Electronic Supplementary Information (ESI)

Multichannel HSO_4^- recognition promoted by a bound cation within a ferrocene-based ion pair receptor.

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1. Experimental section.

1.1. General and computational comments.

Melting points were determined on a hot-plate melting point apparatus and are uncorrected. ^{1}H- and ^{13}C-NMR spectra were recorded at 400, and 100 MHz, respectively. Chemical shifts refer to signals of tetramethylsilane in the case of ^{1}H and ^{13}C spectra.

UV-vis spectra were carried out in a UV-vis-NIR spectrophotometer using a dissolution cell of 10 mm path. The samples were solved in CH_3CN ($c = 1x10^{-5}$ M) and the spectra were recorded with the spectra background corrected before and after of the sequential additions of aliquots of 0.1 equiv of cations/anions in CH_3CN ($c = 1x\ 10^{-3}$ M).

Fluorescence spectra were carried out in a fluorescence spectrophotometer using a fluorescence cell 10 mm ($c = 2x10^{-6}$ M in CH_3CN), as it is stated in the corresponding figure captions. Before recording the spectra, the samples were deoxygenated, to remove fluorescence quenching via oxygen, by bubbling nitrogen for at least 10 min. All the spectra were recorded before and after the sequential additions of aliquots of 0.1 equiv of a solution of cations in CH_3CN ($c = 10^{-3}$ M). Quantum yield values were measured with respect to anthracene as standard ($\Phi = 0.27\pm0.01$)[1], using the equation $\Phi_x/\Phi_s = (S_x/S_s)\ [(1\text{-}10^{-As})/(1\text{-}10^{-Ax})]^2(n_s^2/n_x^2)$ where x and s indicate the unknown and standard solution, respectively, Φ is the quantum yield, S is the area under the emission curve A is the absorbance at the excitation wavelength and n is the index of refraction.

CV and OSWV techniques were performed with a conventional three-electrode configuration consisting of platinum working and auxiliary electrodes and a Ag/AgCl reference electrode. The experiments were carried out with a $1x10^{-3}$ M and $5x10^{-4}$ M solution of sample in CH_3CN containing 0.1 M $(n\text{-}C_4H_9)_4PF_6$ ($TBAPF_6$) as supporting electrolyte. All the potential values reported are relative to the decamethylferrocene (DMFc) couple at room temperature. Deoxygenation of the solutions was achieved by bubbling nitrogen for at least 10 min and the working electrode was cleaned after each run. The cyclic voltammograms were recorded with a scan rate increasing from 0.05 to 1.00 Vs^{-1}, while the OSWV were recorded at a scan rate of 100 mVs^{-1} with a pulse hight of 10 mV and a step time of 50 ms. Typically, receptor ($1x10^{-3}$ M or $5x10^{-4}$ M) was dissolved in CH_3CN (5 mL) and $TBAPF_6$ (base electrolyte) (0.190 g or 0.095g) added. The guest under investigation was then added as a $2.5x10^{-2}$ M solution in CH_3CN using a microsyringe whilst the cyclic voltammetric properties of the solution were monitored. DMFc was used as an external reference both for potential calibration and for reversibility criteria.

All calculations have been carried out with the ORCA electronic structure program package[2] with all structures being optimized in redundant internal coordinates with tight criteria[3] at the density functional theory (DFT) level using the B3LYP[4] functional together with the new efficient RIJCOSX algorithm[5] and the def2-TZVP[6]

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[1] W. R. Dawson and M. W. Windsor, *J. Phys.Chem.* 1968, **72**, 3251.

[2] ORCA — An ab initio, density functional and semiempirical program package. Written by F. Neese. Version 2.8.0, Universität Bonn, 2010. Web page: http://www.thch.uni-bonn.de/tc/orca/

[3] Default tight convergence criteria for optimizations in ORCA: energy change $1.0\cdot10^{-6}$ hartree; maximum gradient $1.0\cdot10^{-4}$ hartree/a_0; RMS gradient $3.0\cdot10^{-5}$ hartree/a_0; maximum displacement $1.0\cdot10^{-3}$ a_0; RMS displacement $6.0\cdot10^{-4}$ a_0.

[4] (a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; (b) C. T. Lee, W. T. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.

[5] F. Neese, F. Wennmohs, A. Hansen, U. Becker, *Chem. Phys.*, **2009,** *356*, 98.

basis set. For Pb the [SD(60,MDF)] effective core potential was employed.[7] A damped semiempirical correction accounting for the major part of the contribution of dispersion forces to the energy was included[8] and denoted with suffix -D after the name of the functional (B3LYP-D). Solvent effects (MeCN) were taken into account via the COSMO solvation model.[9] Reported energies are uncorrected for the zero-point vibrational term. Bond strengths were characterized by Wiberg's Bond Indices (WBI)[10] and calculated with the natural bond orbital (NBO) method as the sum of squares of the off-diagonal density matrix elements between atoms. Electron densities at bond critical points (BCP) that were computed with the AIM2000 program[11] and the wavefunctions generated at the B3LYP/def2-TZVP level with the Gaussian09 software package.[12] Figure 2 was drawn with VMD.[13]

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[6] F. Weigend, R. Ahlrichs, Phys. *Chem. Chem. Phys.*, **2005**, *7*, 3297.

[7] Metz, B.; Stoll, H.; Dolg, M. *J. Chem. Phys.*, **2000**, *113*, 2563. ECP parameters for Pb [SD(60,MDF)] have been obtained from the pseudopotential library of the Stuttgart/Cologne group, at http://www.theochem.uni-stuttgart.de/pseudopotentials/.

[8] (a) S. Grimme, *J. Comput. Chem.*, **2004**, *25*, 1463. (b) S. Grimme, *J. Comput. Chem.*, **2006**, *27*, 1787.

[9] (a) A. Klamt, G. Schüürmann, *J. Chem. Soc. Perkin Trans. 2*, **1993**, *220*, 799. (b) A. Klamt, *J. Phys. Chem.*, **1995**, *99*, 2224.

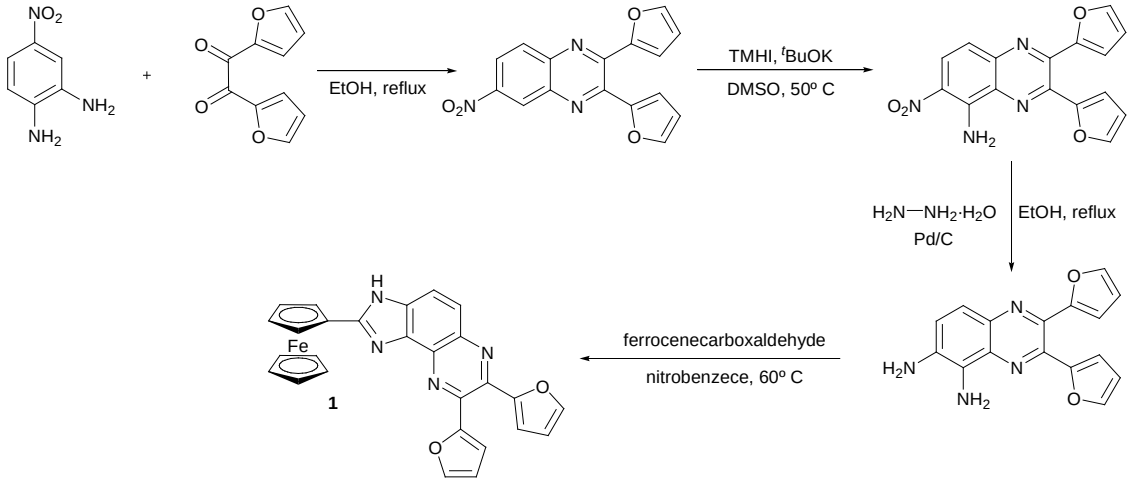
[10] Wiberg, K. *Tetrahedron* **1968**, *24*, 1083.

[11] AIM2000 v. 2.0, designed by F. Biegler-König, and J. Schönbohm, 2002. Home page http://www.aim2000.de/. F. Biegler-König, J. Schönbohm, D. J. Bayles, *Comp. Chem.* **2001**, *22*, 545. (b) F. Biegler-König, J. Schönbohm, *J. Comp. Chem.* **2002**, *23*, 1489.

[12] Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

[13] VMD — Visual Molecular Dynamics. W. Humphrey, A. Dalke, K. Schulten, *J. Molec. Graphics*, 1996, **14**, 33. Home page http://www.ks.uiuc.edu/Research/vmd/.

1.2. Synthetic methodology for the preparation of 1 and NMR spectra.

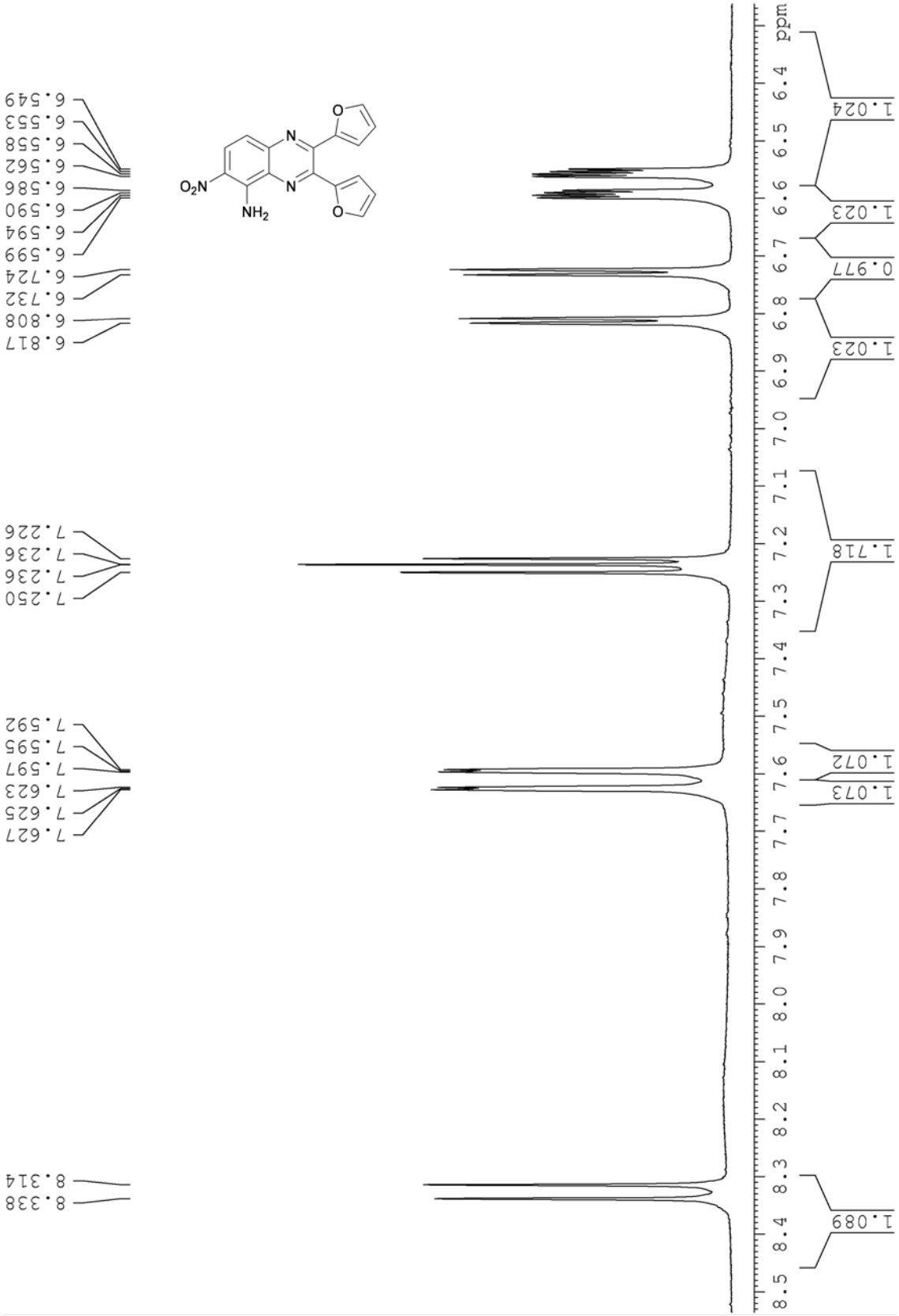


6-Nitro-2,3-bis(furan-2-yl)quinoxaline has been previously reported.[14]

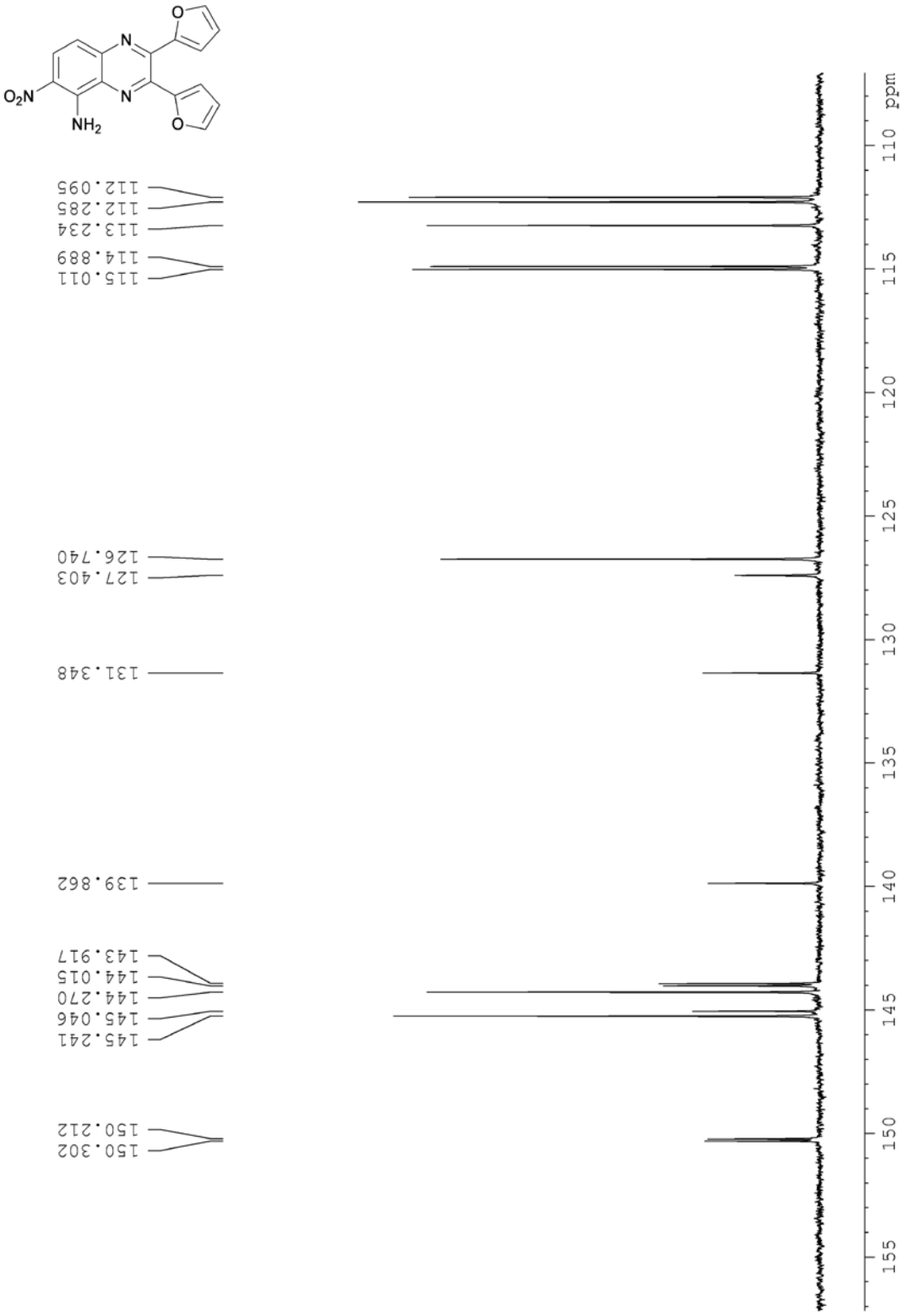
[14] J. Ji and K.-I. Lee, *J. Korean Chem. Soc.*, 2005, **49**, 150.

5-Amino-6-nitro-2,3-bis(furan-2-yl)quinoxaline.

^{1}H NMR (400 MHz, $CDCl_3$):

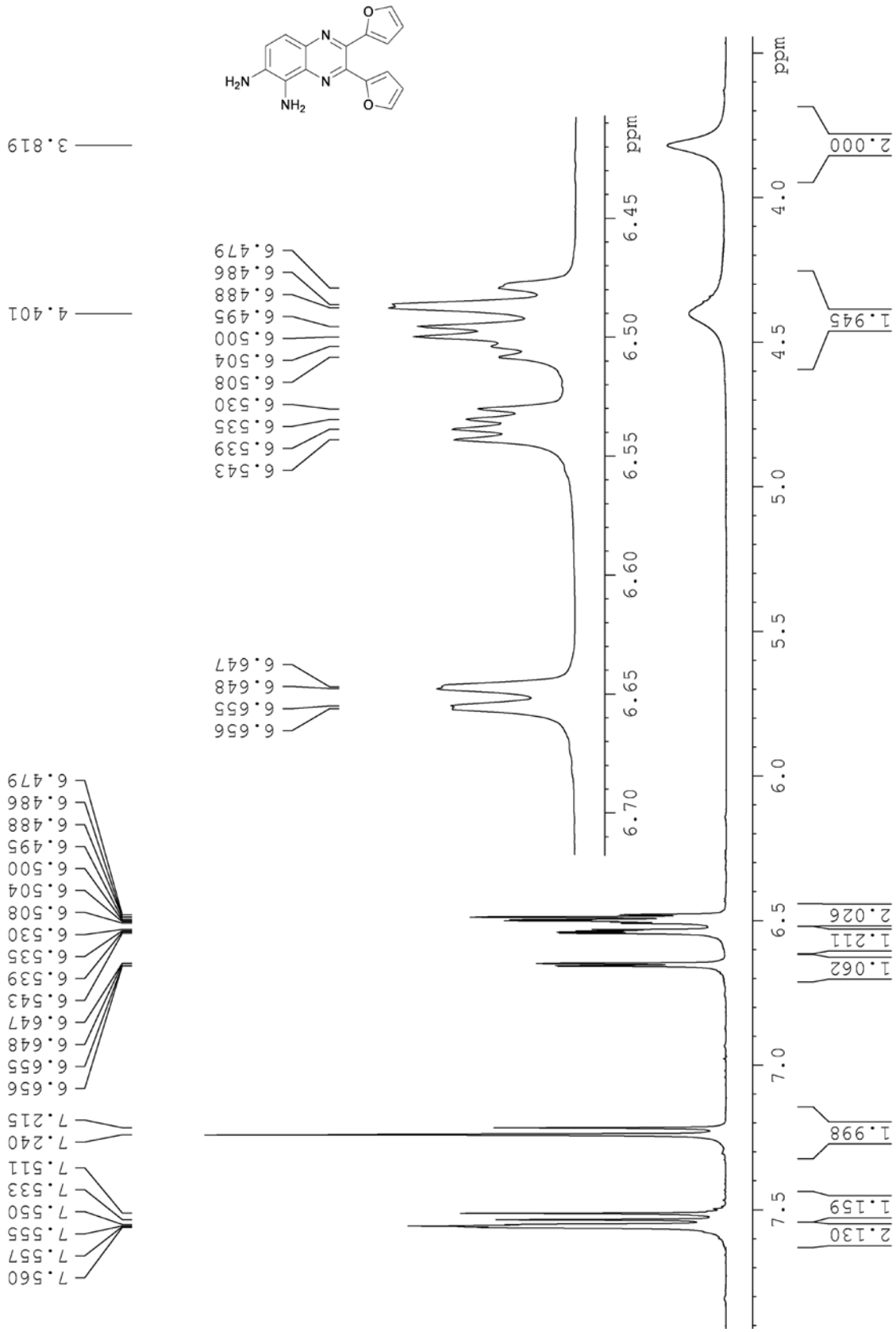


^{13}C NMR (100 MHz, $CDCl_3$):

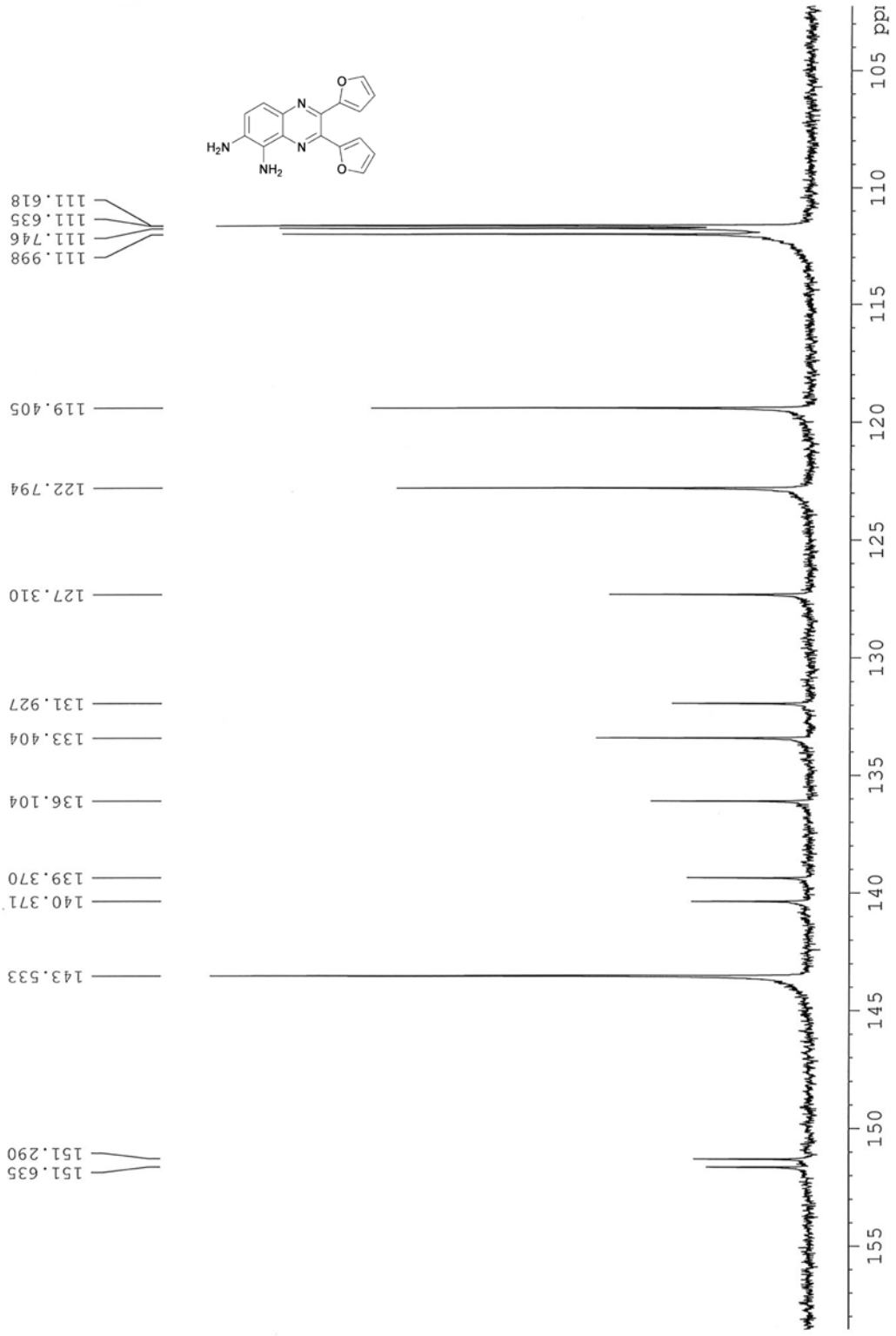


5,6-Diamino-2,3-bis(furan-2-yl)quinoxaline.

^{1}H NMR (400 MHz, $CDCl_3$):

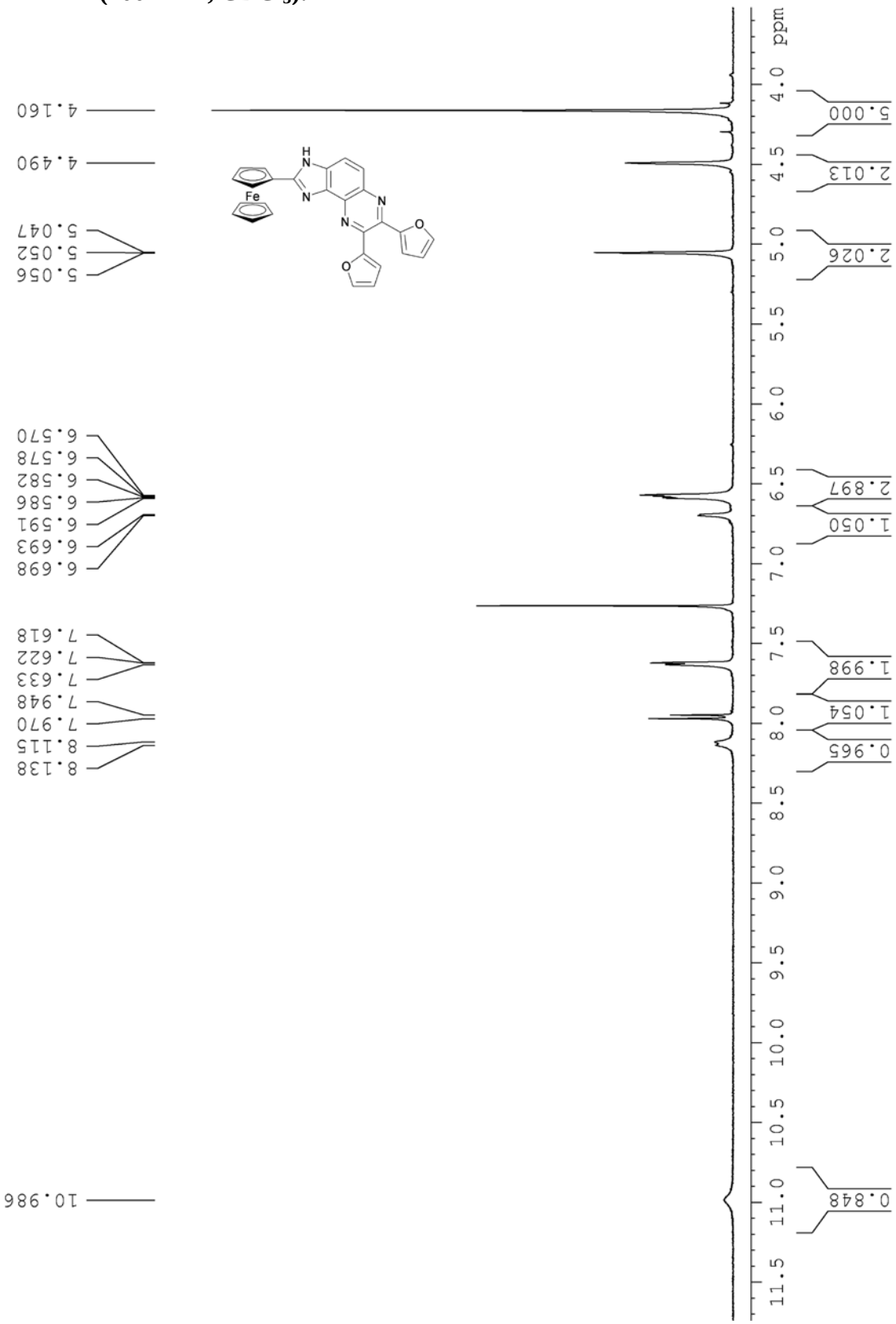


^{13}C NMR (100 MHz, $CDCl_3$):

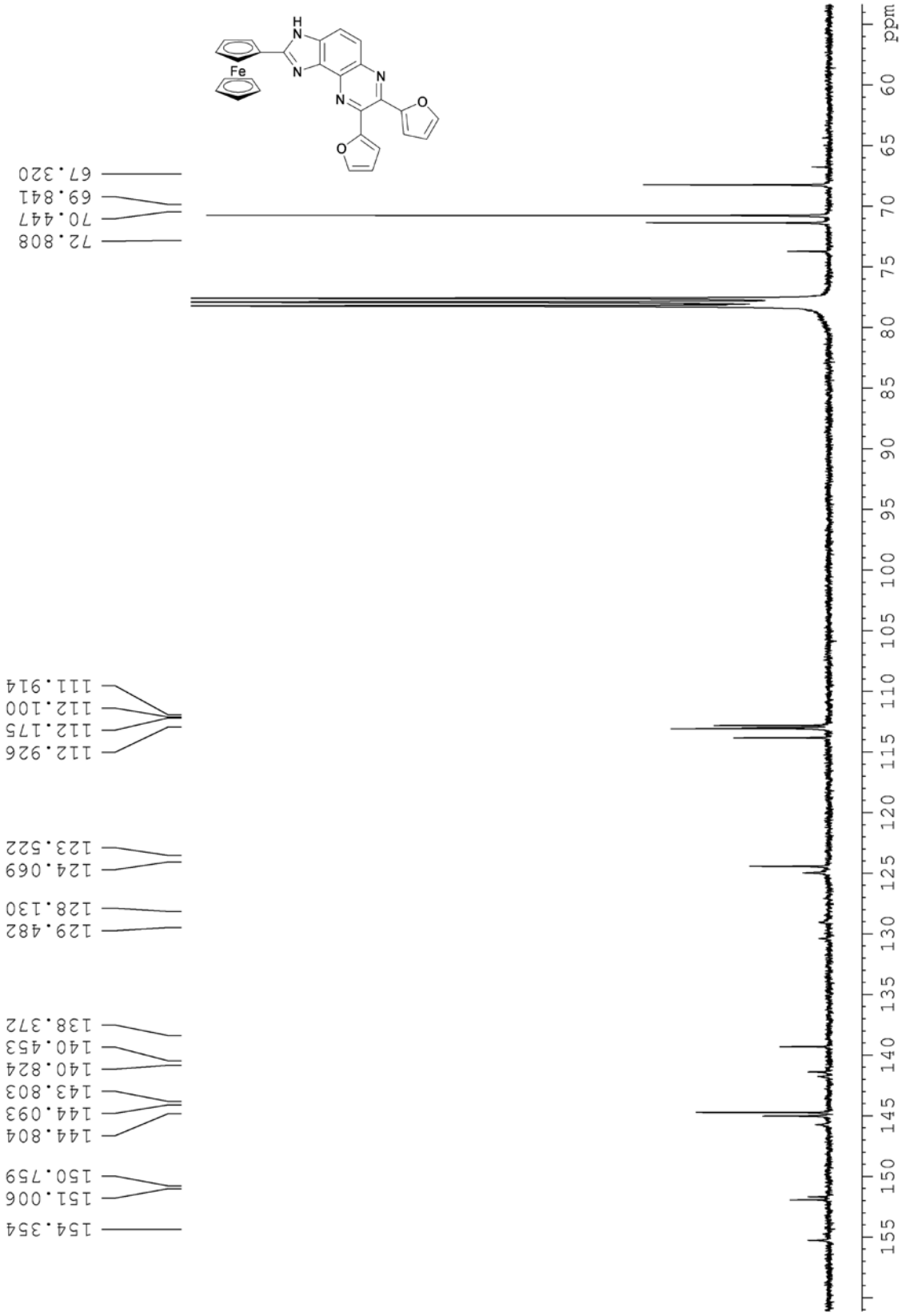


2-Ferrocenyl-7,8-bis(furan-2-yl)-3*H*-imidazo[4,5-*f*]quinoxaline

^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):



2. Titration experimental data.

2.1. Electrochemical titration.

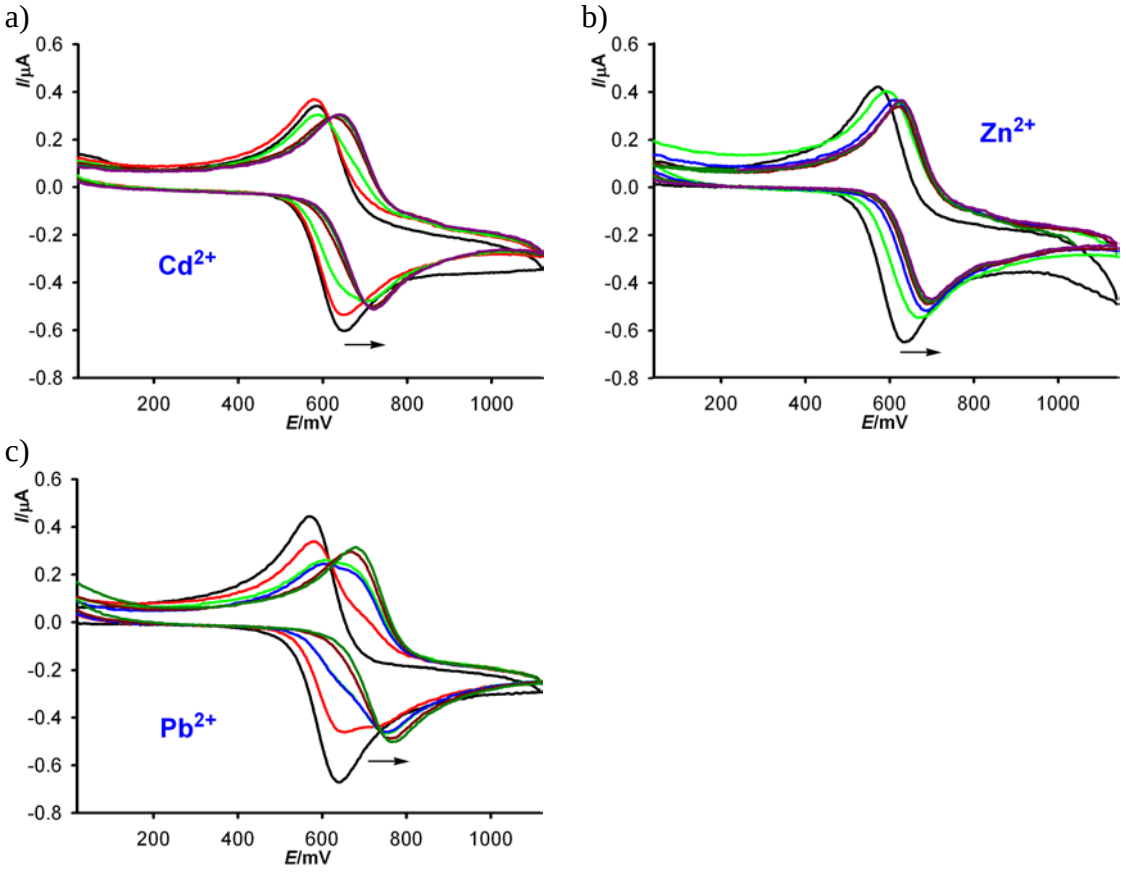


Figure S1. Evolution of the CV of **1** ($1x10^{-3}$ M) in CH_3CN//$[(n\text{-}Bu)_4]PF_6$ scanned at 0.1 $V{\cdot}s^{-1}$ in the presence of increasing amounts of : (a) $Cd(ClO_4)_2$; (b) $Zn(OTf)_2$; (c) $Pb(ClO_4)_2$, until 1 equiv. were added.

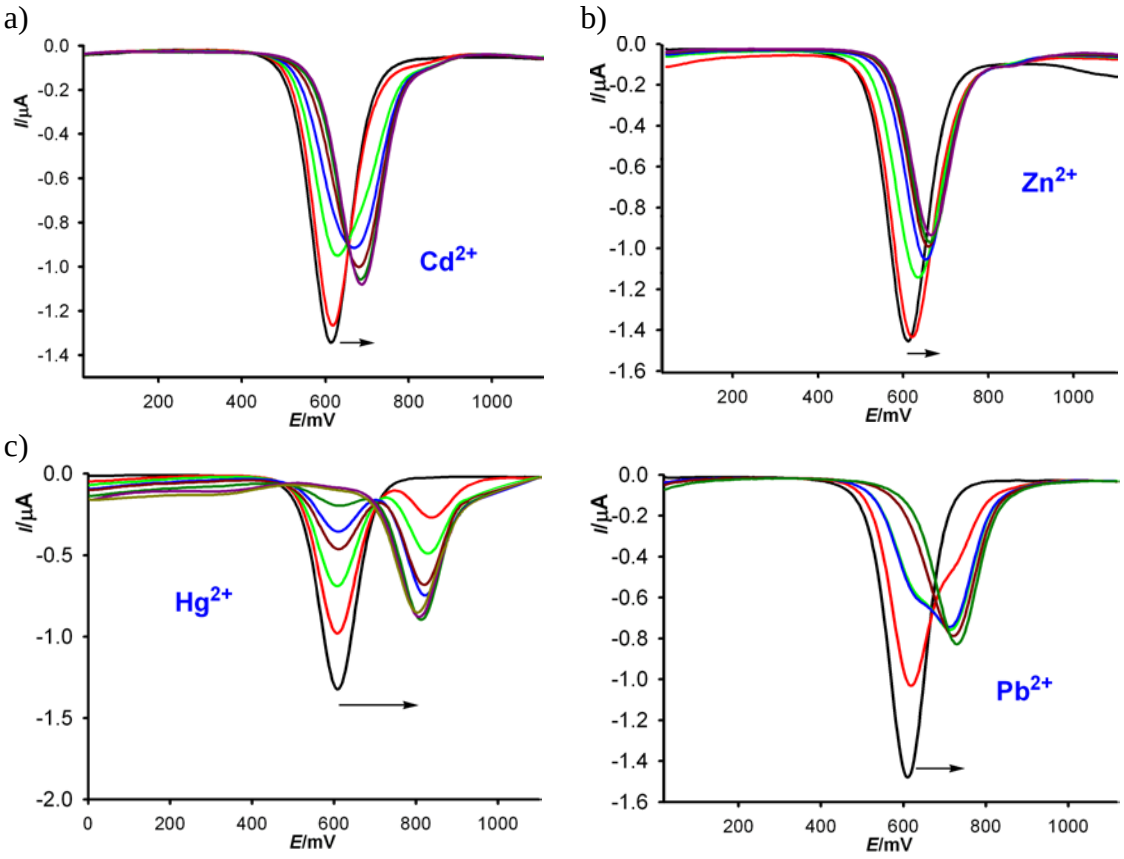


Figure S2. Evolution of the OSWV of **1** ($1x10^{-3}$ M) in CH_3CN//$[(n\text{-}Bu)_4]PF_6$ scanned at 0.1 $V{\cdot}s^{-1}$ in the presence of increasing amounts of : (a) $Cd(ClO_4)_2$; (b) $Zn(OTf)_2$; (c) $Hg(OTf)_2$; (d) $Pb(ClO_4)_2$ until 1 equiv. were added.

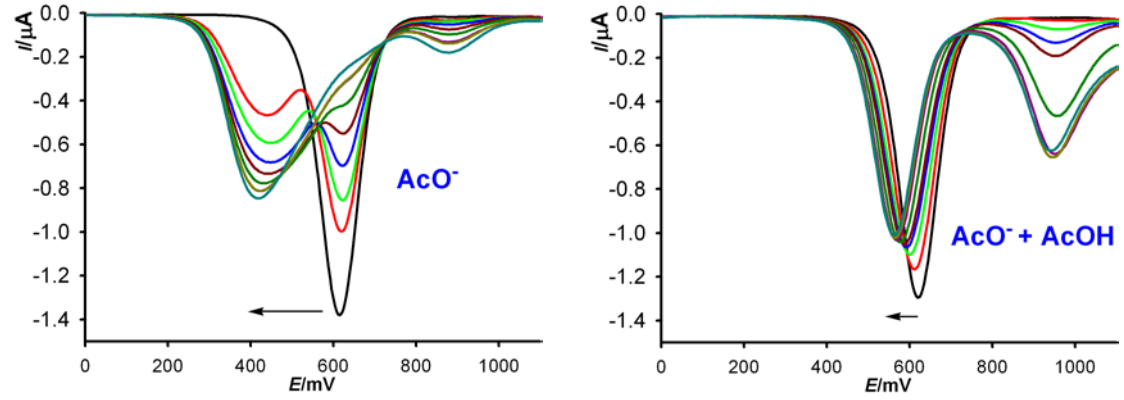


Figure S3. Evolution of the OSWV of **1** ($1x10^{-3}$ M) in CH_3CN//$[(n\text{-}Bu)_4]PF_6$ scanned at 0.1 $V{\cdot}s^{-1}$ in the presence of increasing amounts of $[(n\text{-}Bu_4N)]AcO$ until 2 equiv, in the absence (left) and in the presence (right) of acetic acid (20 equiv).

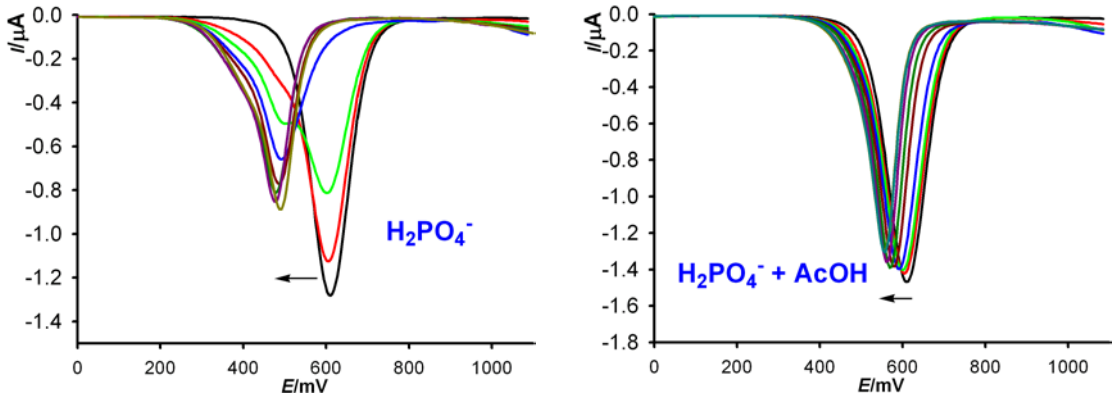


Figure S4. Evolution of the OSWV of **1** ($1x10^{-3}$ M) in CH_3CN//$[(n\text{-}Bu)_4]PF_6$ scanned at 0.1 $V{\cdot}s^{-1}$ in the presence of increasing amounts of $[(n\text{-}Bu_4N)]H_2PO_4$ until 2 equiv, in the absence (left) and in the presence (right) of acetic acid (20 equiv).

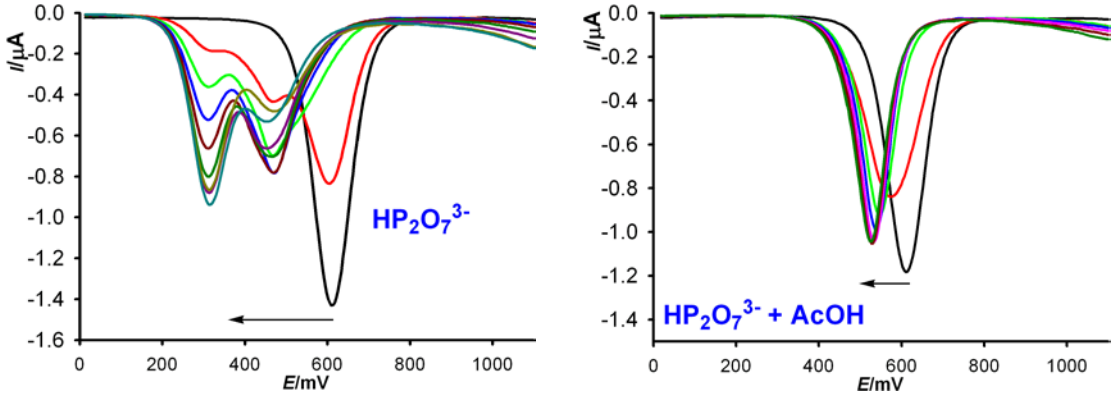


Figure S5. Evolution of the OSWV of **1** ($1x10^{-3}$ M) in CH_3CN//$[(n\text{-}Bu)_4]PF_6$ scanned at 0.1 $V{\cdot}s^{-1}$ in the presence of increasing amounts of $[(n\text{-}Bu_4N)]_3HP_2O_7$ until 2 equiv in the absence (left) and in the presence (right) of acetic acid (20 equiv).

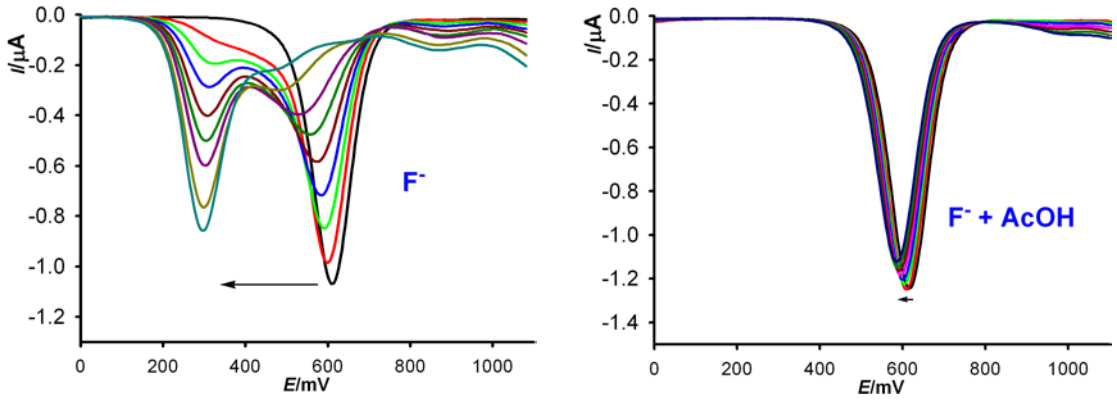


Figure S6. Evolution of the OSWV of **1** ($1x10^{-3}$ M) in CH_3CN//$[(n\text{-}Bu)_4]PF_6$ scanned at 0.1 $V{\cdot}s^{-1}$ in the presence of increasing amounts of $[(n\text{-}Bu_4N)]F$ until 2 equiv in the absence (left) and in the presence (right) of acetic acid (20 equiv).

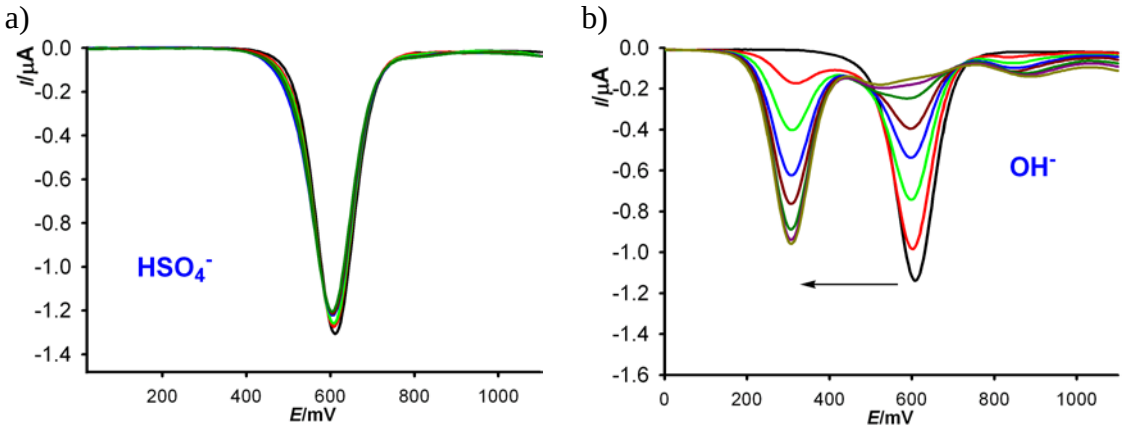


Figure S7. Evolution of the OSWV of **1** ($1x10^{-3}$ M) in CH_3CN//[(*n*-Bu)$_4$]PF_6 scanned at 0.1 $V \cdot s^{-1}$ in the presence of increasing amounts of: (a) [(*n*-Bu_4N)]HSO_4; (b) [(*n*-Bu_4N)]OH, until 2 equiv.

Table S1. Electrochemical data of receptor **1** in the presence of several anions.

Receptor	Anion added	$E_{1/2}$ (V)	$\Delta E_{1/2}$ (mV)	Acetic acid added
1	--	0.61	--	no
1	AcO^-	0.40	-206	no
1	AcO^-	0.55	-61	yes
1	$H_2PO_4^-$	0.47	-135	no
1	$H_2PO_4^-$	0.55	-57	yes
1	$HP_2O_7^{3-}$	0.45	-142; -298	no
1	$HP_2O_7^{3-}$	0.52	-85	yes
1	F^-	0.30	-305	no
1	F^-	0.58	-25	yes
1	HSO_4^-	0.61	-5	no
1	OH^-	0.30	-303	no

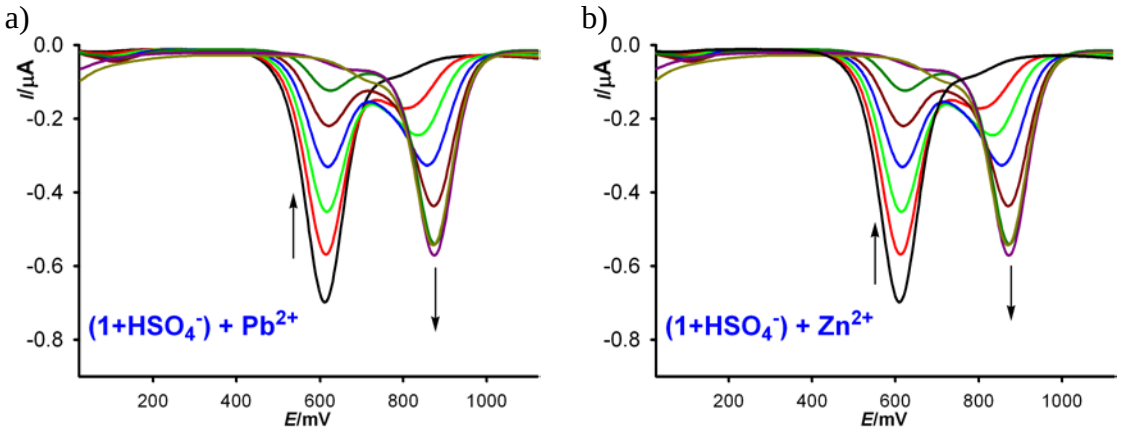


Figure S8. Evolution of the OSWV of the [**1**·HSO_4^-] complex, in CH_3CN//[(*n*-Bu)$_4$]PF_6 scanned at 0.1 $V \cdot s^{-1}$, in the presence of increasing amounts of: (a) $Pb(ClO_4)_2$; (b) $Zn(OTf)_2$.

2.2. UV-Visible titration data.

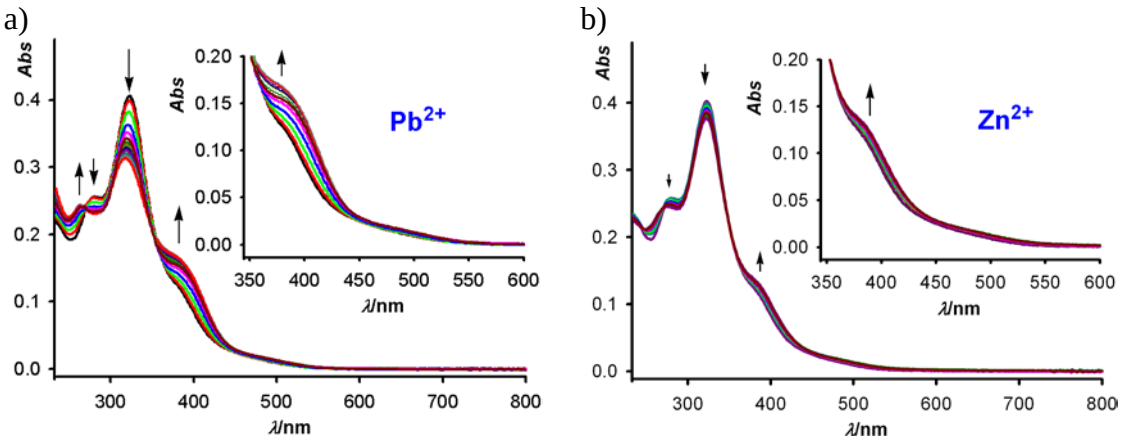


Figure S9. Changes in the absorption spectra of **1** ($1x10^{-5}$ M in CH_3CN) upon addition of increasing amounts of: (a) $Pb(ClO_4)_2$; (b) $Zn(OTf)_2$ until 1 equiv. Arrows indicate absorptions that increase or decrease during the experiment.

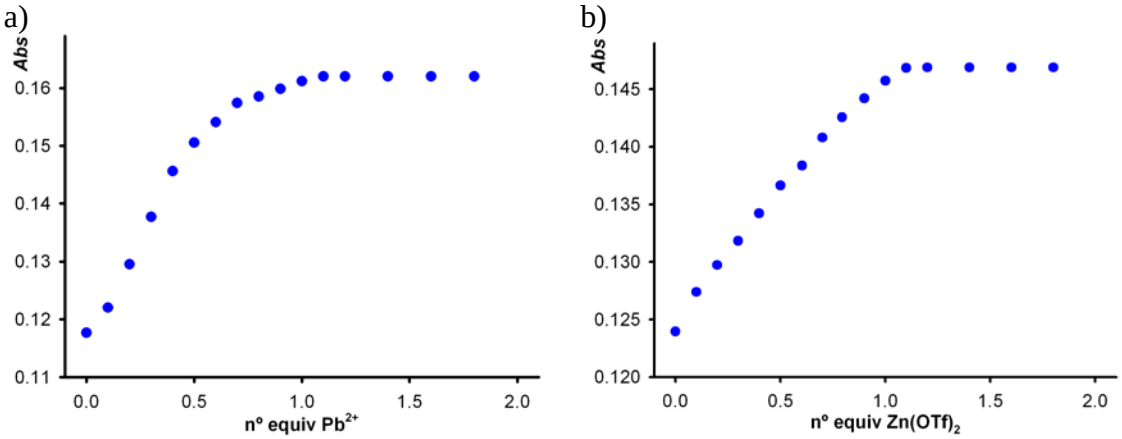


Figure S10. Titration profile showing the absorbance change as a function of the equivalents of: (a) $Pb(ClO_4)_2$; (b) $Zn(OTf)_2$ added.

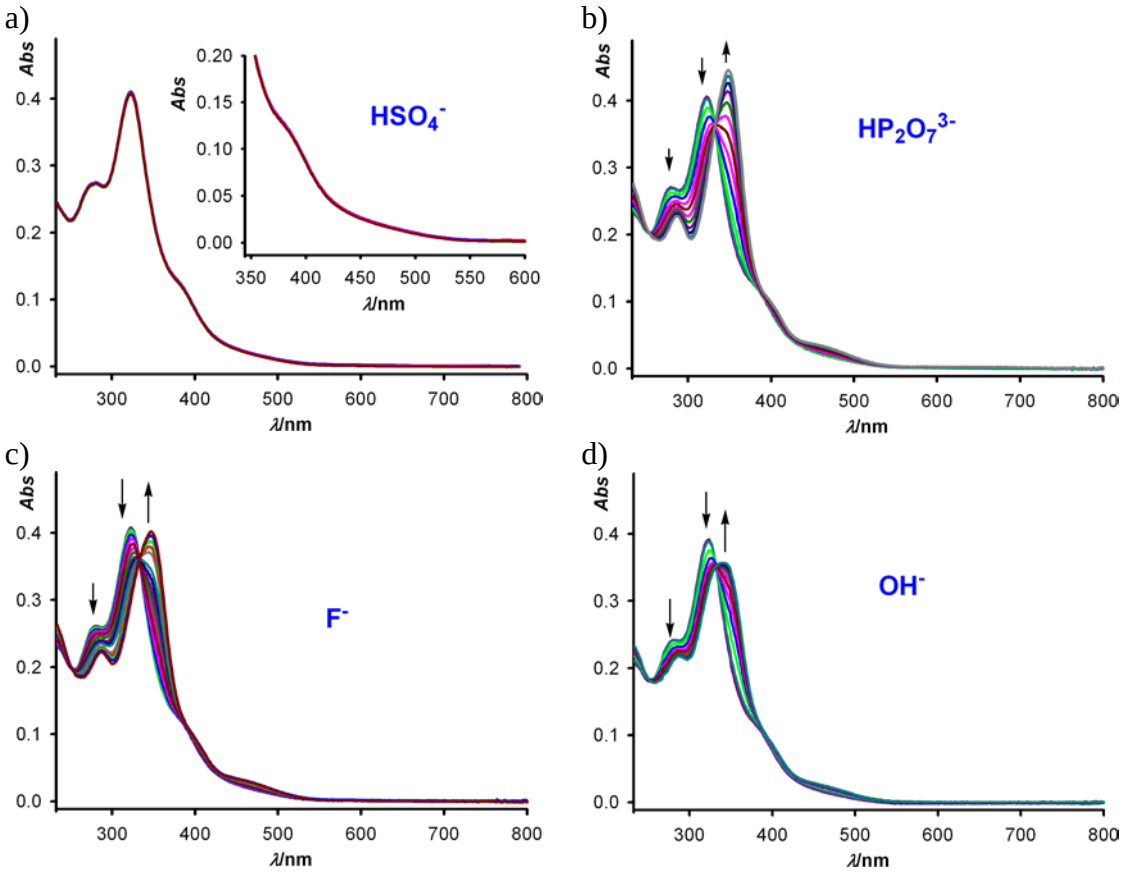


Figure S11. Changes in the absorption spectra of **1** ($1x10^{-5}$ M in CH_3CN) upon addition of increasing amounts of: (a) [(*n*-Bu_4N)]HSO_4; (b) [(*n*-Bu_4N)]$_3HP_2O_7$; (c) [(*n*-Bu_4N)]F; and (d) [(*n*-Bu_4N)]OH until 2 equiv. Arrows indicate absorptions that increase or decrease during the experiment.

Table S2. UV-visible titration data of receptor **1** in the presence of several cations and anions.

COMPOUND	λ/nm (ε/$cm^3 \cdot M^{-1} \cdot cm^{-1}$)	PI /nm
1	280 (0.260); 323 (0.405); 380 (sh)	
1 + Pb^{2+}	265 (0.243); 320 (0.313); 385 (sh)	270; 355
1+ Zn^{2+}	272 (0.244); 322 (0.368); 380 (sh	270; 350
1 + HSO_4^-	280 (0.260); 323 (0.405); 380 (sh)	--
1 + $HP_2O_7^{3-}$	288 (0.228); 349 (0.446)	250; 335
1 + F^-	288 (0.223); 347 (0.402)	250; 335
1+ OH^-	288 (0.220); 340 (0.357)	250; 335

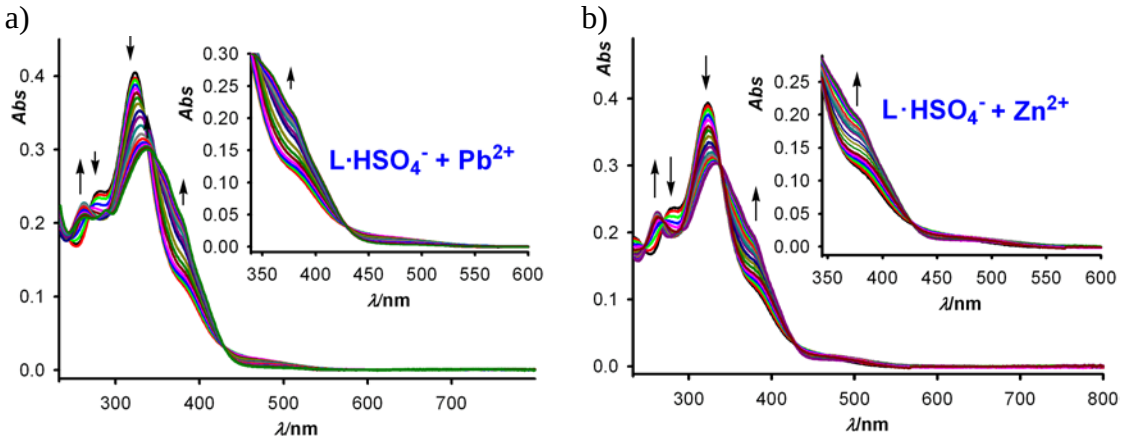


Figure S12. Changes in the absorption spectra of [**1**·HSO_4^-] ($1x10^{-5}$ M in CH_3CN) upon addition from 0 to 2 equiv of: (a) $Pb(ClO_4)_2$, and (b) $Zn(OTf)_2$. Arrows indicate absorptions that increase or decrease during the experiment.

Table S3. UV-visible data of the complex [**1**·HSO_4^-] in the presence of cations.

COMPUESTO	λ/nm (ε/$cm^3 \cdot M^{-1} \cdot cm^{-1}$)	PI/nm
1	280 (0.260); 323 (0.405); 380 (sh)	
1 + HSO_4^- + Pb^{2+}	260 (0.208); 289 (0.217); 335 (0.300); 380 (sh)	430
1 + HSO_4^- + Zn^{2+}	260 (0.209); 289 (0.205); 335 (0.301), 380 (sh)	340; 430

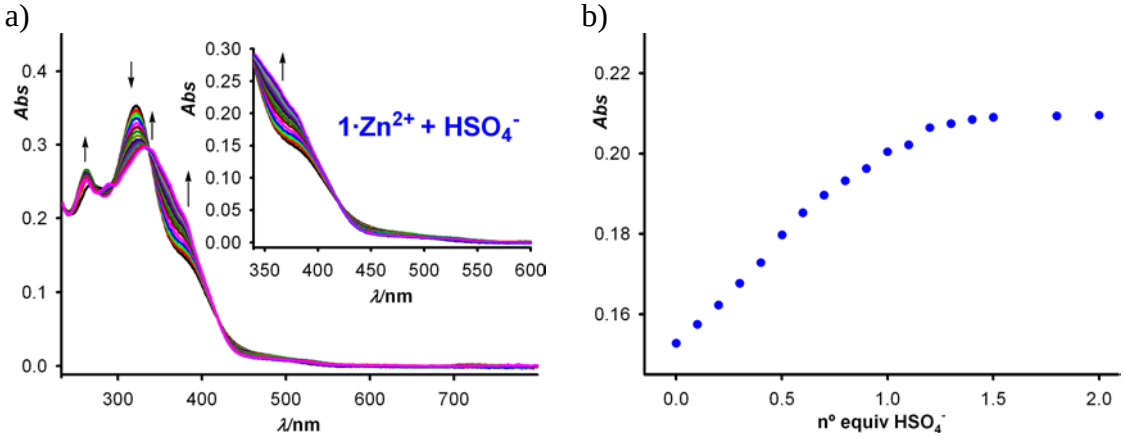


Figure S13. (a) Changes in the absorption spectrum of [**1**·Zn^{2+}] ($1x10^{-5}$ M in CH_3CN) upon addition of increasing amounts of [(*n*-Bu_4N)]HSO_4. Arrows indicate absorptions that increase or decrease during the experiment. (b) Titration profile showing the absorbance changes as a function of the equivalents of [(*n*-Bu_4N)]HSO_4.

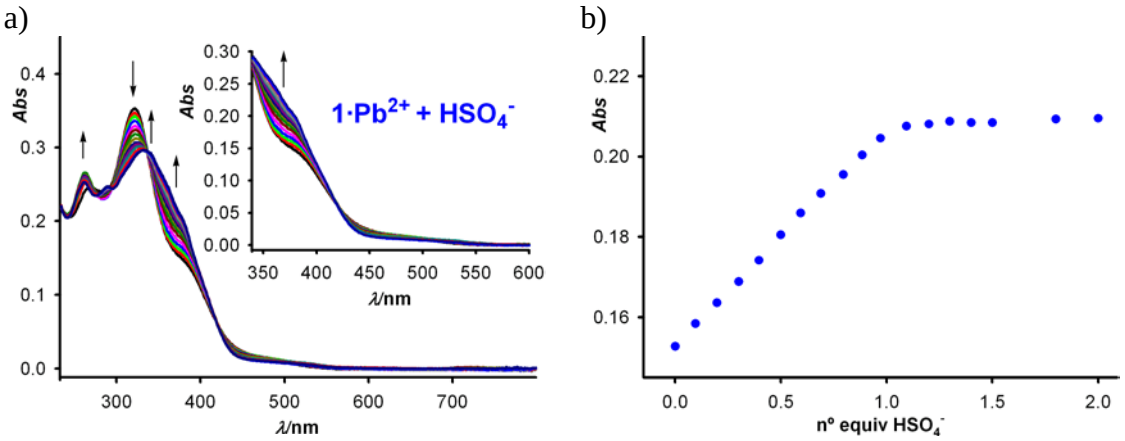


Figure S14. (a) Changes in the absorption spectrum of [**1·Pb^{2+}**] (1x10^{-5} M in CH_3CN) upon addition of increasing amounts of [(*n*-Bu_4N)]HSO_4. Arrows indicate absorptions that increase or decrease during the experiment. (b) Titration profile showing the absorbance changes as a function of the equivalents of ([(*n*-Bu_4N)]HSO_4.

Table S4. UV-visible data of receptor [**1·M^{2+}**] in the presence of HSO_4^-.

COMPOUND	λ/nm (ε/cm^3·M^{-1}·cm^{-1})	PI/nm
1	280 (0.260); 323 (0.405); 380 (sh)	
1·Pb^{2+}+ HSO$_4^-$	260 (0.249); 289 (0.228); 335 (0.300); 380 (sh)	335; 420
1·Zn^{2+}+ HSO$_4^-$	260 (0.252); 289 (0.246); 335 (0.297), 380 (sh)	335; 420

2.2. Emission titration data.

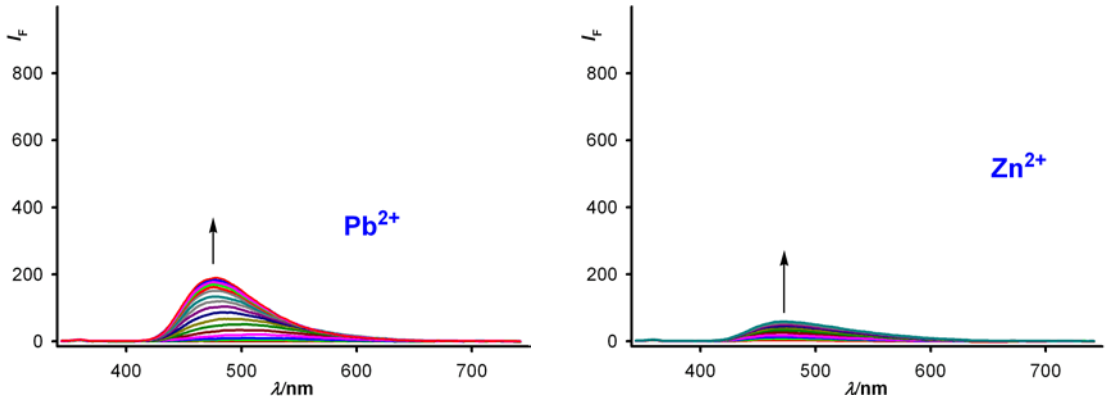


Figure S15. Changes in the fluorescence emission spectrum of **1** (c = $2x10^{-6}$ M) in CH_3CN upon addition of: (a) $Pb(ClO_4)_2$; (b) $Zn(OTf)_2$, from 0 to 1 equiv. Emission is monitored at λ_{exc} = 325 nm.

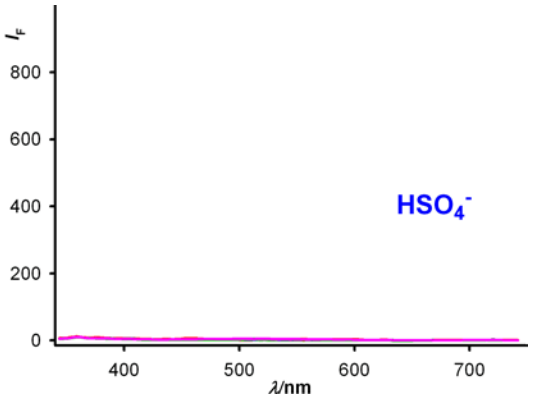


Figure S16. Changes in the fluorescence emission spectrum of **1** (c = $2x10^{-6}$ M) in CH_3CN upon addition of: [(*n*-Bu_4N)]HSO_4 from 0 to 2 equiv. Emission is monitored at λ_{exc} = 325 nm.

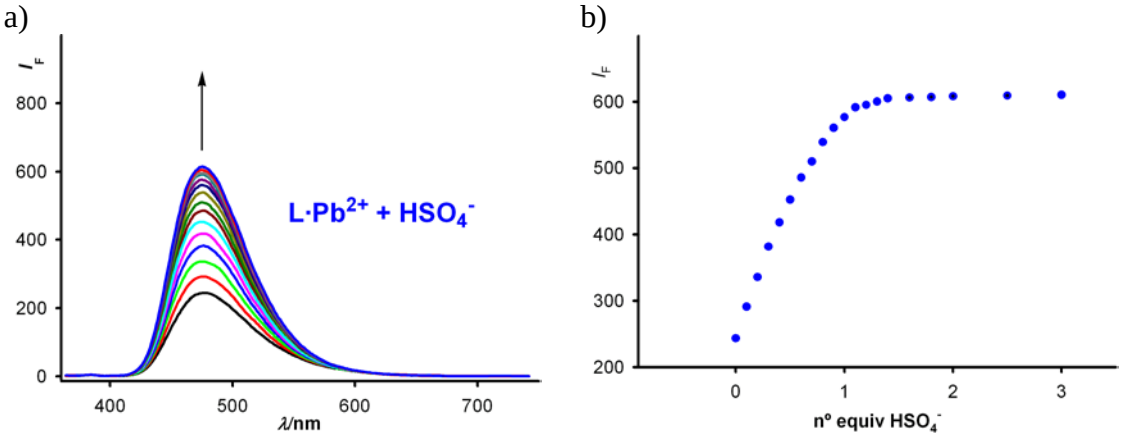


Figure S17. (a) Changes in the fluorescence emission spectrum of **1·Pb**$^{2+}$ ($2{\cdot}10^{-6}$ M in CH_3CN) upon titration with [(*n*-Bu_4N)]HSO_4.. Emission is monitored at λ_{exc} = 345 nm. (b) Titration profile showing the absrobance change as a function of the equivalents of ([(*n*-Bu_4N)]HSO_4.

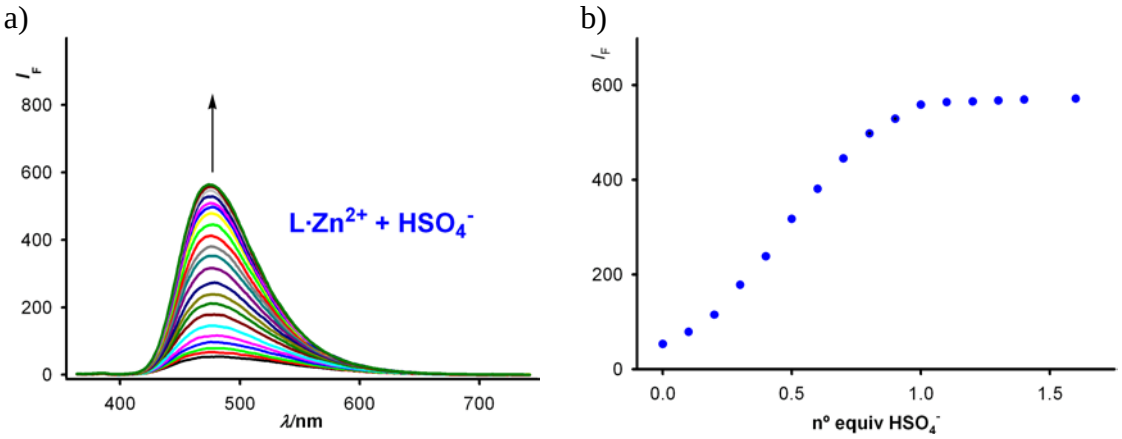


Figure S18. (a) Changes in the fluorescence emission spectrum of **1·Zn^{2+}** ($2\cdot10^{-6}$ M in CH_3CN) upon titration with [(*n*-Bu_4N)]HSO_4.. Emission is monitored at λ_{exc} = 345 nm. (b) Titration profile showing the absorbance change as a function of the equivalents of ([(*n*-Bu_4N)]HSO_4.

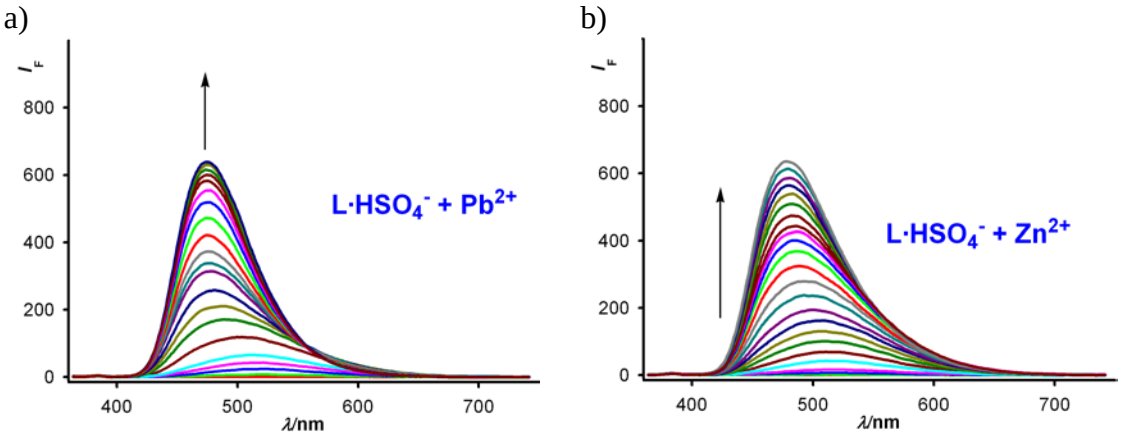


Figure S19. Changes in the fluorescence emission spectrum of [**1**·HSO_4^-] ($2\cdot10^{-6}$ M in CH_3CN) upon titration with: (a) $Pb(ClO_4)_2$; (b) $Zn(OTf)_2$. Emission is monitored at λ_{exc} = 345 nm.

Table S5. Fluorescence emission data of receptor **1** in the presence of cations and anions simultaneously.

COMPOUND	**λ_{em}/nm**	**Φ (CHEF)**
1	475	$7\cdot10^{-4}$
(1 + HSO_4^-) + Pb^{2+}	475	0.271 (640)
(1 + HSO_4^-) + Zn^{2+}	475	0.196 (635)

2.4. NMR study.

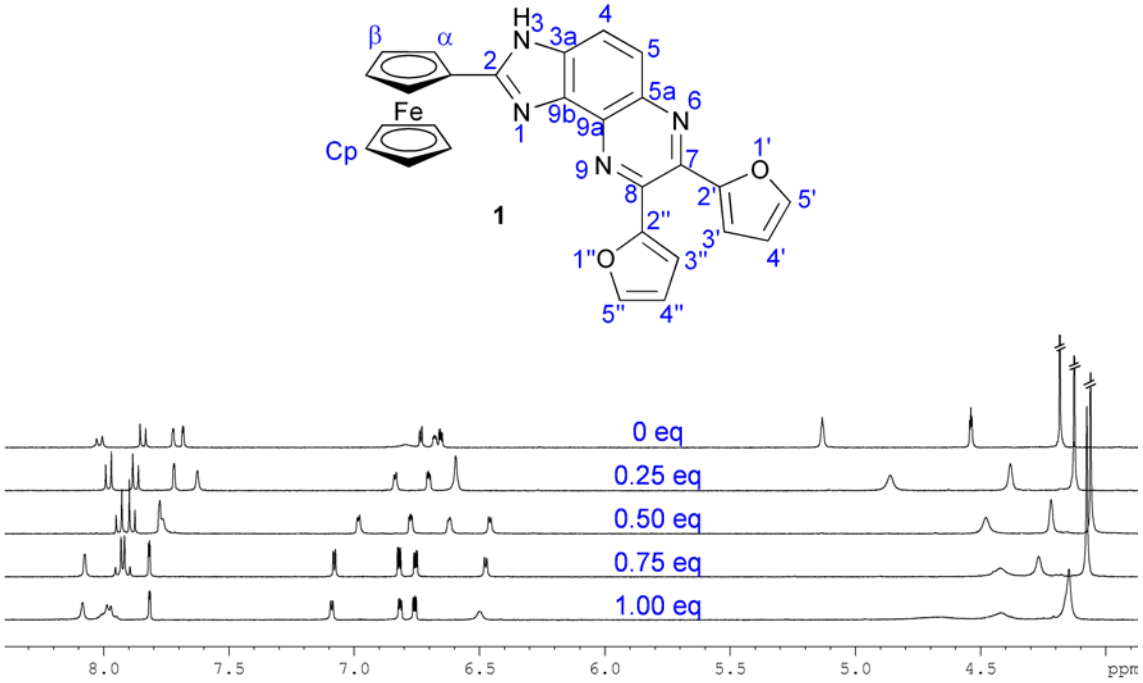


Figure S20. Changes in the ^{1}H NMR (in CD_3CN) spectrum of **1** (top) upon addition of $Pb(ClO_4)_2$ from 0 to 1 equiv (bottom).

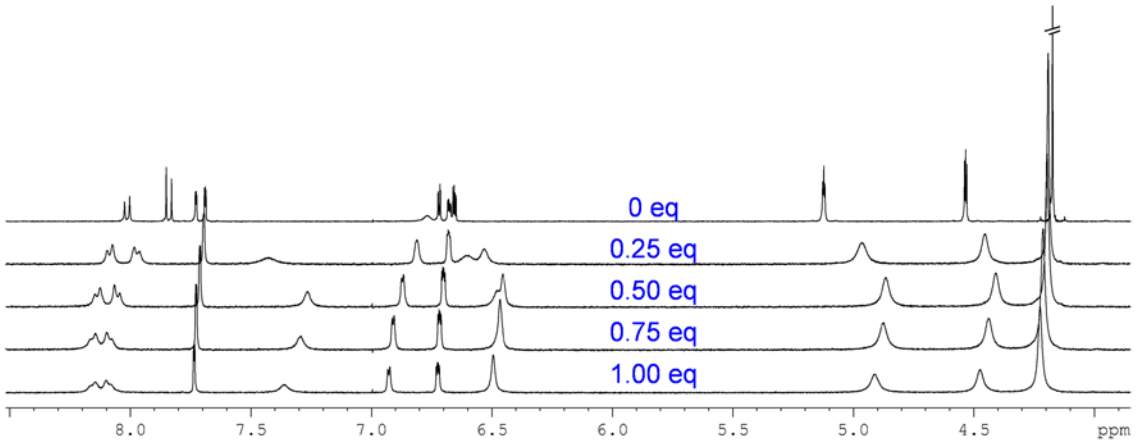


Figure S21. Changes in the ^{1}H NMR (in CD_3CN) spectrum of **1** (top) upon addition of $Zn(OTf)_2$ from 0 to 1 equiv (bottom).

Table S6. NMR data of receptor **1** in the presence of several cations.

	H^5	H^4	$H^{5''}$	$H^{5'}$	$H^{3''}$	$H^{3'}$	$H^{4''}$	$H^{4'}$
1	8.02	7.84	7.72	7.68	6.79	6.73	6.68	6.65
1 + Pb^{2+}	8.00 (-0.02)	7.96 (0.12)	8.08 (0.36)	7.82 (0.14)	7.09 (0.30)	6.5 (-0.23)	6.82 (0.14)	6.76 (0.11)
1 + Zn^{2+}	8.15 (0.13)	8.10 (0.26)	7.36 (-0.36)	7.73 (0.05)	6.49 (-0.3)	6.49 (-0.24)	6.93 (0.25)	6.72 (0.07)

	H^{α}	H^{β}	H^{Cp}
1	5.13	4.54	4.18
1+ Pb^{2+}	4.66 (-0.47)	4.42 (-0.12)	4.15 (-0.03)
1 + Zn^{2+}	4.91 (-0.22)	4.47 (-0.07)	4.37 (0.03)

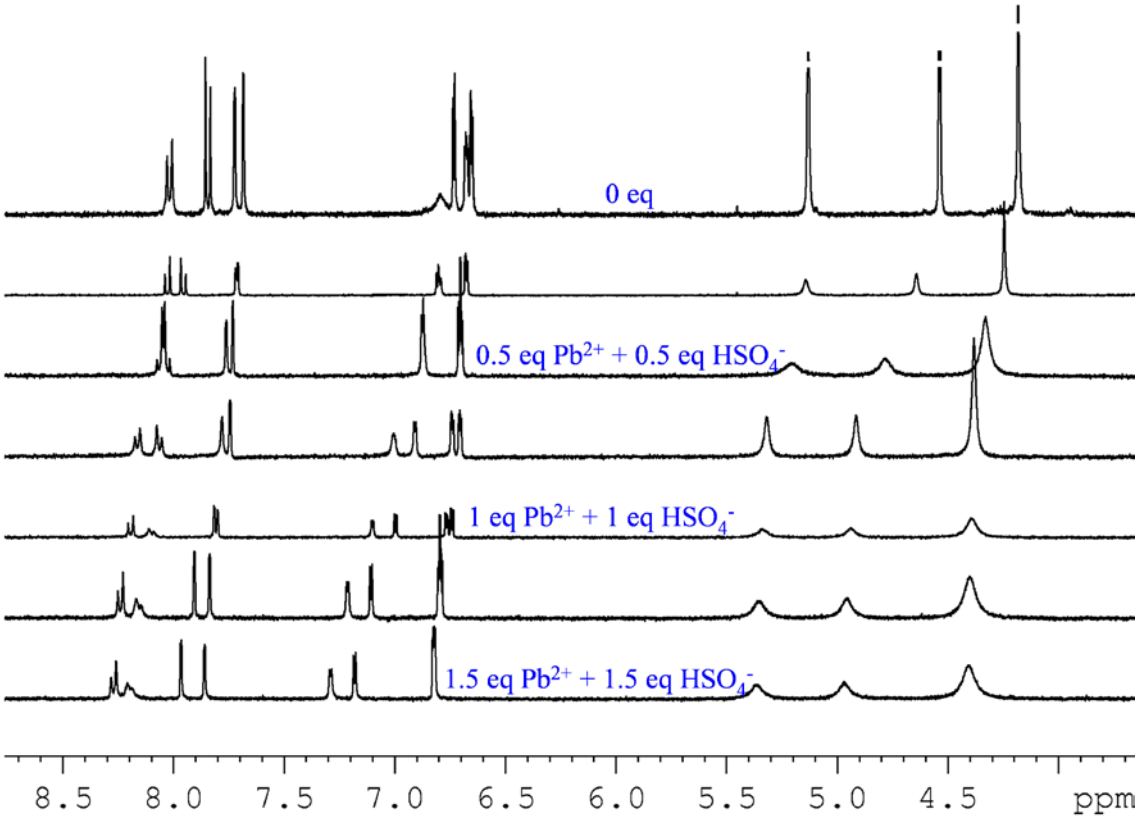


Figure S22. Changes in the ^1H NMR (in CD_3CN) spectrum of **1** (top) upon gradual addition of increasing amounts of [(*n*-Bu_4N)]HSO_4 followed by $Pb(ClO_4)_2$ until achieving 1.5 equiv (bottom).

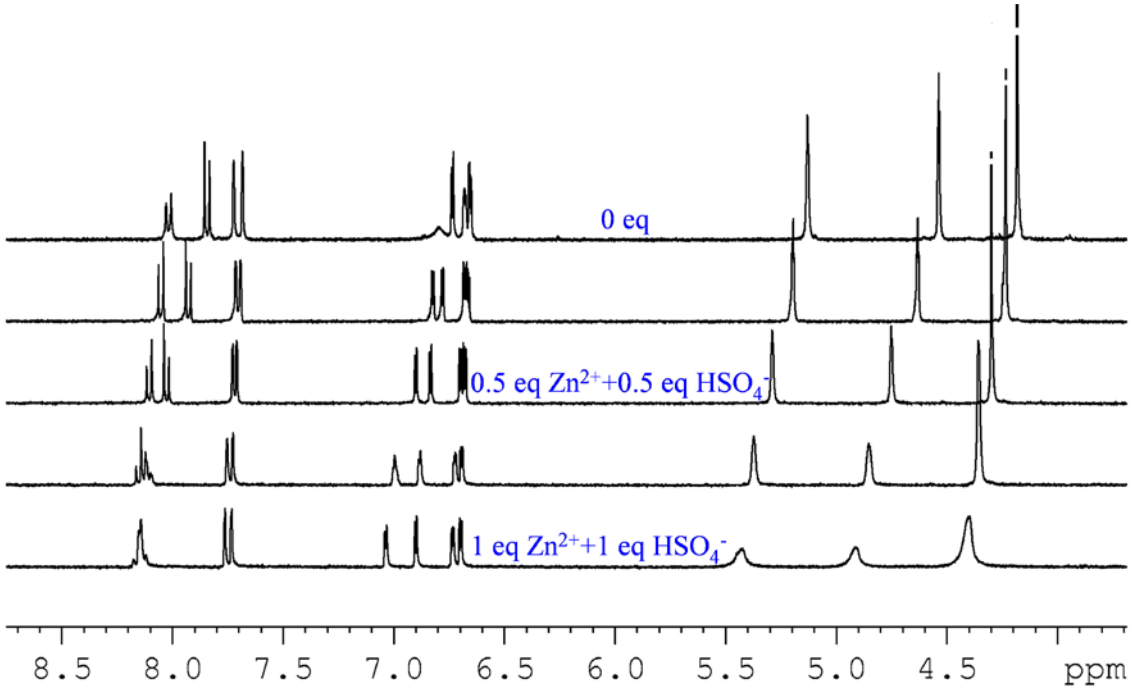


Figure S23. Changes in the ^{1}H NMR (in CD_3CN) spectrum of **1** (top) upon gradual addition of increasing amounts of [(*n*-Bu_4N)]HSO_4 followed by $Zn(OTf)_2$ until achieving 1.0 equiv (bottom).

Table S7. NMR data of receptor **1**.

	H^5	H^4	$H^{5''}$	$H^{5'}$	$H^{3''}$	$H^{3'}$	$H^{4''}$	$H^{4'}$
1	8.02	7.84	7.72	7.68	6.79	6.73	6.68	6.65
1 + Zn^{2+} + HSO_4^-	8.16 (0.14)	8.08 (0.24)	7.78 (0.06)	7.74 (0.06)	7.01 (0.22)	6.91 (0.18)	6.74 (0.06)	6.70 (0.05)
1 + Pb^{2+} + HSO_4^-	8.27 (0.25)	8.21 (0.37)	7.96 (0.24)	7.86 (0.18)	7.29 (0.5)	7.18 (0.27)	6.82 (0.44)	6.82 (0.17)

	H^{α}	H^{β}	H^{Cp}
1	5.13	4.54	4.18
1 + Zn^{2+} + HSO_4^-	5.33 (0.20)	4.91 (0.37)	4.38 (0.20)
1 + Pb^{2+} + HSO_4^-	5.36 (0.23)	4.97 (0.43)	4.40 (0.22)

2.5. ESI-MS study.

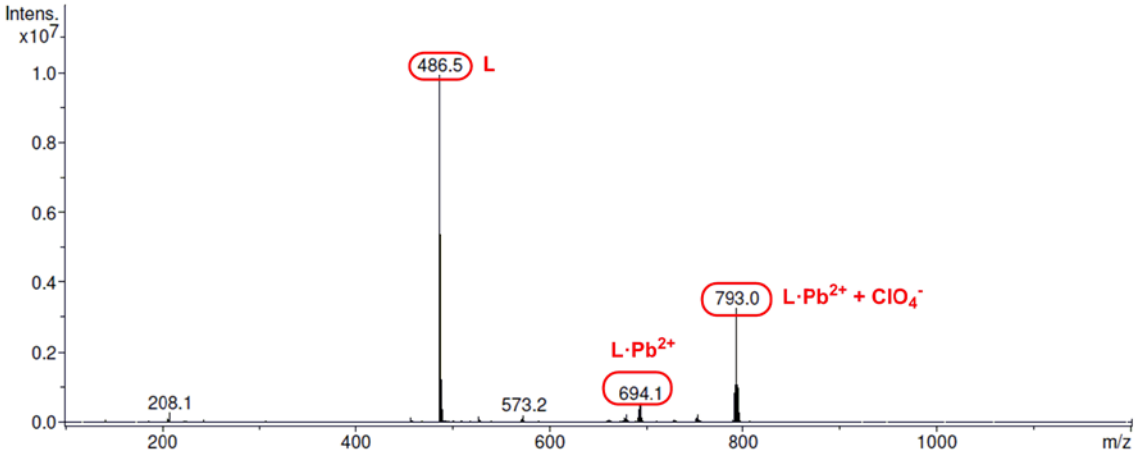


Figure S24. ESI-MS spectrum of an acetonitrile solution of an equimolecular amount of $Pb(ClO_4)_2$ and ligand **1**.

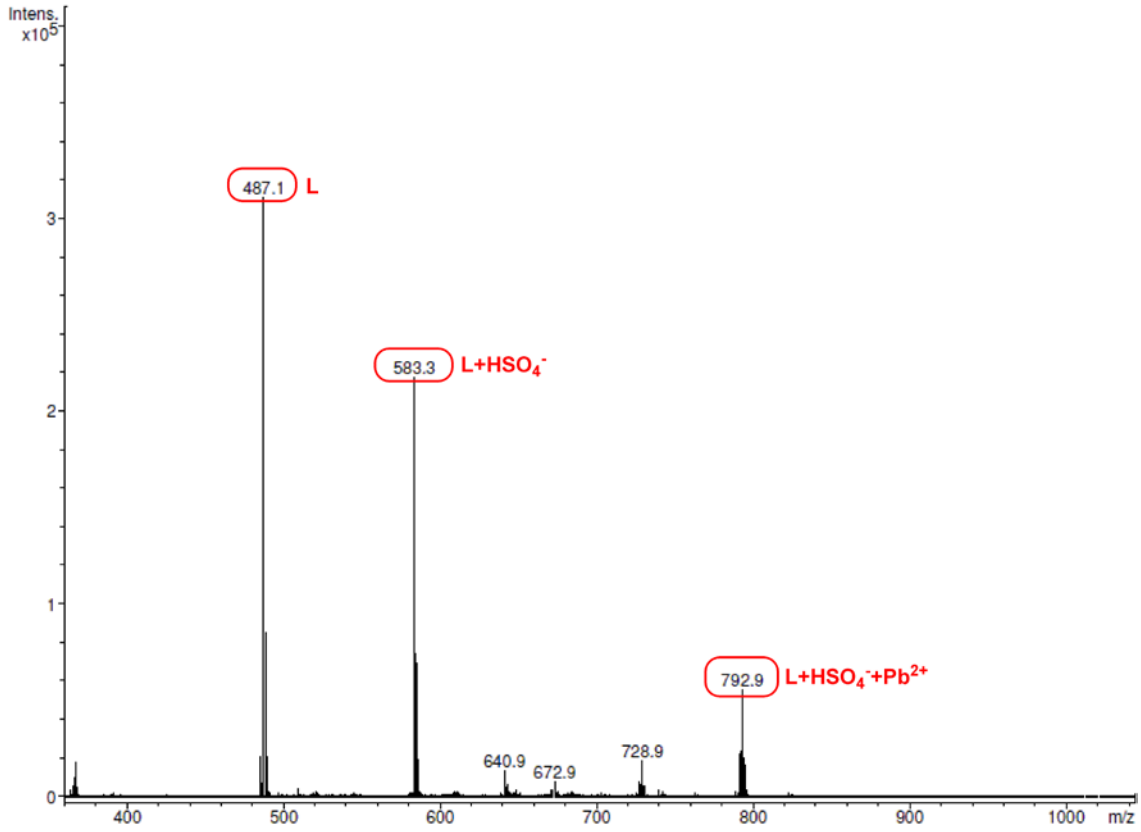


Figure S25. ESI-MS spectrum of a acetonitrile solution of an equimolecular amount of $Pb(ClO_4)_2$ and $[(n\text{-}Bu_4N)]HSO_4$ ligand **1**.

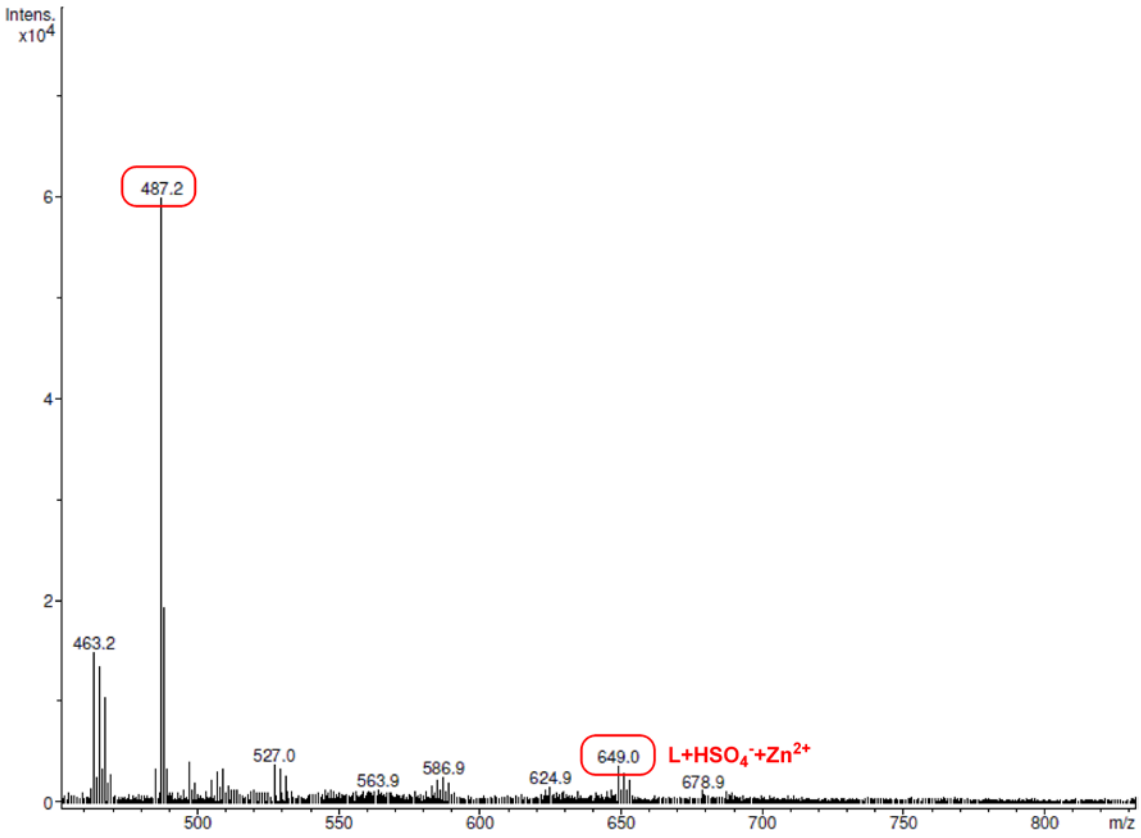


Figure S26. ESI-MS spectrum of a acetonitrile solution of an equimolecular amount of $Zn(OTf)_2$ and $[(n\text{-}Bu_4N)]HSO_4$ ligand **1**.

Cartesian coordinates (Å) and energies for the computed most stable geometries of ligand **1** and reported complexes**.**

Compound **1**: E_{MeCN} = -2672.591800647 au

N	-0.005199	-0.007724	0.015066	C	3.087832	-0.564699	2.999721
C	1.360253	-0.029852	-0.090286	C	2.755809	-1.874161	3.454424
N	1.872994	1.184344	-0.162207	C	3.896119	-2.708360	3.262523
C	0.797693	2.032964	-0.088012	C	4.931328	-1.915088	2.687500
C	-0.397707	1.307821	0.016044	C	4.430566	-0.589263	2.523295
H	-0.606267	-0.815700	0.053478	H	2.422178	0.283544	2.967787
C	0.752809	3.450766	-0.054390	H	1.798888	-2.188508	3.840029
N	1.874012	4.194686	-0.033190	H	3.956749	-3.762431	3.483163
C	1.768100	5.510503	0.024450	H	5.905491	-2.268504	2.388339
C	0.470272	6.139944	-0.016088	H	4.958228	0.238453	2.077273
N	-0.629866	5.412485	0.019752	C	3.013739	6.249800	0.204829
C	-0.534072	4.063690	0.031589	O	4.169316	5.606753	-0.157800
C	-1.721428	3.281000	0.101189	C	5.207082	6.408806	0.189461
C	-1.667605	1.908278	0.101379	C	4.752103	7.546247	0.778507
H	-2.668571	3.801689	0.157209	C	3.331384	7.446177	0.786657
H	-2.567649	1.310571	0.163991	H	6.189327	6.040819	-0.056119
C	2.106786	-1.270162	-0.100546	H	5.352174	8.357462	1.157914
C	3.464462	-1.422325	-0.526326	H	2.634598	8.165228	1.178434
C	3.830005	-2.783304	-0.338610	C	0.285526	7.584558	-0.143715
C	2.710680	-3.473817	0.213144	O	-0.809269	8.131741	0.472497
C	1.645452	-2.544419	0.363332	C	-0.831235	9.453617	0.155841
H	4.089271	-0.627907	-0.898554	C	0.210589	9.763011	-0.659851
H	4.800073	-3.209094	-0.539719	C	0.935203	8.550184	-0.854484
H	2.686879	-4.510983	0.507835	H	-1.632044	10.029819	0.587916
H	0.675841	-2.753311	0.787264	H	0.440895	10.732391	-1.071545
Fe	3.277716	-1.921208	1.457380	H	1.828794	8.412445	-1.438474

Complex **1**·HSO_4^-: E_{MeCN} = -3372.459914526 au

N	0.172645	0.186703	-0.181929	C	2.175225	-2.591513	-3.585005
C	1.533872	0.115398	-0.130816	H	1.409367	-0.497362	-3.452964
N	2.087352	1.318190	-0.089318	H	3.999342	0.191597	-3.173076
C	1.035176	2.206511	-0.112985	H	5.462152	-2.076828	-3.228867
C	-0.179509	1.511018	-0.170403	H	3.781255	-4.150156	-3.521049
H	-0.455768	-0.600652	-0.193995	H	1.272014	-3.173882	-3.669828
C	1.011168	3.626660	-0.067915	C	3.290898	6.395053	0.270994
N	2.131739	4.362683	0.054650	O	3.316094	7.504249	1.070998
C	2.030763	5.679734	0.087964	C	4.593944	7.966997	1.078716
C	0.749406	6.326533	-0.060332	C	5.386569	7.178711	0.305334
N	-0.355862	5.604452	-0.116895	C	4.544126	6.148229	-0.210495
C	-0.271386	4.258895	-0.104022	H	4.775694	8.846352	1.673490
C	-1.474995	3.498887	-0.158485	H	6.439947	7.318716	0.121747
C	-1.442903	2.129186	-0.190584	H	4.815789	5.330255	-0.857553
H	-2.412764	4.038564	-0.181331	C	0.584535	7.766125	-0.225117
H	-2.351180	1.542482	-0.233297	O	-0.674604	8.264556	-0.008150
C	2.212726	-1.161101	-0.117678	C	-0.645548	9.587973	-0.310301
C	1.603715	-2.440108	-0.342684	C	0.595487	9.953447	-0.724823
C	2.623323	-3.426937	-0.272449	C	1.393619	8.774349	-0.669274
C	3.859748	-2.769247	-0.007224	H	-1.569545	10.124402	-0.173047
C	3.609854	-1.374456	0.089096	H	0.907321	10.937714	-1.035156
H	0.564437	-2.621279	-0.568821	H	2.431823	8.689518	-0.938078
H	2.484382	-4.483813	-0.435975	O	7.127552	2.226353	-0.954635
H	4.824743	-3.241688	0.080977	P	5.807335	1.589542	-1.250127
H	4.327023	-0.602320	0.306568	O	5.020894	1.979388	-2.465260
Fe	3.023359	-2.065195	-1.779411	O	6.133448	-0.020986	-1.328486
C	2.249040	-1.174238	-3.471468	H	5.340821	-0.535998	-1.541544
C	3.617909	-0.809469	-3.320932	O	4.876411	1.722070	0.062782
C	4.390899	-2.009599	-3.343230	H	3.899058	1.663253	-0.104415
C	3.500510	-3.108947	-3.501678				

Complex (TfO)·**1**·Zn(OTf): E_{MeCN} = -6375.042803020 au

N	0.014373	0.049436	-0.063461	H	1.527744	-3.068672	-3.782239
C	1.375076	0.039363	-0.048542	C	3.269955	6.068905	0.056820
N	1.849006	1.292337	-0.002848	O	3.597105	6.967650	1.031178
C	0.739411	2.095563	-0.006570	C	4.836435	7.441272	0.726645
C	-0.423652	1.359496	-0.055278	C	5.301765	6.861871	-0.409769
H	-0.558592	-0.793972	-0.197854	C	4.283660	5.964030	-0.847578
C	0.747308	3.482377	0.022154	H	5.250865	8.156855	1.417033
N	1.940238	4.118055	0.049309	H	6.251820	7.047959	-0.884045
C	1.958053	5.440078	0.080559	H	4.284310	5.347368	-1.730766
C	0.698001	6.155583	0.065192	C	0.666936	7.605185	-0.028566
N	-0.466040	5.517491	0.057131	O	-0.543173	8.207658	0.191279
C	-0.482089	4.168525	0.035513	C	-0.386011	9.531733	-0.049262
C	-1.687595	3.401376	-0.019115	C	0.893513	9.801058	-0.421032
C	-1.675176	2.020654	-0.072373	C	1.578953	8.556366	-0.409506
H	-2.627839	3.937055	-0.028216	H	-1.259298	10.145963	0.096173
H	-2.602740	1.465771	-0.129463	H	1.301337	10.765633	-0.678527
C	2.171300	-1.156131	-0.068452	H	2.608725	8.400200	-0.679570
C	1.713454	-2.486505	-0.351628	Zn	3.352776	2.596834	-0.057999
C	2.844140	-3.339455	-0.334836	O	4.699793	2.791363	-1.667599
C	3.999329	-2.556598	-0.049051	S	5.883714	2.761911	-0.768539
C	3.594287	-1.207993	0.108875	O	5.332206	2.465543	0.587586
H	0.700017	-2.772605	-0.569823	O	6.822430	3.834646	-0.865059
H	2.833530	-4.396388	-0.550404	C	6.804336	1.223778	-1.290163
H	5.013615	-2.919549	0.003651	F	6.004055	0.166984	-1.183116
H	4.230689	-0.370798	0.337479	F	7.181827	1.359067	-2.560904
Fe	3.063614	-1.851546	-1.771581	F	7.875809	1.053646	-0.523208
C	2.183239	-0.968554	-3.415536	O	-1.465743	-2.203222	-0.941968
C	3.478813	-0.414375	-3.191214	S	-1.677721	-2.059619	-2.385393
C	4.429080	-1.472255	-3.278166	O	-1.456743	-3.268991	-3.154406
C	3.722366	-2.679244	-3.551422	O	-1.117872	-0.843843	-2.943679
C	2.333692	-2.366573	-3.632961	C	-3.522681	-1.799991	-2.453163
H	1.239112	-0.448786	-3.383814	F	-4.168027	-2.887994	-2.006376
H	3.701262	0.617188	-2.964510	F	-3.876521	-0.761811	-1.677037
H	5.491853	-1.385322	-3.120328	F	-3.943563	-1.551835	-3.704348
H	4.156492	-3.662976	-3.641388				

Complex (TfO)·**1**·Zn(HSO_4): E_{MeCN} = -6113.231754822 au

N	-0.028989	-0.185153	0.070562	H	-0.423287	0.357197	4.251006
C	-0.029292	-0.163367	1.428586	Fe	-1.831944	-1.883226	3.248771
N	1.225822	-0.080459	1.894717	C	-0.804274	-3.543150	2.570894
C	2.020977	-0.063953	0.780229	C	-0.375775	-3.196198	3.886973
C	1.277037	-0.121459	-0.376983	C	-1.510214	-3.265848	4.746274
H	-0.873688	-0.288451	-0.515614	C	-2.635701	-3.652670	3.963164
C	3.408455	-0.024230	0.777461	C	-2.198869	-3.822118	2.617680
N	4.056753	0.025941	1.962904	H	-0.187134	-3.552949	1.686611
C	5.380904	0.047609	1.957148	H	0.622058	-2.906271	4.173924
C	6.077561	-0.046825	0.691714	H	-1.527002	-3.018186	5.795726
N	5.427142	-0.048166	-0.464408	H	-3.647894	-3.759271	4.319956
C	4.080129	-0.024939	-0.461260	H	-2.823878	-4.073915	1.776230
C	3.302553	-0.050814	-1.659511	C	6.045546	0.132706	3.244394
C	1.924474	-0.097499	-1.636061	O	7.003673	1.090441	3.415719
H	3.830394	-0.049106	-2.603813	C	7.491683	0.935923	4.675998
H	1.355426	-0.141507	-2.550832	C	6.869200	-0.094655	5.304698
C	-1.216490	-0.208329	2.234997	C	5.923112	-0.617692	4.374531
C	-2.535664	-0.582043	1.812891	H	8.253307	1.636176	4.975721
C	-3.376453	-0.527288	2.954371	H	7.059688	-0.446448	6.304769
C	-2.592998	-0.135545	4.078293	H	5.271108	-1.464311	4.506276
C	-1.257644	0.054223	3.643613	C	7.515699	-0.243310	0.645348
H	-2.819749	-0.872770	0.814177	O	8.114092	-0.090963	-0.575937
H	-4.422881	-0.787283	2.975921	C	9.416487	-0.438163	-0.434608
H	-2.946092	-0.035384	5.091789	C	9.673745	-0.816016	0.845708

C	8.445846	-0.684603	1.550939	F	0.157858	-1.005517	6.186115
H	10.025293	-0.359138	-1.319557	F	1.370317	-2.426785	7.290264
H	10.618892	-1.150760	1.241492	F	1.149534	-0.393607	8.023420
H	8.279569	-0.919645	2.587965	O	-2.215427	-0.693538	-1.597878
Zn	2.534308	-0.055152	3.390654	S	-1.812028	-1.661439	-2.634884
O	2.760327	-1.600453	4.798905	O	-0.378231	-1.717113	-2.847017
S	2.761777	-0.654598	5.948823	O	-2.110262	-3.128444	-2.003032
O	2.445030	0.676018	5.354533	H	-3.061856	-3.215169	-1.835657
O	3.867333	-0.718462	6.851379	O	-2.619259	-1.555694	-3.838876
C	1.249502	-1.148596	6.934908				

Complex $(HSO_4)\cdot\mathbf{1}\cdot Zn(OTf)$: E_{MeCN} = -6113.221840054 au

N	0.022440	0.055804	0.041618	H	-3.808376	-3.584969	3.681184
C	0.026183	0.027803	1.402646	H	-2.804079	-3.438356	1.182390
N	1.276363	-0.003572	1.868909	C	5.996083	0.135923	3.339619
C	2.073411	0.007522	0.762600	O	6.967590	1.059700	3.586618
C	1.337335	0.049442	-0.401264	C	7.321102	0.921284	4.892043
H	-0.832923	0.151715	-0.521258	C	6.596687	-0.067050	5.479961
C	3.460281	0.013970	0.784322	C	5.724878	-0.576016	4.473293
N	4.080922	0.027758	1.984828	H	8.083477	1.593388	5.248031
C	5.403656	0.074277	2.017909	H	6.682290	-0.403315	6.500407
C	6.131671	0.040696	0.762883	H	5.024454	-1.391400	4.562850
N	5.505060	0.067133	-0.406882	C	7.575898	-0.111261	0.742897
C	4.155874	0.071984	-0.436717	O	8.197658	0.089093	-0.460794
C	3.393303	0.101338	-1.646790	C	9.506552	-0.219164	-0.296232
C	2.010385	0.088892	-1.647013	C	9.747013	-0.618193	0.981250
H	3.933314	0.131537	-2.583718	C	8.499758	-0.546767	1.658382
H	1.467528	0.112437	-2.581629	H	10.134260	-0.097357	-1.162994
C	-1.140929	0.010200	2.239653	H	10.693911	-0.929217	1.391704
C	-2.488178	-0.280914	1.859351	H	8.319200	-0.814216	2.684309
C	-3.272683	-0.291195	3.042701	Zn	2.579035	-0.096385	3.399189
C	-2.425375	-0.014063	4.150472	O	-2.386338	0.512411	-1.398151
C	-1.104494	0.168339	3.665303	S	-3.256356	-0.538726	-1.937387
H	-2.804822	-0.540206	0.865323	O	-4.317773	-0.055022	-2.797616
H	-4.324374	-0.521740	3.097183	O	-3.640588	-1.549731	-0.967974
H	-2.727519	0.034447	5.183957	C	-2.089055	-1.436692	-3.088427
H	-0.249193	0.484692	4.237814	F	-1.675348	-0.627730	-4.075713
Fe	-1.771114	-1.724653	3.131049	F	-0.999071	-1.847579	-2.410523
C	-0.822343	-3.309793	2.198995	F	-2.669923	-2.510144	-3.642599
C	-0.475763	-3.293097	3.579762	O	2.453866	-1.780872	4.650223
C	-1.682178	-3.421421	4.335527	S	1.898655	-0.989459	5.789451
C	-2.764659	-3.516913	3.418604	O	1.933754	0.423889	5.286067
C	-2.234075	-3.446986	2.097605	O	0.386713	-1.408346	5.953790
H	-0.135197	-3.200601	1.375024	H	-0.098456	-1.432200	5.095552
H	0.525177	-3.226957	3.974268	O	2.478689	-1.201015	7.075850
H	-1.763826	-3.429262	5.411087				

Complex $(ClO_4)\cdot\mathbf{1}\cdot Pb(ClO_4)(MeCN)_2$: E_{MeCN} = -4652.671876791 au

N	-0.096465	-0.065415	-0.066281	H	1.138571	0.011334	-2.696459
C	-0.080334	-0.104399	1.292563	C	-1.295769	-0.070225	2.064982
N	1.179502	-0.114640	1.748970	C	-2.609147	-0.389805	1.580183
C	1.975722	-0.089885	0.625399	C	-3.518869	-0.203754	2.652581
C	1.196532	-0.060759	-0.524341	C	-2.783284	0.220627	3.799340
H	-0.926638	-0.182360	-0.639909	C	-1.413670	0.303031	3.444197
C	3.375026	-0.095818	0.526879	H	-2.849343	-0.746283	0.591268
N	4.142281	-0.176848	1.633197	H	-4.578158	-0.402789	2.618637
C	5.454520	-0.139381	1.527886	H	-3.186831	0.409249	4.780874
C	6.061251	-0.027727	0.221560	H	-0.607577	0.609738	4.082839
N	5.310967	0.038139	-0.868548	Fe	-2.085684	-1.616333	3.150200
C	3.966069	0.001261	-0.759233	C	-1.003056	-3.325793	2.781360
C	3.134048	0.033356	-1.916692	C	-0.838158	-2.922178	4.138404
C	1.763124	-0.008519	-1.814018	C	-2.124274	-2.912141	4.752165
H	3.613022	0.091906	-2.884434	C	-3.080531	-3.316114	3.775187

C	-2.386890	-3.567067	2.553797	O	-2.093266	-1.350147	-1.793348
H	-0.233467	-3.381687	2.030174	Cl	-1.869643	-2.784547	-1.581524
H	0.081104	-2.636979	4.622053	O	-0.958277	-2.954184	-0.463642
H	-2.340800	-2.598514	5.761126	O	-3.142938	-3.419059	-1.292821
H	-4.147198	-3.375075	3.925520	O	-1.290685	-3.364201	-2.780824
H	-2.828615	-3.829552	1.605609	O	1.380474	-1.245625	6.126353
C	6.189667	-0.268660	2.785702	Cl	0.765296	0.023890	6.531815
O	7.068749	0.710539	3.142676	O	1.117444	1.022353	5.490527
C	7.620245	0.336167	4.330614	O	-0.665242	-0.112629	6.598159
C	7.107692	-0.852862	4.737313	O	1.311447	0.454035	7.793322
C	6.167028	-1.247341	3.736405	N	2.922717	2.190807	3.065676
H	8.337824	1.019655	4.752481	C	2.797677	2.799339	2.097290
H	7.370471	-1.390884	5.633954	C	2.632450	3.520755	0.853280
H	5.596258	-2.162346	3.695989	H	1.570440	3.689939	0.664616
C	7.502219	-0.042933	0.041556	H	3.149240	4.480066	0.916574
O	7.962703	0.290703	-1.204509	H	3.061231	2.930260	0.040214
C	9.308694	0.139927	-1.193221	N	2.636306	-2.799817	2.608180
C	9.732166	-0.289110	0.025757	C	2.534535	-3.128409	1.509865
C	8.564754	-0.405466	0.828105	C	2.390797	-3.494051	0.116187
H	9.817966	0.379086	-2.111966	H	2.818069	-4.484301	-0.053866
H	10.746963	-0.499463	0.322136	H	1.330895	-3.499060	-0.152105
H	8.534162	-0.741122	1.848904	H	2.919639	-2.765040	-0.502217
Pb	2.676528	-0.310622	3.749135				

Complex $(ClO_4)\cdot\mathbf{1}\cdot Pb(HSO_4)(MeCN)_2$: E_{MeCN} = -4591.567856032 au

N	-0.098691	-0.031942	0.007508	C	7.724334	0.602781	4.224237
C	-0.074090	-0.032362	1.364284	C	7.210677	-0.534139	4.755395
N	1.184557	-0.044671	1.817705	C	6.230904	-1.002626	3.829213
C	1.976083	-0.067027	0.689768	H	8.463274	1.311668	4.554829
C	1.189578	-0.063855	-0.456982	H	7.493701	-0.990010	5.688958
H	-0.944667	-0.141332	-0.545089	H	5.641952	-1.903891	3.894632
C	3.376494	-0.088598	0.580590	C	7.497221	-0.128793	0.027776
N	4.158812	-0.123292	1.678708	O	7.946188	0.143251	-1.237206
C	5.469218	-0.094646	1.543603	C	9.289180	-0.045339	-1.237840
C	6.059358	-0.065989	0.228083	C	9.721801	-0.431962	-0.007315
N	5.293456	-0.040341	-0.852989	C	8.563809	-0.487029	0.813347
C	3.950834	-0.047400	-0.718784	H	9.791058	0.144402	-2.170722
C	3.109239	-0.041821	-1.871152	H	10.736310	-0.659437	0.284652
C	1.739487	-0.062134	-1.755091	H	8.543017	-0.785239	1.846887
H	3.581397	-0.029228	-2.844044	Pb	2.637071	-0.201128	3.869884
H	1.104839	-0.064641	-2.630827	O	-2.194160	-1.110167	-1.672163
C	-1.301012	-0.001616	2.126917	Cl	-2.006787	-2.569571	-1.572344
C	-2.600164	-0.348836	1.624154	O	-0.881213	-2.841635	-0.690743
C	-3.529155	-0.202386	2.685908	O	-3.212772	-3.165224	-1.028570
C	-2.823155	0.232865	3.842007	O	-1.750043	-3.094486	-2.901315
C	-1.449852	0.362665	3.502168	O	1.458325	-1.477867	6.130558
H	-2.826112	-0.702372	0.631298	S	0.711965	-0.290039	6.561651
H	-4.581474	-0.431359	2.632583	O	0.930510	0.797391	5.575370
H	-3.247511	0.420427	4.814757	O	-0.847205	-0.665701	6.480977
H	-0.672183	0.719480	4.153396	H	-1.096832	-0.939251	5.575772
Fe	-2.062341	-1.589796	3.171447	O	0.890268	0.099459	7.935838
C	-0.957247	-3.262274	2.693399	N	2.913087	2.329316	3.073085
C	-0.834779	-2.986981	4.085095	C	2.816516	2.802497	2.030529
C	-2.143619	-3.041338	4.654455	C	2.712384	3.346700	0.691788
C	-3.065172	-3.346201	3.611422	H	1.656987	3.421943	0.404072
C	-2.331504	-3.483897	2.396727	H	3.170654	4.338140	0.649352
H	-0.152631	-3.267677	1.980315	H	3.235282	2.686770	-0.006461
H	0.080923	-2.777578	4.616783	N	2.608008	-2.700850	2.694829
H	-2.398890	-2.868003	5.688244	C	2.550983	-3.065305	1.604830
H	-4.136131	-3.419431	3.718223	C	2.472585	-3.466642	0.218114
H	-2.740871	-3.654735	1.412413	H	2.884969	-4.471349	0.098151
C	6.236110	-0.121712	2.789655	H	1.431901	-3.459481	-0.119832
O	7.140074	0.870485	3.024375	H	3.053759	-2.771463	-0.392815

Complex $(HSO_4)\cdot 1\cdot Pb(ClO_4)(MeCN)_2$: E_{MeCN} = -4591.562587375 au

N	-0.011307	0.032488	0.018109	C	7.784023	0.941857	4.281669
C	-0.012148	-0.007018	1.373453	C	7.212965	-0.114377	4.915939
N	1.241638	-0.024267	1.847265	C	6.222019	-0.628237	4.024379
C	2.053786	-0.008373	0.734241	H	8.554063	1.643702	4.554376
C	1.284704	0.015109	-0.421274	H	7.469907	-0.490612	5.892624
H	-0.833267	-0.054928	-0.595608	H	5.597892	-1.496347	4.168644
C	3.453313	0.013804	0.652930	C	7.573035	-0.059243	0.165386
N	4.209291	0.053851	1.768090	O	8.041698	0.148284	-1.105044
C	5.525241	0.095109	1.654930	C	9.375313	-0.095345	-1.089872
C	6.134885	0.052975	0.347584	C	9.780024	-0.459919	0.155601
N	5.390215	0.050570	-0.747330	C	8.614138	-0.437916	0.970637
C	4.047725	0.044840	-0.637458	H	9.890750	0.040640	-2.025806
C	3.225903	0.045481	-1.802816	H	10.781199	-0.718362	0.460295
C	1.856272	0.032058	-1.710076	H	8.565876	-0.693060	2.014656
H	3.716252	0.056079	-2.766907	Pb	2.604983	0.053498	3.886474
H	1.234457	0.032288	-2.594153	O	1.057807	-1.435424	5.378341
C	-1.241477	-0.020981	2.125689	Cl	0.666254	-0.776536	6.656013
C	-2.559987	-0.005286	1.553272	O	1.138071	0.600155	6.587098
C	-3.493121	-0.053915	2.618919	O	-0.769155	-0.815087	6.779416
C	-2.771759	-0.120930	3.846056	O	1.298911	-1.473478	7.751131
C	-1.386786	-0.103677	3.547895	O	-1.946424	-0.561166	-1.851339
H	-2.791801	0.016483	0.500052	S	-1.664748	-1.940224	-2.286481
H	-4.565534	-0.081898	2.509315	O	-0.497301	-2.524724	-1.645975
H	-3.196016	-0.210260	4.832791	O	-2.873204	-2.836015	-1.676794
H	-0.594975	-0.187672	4.263950	H	-3.712499	-2.543086	-2.065808
Fe	-2.247732	-1.730158	2.645989	O	-1.726437	-2.090745	-3.731394
C	-1.512701	-3.332240	1.574612	N	1.133257	2.299774	3.867584
C	-1.025717	-3.361873	2.916695	C	0.077336	2.747682	3.786266
C	-2.147836	-3.450334	3.789376	C	-1.261860	3.293823	3.695302
C	-3.326738	-3.471230	2.990828	H	-1.915668	2.551778	3.231722
C	-2.932780	-3.401233	1.623695	H	-1.628114	3.527962	4.696669
H	-0.939139	-3.212774	0.669133	H	-1.250873	4.202621	3.091568
H	-0.000094	-3.278607	3.238101	N	2.771733	-2.454318	2.987200
H	-2.109746	-3.448604	4.867302	C	2.398527	-3.046886	2.075229
H	-4.339560	-3.499304	3.360323	C	1.884260	-3.761452	0.925704
H	-3.583688	-3.351865	0.766960	H	1.225952	-4.563452	1.264364
C	6.274259	0.149819	2.905025	H	1.314550	-3.069888	0.297918
O	7.222699	1.118721	3.053572	H	2.707286	-4.185636	0.347441

Electronic Supplementary Material (ESI) for Chemical Communications