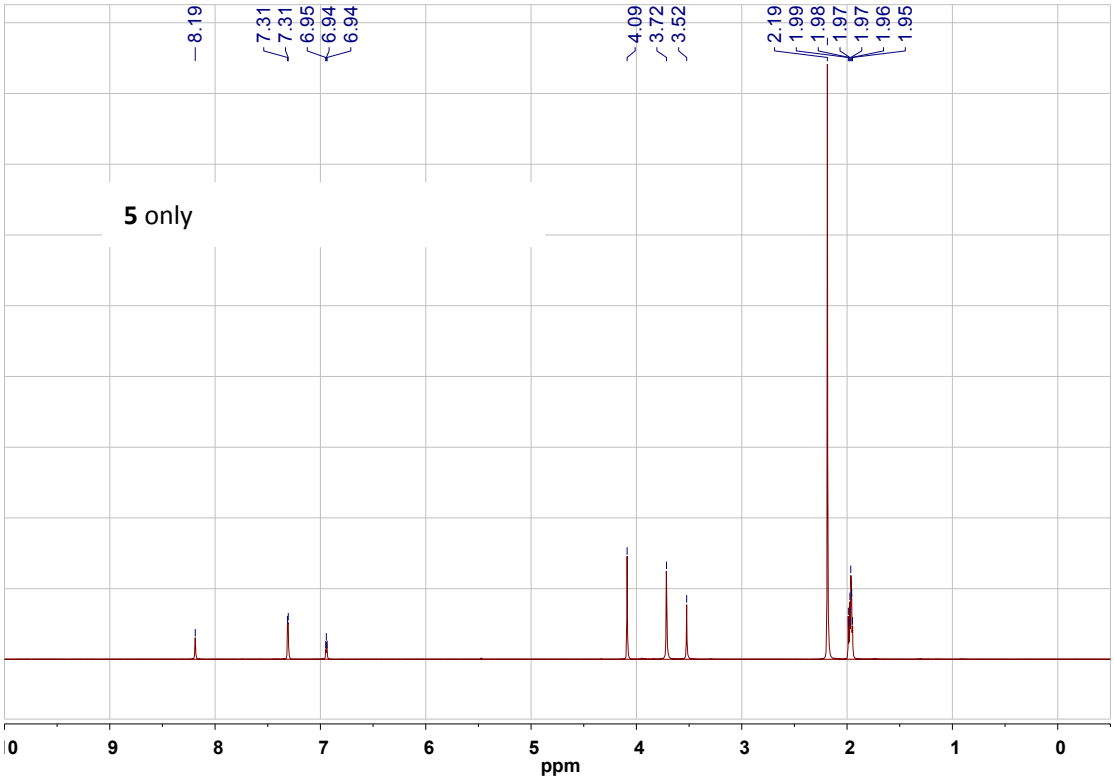
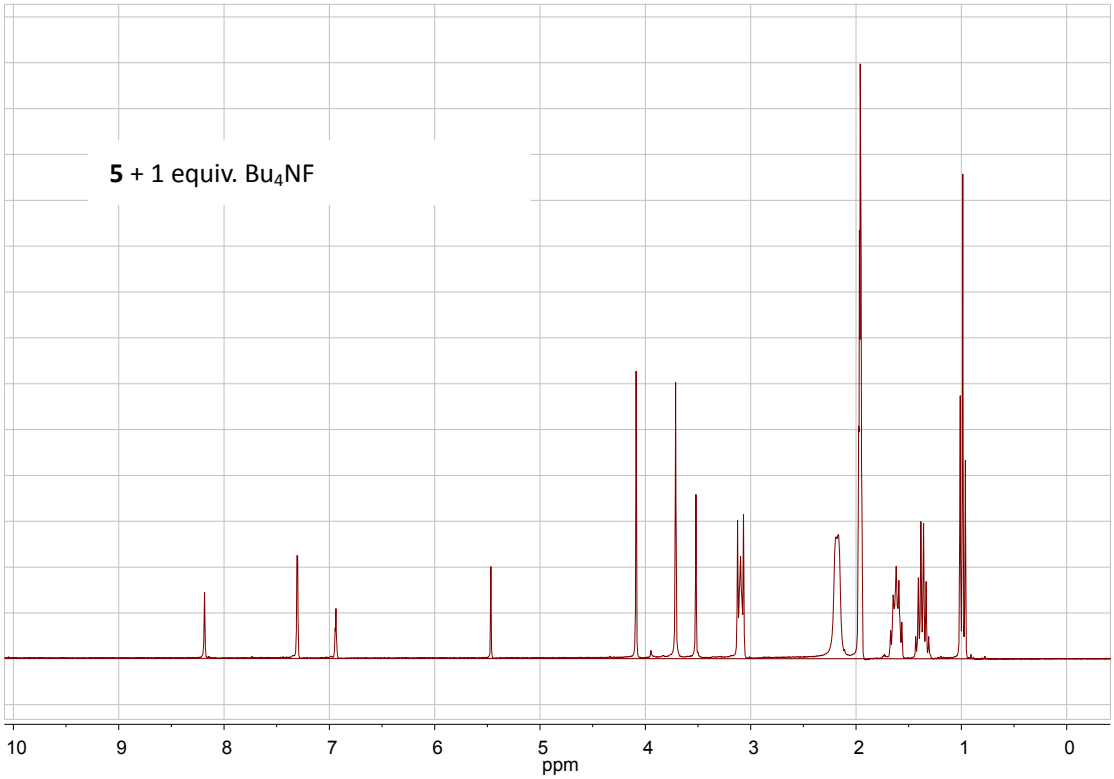


Figure S14: Fluorescence titration curves of the complex of **5** (3.984×10^{-4} M) and zinc ion (4.011×10^{-4}M) in acetonitrile (2ml) with increasing of Bu_4NO_3 (a) 0~3.605×10^{-4} M, (b) 3.605~14.42×10^{-4} M.

5. ^{1}H NMR titration data





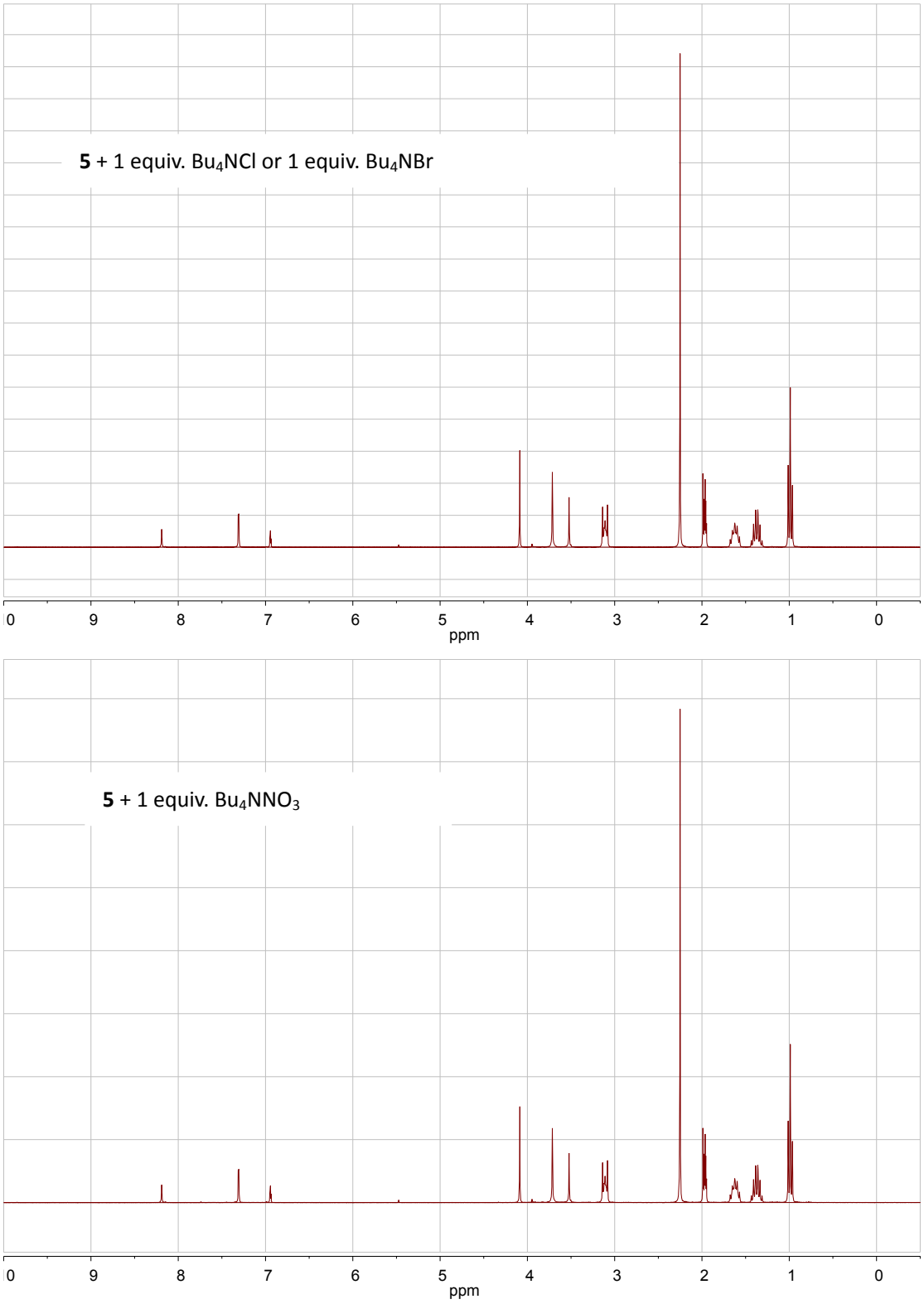


Figure S15 ^{1}H NMR spectra of **5** with the addition of anions.

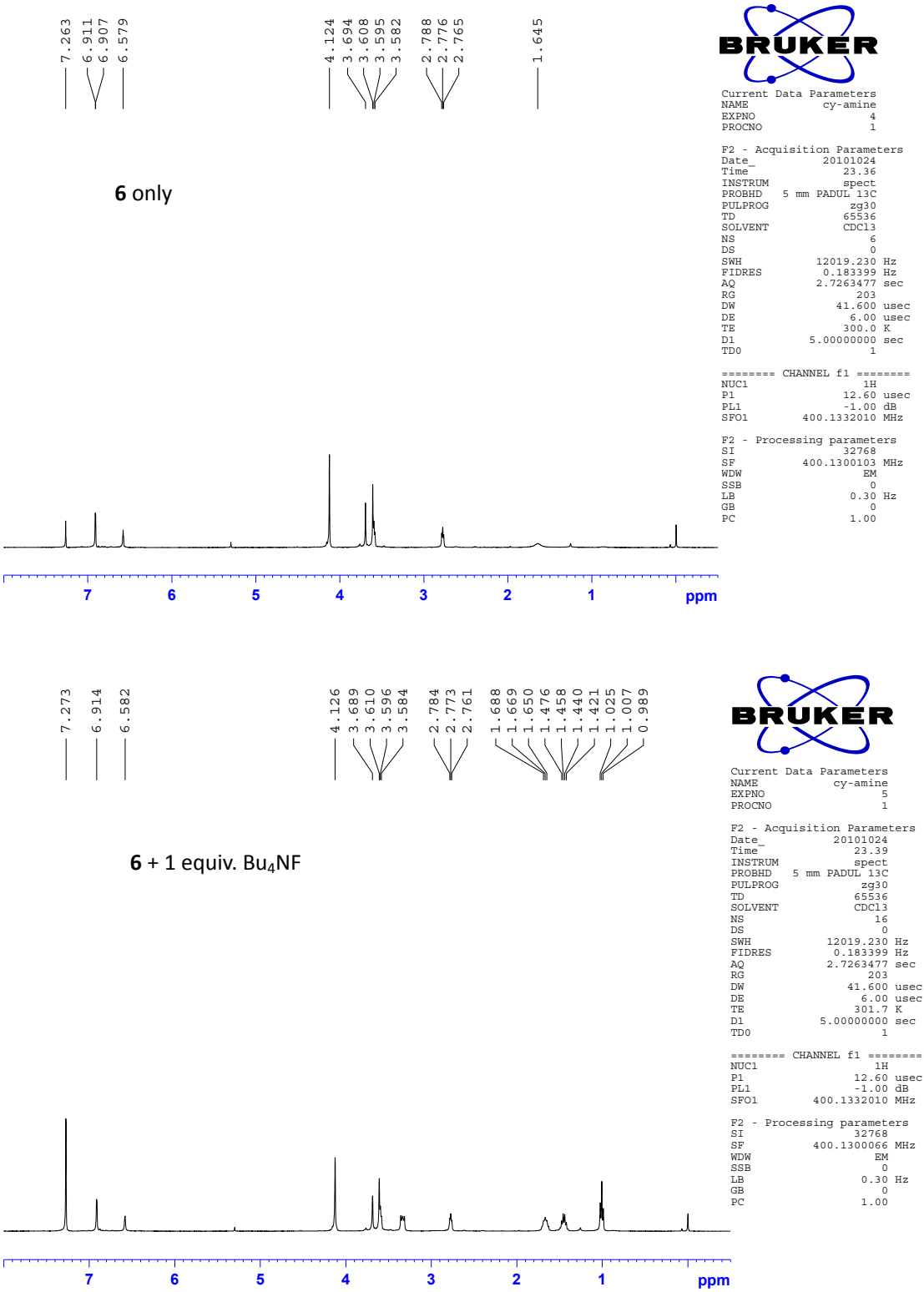
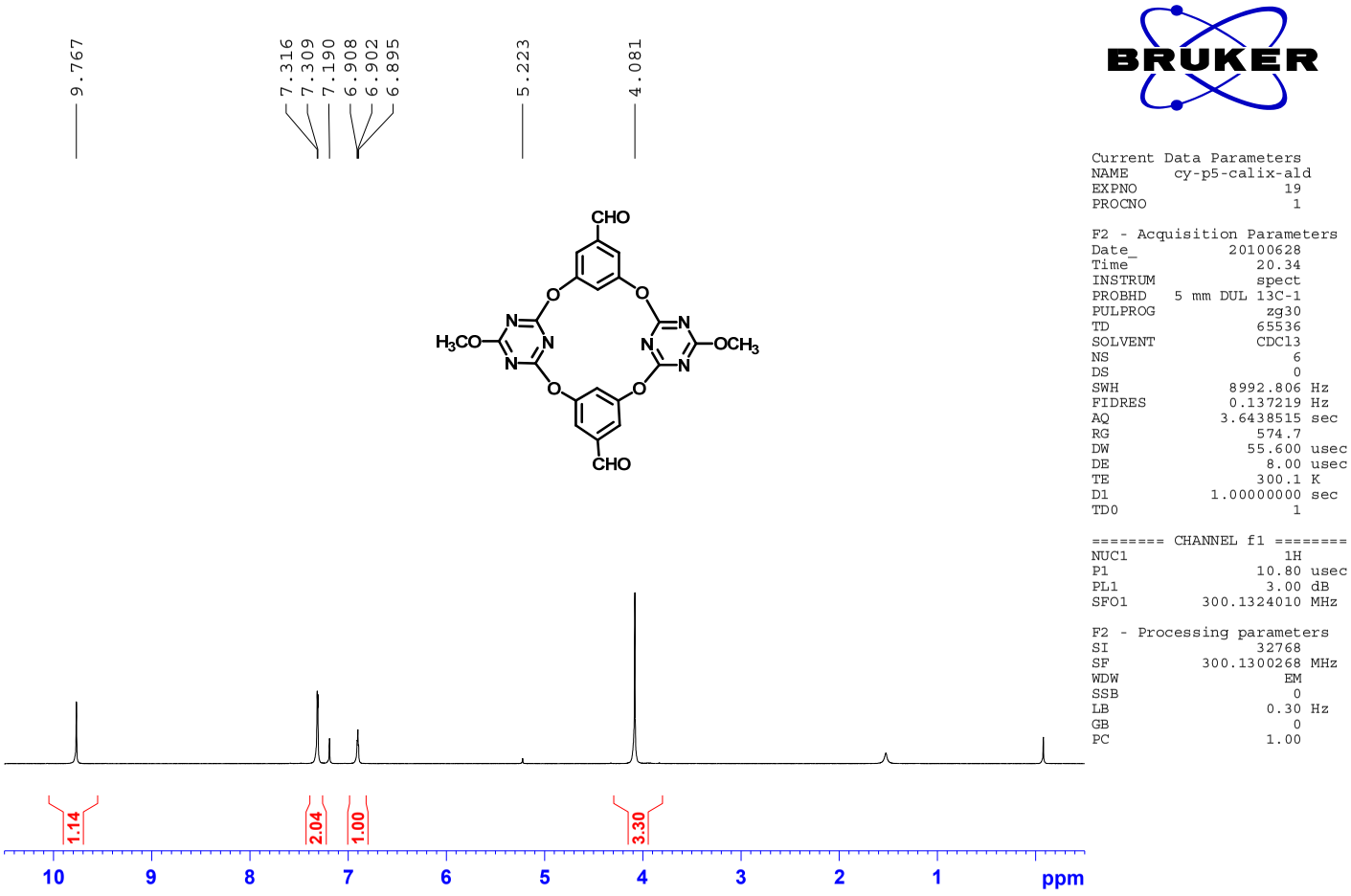


Figure S16 ^{1}H NMR spectra of **6** with the addition of F^{-}.

6. Copies of ^{1}H and ^{13}C NMR Spectra

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DE                 8.00 usec
TE                 300.1 K
D1             1.00000000 sec
TD0                    1

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PL1                 3.00 dB
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F2 - Processing parameters
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LB                  0.30 Hz
GB                     0
PC                  1.00
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Figure S17 ^{1}H spectra of **3**.

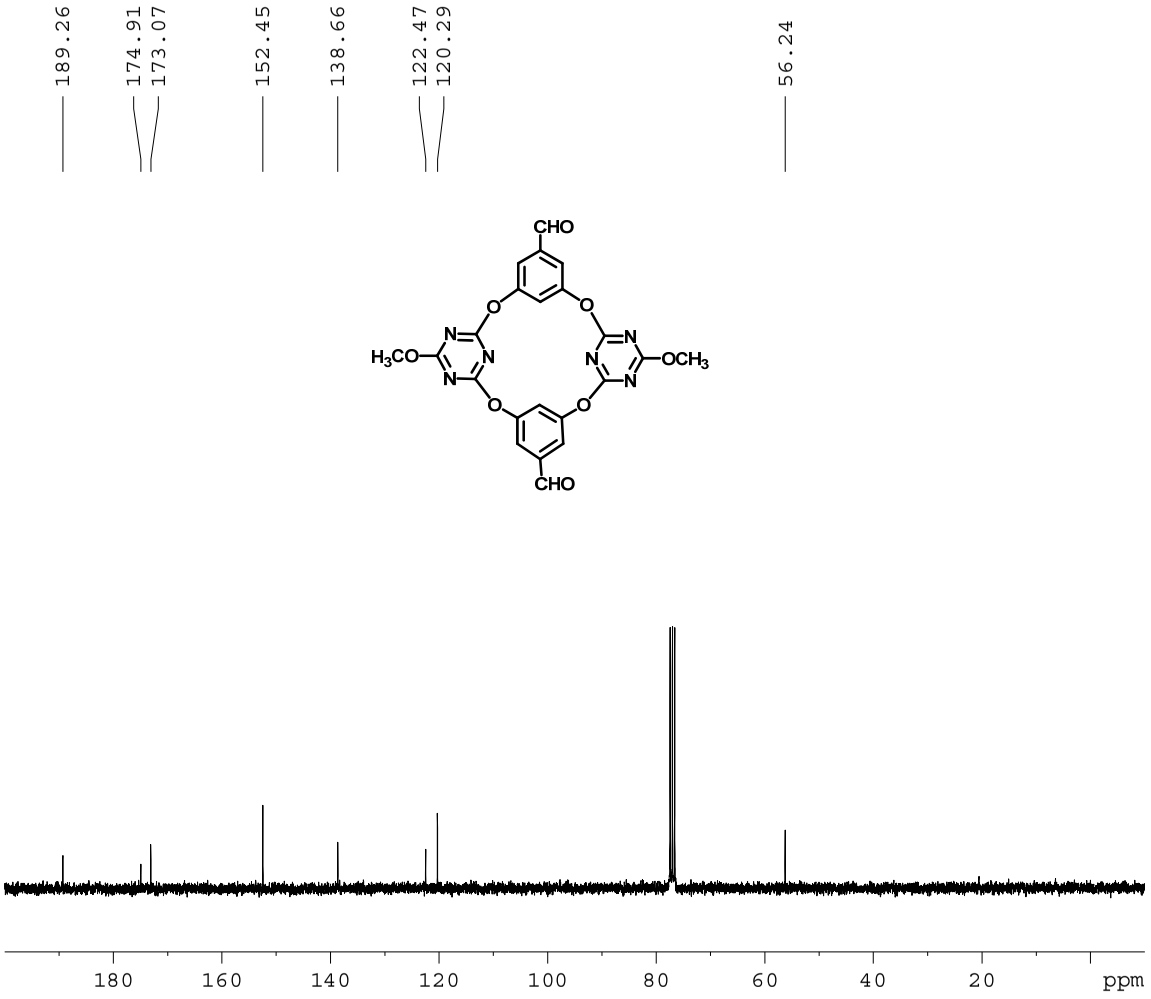
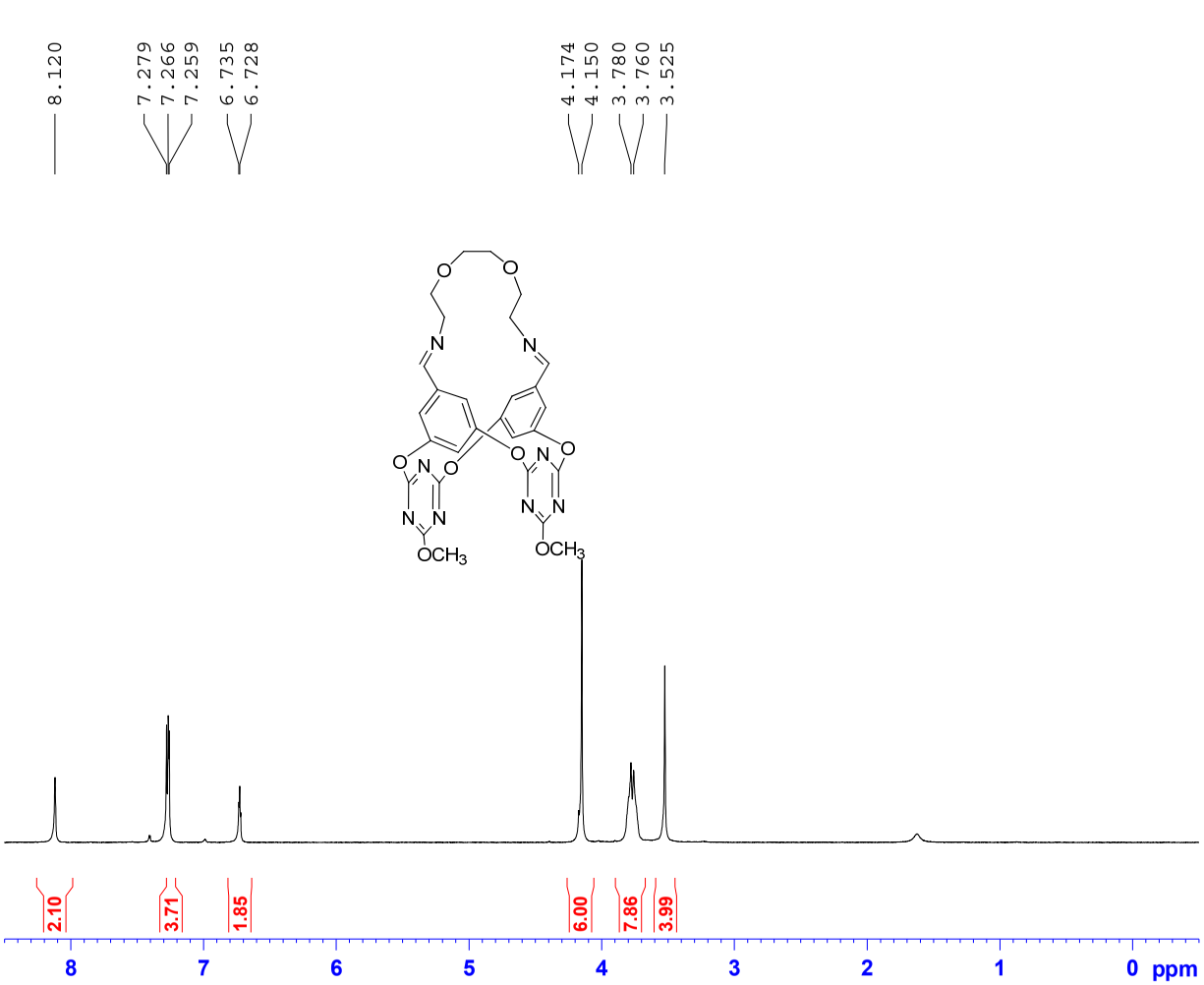


Figure S18 ^{13}C spectra of **3**.

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TD                    32768
SOLVENT               CDCl3
NS                       16
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RG                      45.3
DW                    55.600 usec
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TE                    298.3 K
D1                 2.00000000 sec
TD0                       1

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PL1                    3.00 dB
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SI                    32768
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SSB                       0
LB                     0.30 Hz
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PC                     1.00
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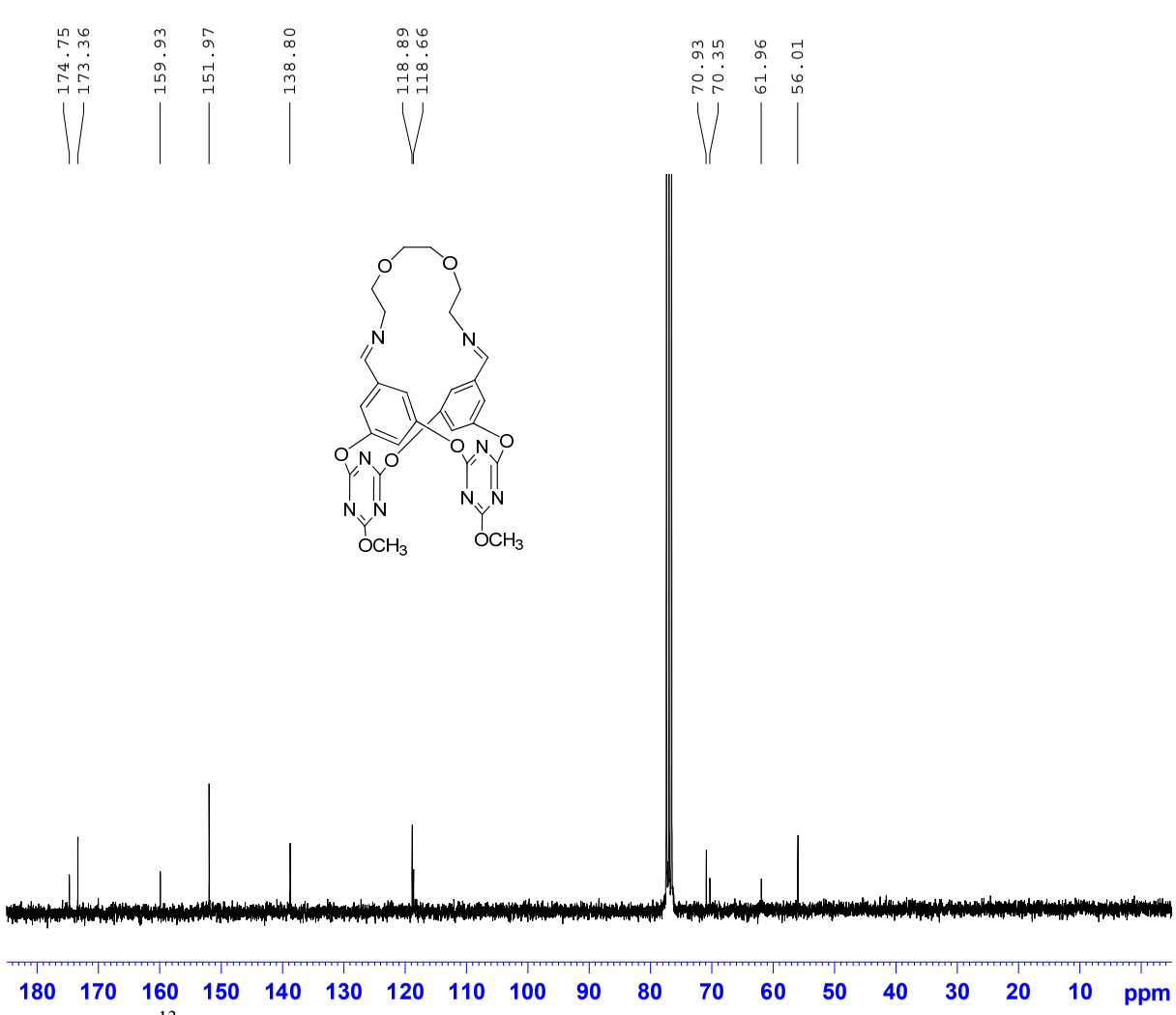
Figure S19 ^{1}H spectra of **5**.



BRUKER

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TD                  32768
SOLVENT             CDCl3
NS                    723
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FIDRES          0.574719 Hz
AQ              0.8700404 sec
RG                14596.5
DW                26.550 usec
DE                 8.00 usec
TE                298.3 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

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PCPD2             100.00 usec
PL2                 3.00 dB
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SI                  32768
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GB                      0
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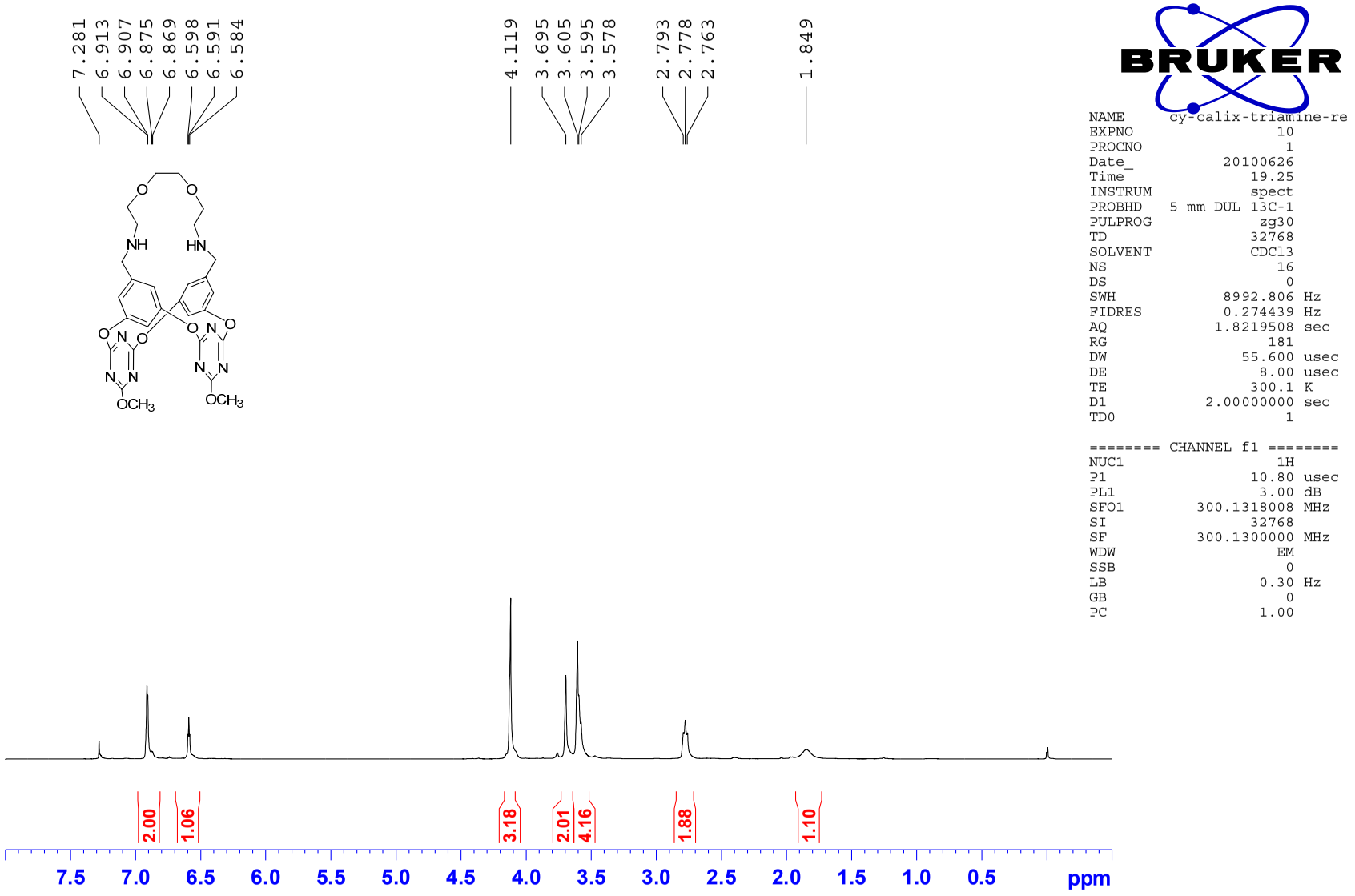
Figure S20 ^{13}C spectra of **5**.



BRUKER

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TD	32768
SOLVENT	CDCl3
NS	16
DS	0
SWH	8992.806 Hz
FIDRES	0.274439 Hz
AQ	1.8219508 sec
RG	181
DW	55.600 usec
DE	8.00 usec
TE	300.1 K
D1	2.00000000 sec
TD0	1
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PL1	3.00 dB
SFO1	300.1318008 MHz
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WDW	EM
SSB	0
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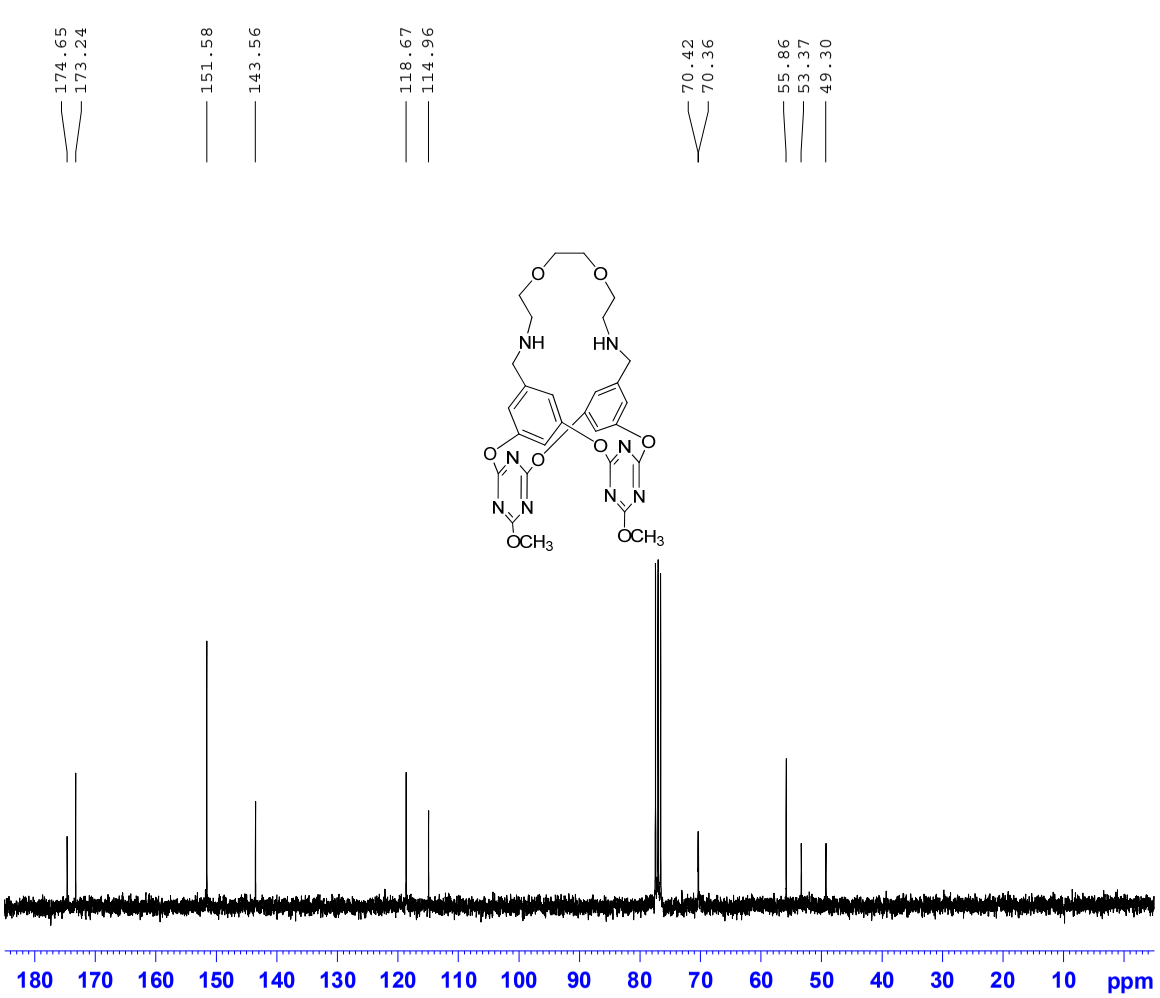
PC	1.00

Figure S21 ^{1}H spectra of **6**.

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PROCNO                      1

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TD                     32768
SOLVENT                CDCl3
NS                       198
DS                         0
SWH               18832.393 Hz
FIDRES             0.574719 Hz
AQ                 0.8700404 sec
RG                      6502
DW                    26.550 usec
DE                     8.00 usec
TE                     300.3 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
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P1                     12.50 usec
PL1                     2.00 dB
SFO1              75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2               waltz16
NUC2                      1H
PCPD2                100.00 usec
PL2                     3.00 dB
PL12                   22.33 dB
SFO2             300.1312005 MHz

F2 - Processing parameters
SI                     32768
SF                75.4677490 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
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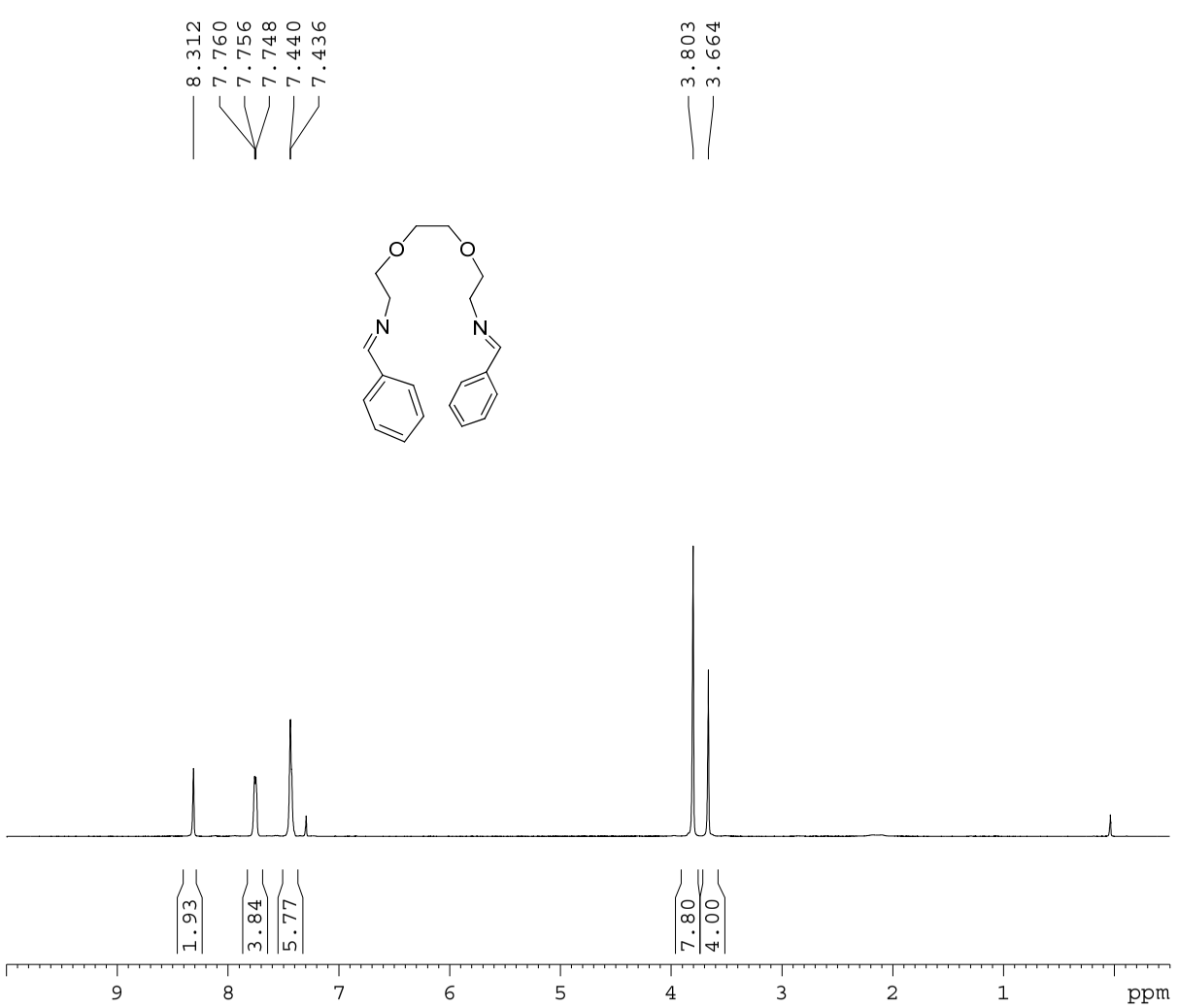
Figure S22 ^{13}C spectra of **6**.

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PROCNO                 1

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TD                 65536
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NS                     3
DS                     0
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RG                   144
DW                41.600 usec
DE                 6.00 usec
TE                300.0 K
D1            5.00000000 sec
TD0                    1

======== CHANNEL f1 ========
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PL1               -1.00 dB
SFO1         400.1332010 MHz

F2 - Processing parameters
SI                 32768
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WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.00
```

Figure S23 ^{1}H spectra of **7**.