Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary information

Bis(2-pyridylmethyl)amine functionalized alizarin: Efficient and simple colorimetric sensor for fluoride and fluorescence turn-on sensor for Al^{3+} in organic solution

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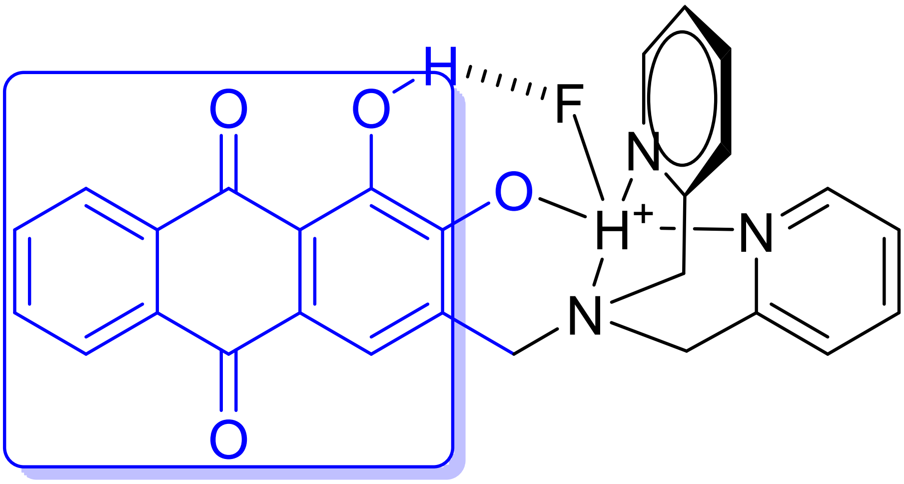
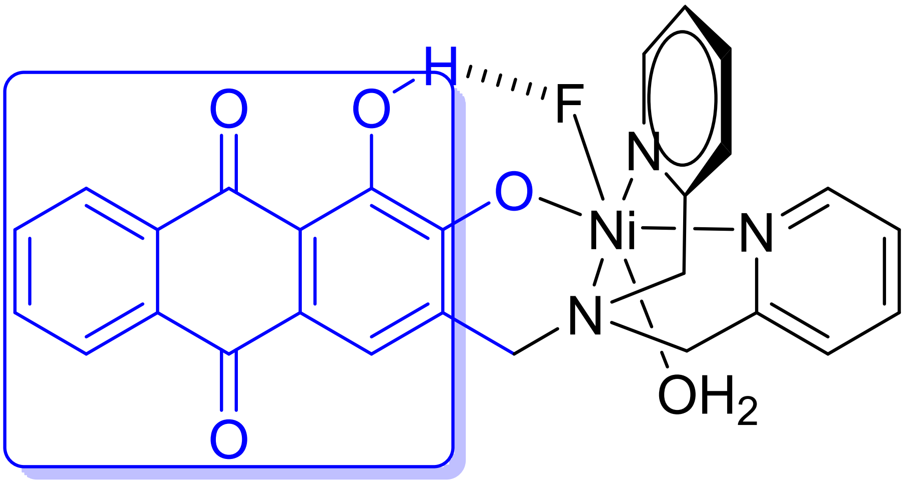




Scheme S1. Proposed structure of $H_2L–F^−$ and $HL^−–Ni^{2+}–F^−$ complex.

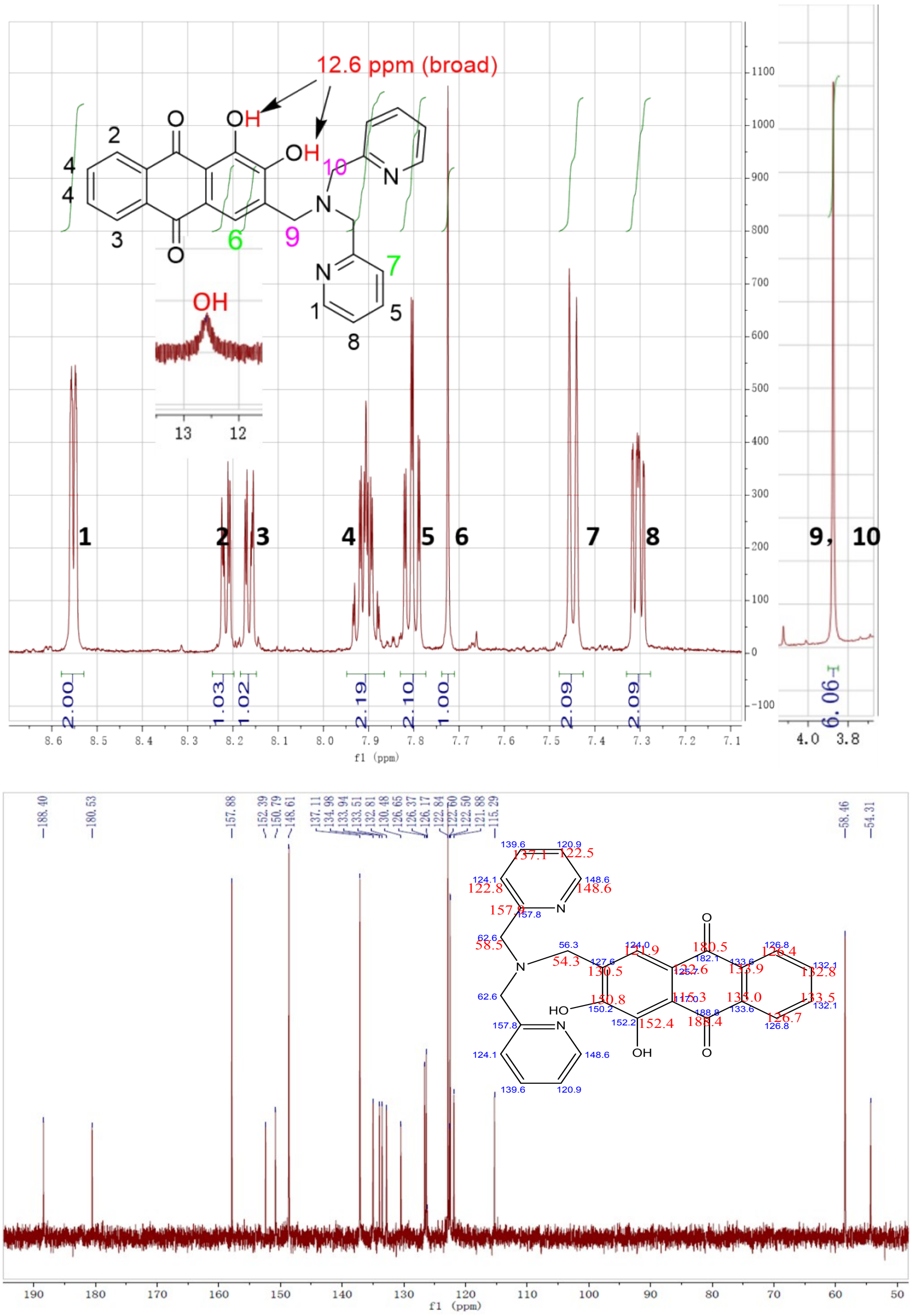
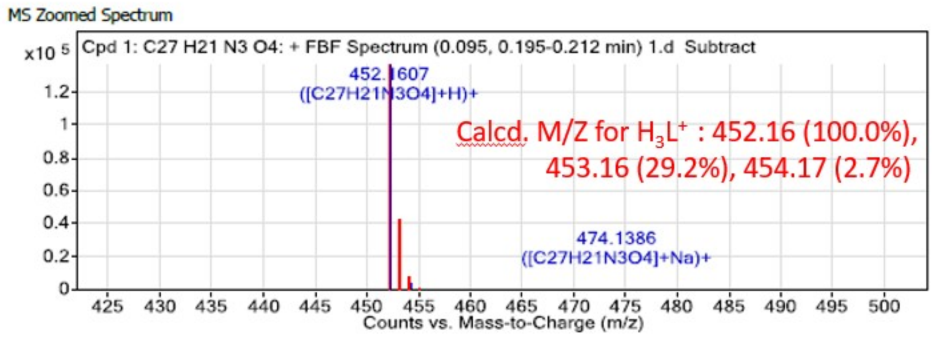


Figure S1. ^{1}H and ^{13}C NMR spectra of H_2L in $(CD_3)SO$



Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)	MFG Formula	DB Formula
Cpd 1: C27 H21 N3 O4	0.128	451.1534	136793	C27 H21 N3 O4	451.1532	0.34	C27 H21 N3 O4	C27 H21 N3 O4

Figure S2. Mass spectral data for H_2L in methanol

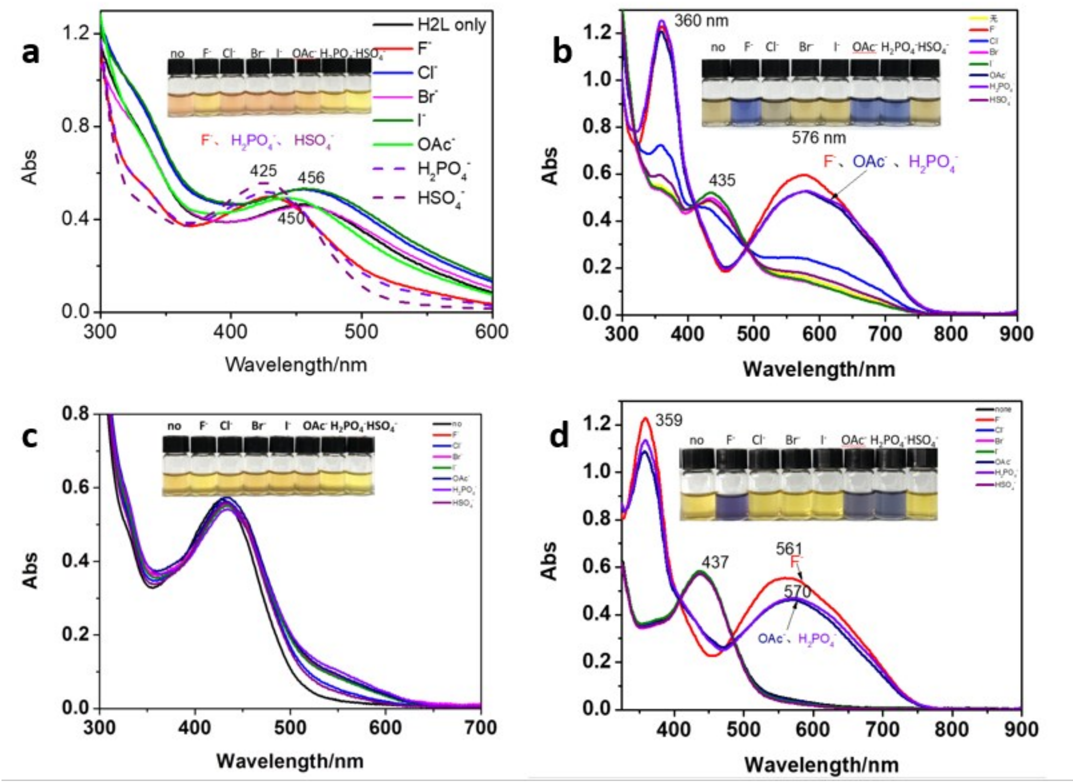


Figure S3. UV-Vis spectra of $1.0{\times}10^{-4}$ M H_2L in the absence and presence of $5.0{\times}10^{-3}$ M different anions (TBA salt) in water(a), DMF(b), methanol(c), acetone(d).

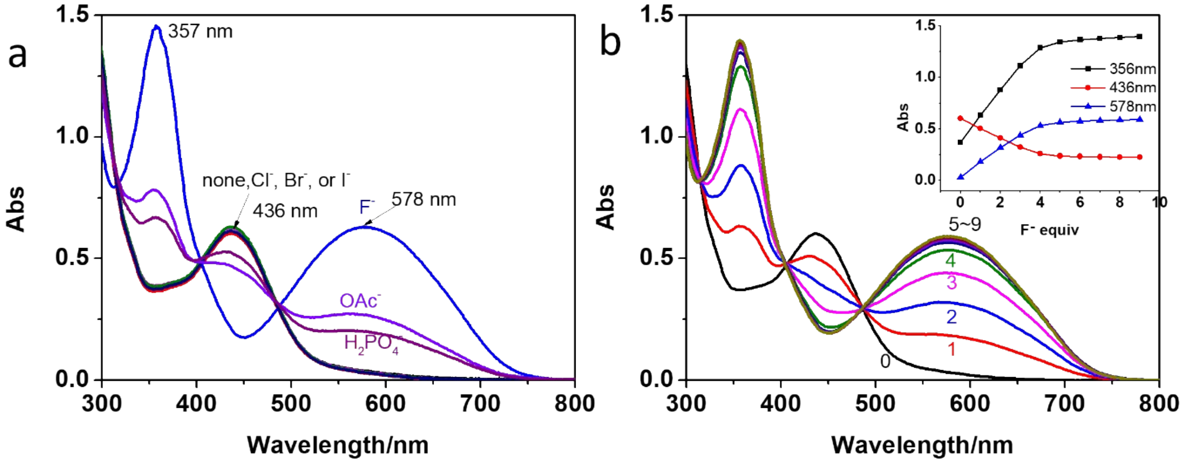


Figure S4. (a) UV-Vis spectra of 1.0×10^{-4} M H_2L in the absence and presence of 5.0×10^{-3} M different anions (TBA salt) in acetonitrile; (b) UV-vis spectral changes of 1.0×10^{-4} M H_2L upon gradually addition of 0 ~ 9 equiv of F^- in acetonitrile. The inset is a plot of 356, 436 and 578 nm absorbance vs F^- eqs.

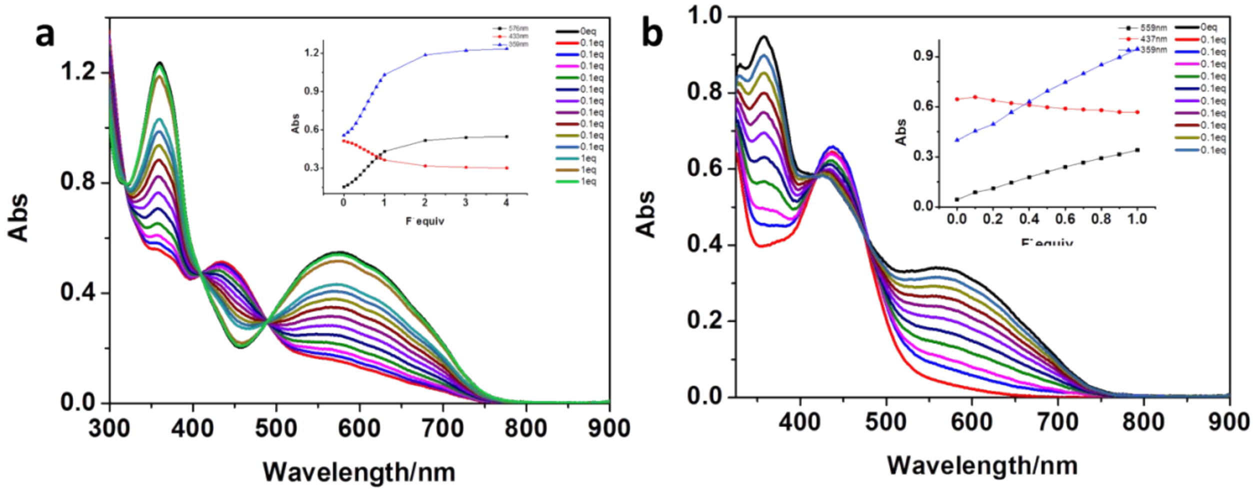


Figure S5. (a)UV-vis spectral changes of 1.0×10^{-4} M H_2L upon gradually addition of 0 ~ 4 equiv of TBAF in DMF. (b) UV-vis spectral changes of 1.0×10^{-4} M H_2L upon gradually addition of 0 ~ 1equiv of TBAF in acetone.

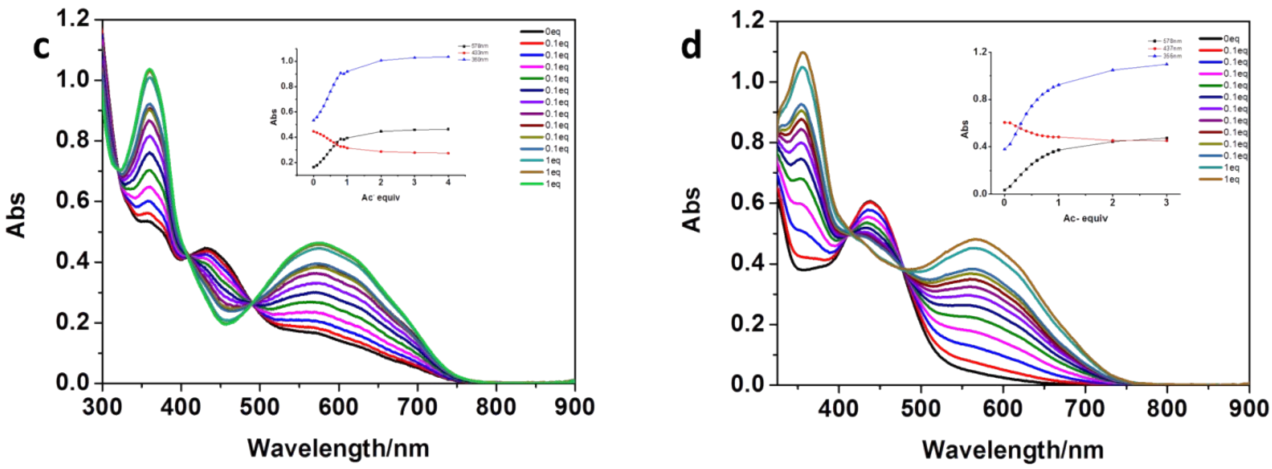


Figure S6. (a)UV-vis spectral changes of 1.0×10^{-4} M H_2L upon gradually addition of 0~4 equiv of Ac^- in DMF. (b) UV-vis spectral changes of 1.0×10^{-4} M H_2L upon gradually addition of 0~ 3equiv of Ac^- in acetone (TBA salt).

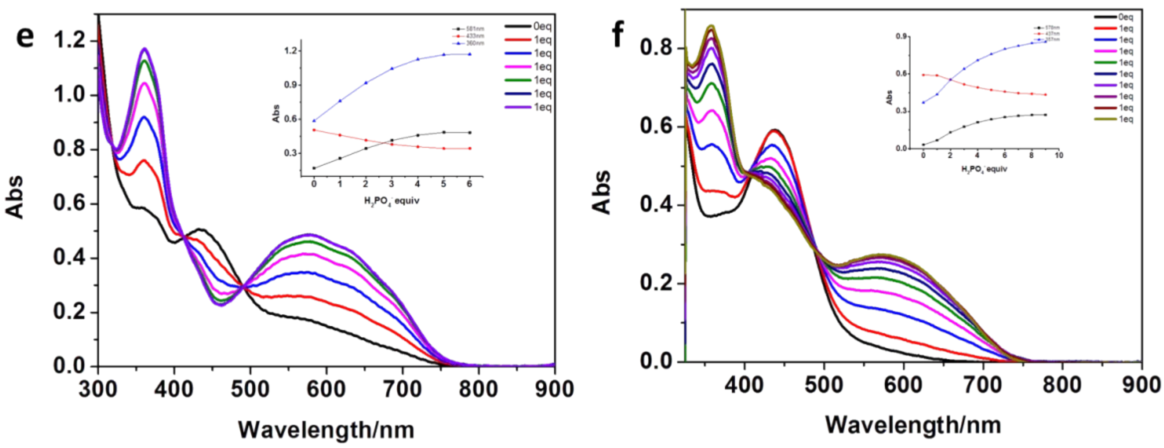


Figure S7. (a)UV-vis spectral changes of 1.0×10^{-4} M H_2L upon gradually addition of 0~6 equiv of $H_2PO_4^-$ in DMF. (b) UV-vis spectral changes of 1.0×10^{-4} M H_2L upon gradually addition of 0 ~ 10equiv of $H_2PO_4^-$ in acetone.

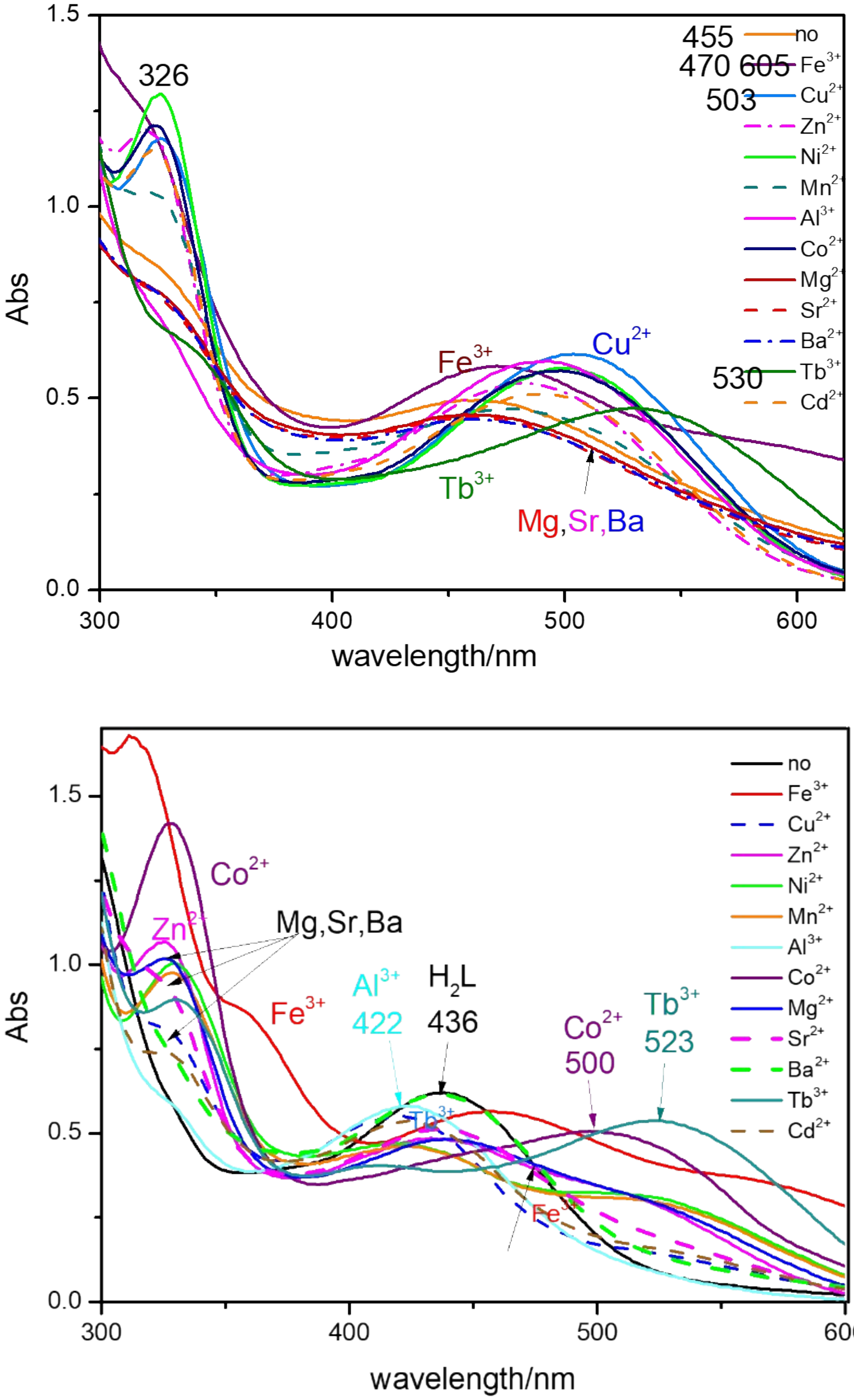


Figure S8. UV-vis spectral of 1.0×10^{-4} M H_2L in the absence (none) and presence of different metal ion (1.0×10^{-4}) in water （top）and acetonitrile (bottom).

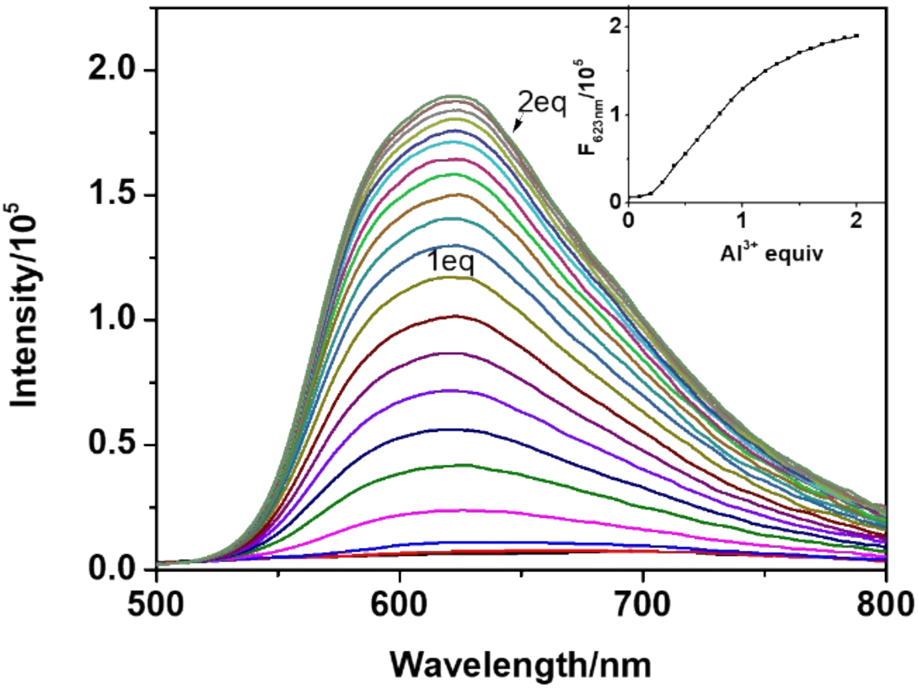


Figure S9. Fluorescence spectra of 1.0×10^{-4} M H_2L in the presence of 2.0×10^{-4} M $AlCl_3$ in DMF (slid width 2 nm)

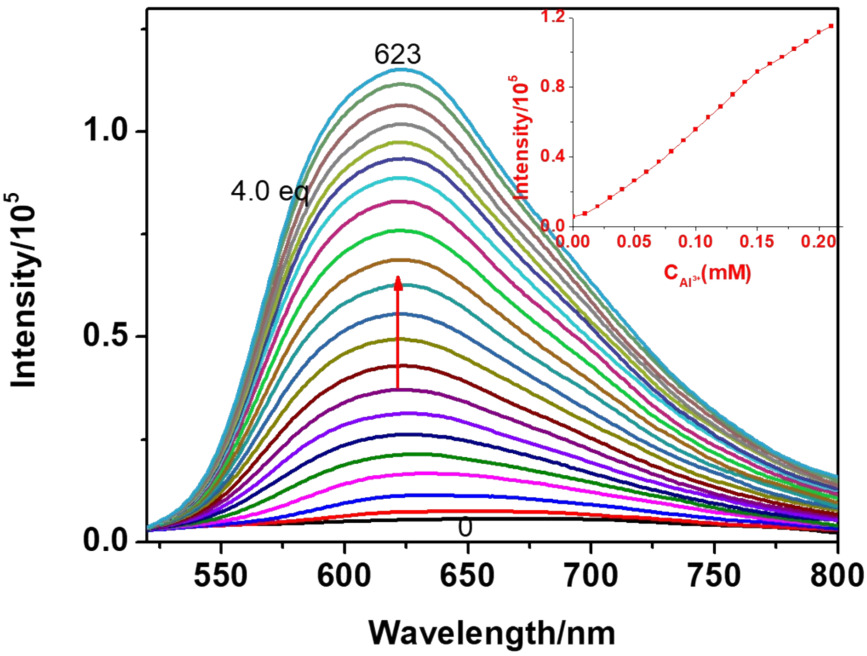


Figure S10. Fluorescent titration of H_2L (5.0×10^{-5} M) in the presence of different concentrations of $AlCl_3$ in DMF. Inset: the fluorescence at 623 nm of H_2L as a function of the $AlCl_3$ concentration. λ_{ex} = 430 nm, slid width 3 nm.

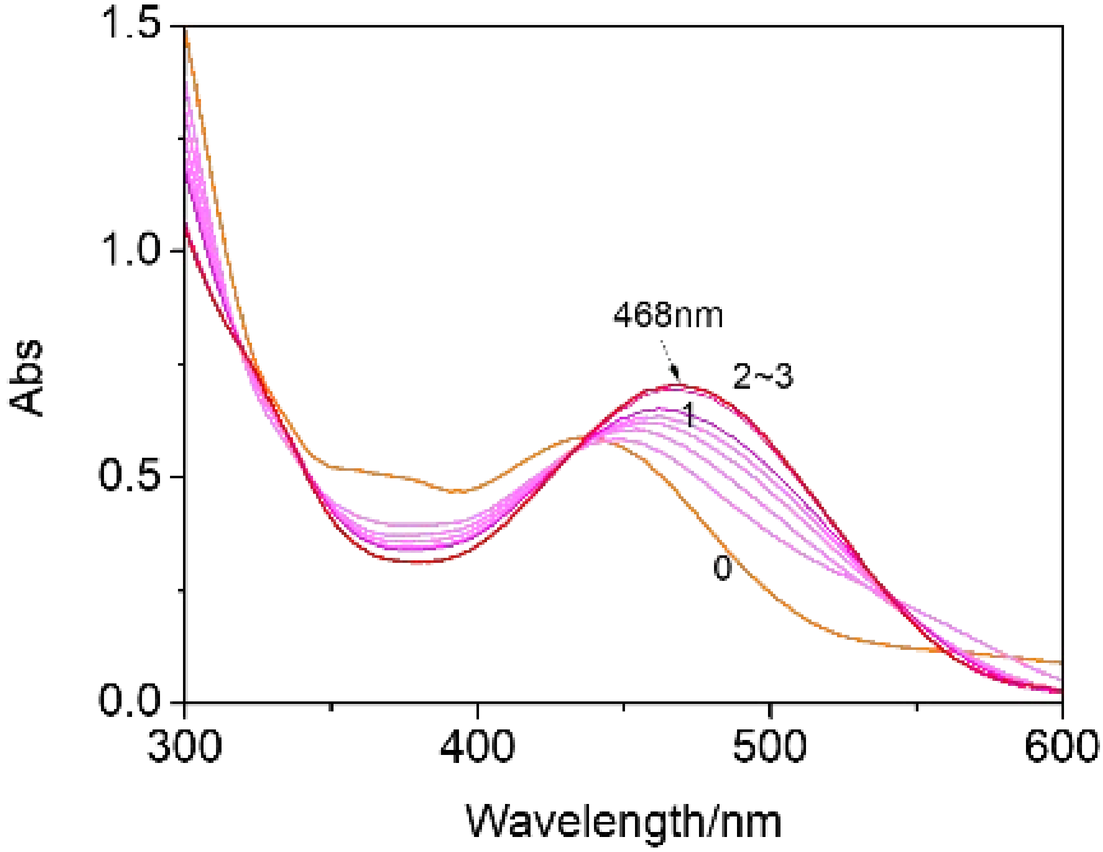


Fig. S11 NaOH titration spectra of 1.0×10^{-4} M H_2L in the presence of 1 eq $Al(NO_3)_3$ in DMF.

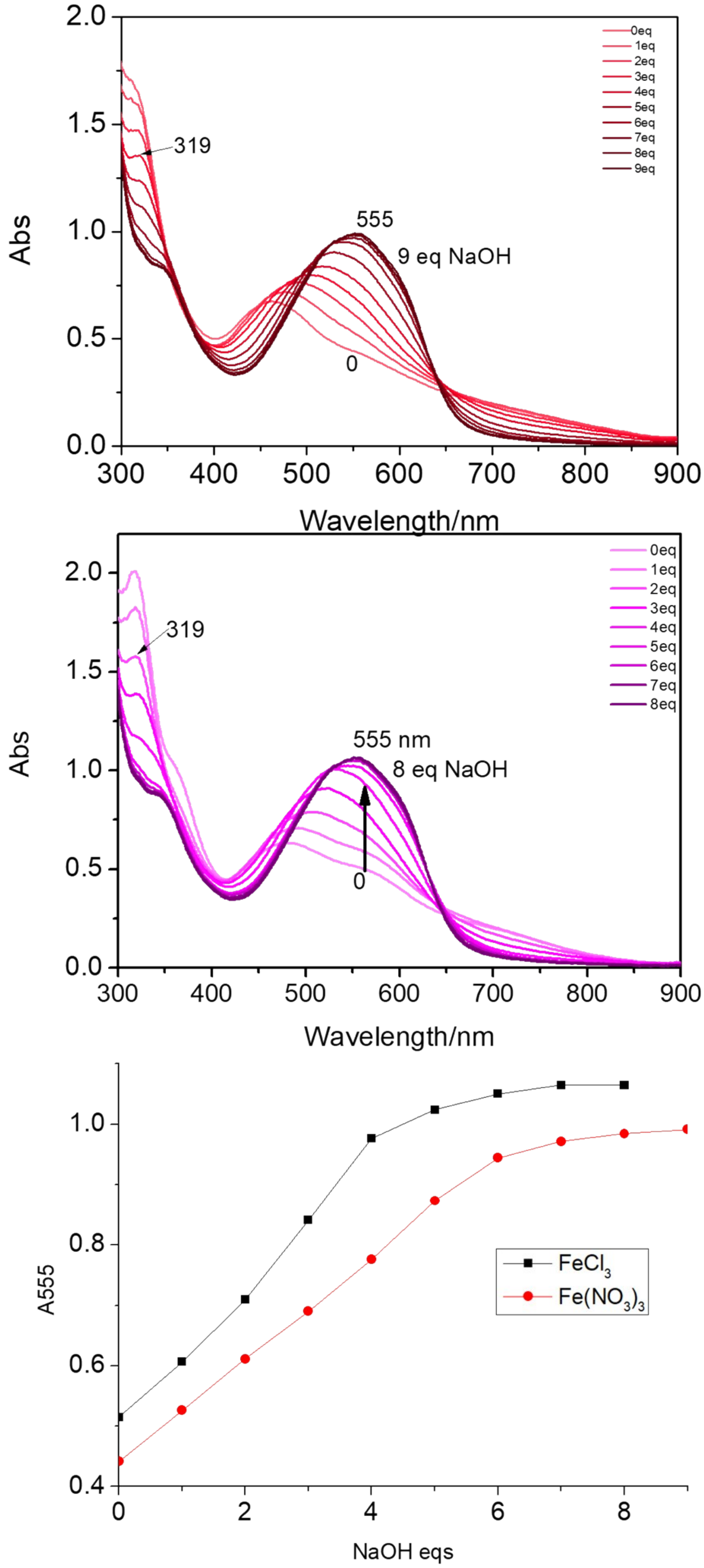


Figure S12. NaOH titration spectra of 1.0×10^{-4} M H_2L in the presence of 1 eq $Fe(NO_3)_3$ (top), $FeCl_3$(middle) and their A_{552} vs NaOH eqs (bottom) in DMF.

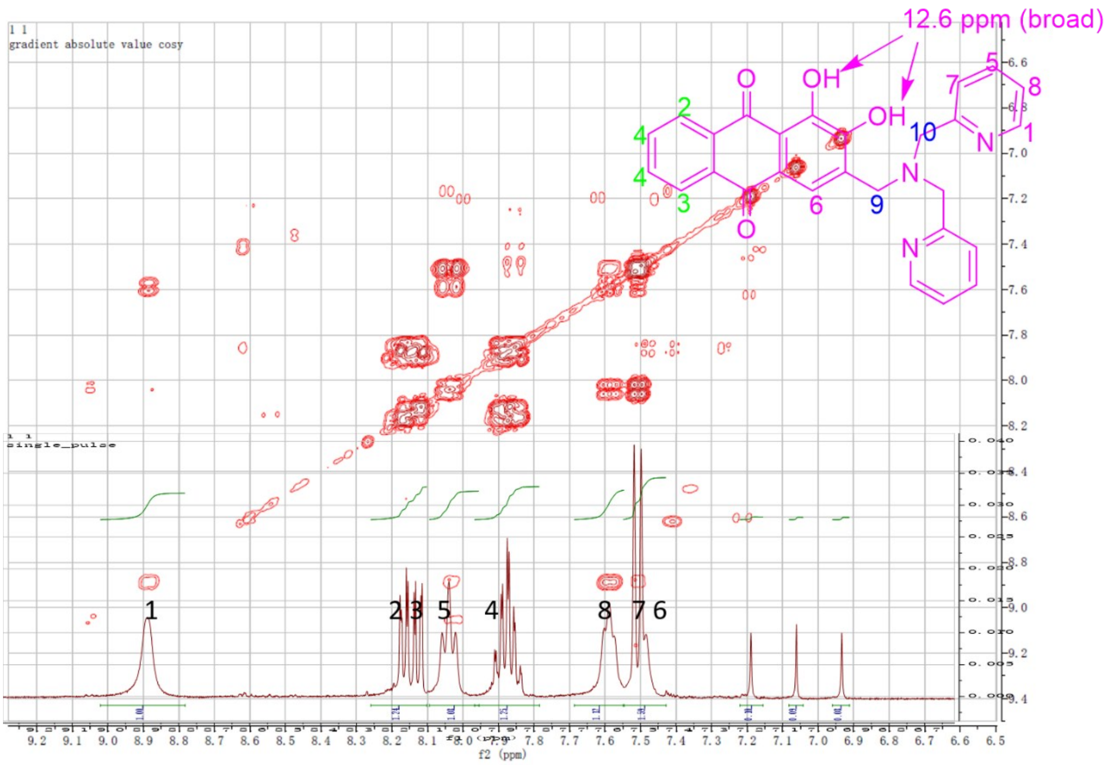


Figure S13. H-H Cosy of ~1×10^{-2} M H_2L-$ZnCl_2$ in d_6-DMSO

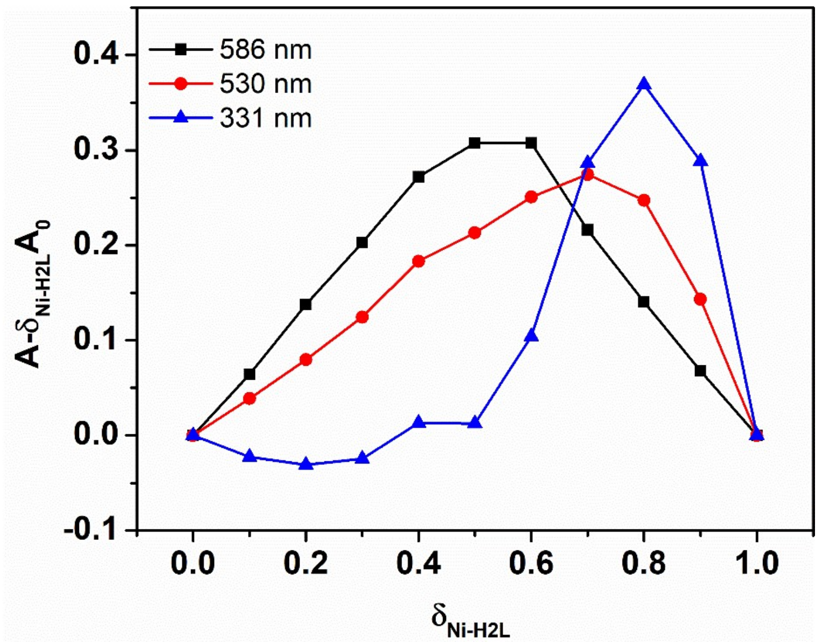


Figure S14. Jobs-plot of 331 nm (corresponding to HL^- species) and 586 nm (corresponding to F^-– $NiCl_2$–HL^- species) for 2.0×10^{-4} M TBAF and 2.0×10^{-4} M $NiCl_2$–H_2L system in acetonitrile.

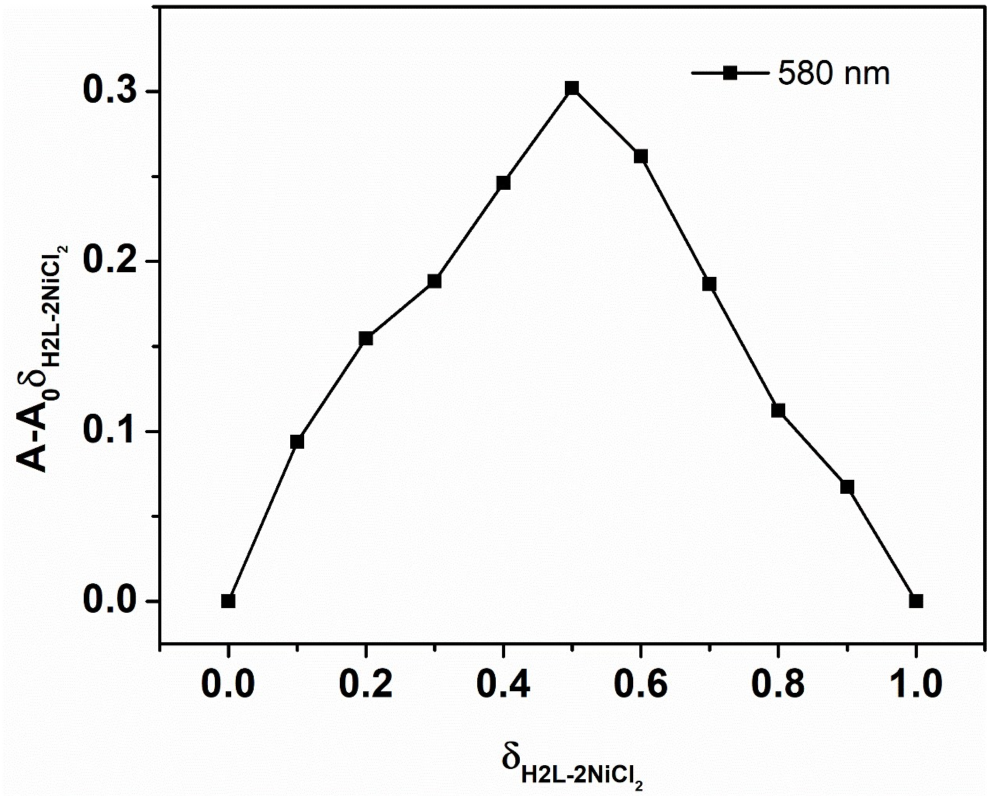


Figure S15. Jobs-plot of 580 nm (corresponding to F^-–$2NiCl_2$–HL^- species) for 2.0×10^{-4} M TBAF and 2.0×10^{-4} M H_2L–$2NiCl_2$ system in acetonitrile.

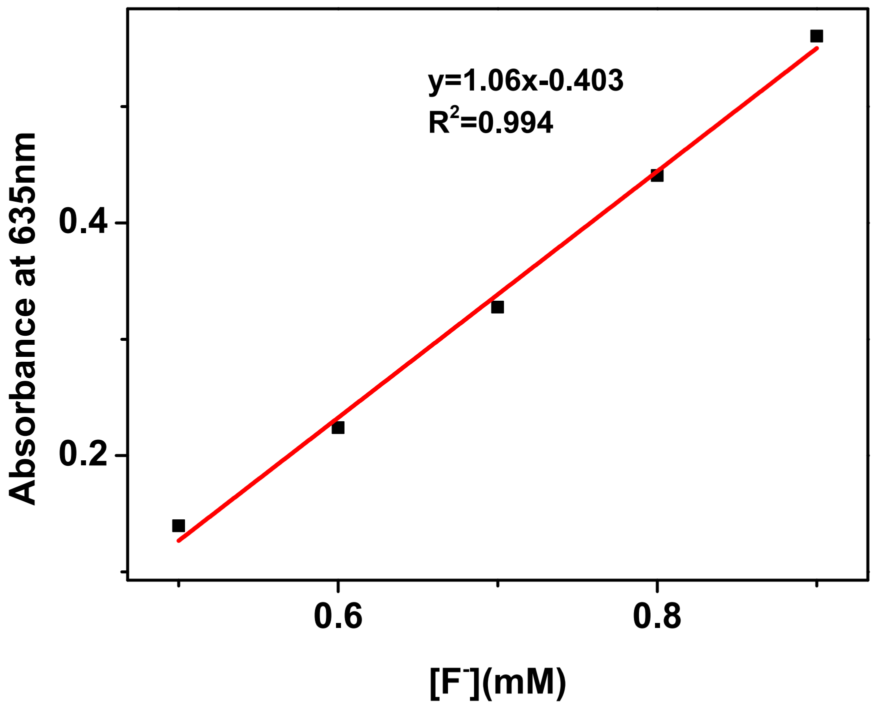


Figure S16. Plot of 635 nm absorbance at different F^- concentrations for 1.0×10^{-4} M H_2L–$2NiCl_2$ system.

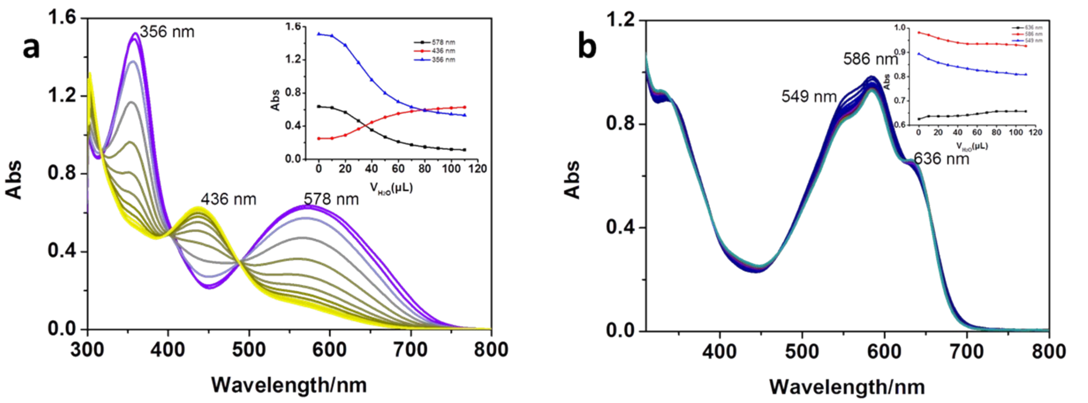


Fig. S17 (a) UV-Vis spectra of 1.0×10^{-4} M H_2L in the presence of 1.0×10^{-3} M TBAF（3.0 ml）upon gradually addition of 0 ~ 120 μL H_2O （0~4%）in acetonitrile; The inset is a plot of 356, 436 and 578 nm absorbance vs V_{H2O} (μL). (b) UV-Vis spectra of 1.0×10^{-4} M $NiCl_2$–H_2L complex in the presence of 1.0×10^{-3} M TBAF (3.0 ml) upon gradually addition of 0 ~ 120μL H_2O in acetonitrile;

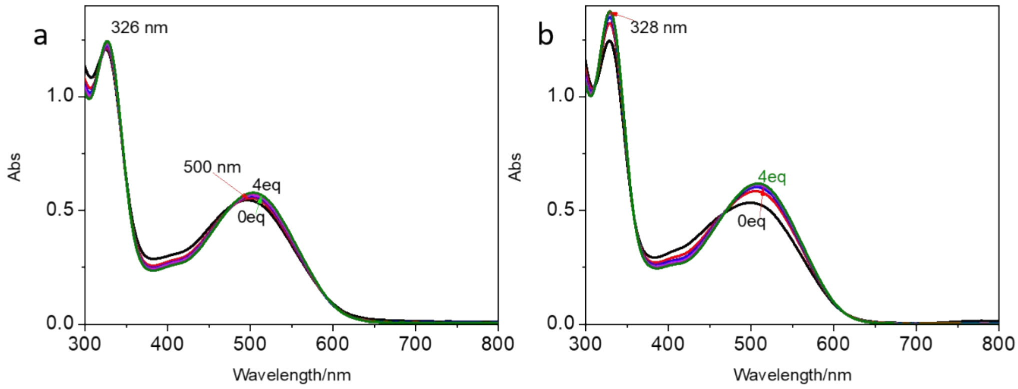


Fig. S18 UV-Vis spectra of 1.0×10^{-4} M H_2L-$NiCl_2$ in the presence of different eqs. of TBAF in H_2O (a) and 20% （V/V）CH_3CN aqueous solution（b）.

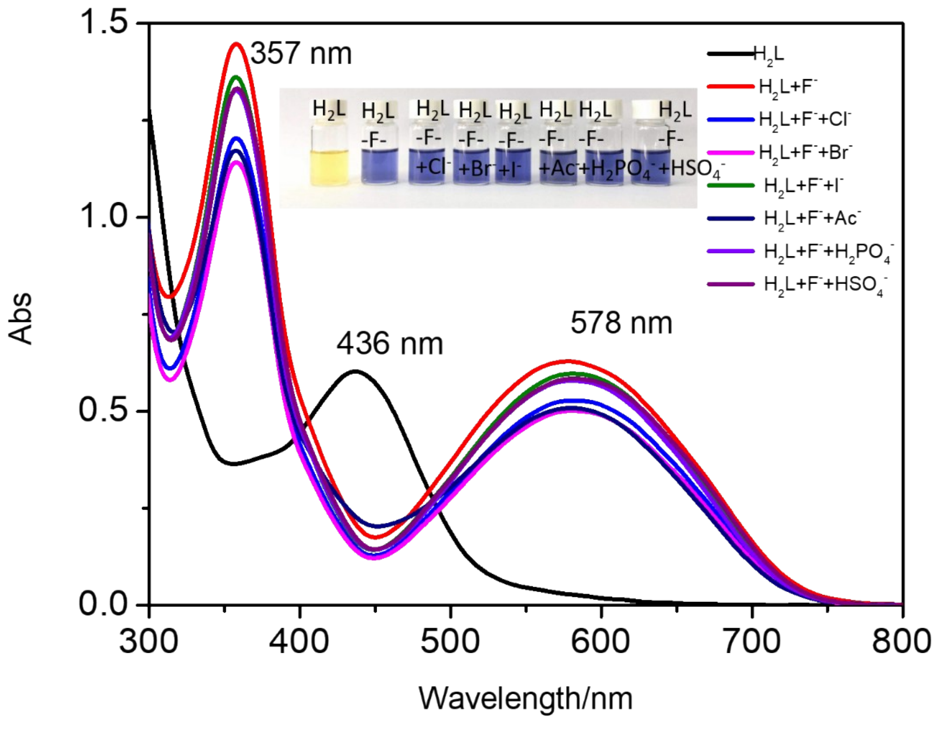


Fig. S19 UV-Vis spectra of 1.0×10^{-4} M H_2L in the presence of 5.0×10^{-3} M F^- and 5.0×10^{-3} M other anions in CH_3CN. All are TBA^+ salt. This figure indicates that 1 eq of Cl^-, Br^-, I^-, Ac^-, $H_2PO_4^-$ and HSO_4- have no significant influence on F^- sensitivity.

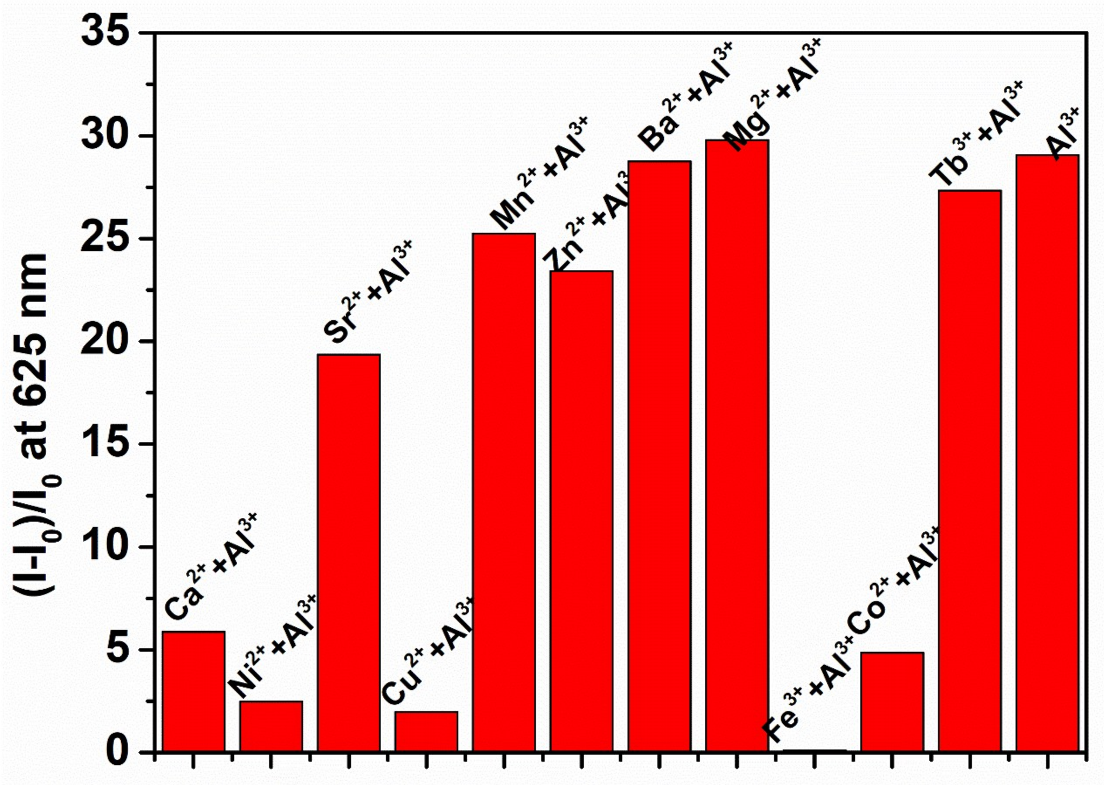


Fig. S20 Relative fluorescence intensity of 1.0×10^{-4} M H_2L in the presence of 2.0×10^{-4} M different metal ion chloride in DMF solution. Of the investigated metal ions, Fe^{3+}, Cu^{2+}, Ni^{2+}， Co^{2+} and Ca^{2+} significantly decrease fluorescence intensity and thus greatly decrease Al^{3+} fluorescence turn-on sensitivity.

Table S1. The limit of detection (3σ/slope) for 1.0×10^{-4} M H_2L in different solvents.

	Acetonitrile	DMF	Acetone
F^-	7.54×10^{-6}	5.276×10^{-6}	3.067×10^{-5}
Ac^-	insensitive	7.666×10^{-6}	2.098×10^{-5}
$H_2PO_4^-$	insensitive	3.055×10^{-5}	2.021×10^{-4}