Supplementary Information

Highly selective recognition of fluoride using a trapezoidal cage

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Materials, methods, and abbreviations

Materials

All salts were purchased from commercial sources and used without further purification. All anions are tetrabutylammonium (TBA) salts. The trapezoidal cage **1** was produced according to the previously reported protocol.[1] Solvents were obtained from commercial sources. Analytical thin layer chromatography (TLC) was performed on silica gel plates (Merck 60F254) visualized with a UV lamp (254 nm). Column chromatography was performed with commercial glass columns using silica gel 200-300 mesh (particle size 0.045-0.075 mm).

NMR spectroscopy

^{1}H NMR spectra were recorded on a Bruker AVANCE III HD 400 or a Bruker AVANCE III HD 600 in DMSO-d_6. Chemical shifts are reported in ppm relative to residual solvent signal of DMSO-d_6 (δ = 2.50 ppm). Spectra of nuclear overhauser effect spectroscopy (NOESY) and correlation spectroscopy (COSY) experiments were recorded on a Bruker AVANCE III HD 400 by means of a BBO (BB-H/F-D) probe, or a Bruker AVANCE III HD 600 by means of a 5 mm BBFO probe with z gradient. Data processing was performed with Topspin software. ^{1}H-^{1}H NOESY acquisitions were performed with a time domain size of 2048 (F2) × 256(F1), 32 scans per increment, a pulse program of noesygpphpp or noesygpph, and a mixing time of 300 ms. ^{1}H-^{1}H COSY acquisitions were performed with a time domain size of 2048(F2) × 128(F1), 4 scans per increment, and a pulse program of cosygpppgf.

Fluorescence spectroscopy

Fluorescence spectra were recorded on an Edinburgh Instruments FLS 980 spectrometer with Xenon Xe1+400 nm lamp and visible PMT detector under following conditions: Dwell time = 0.1s, step = 1 nm, number of scans = 1, without polarizers. Stock solutions of anions were prepared with concentrations of 5 mM, 50 mM or 250 mM (all containing 50 μM **1**) in DMSO. The detailed conditions for each sample are

as follows: excitation wavelength (Ex) = 303 nm, excitation bandwidth (ExBW) = 2.0 nm and emission bandwidth (EmBW) = 1.5 nm with a 330 nm filter for the emission spectra of F^-+**1**; Ex = 300 nm, ExBW = 2.7 nm and EmBW = 2.65 nm with a 330 nm filter for the emission spectra of Cl^-+**1**, Br^-+**1**, I^-+**1**, NO_3^-+**1**, SCN^-+**1**, HSO_4^-+**1**, HCO_3^-+**1**, Ex = 300 nm, ExBW = 2.2 nm and EmBW = 2.2 nm with a 330 nm filter for the emission spectra of ClO_4^-+**1**, BF_4^-+**1**, PF_6^-+**1**. Organic solvents for spectroscopic studies were of spectroscopic grade and all anions were prepared as tetrabutylammonium (TBA) salts. Cuvette specification: 10 mm × 10 mm.

Mass spectrometry

High resolution electrospray ionization time-of-flight (HRESI-TOF) mass spectra were measured in the positive/negative ion mode on a Bruler Daltonic microTOF focus spectrometer.

Abbreviations

DMSO = dimethyl sulfoxide, TBA = tetrabutylammonium.

NMR, fluorescence, and HRMS studies

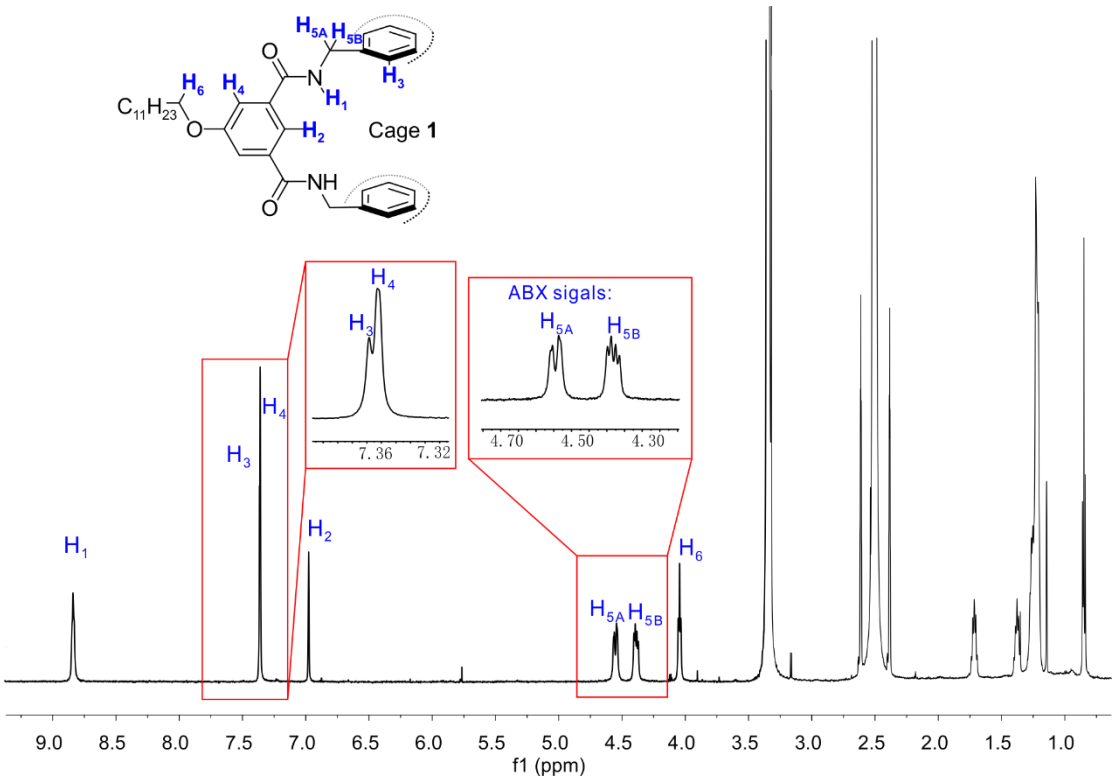

Figure S1. ^{1}H NMR spectrum (600 MHz) of **1** in DMSO-d_6 at 298K.

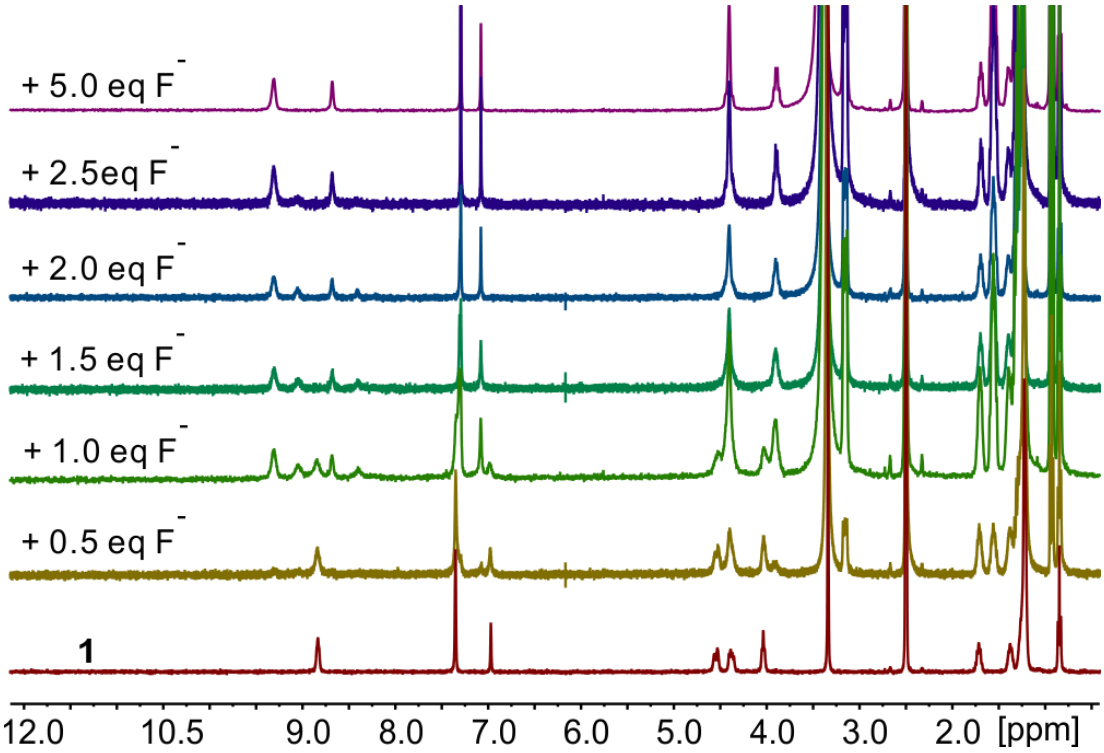

Figure S2. ^{1}H NMR (400 MHz) titration of **1** (1 mM) with F^- in DMSO-d_6.

Assessing binding constants through NMR titration (Figure S3):

$[H] + [G] \overset{K_1}{\rightleftharpoons} [HG]$ $\quad K_1 = [HG]/([H][G])$

$[HG] + [G] \overset{K_2}{\rightleftharpoons} [HG_2]$ $\quad K_2 = [HG_2]/([HG][G])$

$[HG_2] + [HG] + [H] = [H_0]$

$2[HG_2] + [HG] + [G] = [G_0]$

The initial concentrations of **1** ($[H_0]$) and F^- ($[G_0]$) are known and the distribution of H can be calculated by integration. Therefore, $[HG_2] = [H_0] * I_{[HG2]}/(I_{[HG2]} + I_{[HG]} + I_{[H]})$, $[HG] = [H_0] * I_{[HG]}/(I_{[HG2]} + I_{[HG]} + I_{[H]})$, $[H] = [H_0] * I_{[H]}/(I_{[HG2]} + I_{[HG]} + I_{[H]})$. Further, the concentration of [G] can be determined as $[G] = [G_0] - 2[HG_2] - [HG]$. Thereby, K_1 can be obtained as 3.3×10^3 M^{-1} from the spectrum of **1**+1eqF^- (the signal of [H] in other spectra is too weak, which may cause significant errors in calculating K_1), K_2 = $1.1(\pm0.3)\times10^4$ M^{-1} (from three independent measurements, 1.4×10^4 M^{-1}, 1.2×10^4 M^{-1} and 7.2×10^3 M^{-1}, respectively.), and $\beta_2 = K_1\times K_2 = 3.6\times10^7$ M^{-2}. Considering that signal broadening can lead to integration errors, it is more appropriate to consider these binding constants as approximate values.

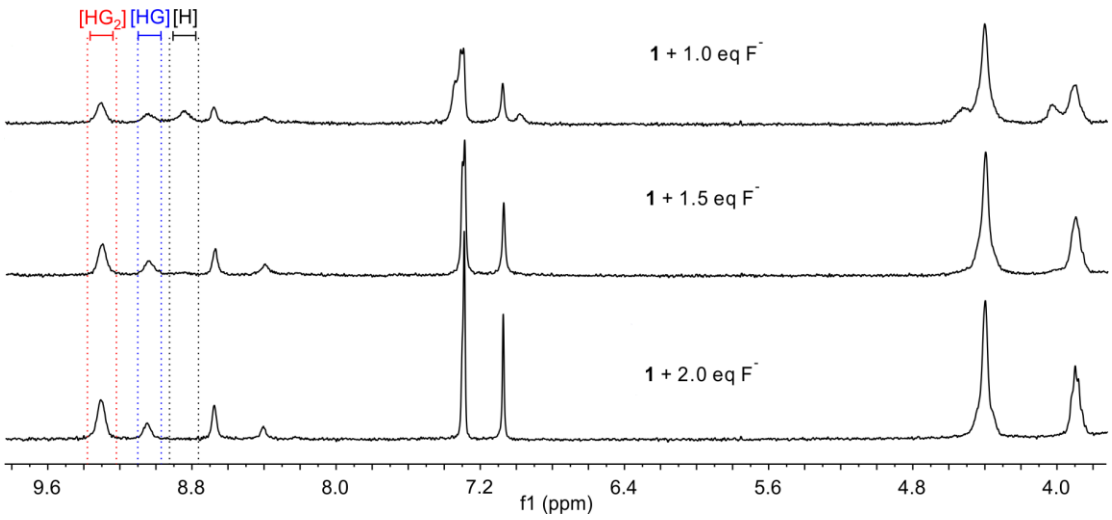

Figure S3. ^{1}H NMR (400 MHz) titration of **1** (1 mM) with F^- in DMSO-d_6.

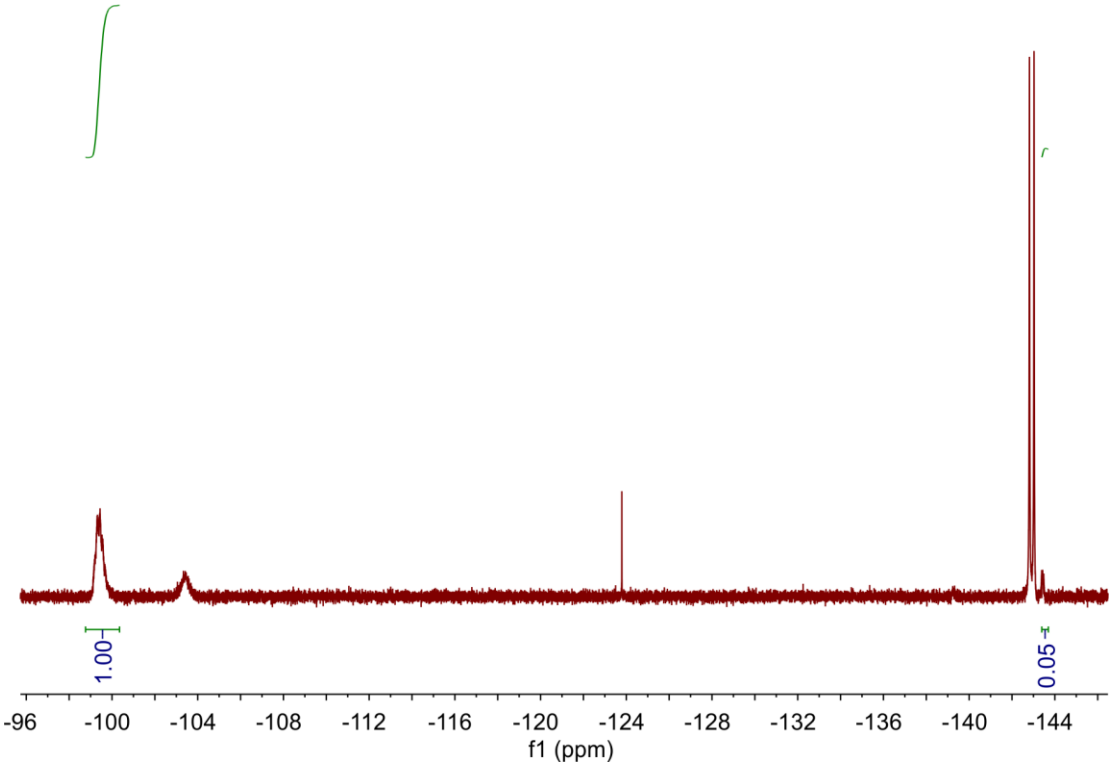

Figure S4. ^{19}F NMR (600 MHz) spectrum of **1** (1 mM) with F^- (5 mM) in DMSO-d_6.

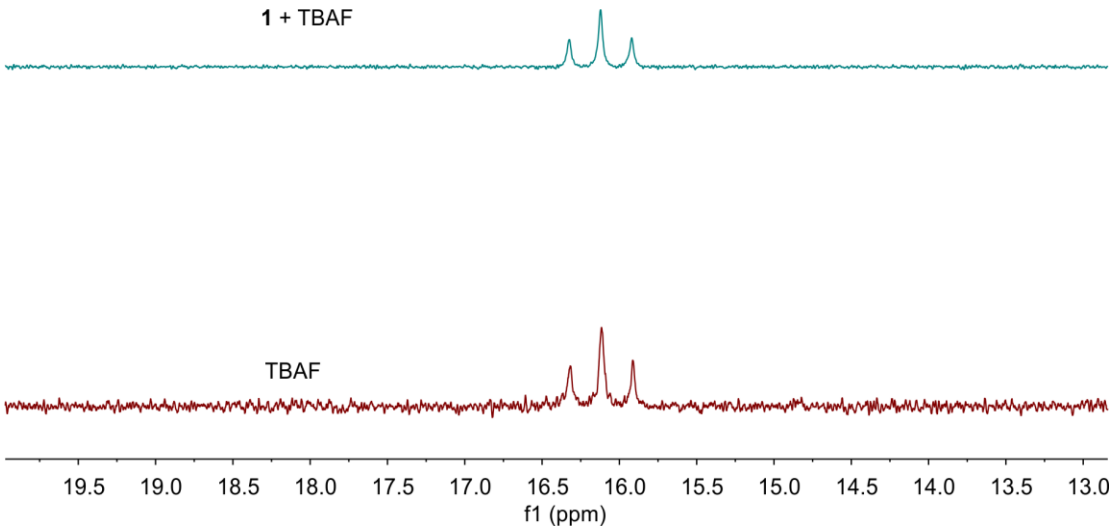

Figure S5. ^{1}H NMR (600 MHz) spectra of **1**+F^- (1 mM + 5 mM) and F^- alone (3 mM) in DMSO-d_6.

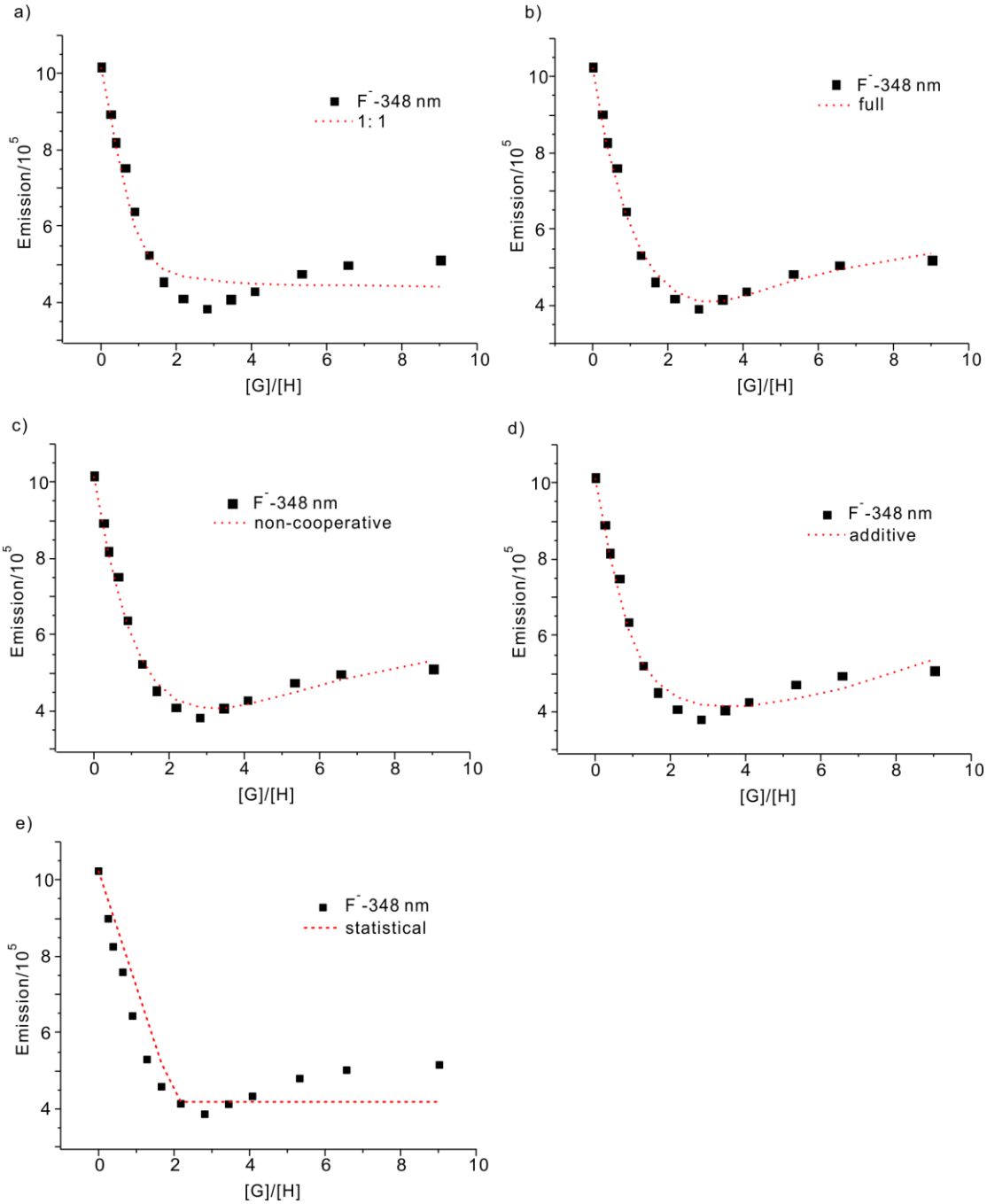

Figure S6. Binding analysis curves of the fluorescence titration between **1** (150 μM) and F^- in DMSO. The analysis was conducted with the help of the website "http://supramolecular.org/". The (a) 1:1, (b) full 1:2 ($K_1 \neq 4K_2$, $\delta_{\Delta HG2} \neq 2\delta_{\Delta HG}$), (c) non-cooperative 1:2 ($K_1 = 4K_2$, $\delta_{\Delta HG2} \neq 2\delta_{\Delta HG}$), (d) additive 1:2 ($K_1 \neq 4K_2$, $\delta_{\Delta HG2} = 2\delta_{\Delta HG}$), and (e) statistical 1:2 ($K_1 = 4K_2$, $\delta_{\Delta HG2} = 2\delta_{\Delta HG}$) binding models (receptor-substrate) are used for the analysis.[2-4] Detailed information on these binding models can be found in references [2-4].

Table S1. Summary of the binding analysis of the fluorescence titration between **1** and F^- in DMSO.

Binding model (host:guest)	K_1 (M^{-1})	K_2 (M^{-1})	β_2 (M^{-2}) ($K_1 \times K_2$)	Covariance	Conclusion[a]
1:1	$8.5(\pm 94.8\%)\times 10^4$	-	8.5×10^4	0.05	
Full (1:2)	$2.7(\pm 16\%)\times 10^3$	$1.4(\pm 20\%)\times 10^4$	3.8×10^7	9.5×10^{-3}	√
Non-cooperative (1:2)	$8.7(\pm 15\%)\times 10^3$	2.2×10^3	1.9×10^7	0.01	
Additive (1:2)	$2.2(\pm 26\%)\times 10^4$	$-185(\pm 18\%)$	-4.1×10^6	0.02	
Statistical (1:2)	$1.3(\pm 1\times 10^{11}\%)\times 10^{20}$	3.3×10^{19}	4.3×10^{39}	0.1	

[a] According to the covariance values and the physical possibility, the full (1:2) binding model should be more appropriate to describe the data. Specifically, to select a more complex model, the covariance value should be at least 3 times lower than a simpler one.[2] Thus, the full, non-cooperative and additive models are better than 1:1 and statistical modes. Since the negative value is physically impossible, the additive model can also be excluded. At last, combined with the NMR titration results which clearly indicate $K_2 > K_1$, the results of the full binding model are therefore chosen.

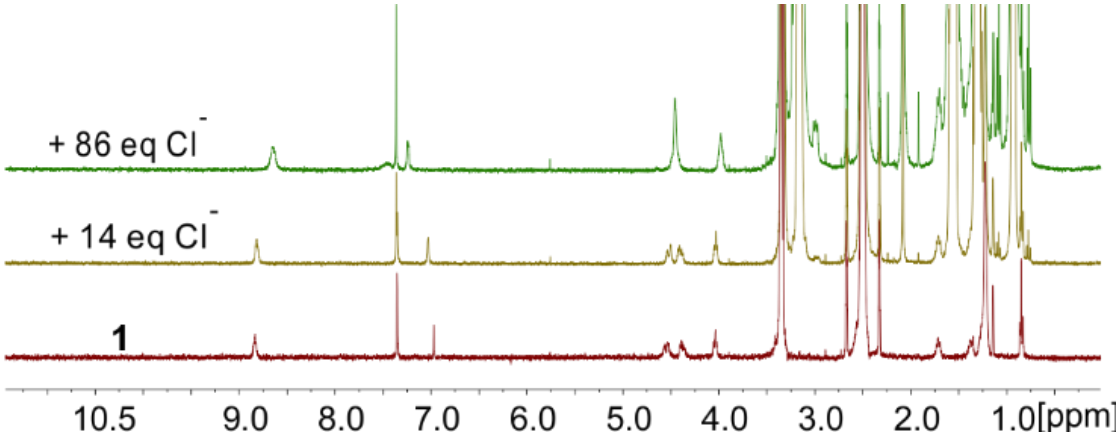

Figure S7. ^{1}H NMR (400 MHz) titration of **1** (1 mM) with Cl^- in DMSO-d_6.

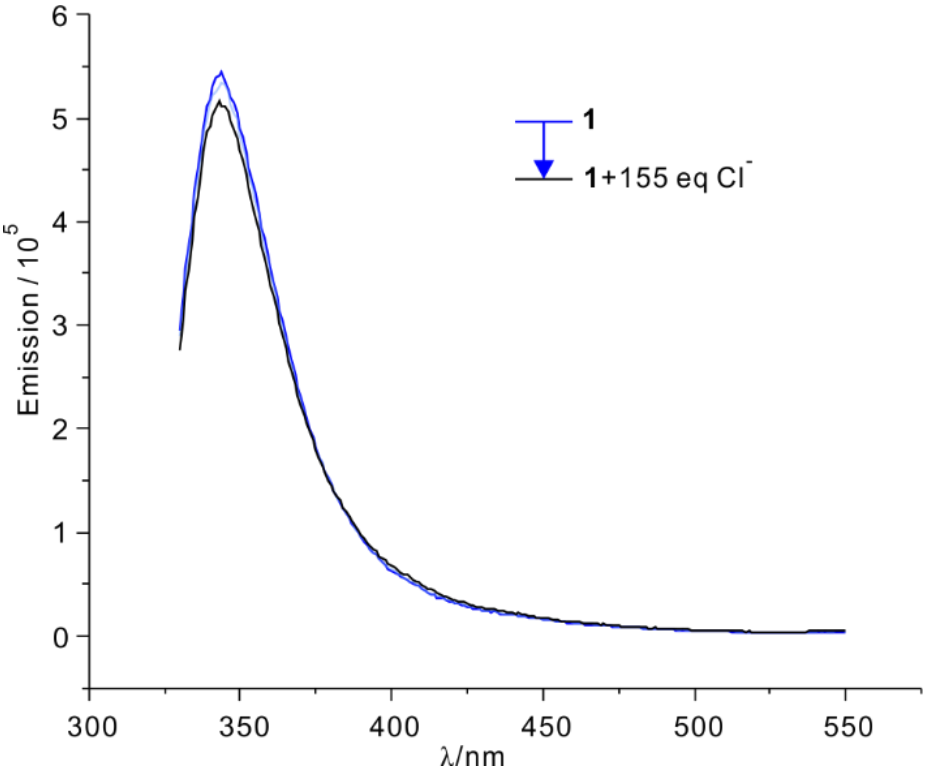

Figure S8. Fluorescence (λ_{ex} = 300 nm) titration of **1** (50 μM) with Cl^- in DMSO.

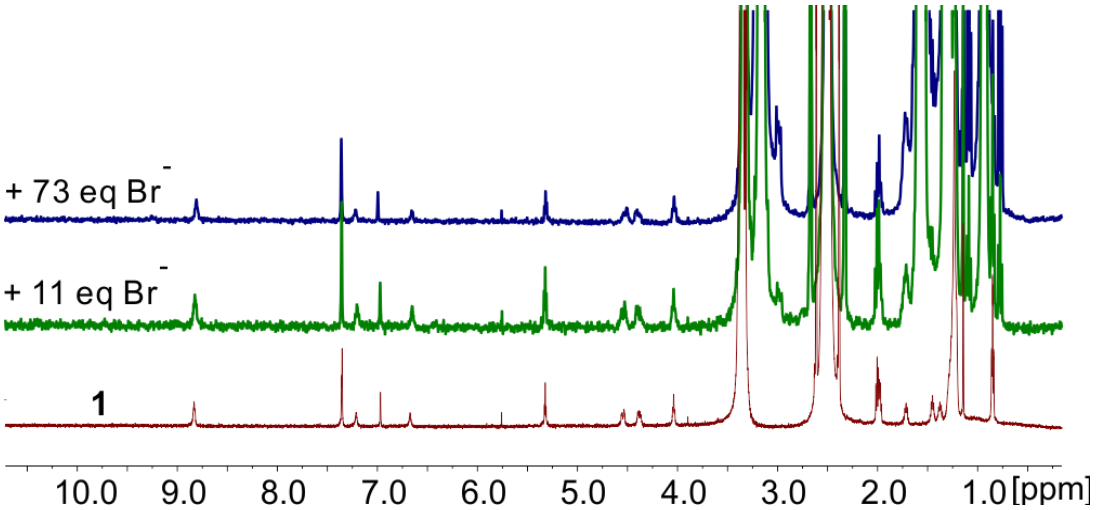

Figure S9. ^{1}H NMR (400 MHz) titration of **1** (1 mM) with Br^- in DMSO-d_6.

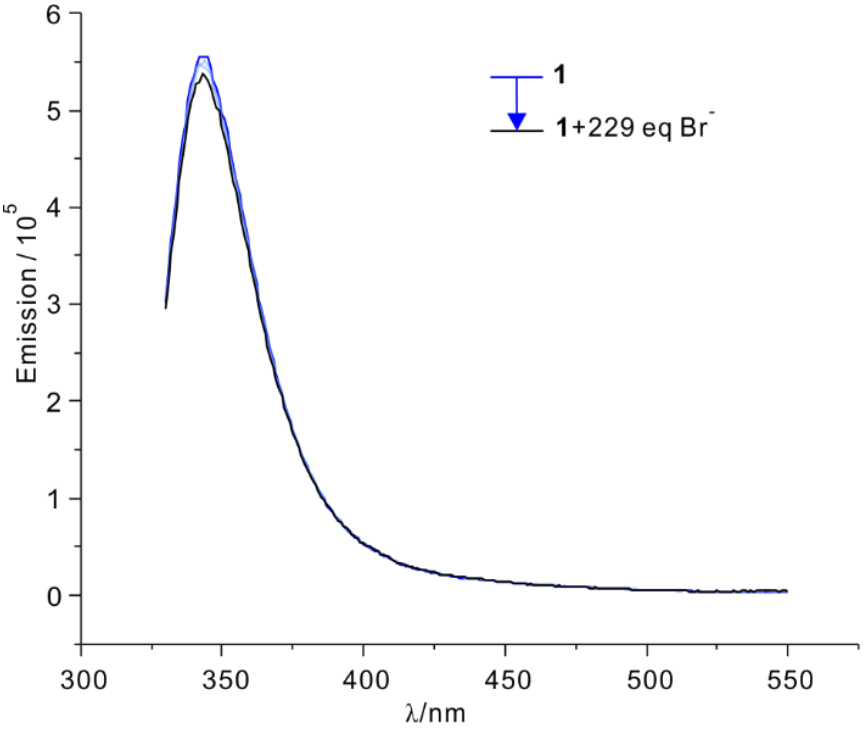

Figure S10. Fluorescence (λ_{ex} = 300 nm) titration of **1** (50 μM) with Br^- in DMSO.

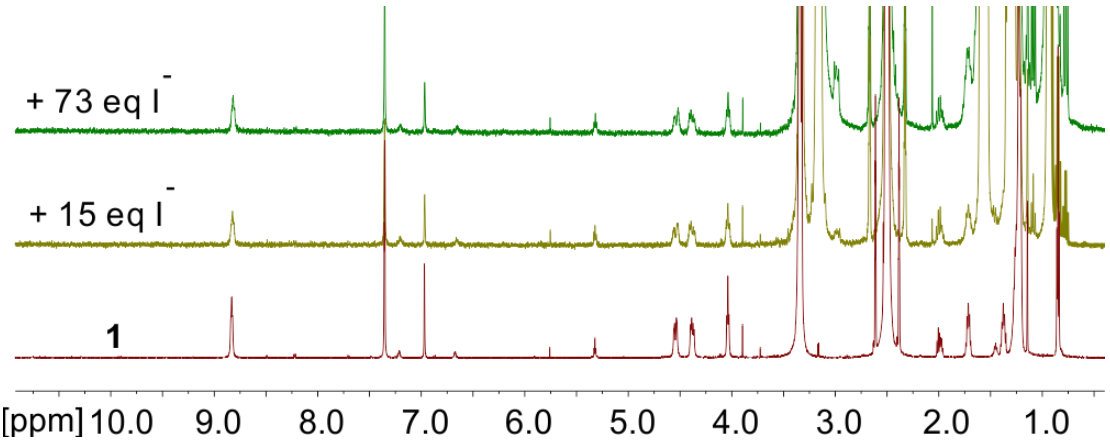

Figure S11. ^{1}H NMR (400 MHz) titration of **1** (1 mM) with I^{-} in DMSO-d_6.

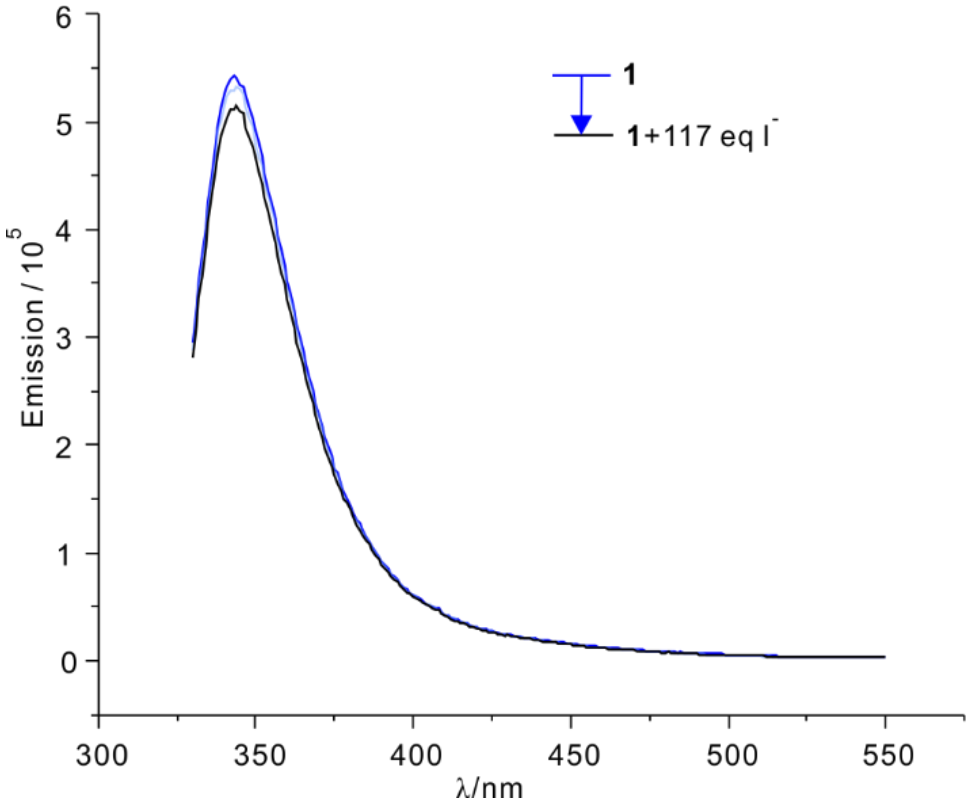

Figure S12. Fluorescence (λ_{ex} = 300 nm) titration of **1** (50 μM) with I^{-} in DMSO.

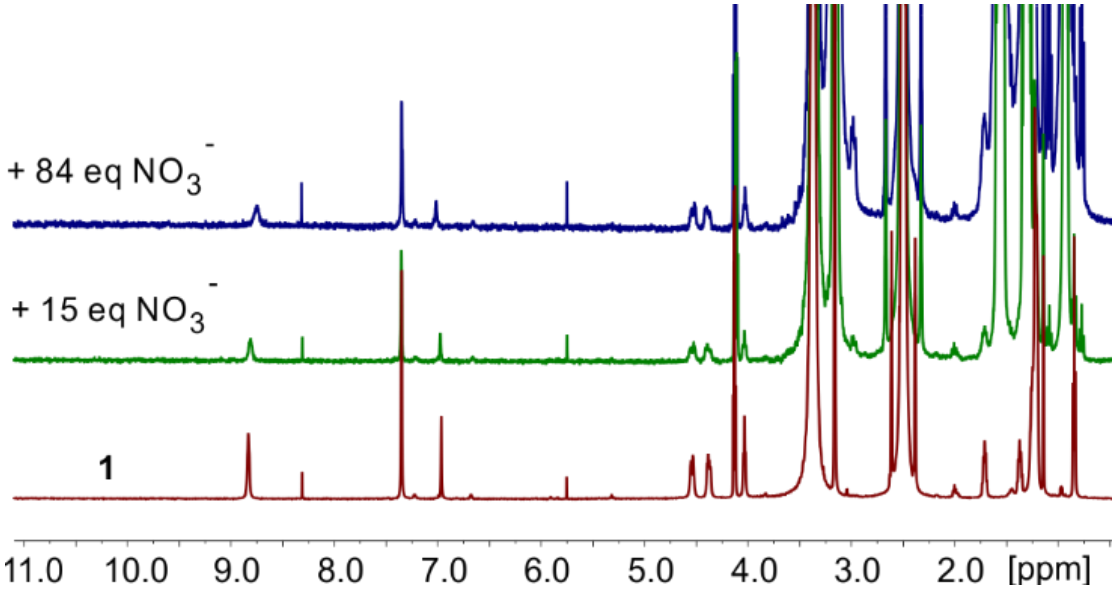

Figure S13. ^{1}H NMR (400 MHz) titration of **1** (1 mM) with NO_3^- in DMSO-d_6.

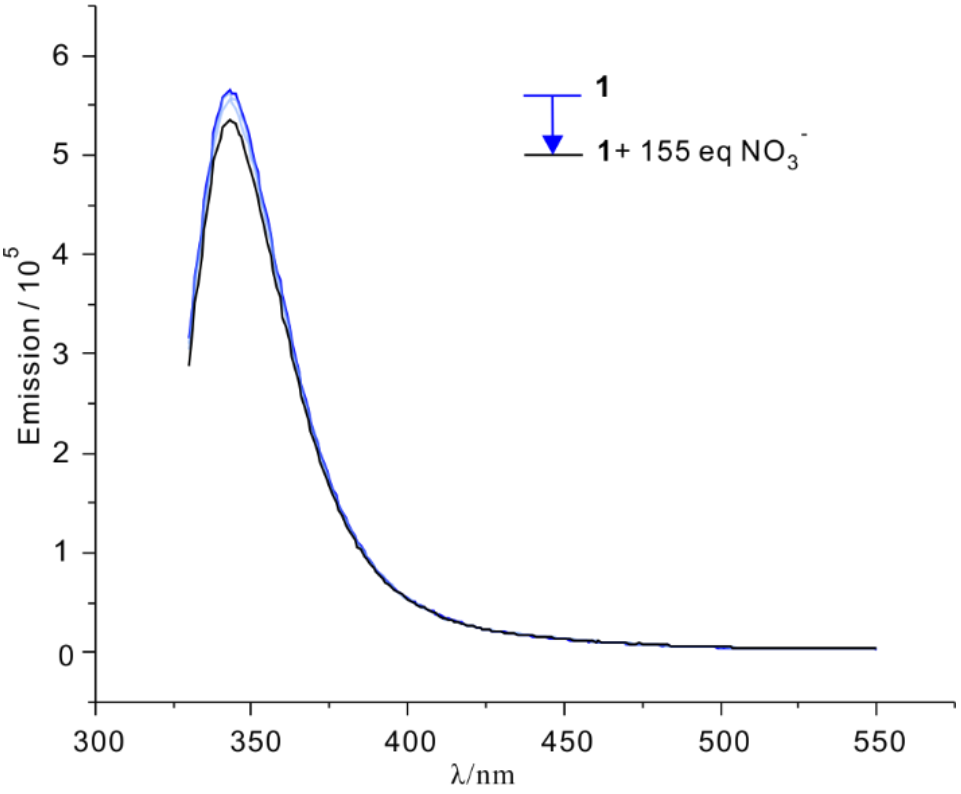

Figure S14. Fluorescence (λ_{ex} = 300 nm) titration of **1** (50 μM) with NO_3^- in DMSO.

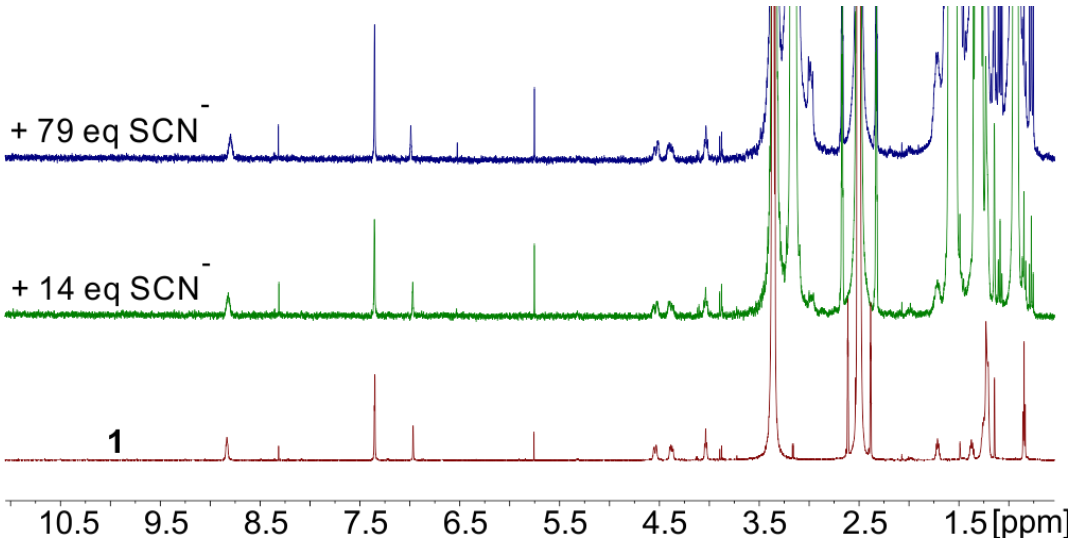

Figure S15. ^{1}H NMR (400 MHz) titration of **1** (1 mM) with SCN^- in DMSO-d_6.

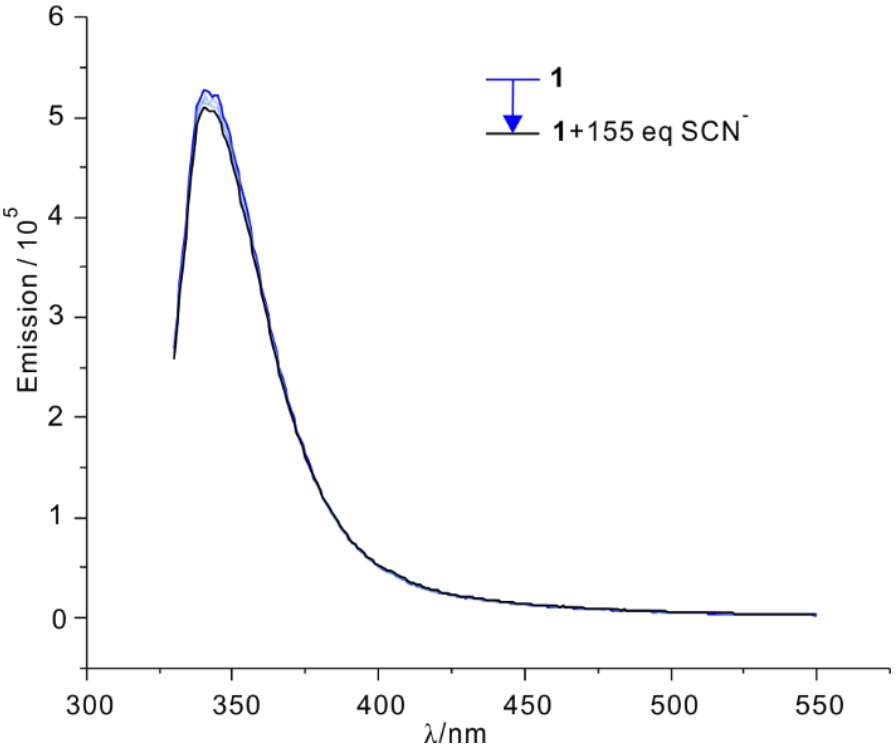

Figure S16. Fluorescence (λ_{ex} = 300 nm) titration of **1** (50 μM) with SCN^- in DMSO.

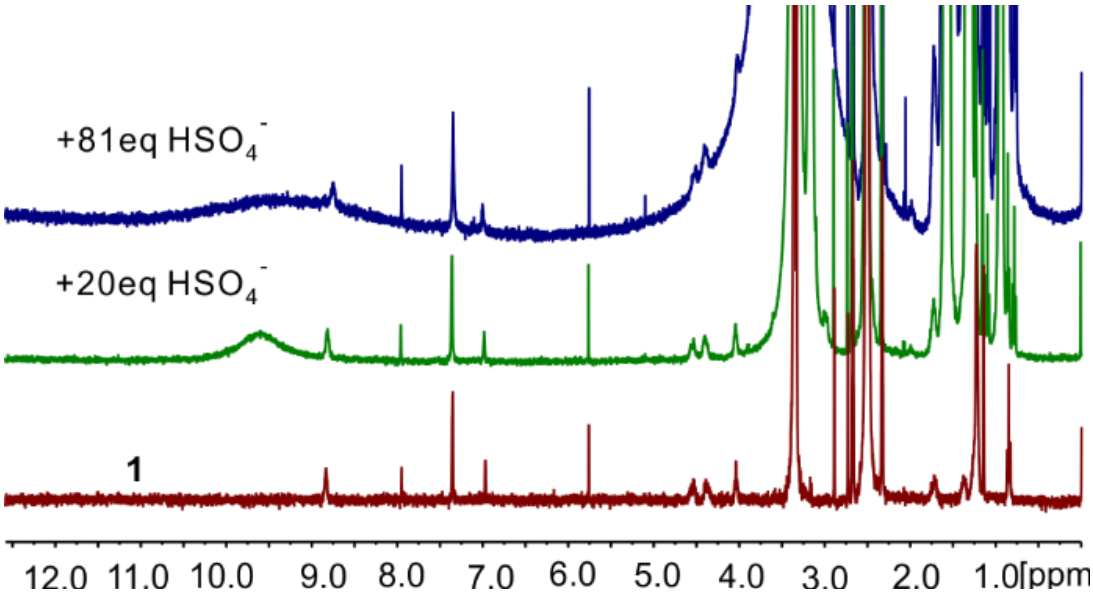

Figure S17. ^{1}H NMR (400 MHz) titration of **1** (1 mM) with HSO_4^- in DMSO-d_6.

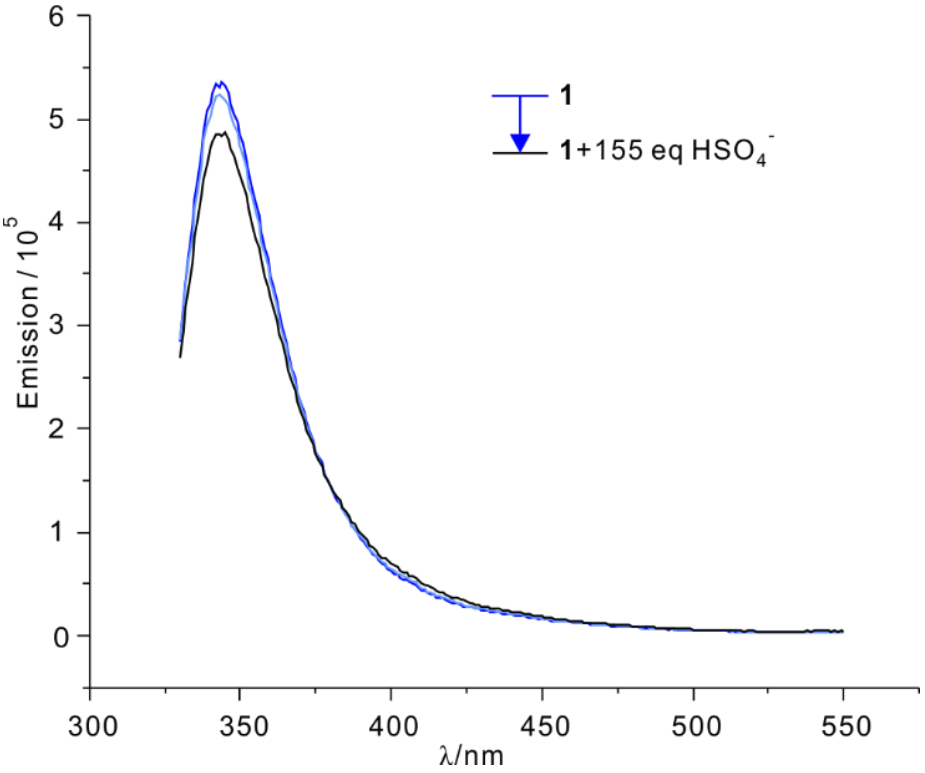

Figure S18. Fluorescence (λ_{ex} = 300 nm) titration of **1** (50 μM) with HSO_4^- in DMSO.

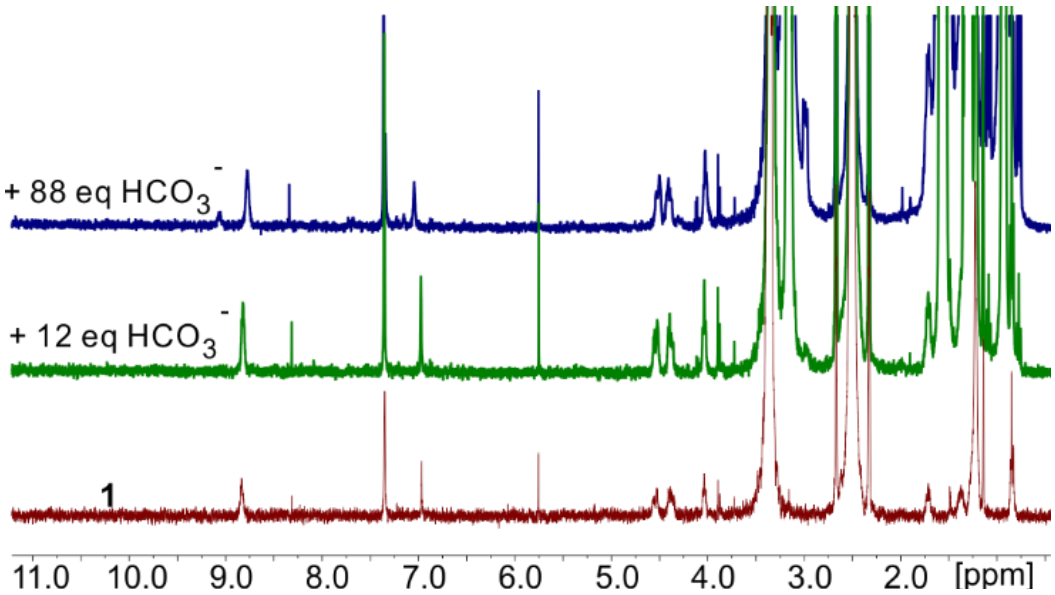

Figure S19. ^{1}H NMR (400 MHz) titration of **1** (1 mM) with HCO_3^- in DMSO-d_6.

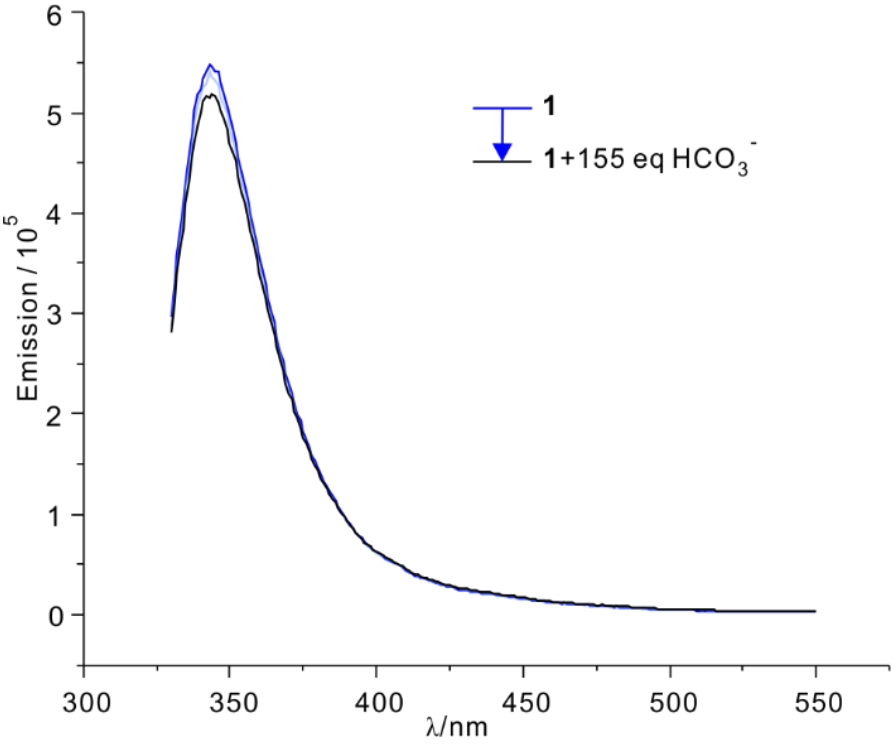

Figure S20. Fluorescence (λ_{ex} = 300 nm) titration of **1** (50 μM) with HCO_3^- in DMSO.

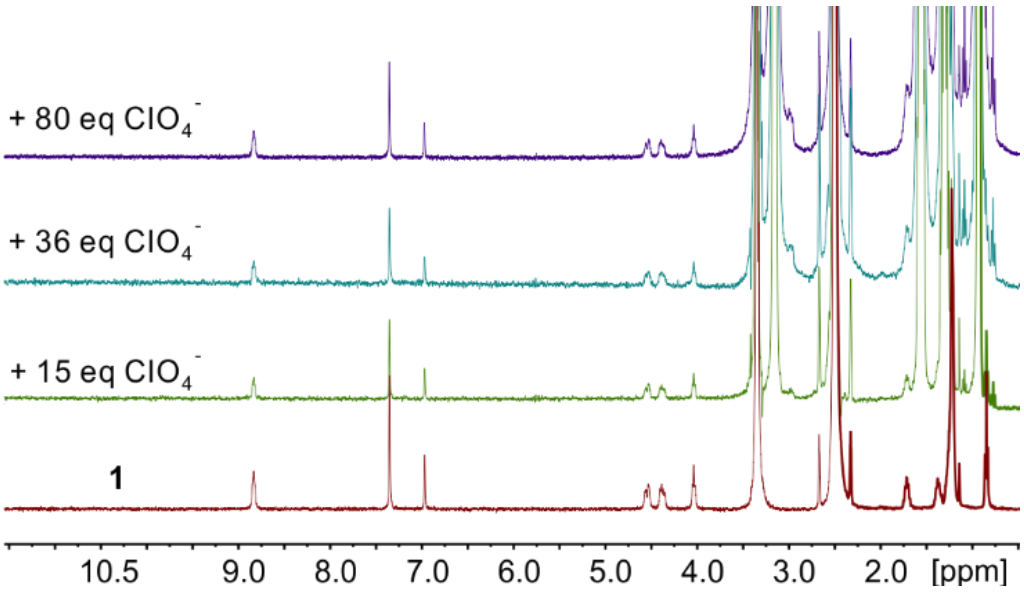

Figure S21. ^{1}H NMR (400 MHz) titration of **1** (1 mM) with ClO_4^- in DMSO-d_6.

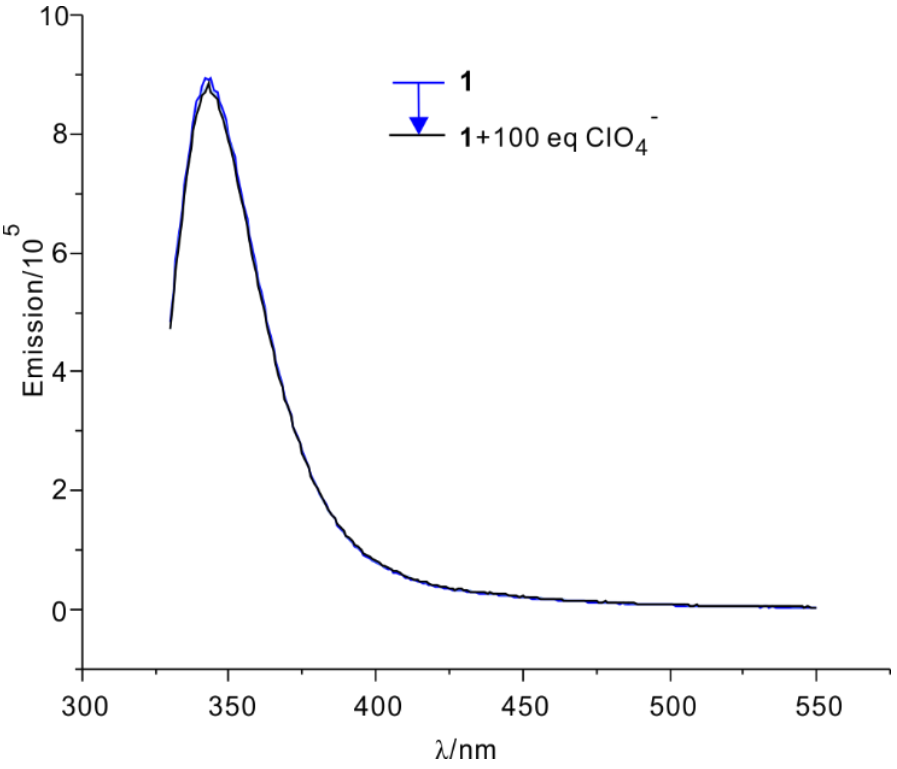

Figure S22. Fluorescence (λ_{ex} = 300 nm) titration of **1** (50 μM) with ClO_4^- in DMSO.

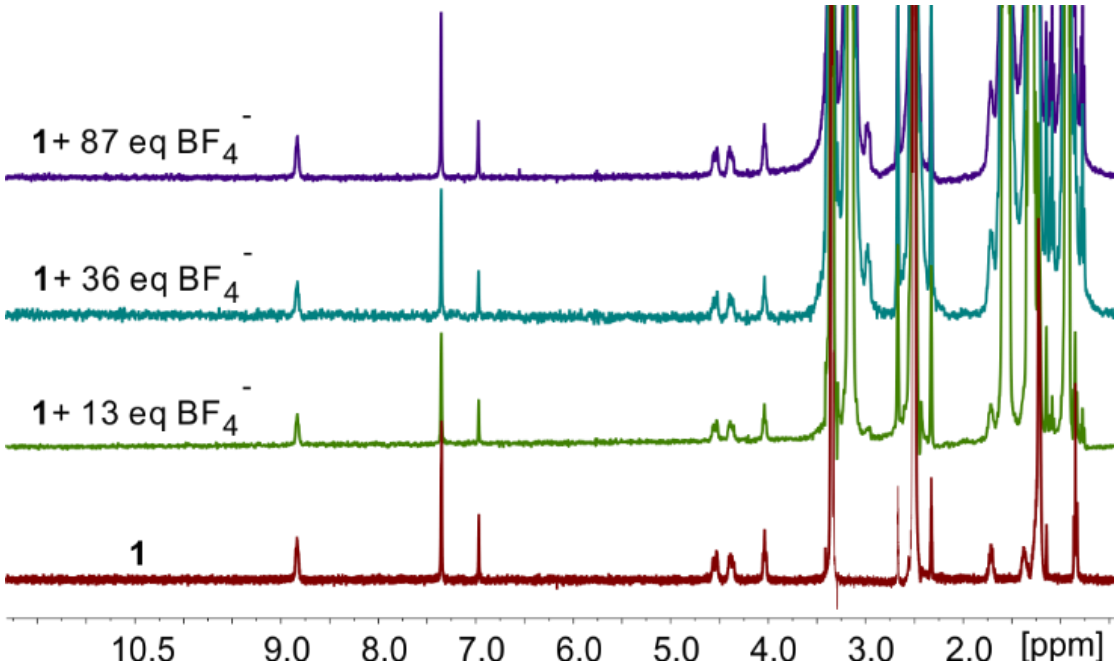

Figure S23. ^{1}H NMR (400 MHz) titration of **1** (1 mM) with BF_4^- in DMSO-d_6.

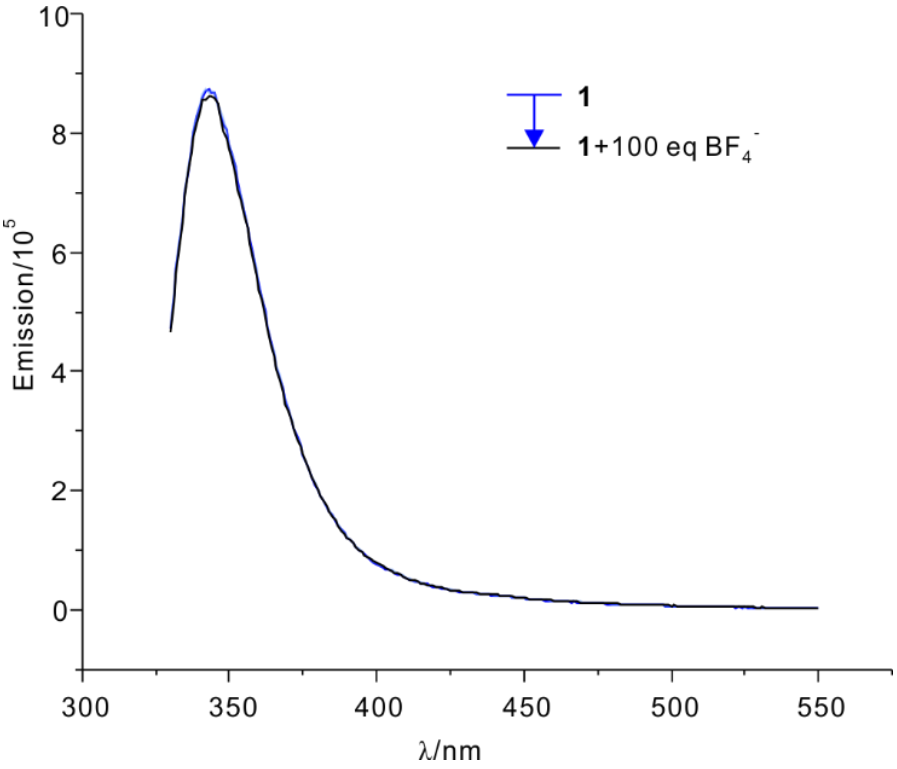

Figure S24. Fluorescence (λ_{ex} = 300 nm) titration of **1** (50 μM) with BF_4^- in DMSO.

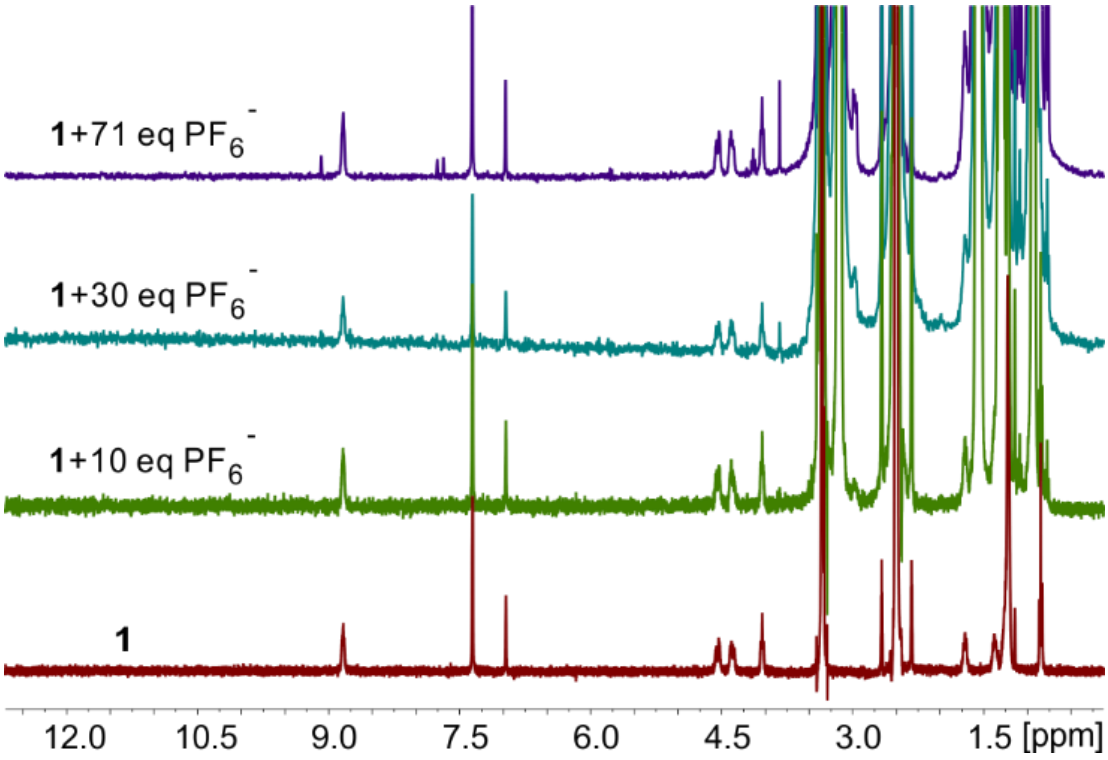

Figure S25. ^{1}H NMR (400 MHz) titration of **1** (1 mM) with PF_6^- in DMSO-d_6.

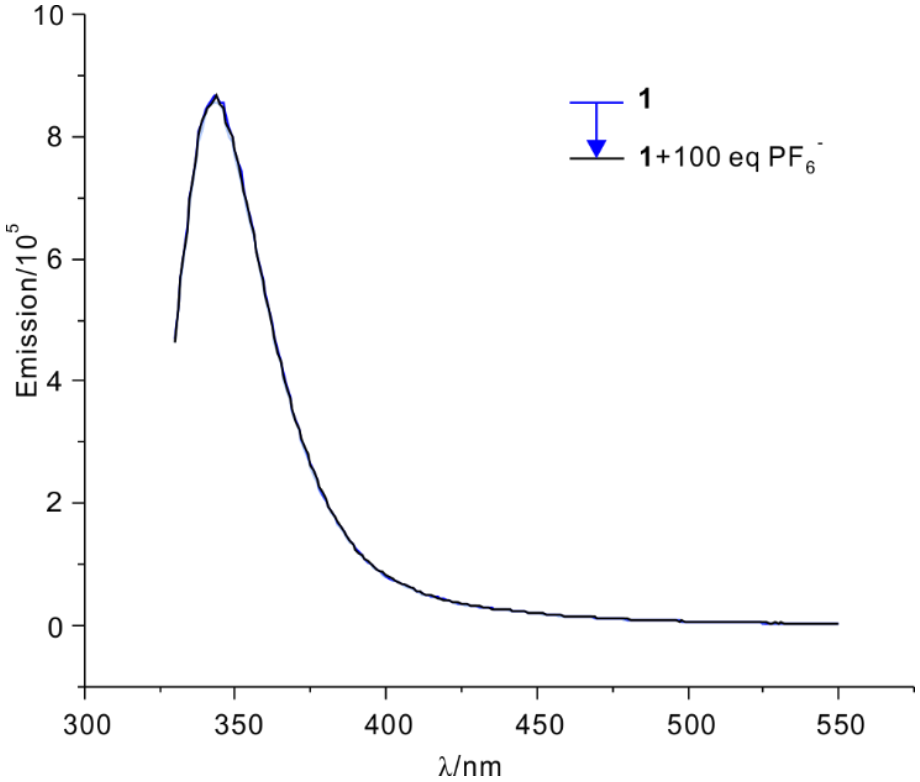

Figure S26. Fluorescence (λ_{ex} = 300 nm) titration of **1** (50 μM) with PF_6^- in DMSO.

Table S2. Summary of stability constants of [**1**-anion] complexes in DMSO.

Anion	K_1 (M^{-1})	K_2 (M^{-1})	β_2 (M^{-2}) ($K_1 \times K_2$)
F^-(NMR)	3.3×10^3	1.1×10^4	3.6×10^7
F^-(fluorescence)	2.7×10^3	1.4×10^4	3.8×10^7
Cl^-	-[a]	-[a]	-[a]
Br^-	-[a]	-[a]	-[a]
I^-	-[a]	-[a]	-[a]
NO_3^-	-[a]	-[a]	-[a]
SCN^-	-[a]	-[a]	-[a]
HSO_4^-	-[a]	-[a]	-[a]
HCO_3^-	-[a]	-[a]	-[a]
ClO_4^-	-[a]	-[a]	-[a]
BF_4^-	-[a]	-[a]	-[a]
PF_6^-	-[a]	-[a]	-[a]

[a] Spectral changes are too small to determine the corresponding stability constants, *i.e.* stability constants are extremely small.

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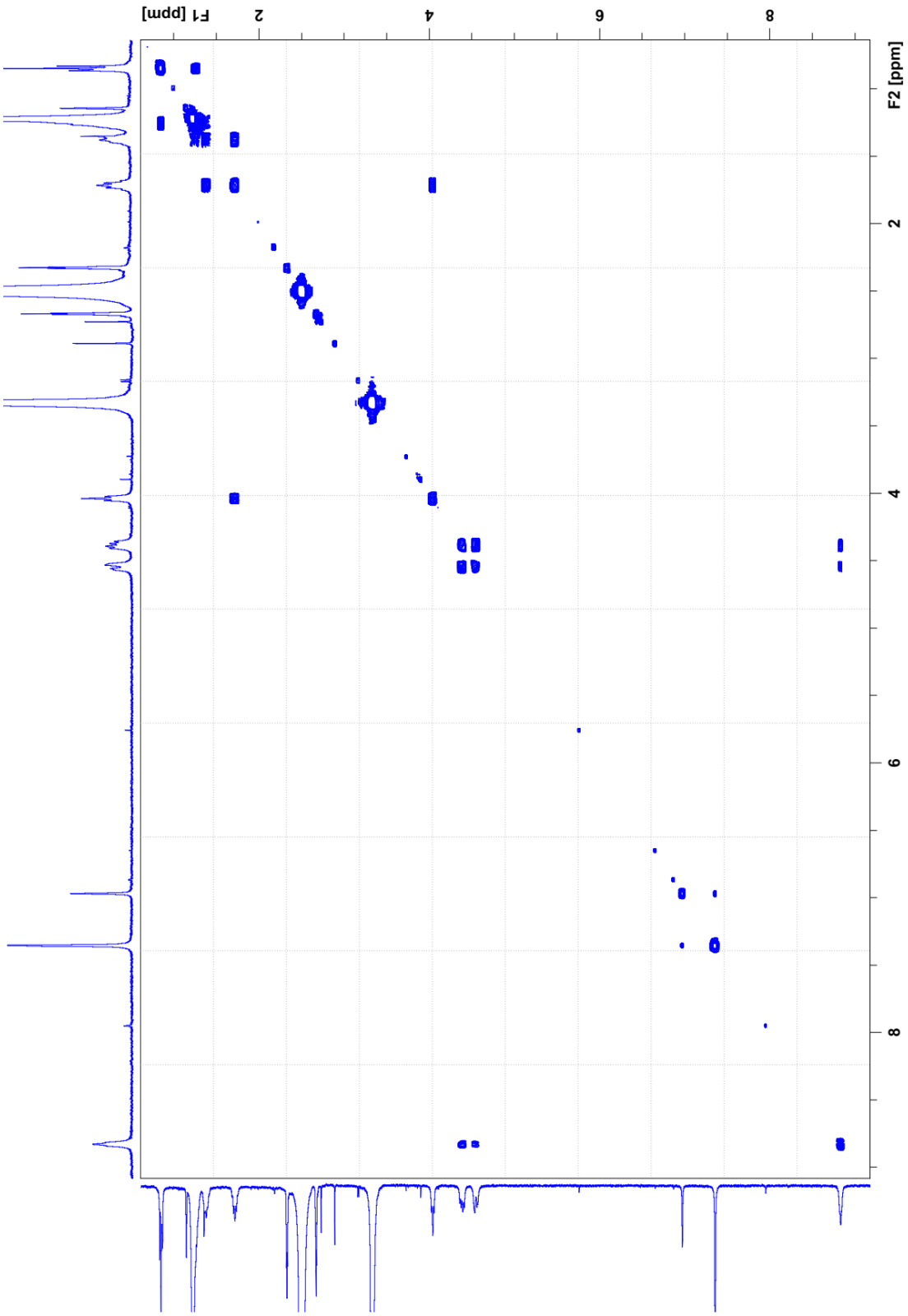

Figure S27. Full ^{1}H-^{1}H COSY (400 MHz) spectrum of **1** (2 mM) in DMSO-d_6 at 298 K.

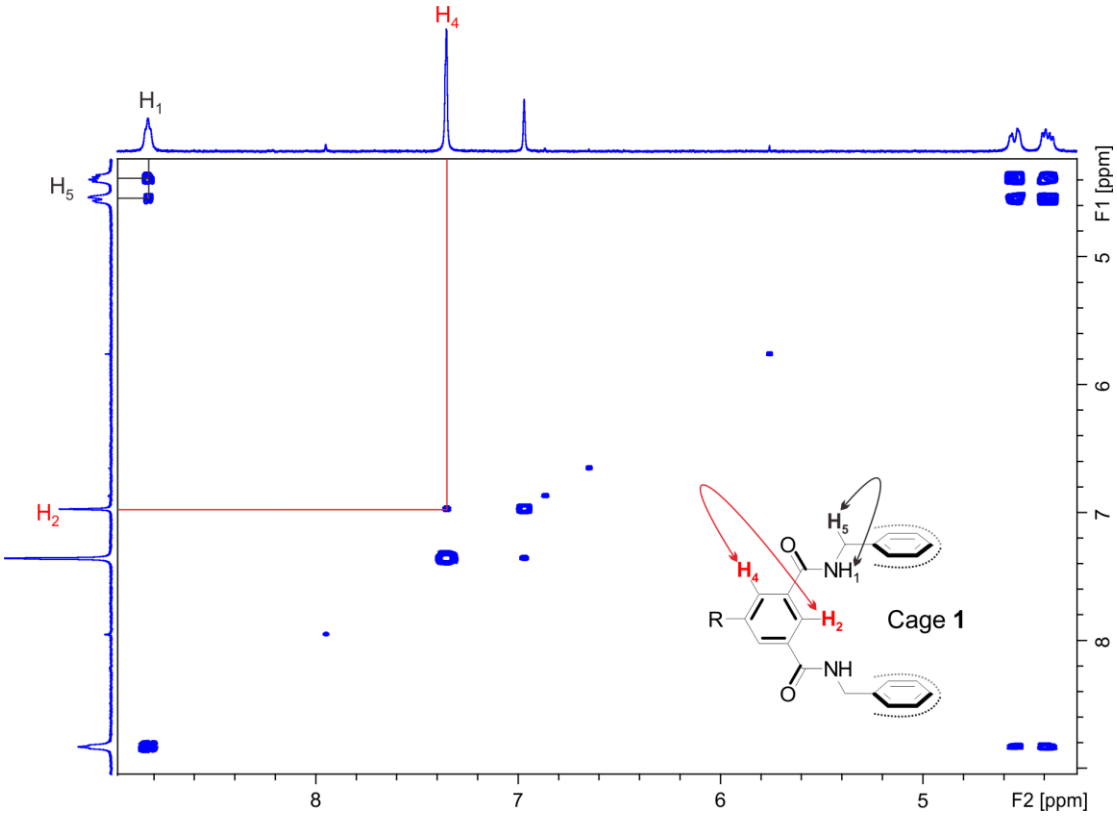

Figure S28. ^{1}H-^{1}H COSY (400 MHz) spectrum of **1** (2 mM) in DMSO-d_6 at 298 K, showing the COSY correlations of H_2↔H_4 and H_1↔H_5.

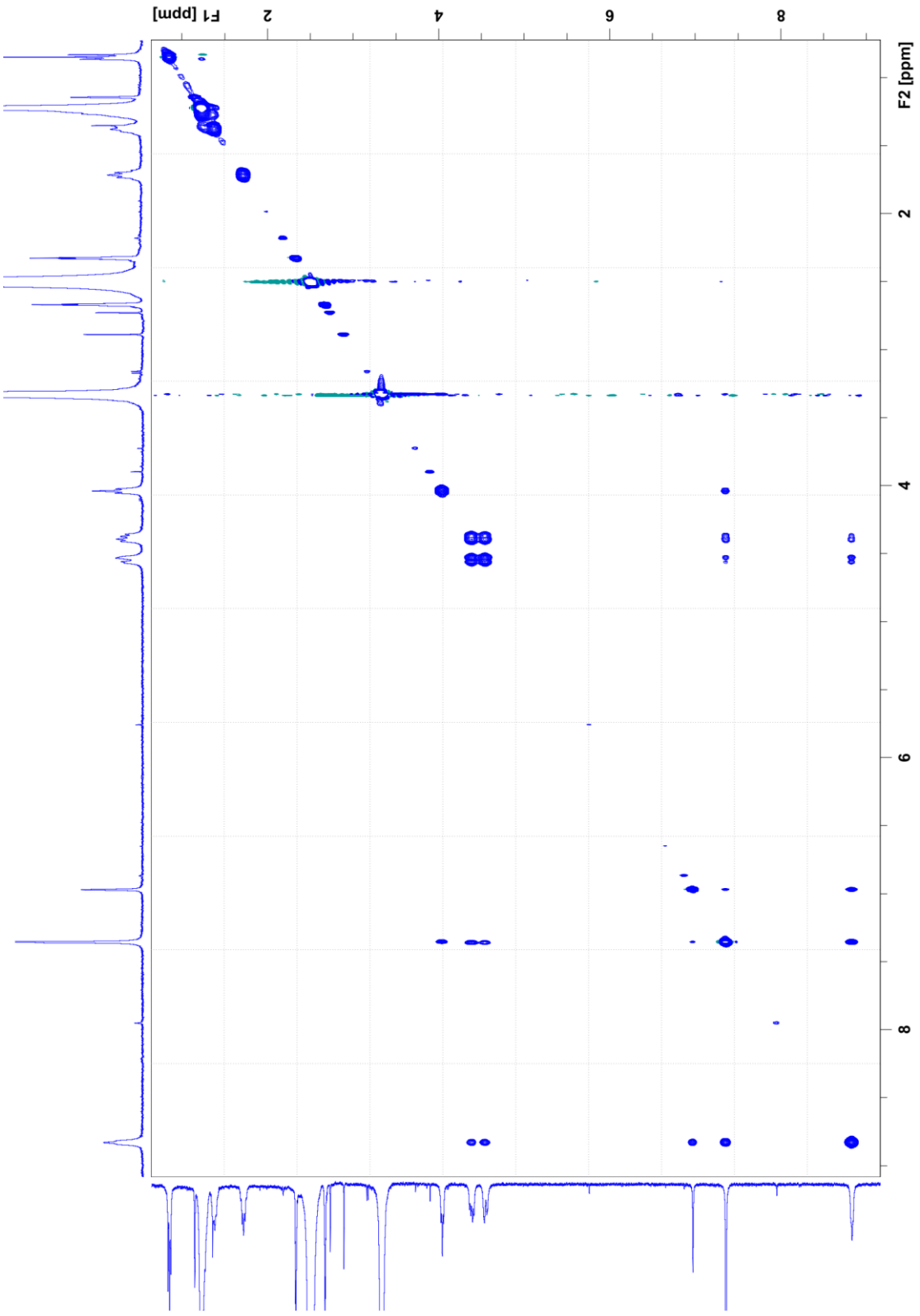

Figure S29. Full ^{1}H-^{1}H NOESY (400 MHz) spectrum of **1** (2 mM) in DMSO-d_6 at 298 K.

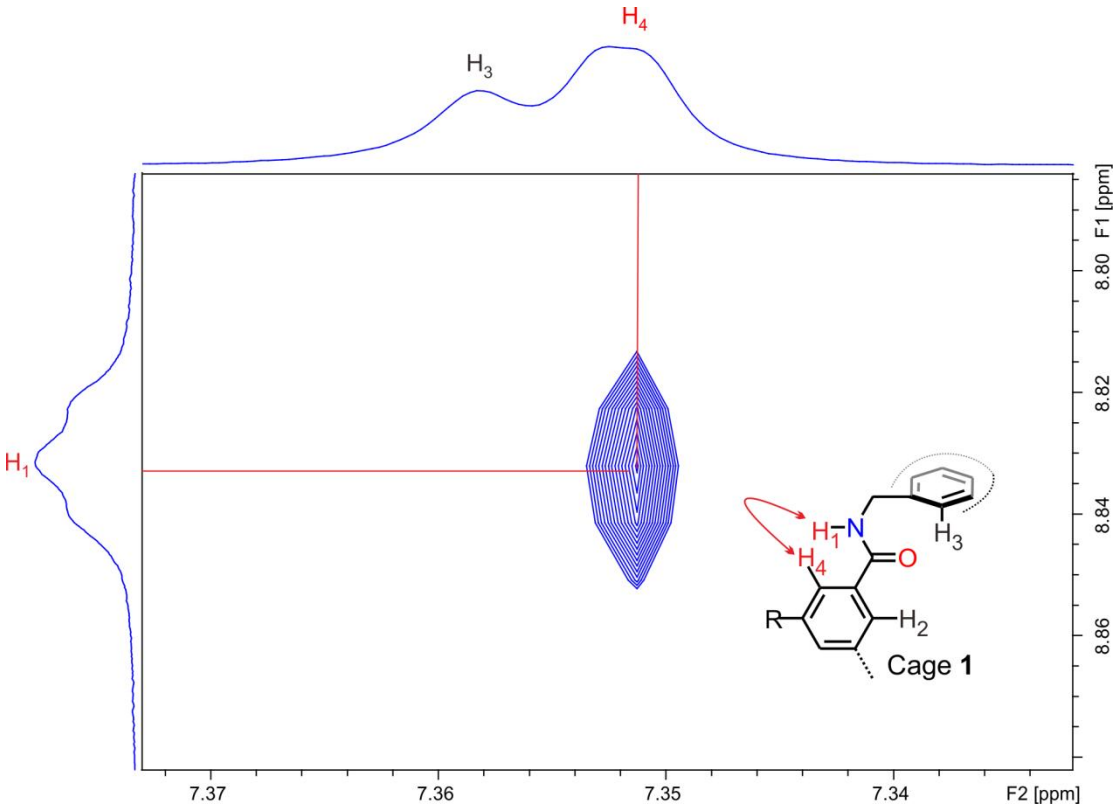

Figure S30. ^{1}H-^{1}H NOESY (400 MHz) spectrum of **1** (2 mM) in DMSO-d_6 at 298 K, showing the NOE correlation of $H_1 \leftrightarrow H_4$.

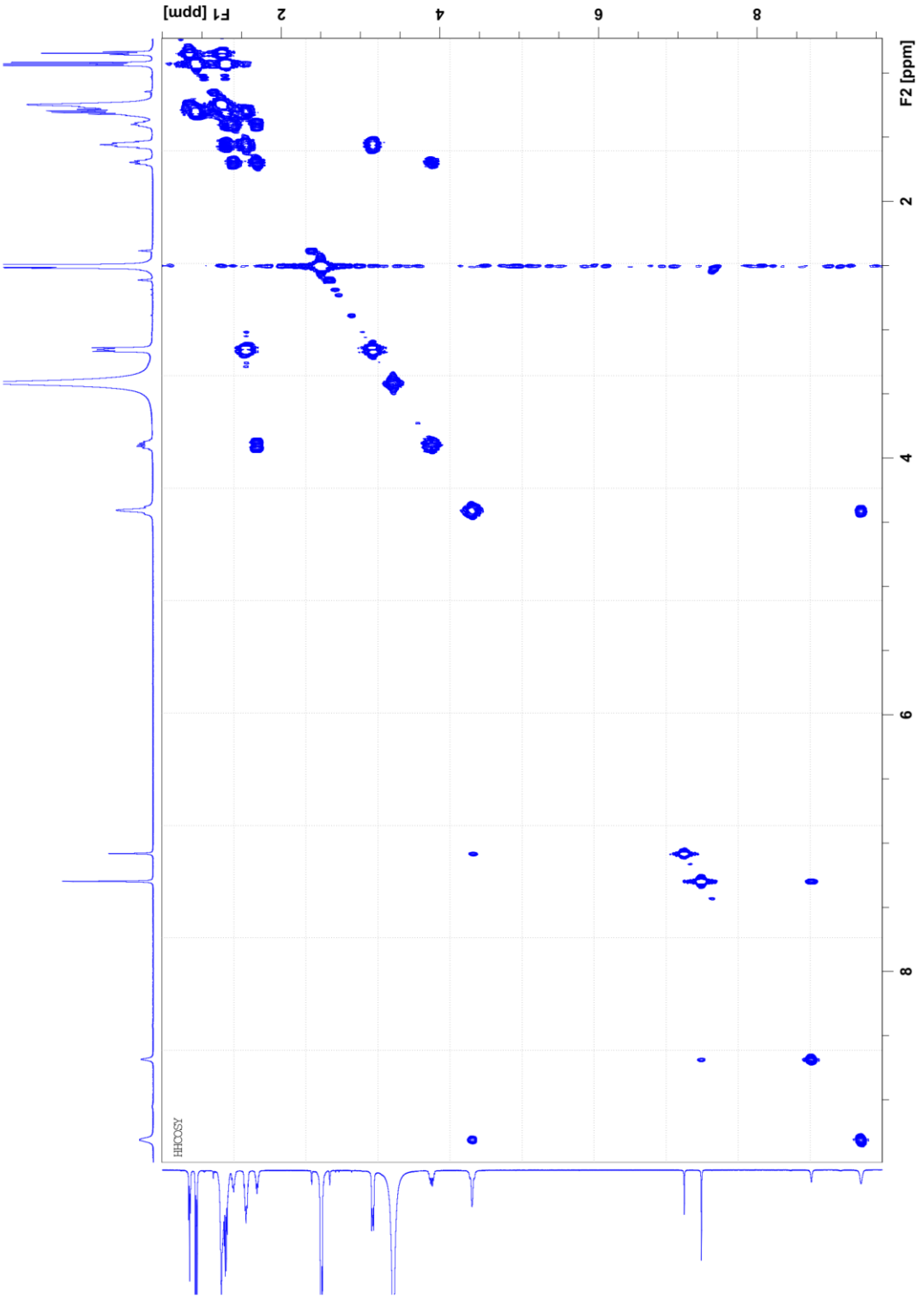

Figure S31. Full ^{1}H-^{1}H COSY (600 MHz) spectrum of **1**+2eqF^{-} (2 mM + 4 mM) in DMSO-d_6 at 298 K.

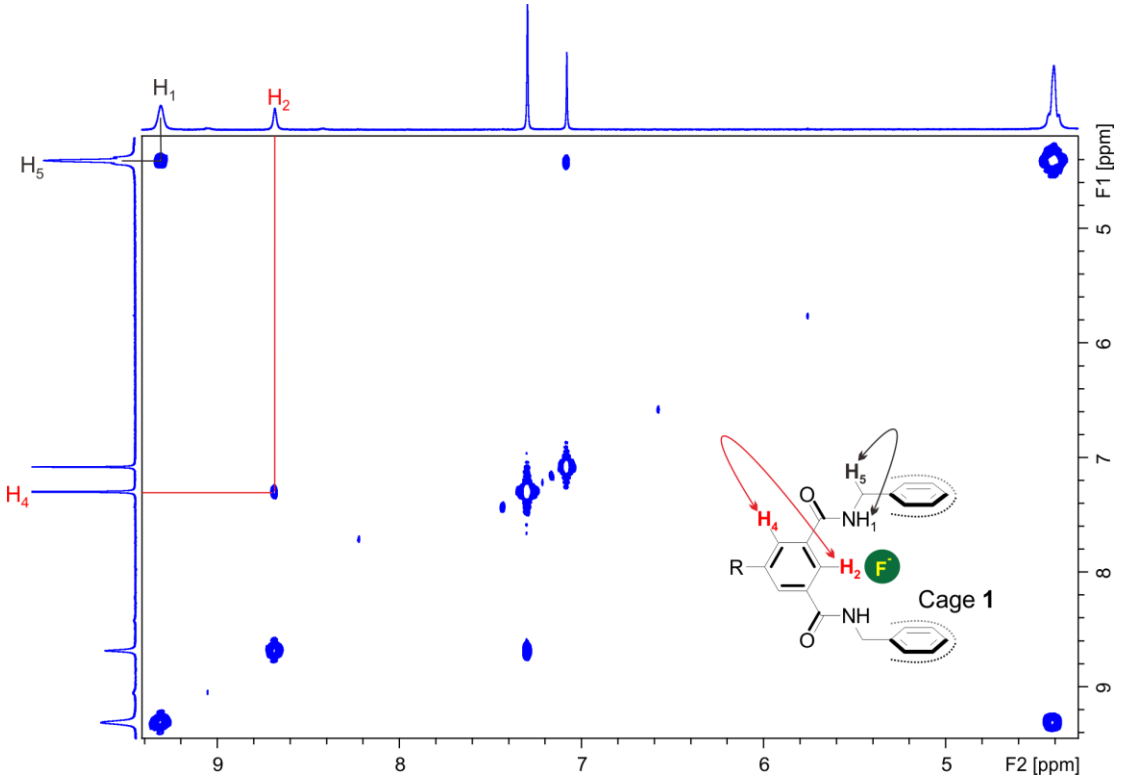

Figure S32. ^{1}H-^{1}H COSY (600 MHz) spectrum of **1**+2eqF^{-} (2 mM + 4 mM) in DMSO-d_6 at 298 K, showing the COSY correlations of H_2↔H_4 and H_1↔H_5.

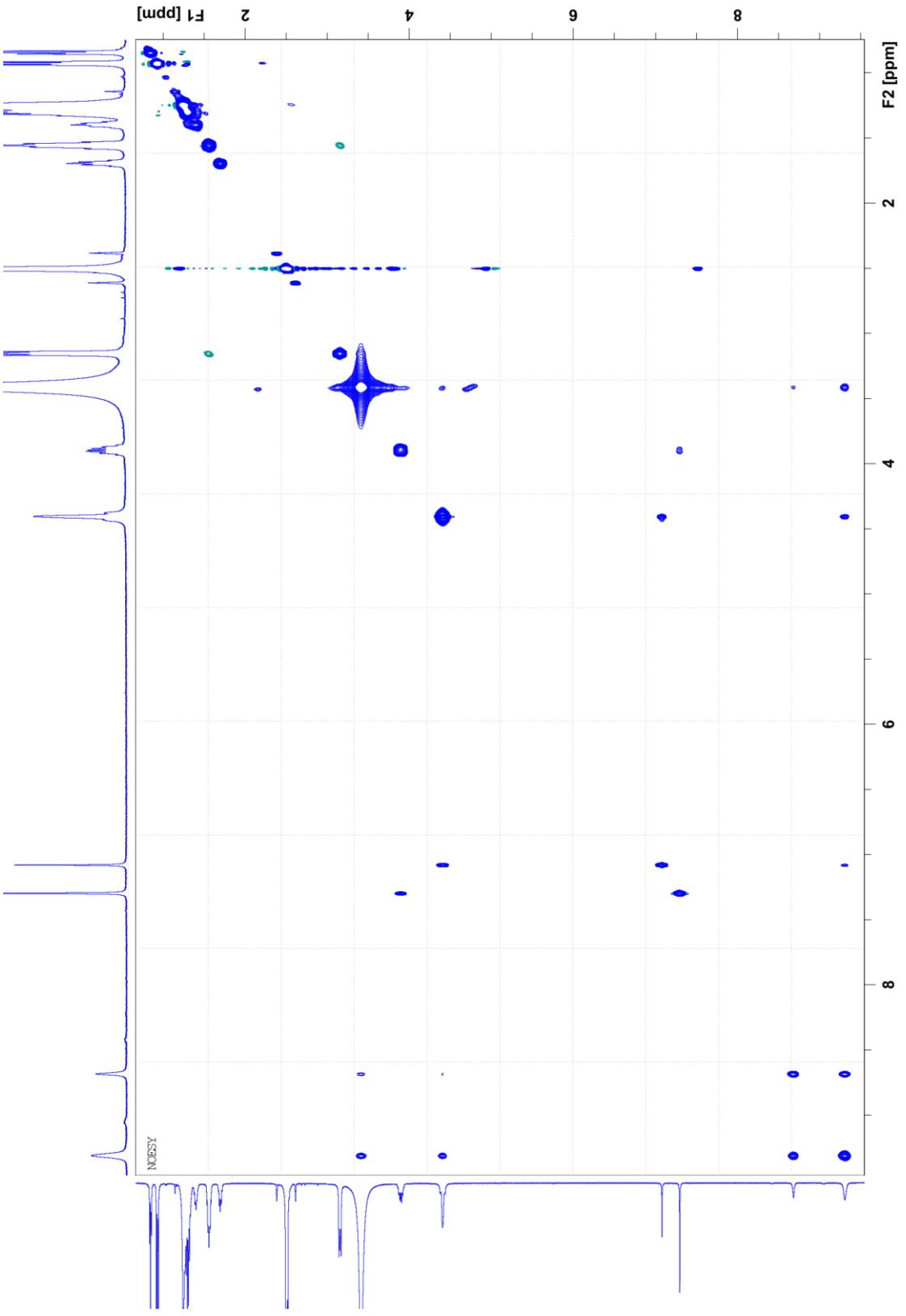

Figure S33. Full ^{1}H-^{1}H NOESY (600 MHz) spectrum of **1**+2eqF^{-} (2 mM + 4 mM) in DMSO-d_6 at 298 K.

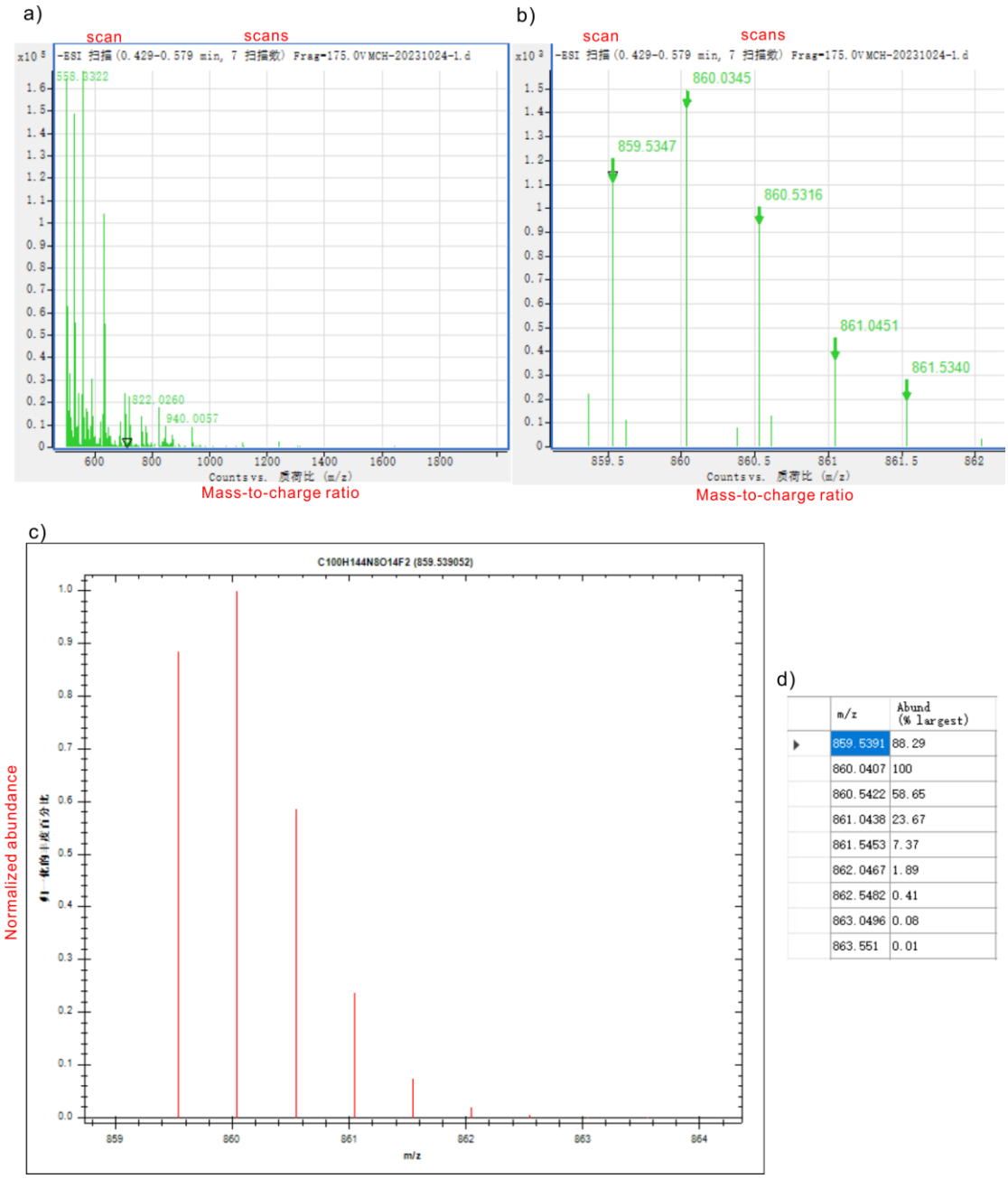

Figure S34. HRMS (ESI-TOF) of **1**+10eqF$^-$ (m/z calcd for $C_{100}H_{144}N_8O_{14}F_2^{2-}$ [**1**+2F+2H_2O]$^{2-}$ = 859.5391, found 859.5347. a) full spectrum, b) target signals, c) and d) theoretical isotopic distribution pattern of the target signals. The red text is the translation of the corresponding Chinese characters.

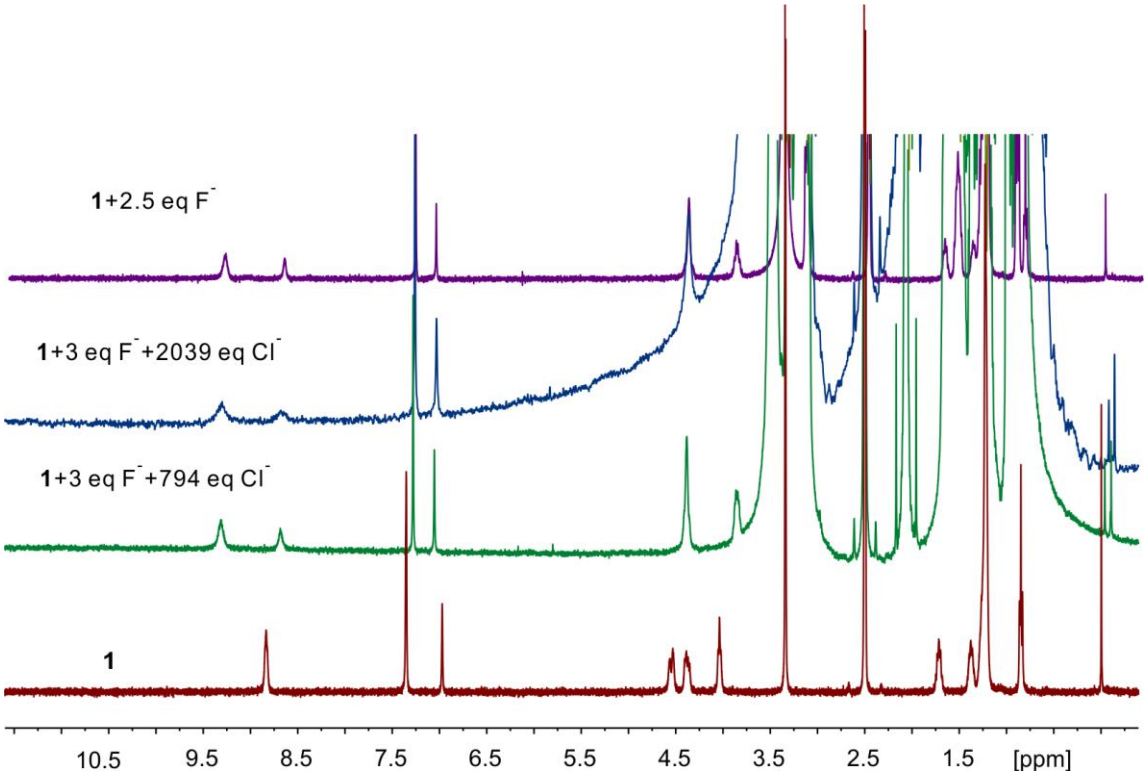

Figure S35. Full ^{1}H NMR spectra of **1** (1 mM), **1**+3eqF^-+794eqCl^-, **1**+3eqF^-+2039eqCl^- and **1**+2.5eqF^- in DMSO-d_6.

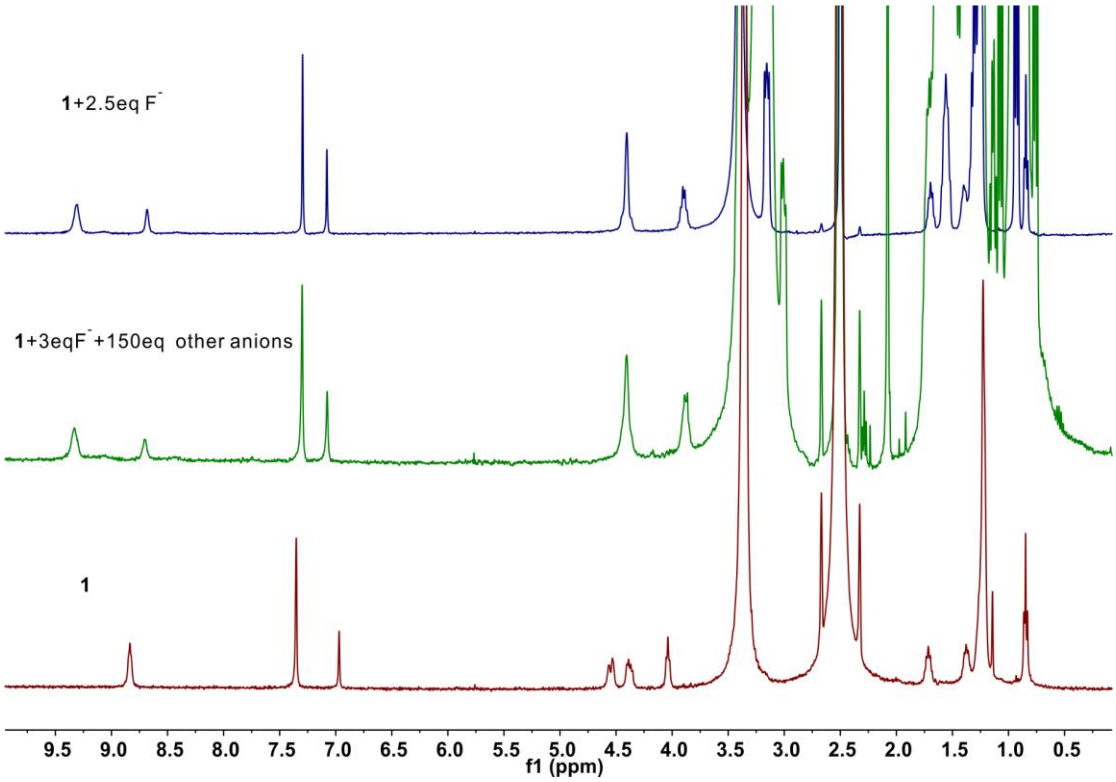

Figure S36. Full ^{1}H NMR spectra of **1**, **1**+3eqF^-+150eq other anions (Cl^-, Br^-, I^-, NO_3^-, SCN^-, HCO_3^-, ClO_4^-, BF_4^-, and PF_6^-), and **1**+2.5eqF^- in DMSO-d_6. The concentration of **1** is 1 mM.

Reference

[1] C. Mao, R. Wu, N. Chen, H. Zheng, Y. Cai, L. Kong and X. Hu, *Org. Chem. Front.*, 2024, **11**, 3348-3357.

[2] D. B. Hibbert and P. Thordarson, *Chem. Commun.*, 2016, **52**, 12792-12805.

[3] P. Thordarson, *Chem. Soc. Rev.*, 2011, **40**, 1305–1323.

[4] E. N., Howe, M. Bhadbhade and P. Thordarson, *J. Am. Chem. Soc.*, 2014, **136**, 7505-7516.