Electronic supplementary materials *Mendeleev Commun.*, 2020, **30**, 445-448

Imidazo[4,5-*f*][1,10]phenanthroline complexes with Fe^{2+}, Cd^{2+}, Co^{2+} and Zn^{2+} ions

Sergey D. Tokarev, Yury V. Fedorov and Olga A. Fedorova

Table of contents

Experimental Section

All reagents were purchased from Acros, Aldrich, Merck and used without additional purification. Solvents were purified by standard procedures. Spectroscopic grade MeCN, was used for spectroscopic and fluorometric measurements.

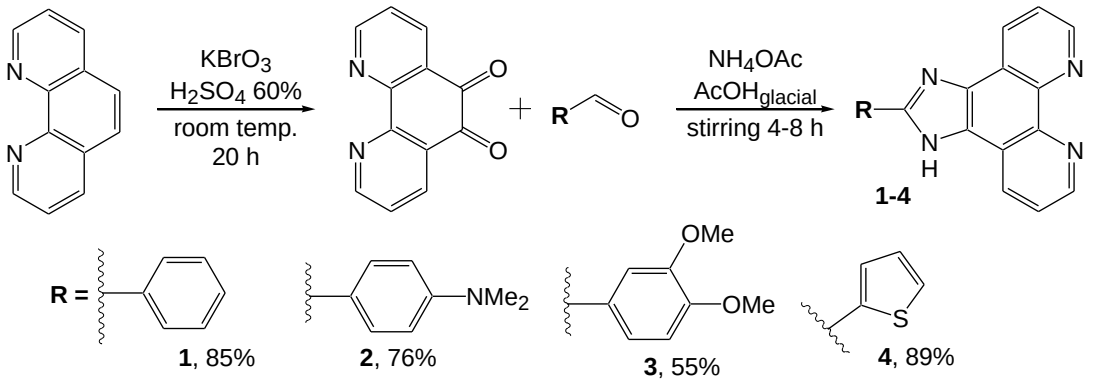
^{1}H and ^{13}C (APT method) NMR spectra were recorded on a Bruker AVANCE-400 spectrometer. The chemical shifts and spin-spin coupling constants were determined with accuracy of 0.01 ppm and 0.1 Hz, respectively.

The electron impact mass spectra of were recorded on a Finnigan Polaris Q instrument. The energy of ionizing electrons was 70 eV. 1 mass. % solutions of compounds in CH_2Cl_2 or $CHCl_3$ (0.2 μl) were loaded into quartz micro-ampoules, which were inserted into the heated tip of the direct input rod. Thermomass spectrograms were filmed in the process of stepped (after 50 ºC) heating of ampoules from 50 to 150 ºC. Before heating the samples in the same temperature range, the thermomass spectrogram of the empty ampoule was usually taken to confirm an absence of any impurities in the ampoule and rod.

Fluorescence spectra were measured at 20±1 °C with an Agilent Cary Eclipse spectrofluorometer. UV-vis spectra were measured using a two-channel spectrophotometer Varian-Cary 300.

Synthesis of ligands

Synthesis of 2-substituted 1*H*-imidazo[4,5-*f*][1,10]phenanthrolines **1-4** was carried out as described [S1] (Scheme S1). The synthetic procedure includes the condensation of phenathroline-5,6-dione with the corresponding aldehyde in glacial acetic acid in the presence of ammonium acetate for 4-8 hours at reflux. 1,10-Phenanthroline-5,6-dione was previously obtained by mixing 1,10-phenanthroline with potassium bromate at room temperature in a solution of 60% sulfuric acid for 20 hours [S2]. The physicochemical characteristics and synthesis techniques of **1-4** are described in literature: (**1**) [S3], (**2**) [S4], (**3**) [S5], (**4**) [S6].



Scheme S1

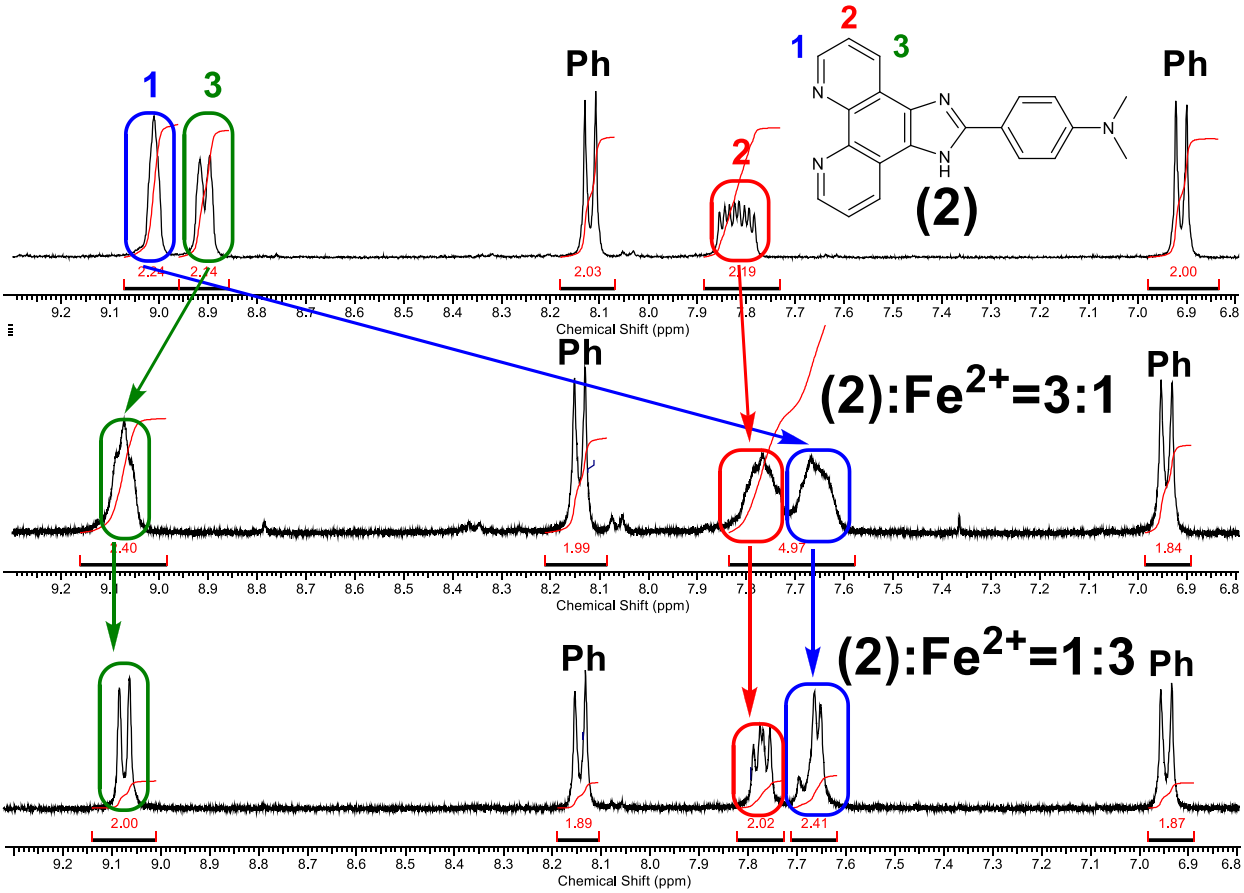


Figure S1 ^{1}H NMR spectral changes of ligand **2** (upper spectrum) upon the addition of 1/3 equivalents (middle spectrum) and 3 equivalents (bottom spectrum) of iron(II) perchlorate.

Table S1. Spectroscopic data of **1-4**, $C_{\mathbf{1\text{-}4}} = 2\times10^{-5}$ M, acetonitrile.

Compound	λ_{abs}, nm	λ_{fl}, nm	Stokes shift, nm	Φ_{fl}, %
1	318	435	117	12.4
2	340	551	211	10.3
3	324	461	137	12.5
4	332	443	111	10.9

ESI-MS data

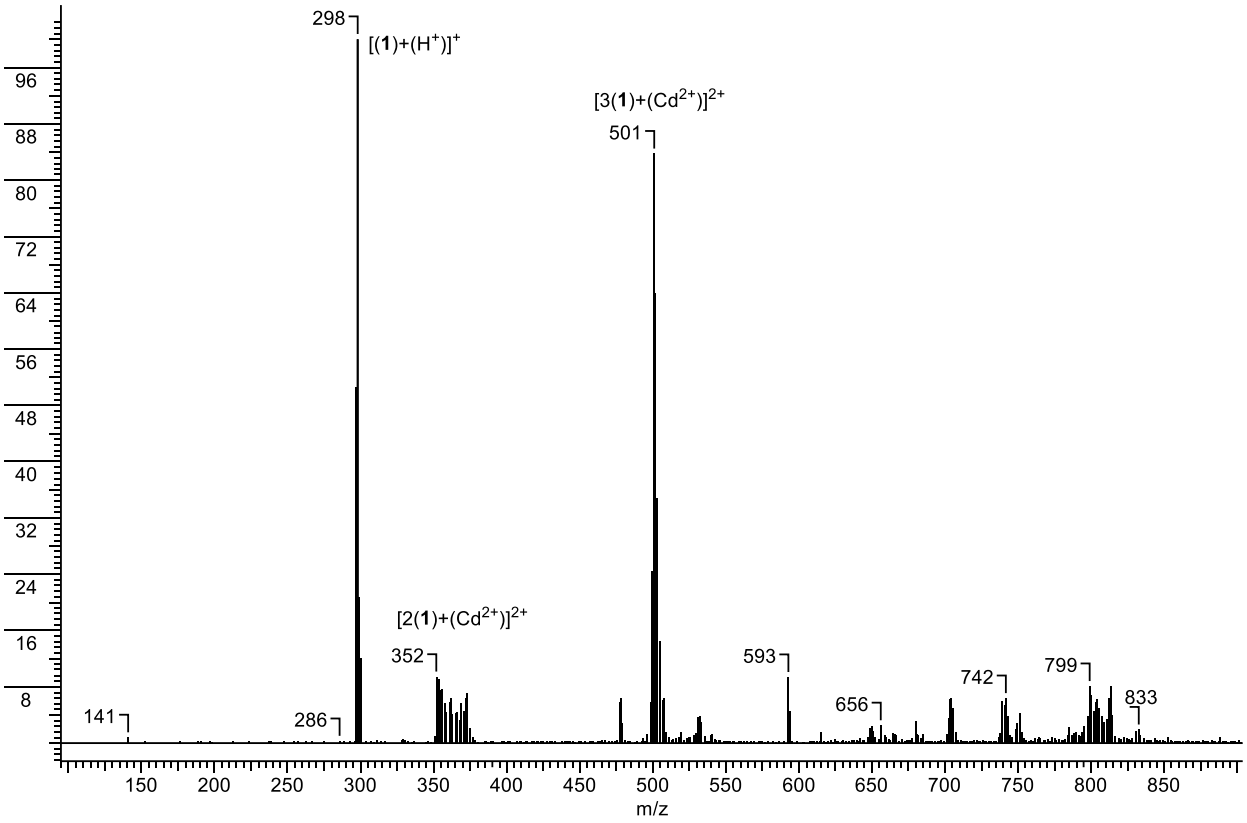


Figure S2. ESI-MS spectrum of mixture ligand **1** with Cd^{2+}, ratio 1:1.

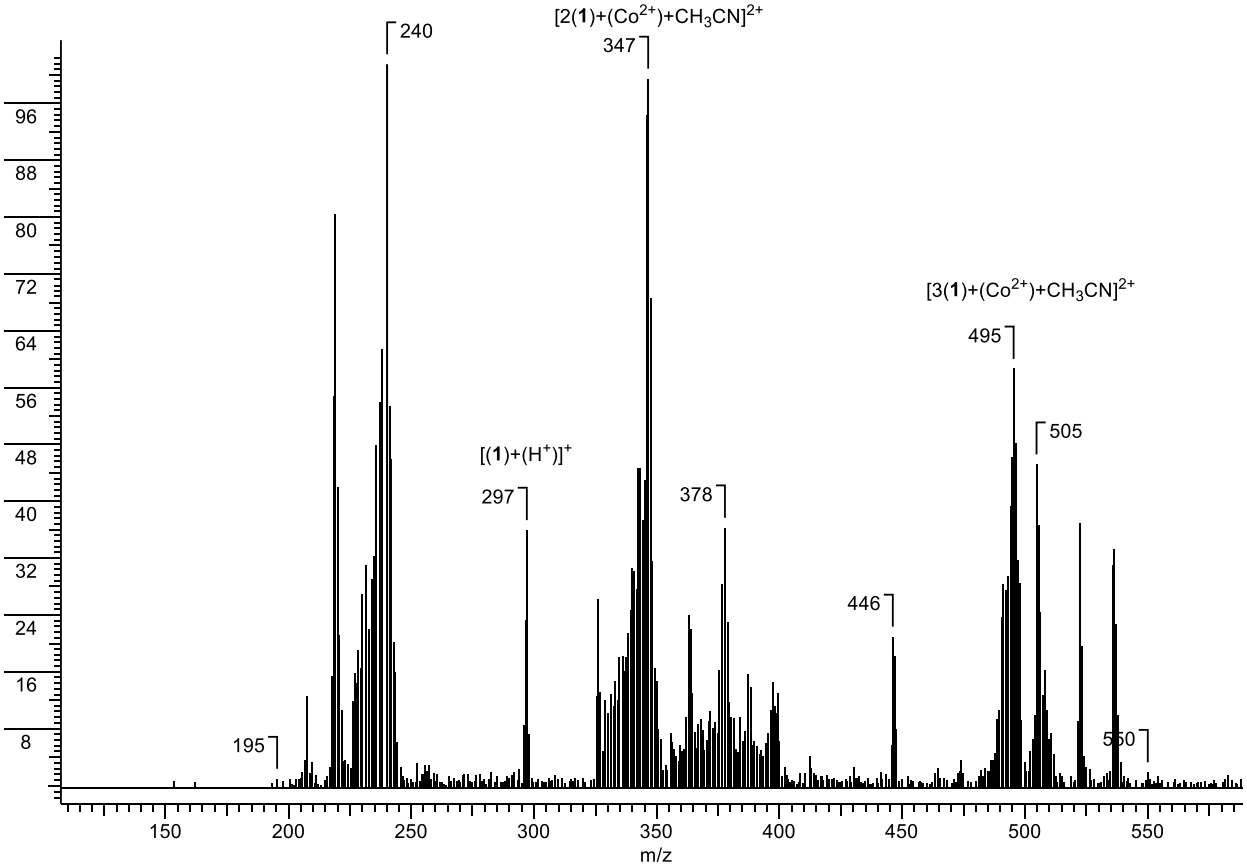


Figure S3. ESI-MS spectrum of mixture ligand **1** with Co^{2+}, ratio 1:1.

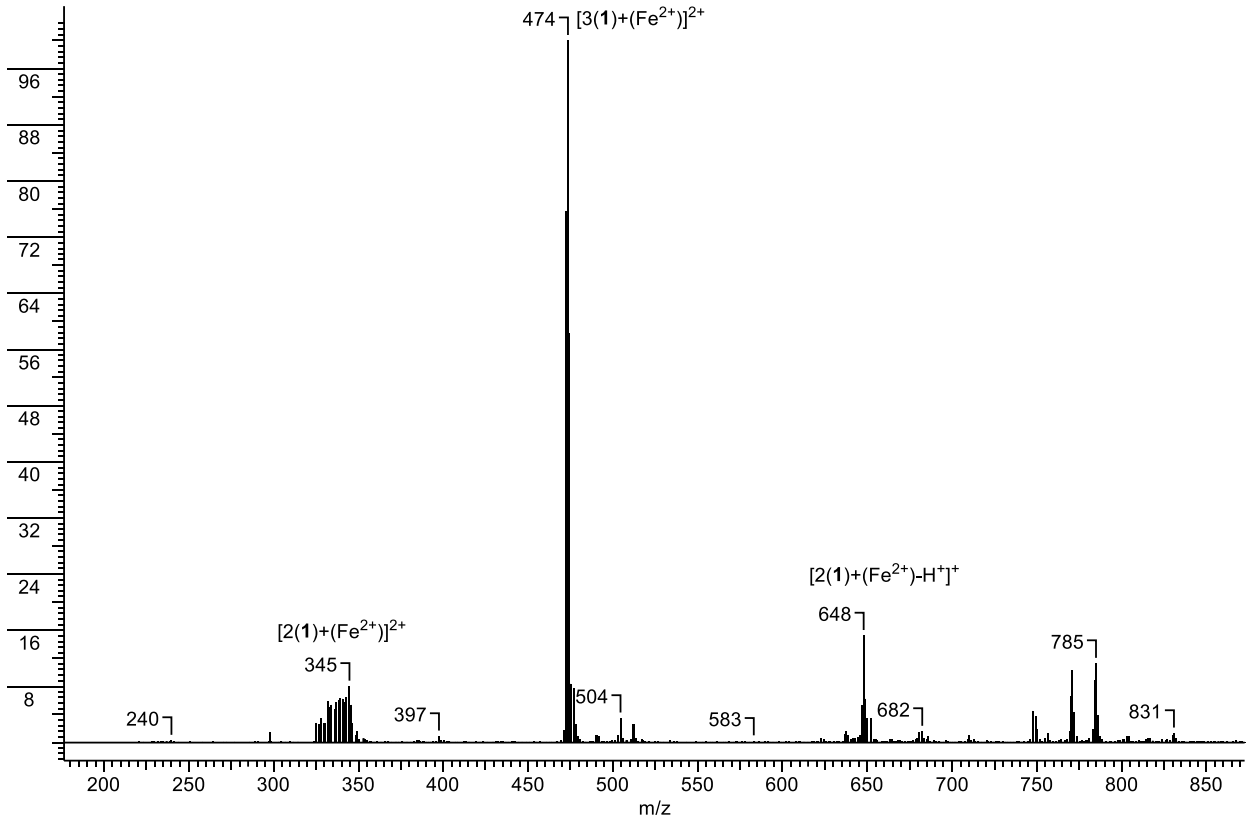


Figure S4. ESI-MS spectrum of mixture ligand **1** with Fe^{2+}, ratio 1:1.

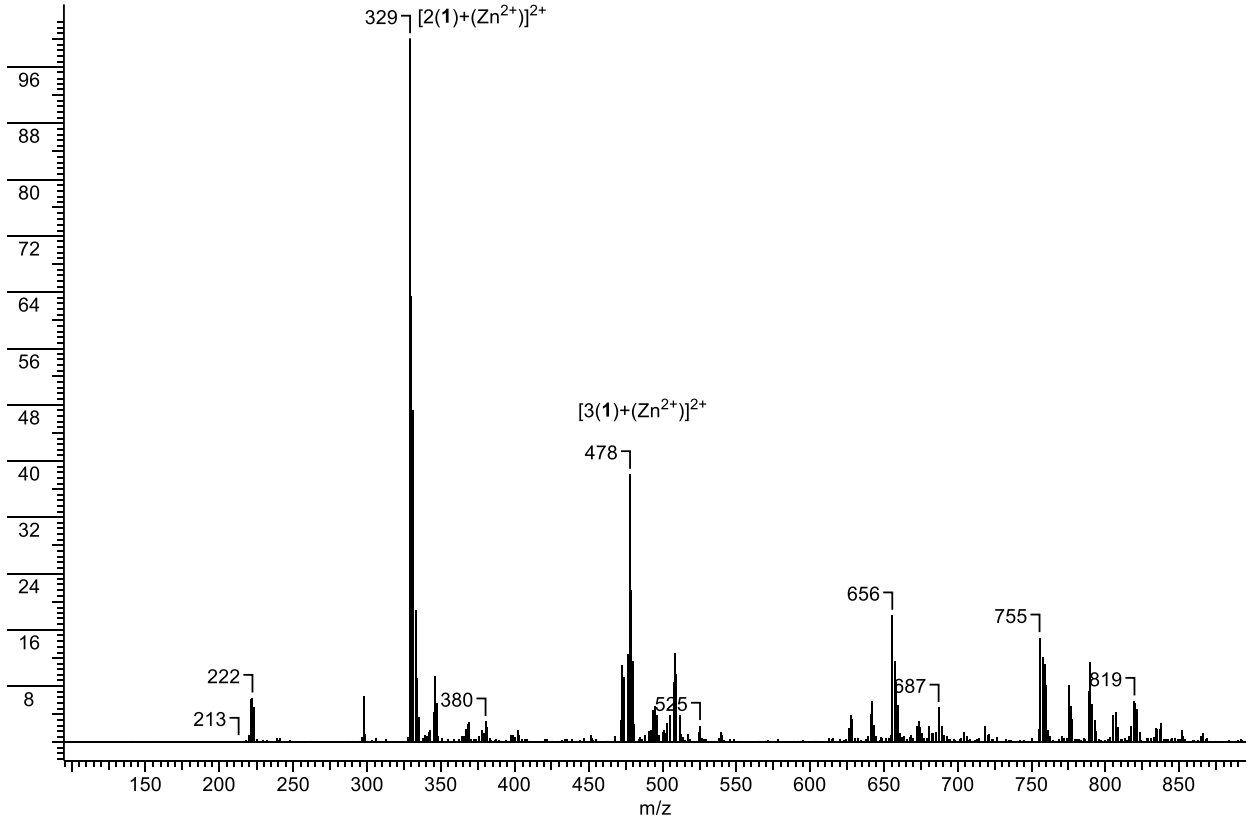


Figure S5. ESI-MS spectrum of mixture ligand **1** with Zn^{2+}, ratio 1:1.

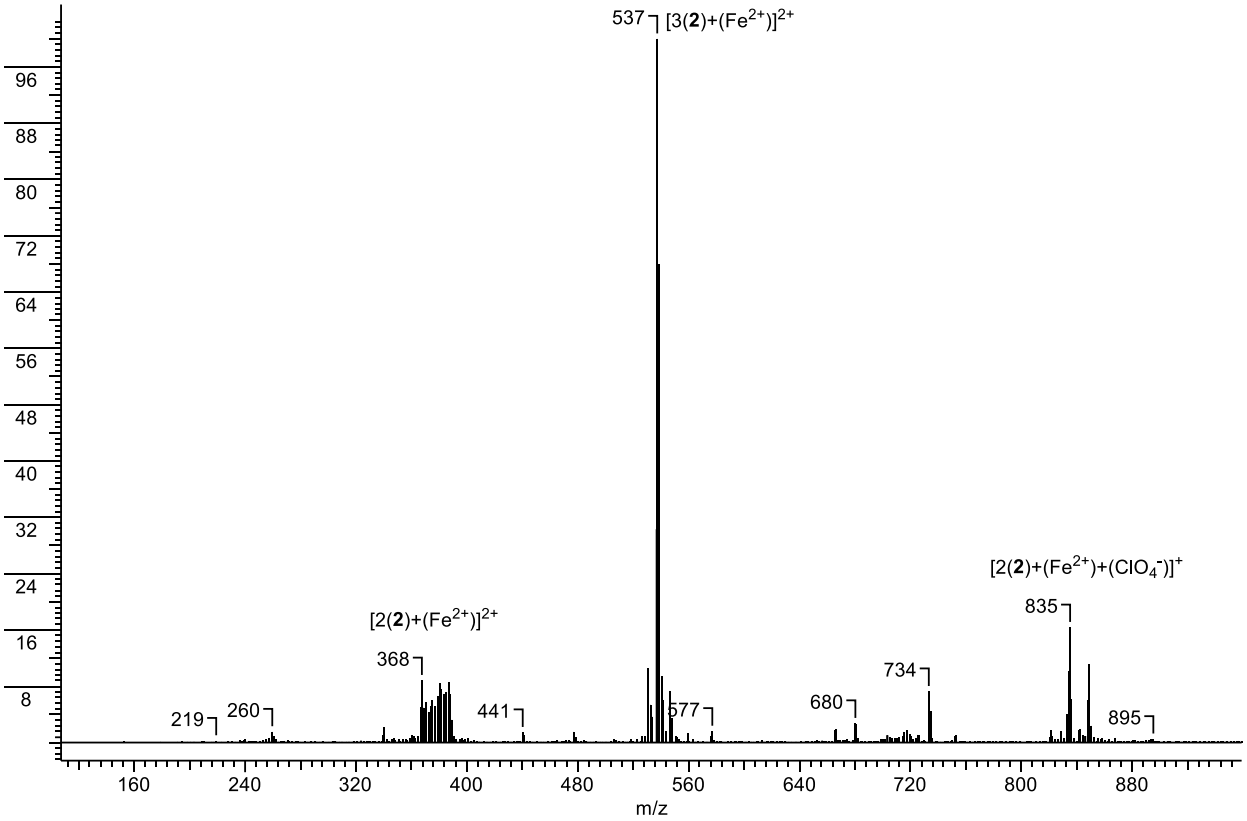


Figure S6. ESI-MS spectrum of mixture ligand **2** with Fe^{2+}, ratio 1:1.

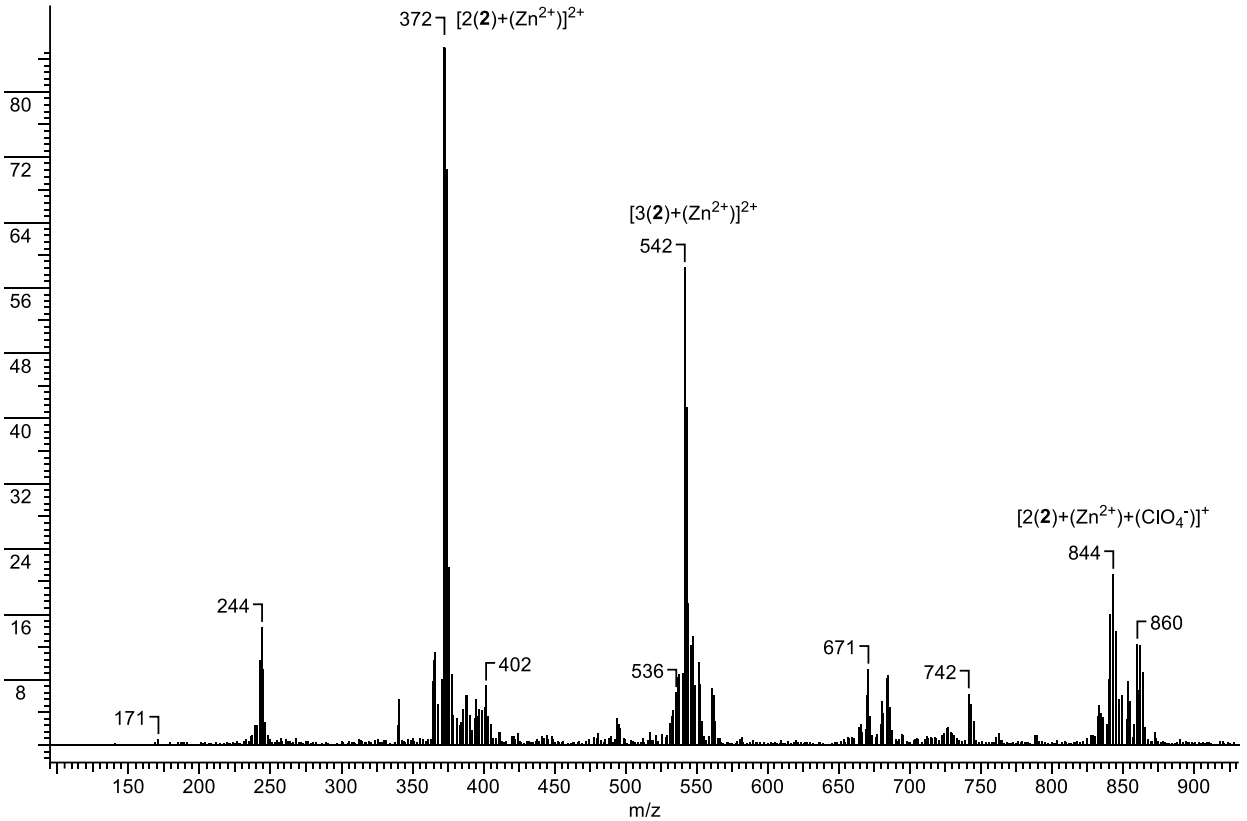


Figure S7. ESI-MS spectrum of mixture ligand **2** with Zn^{2+}, ratio 1:1.

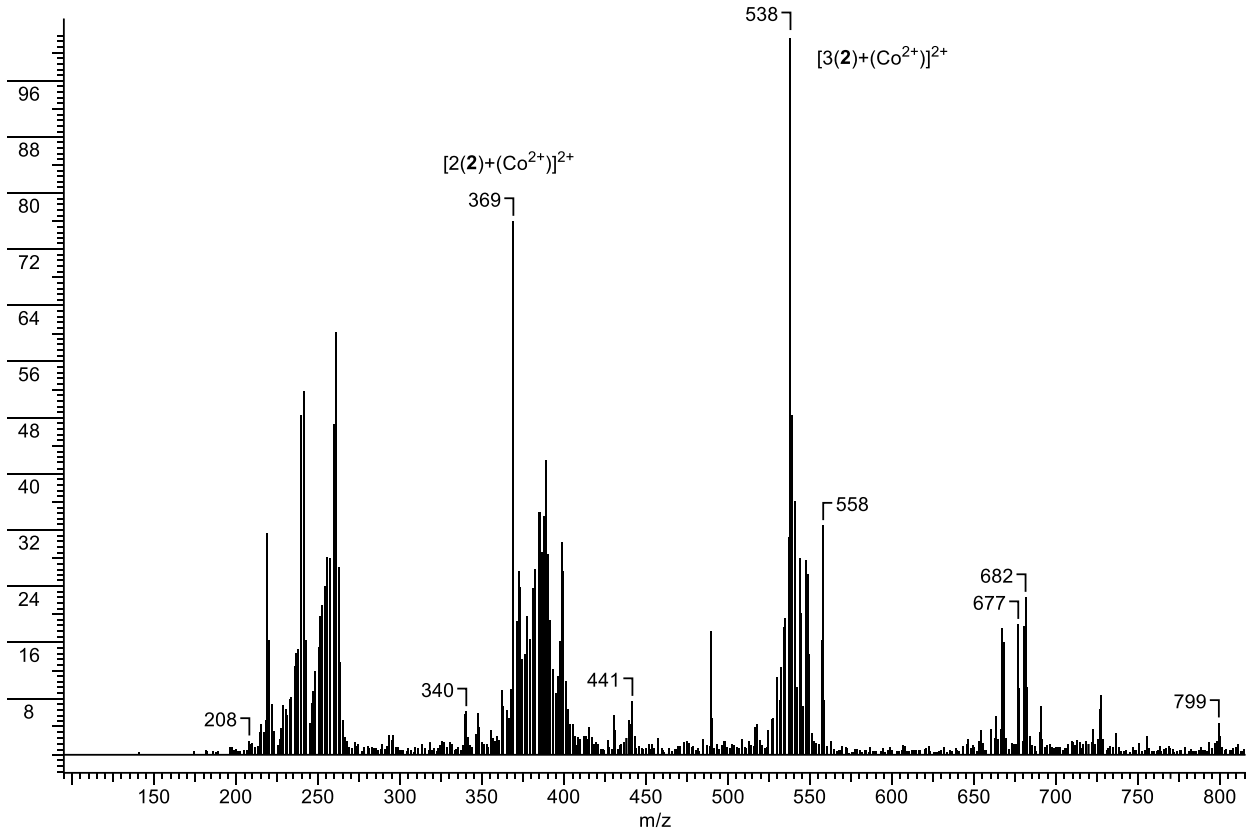


Figure S8. ESI-MS spectrum of mixture ligand **2** with Co^{2+}, ratio 1:1.

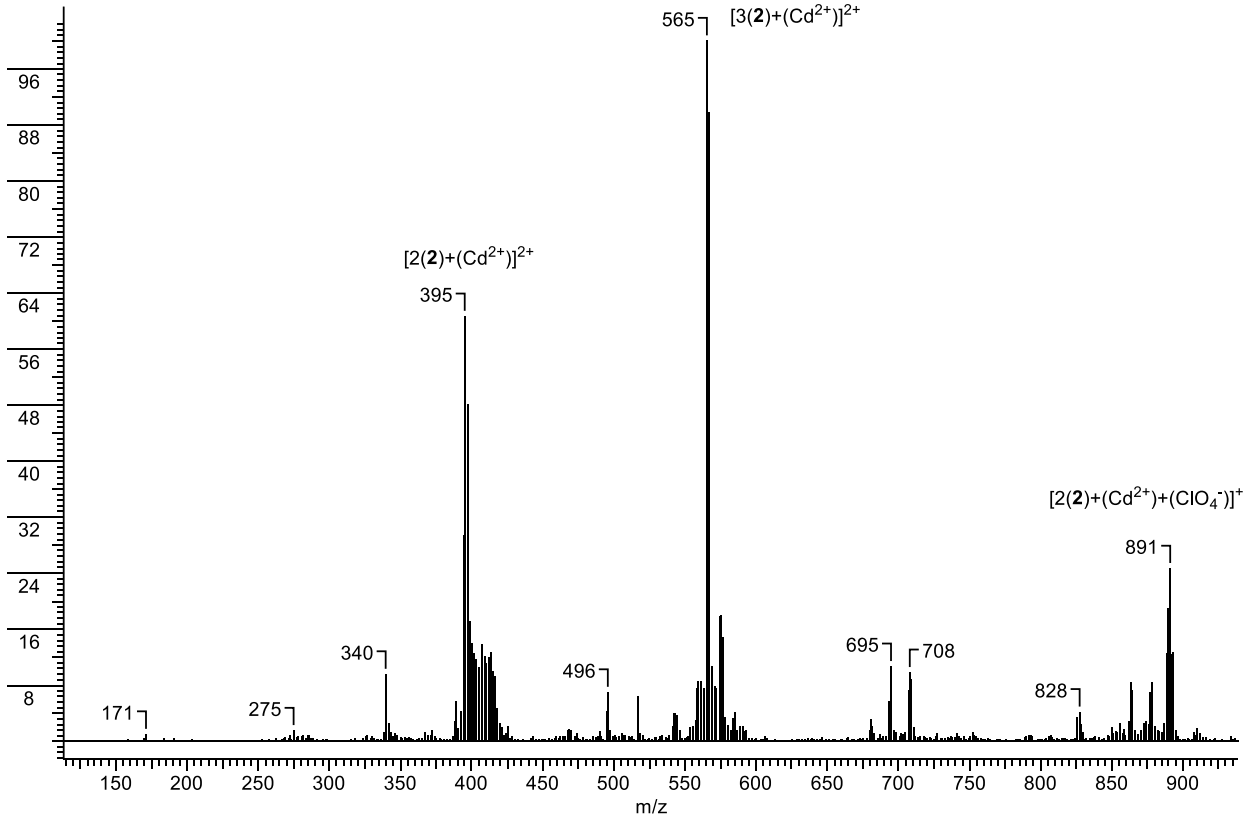


Figure S9. ESI-MS spectrum of mixture ligand **2** with Cd^{2+}, ratio 1:1.

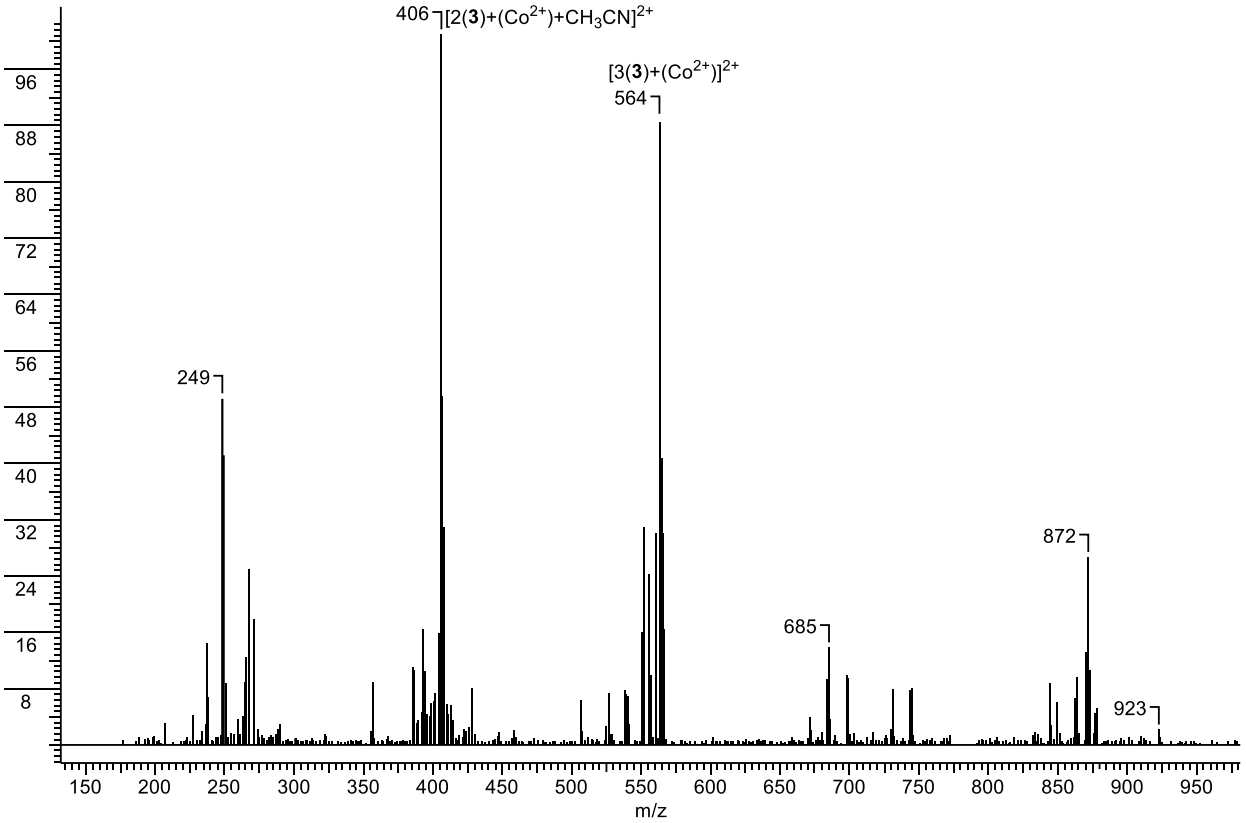


Figure S10. ESI-MS spectrum of mixture ligand **3** with Co^{2+}, ratio 1:1.

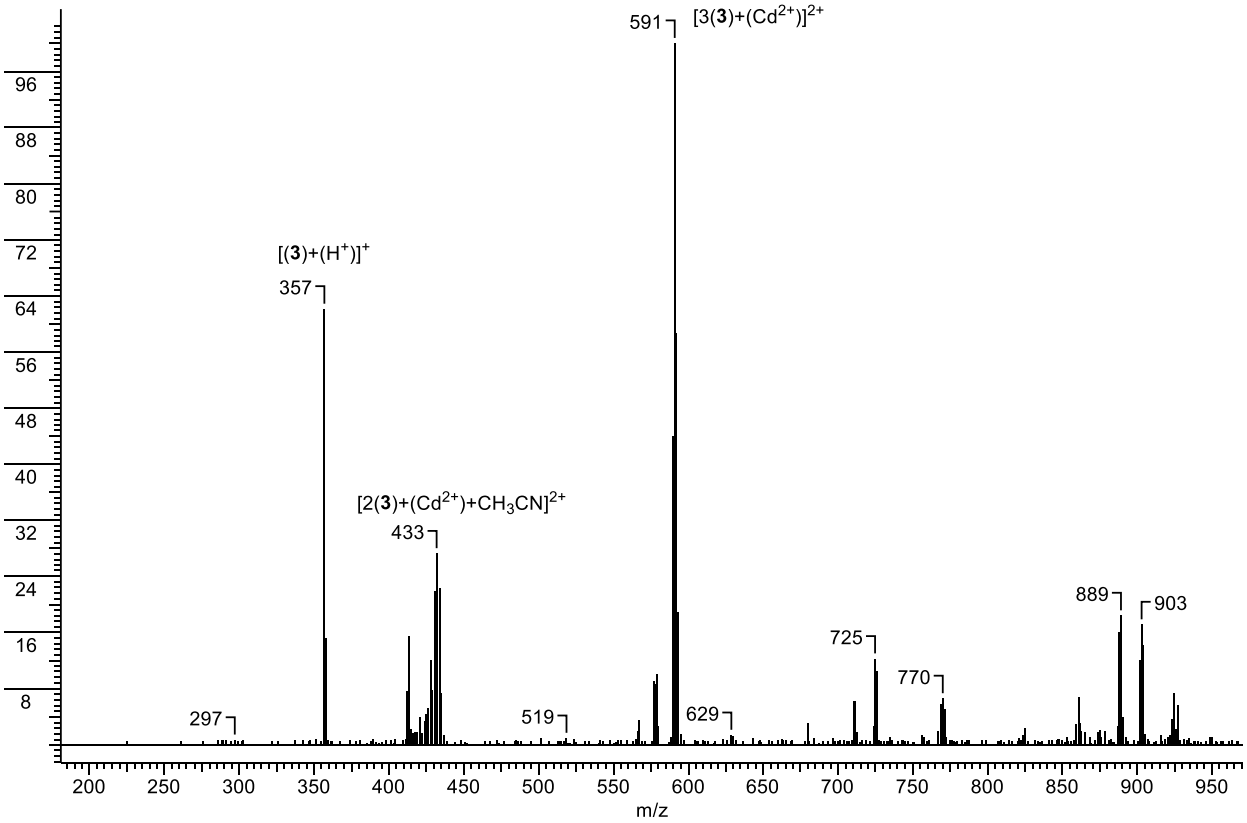


Figure S11. ESI-MS spectrum of mixture ligand **3** with Cd^{2+}, ratio 1:1.

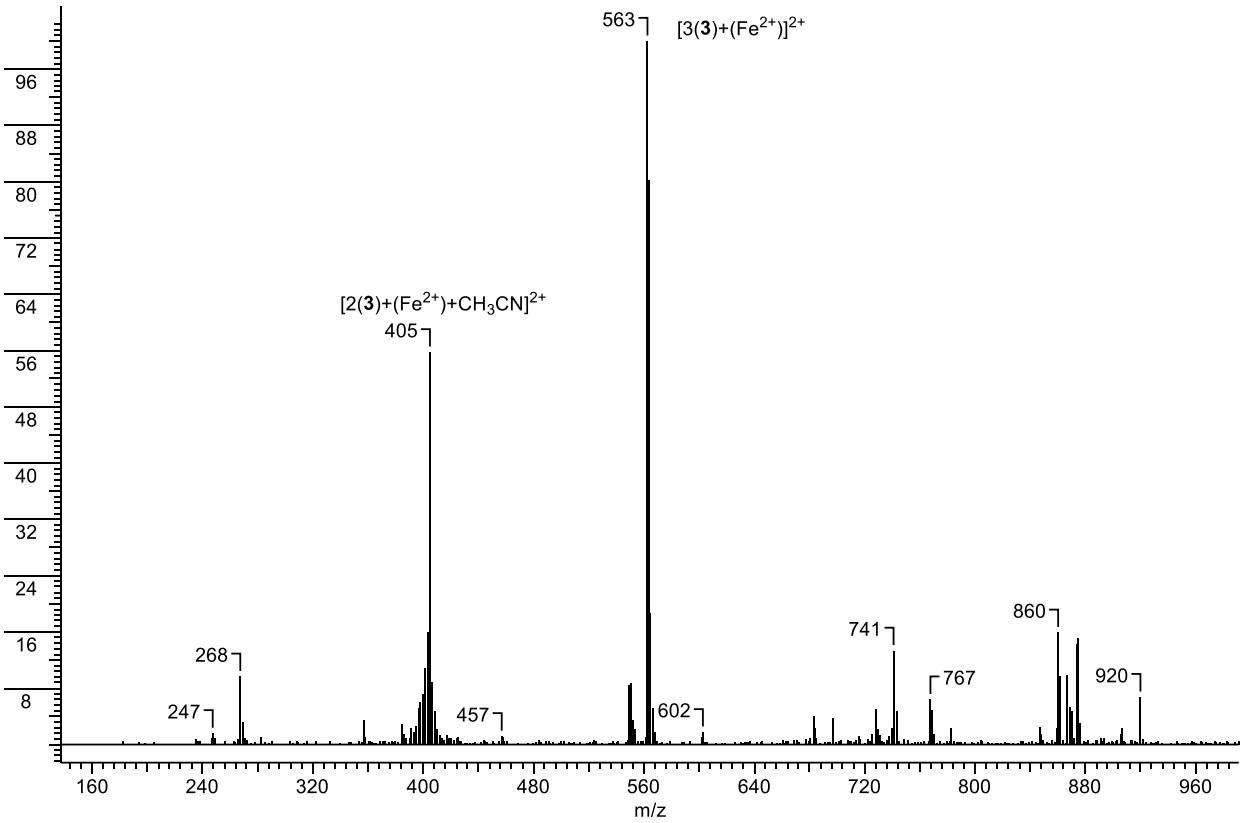


Figure S12. ESI-MS spectrum of mixture ligand **3** with Fe^{2+}, ratio 1:1.

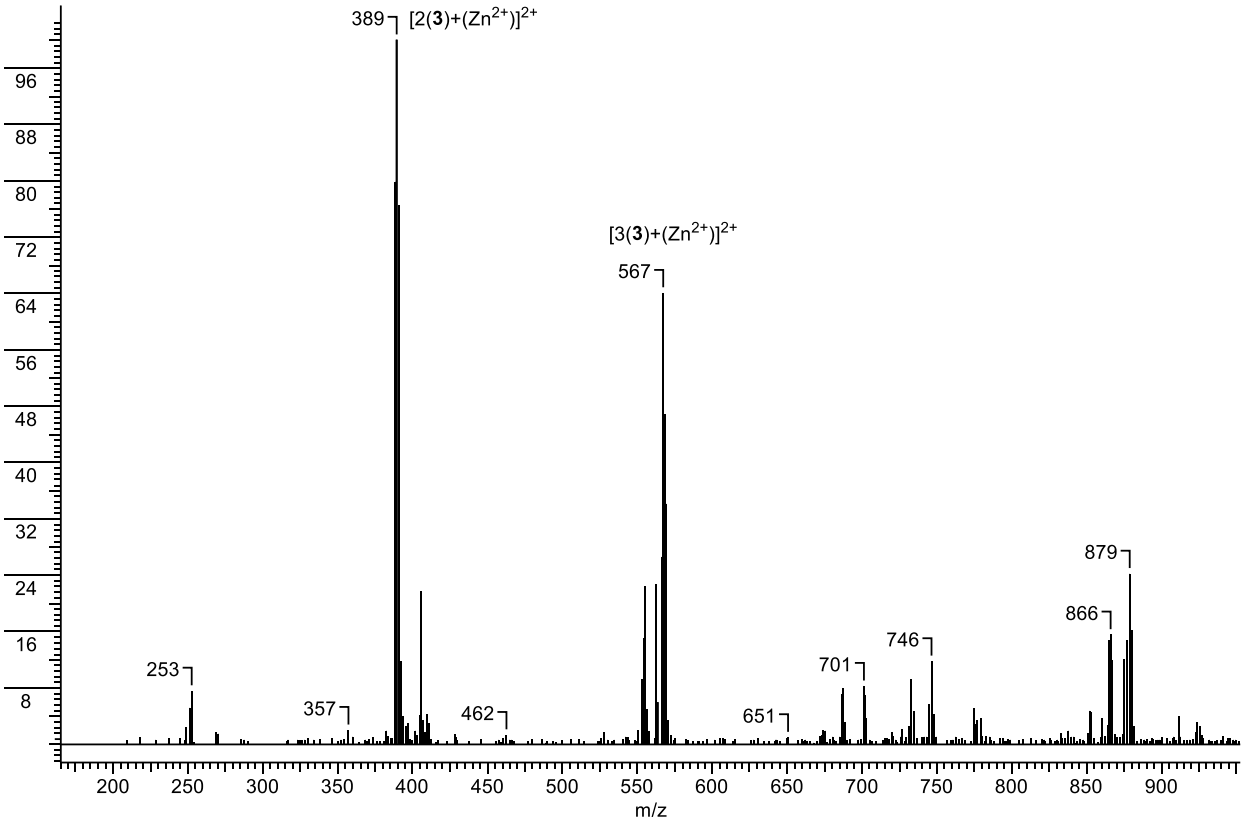


Figure S13. ESI-MS spectrum of mixture ligand **3** with Zn^{2+}, ratio 1:1.

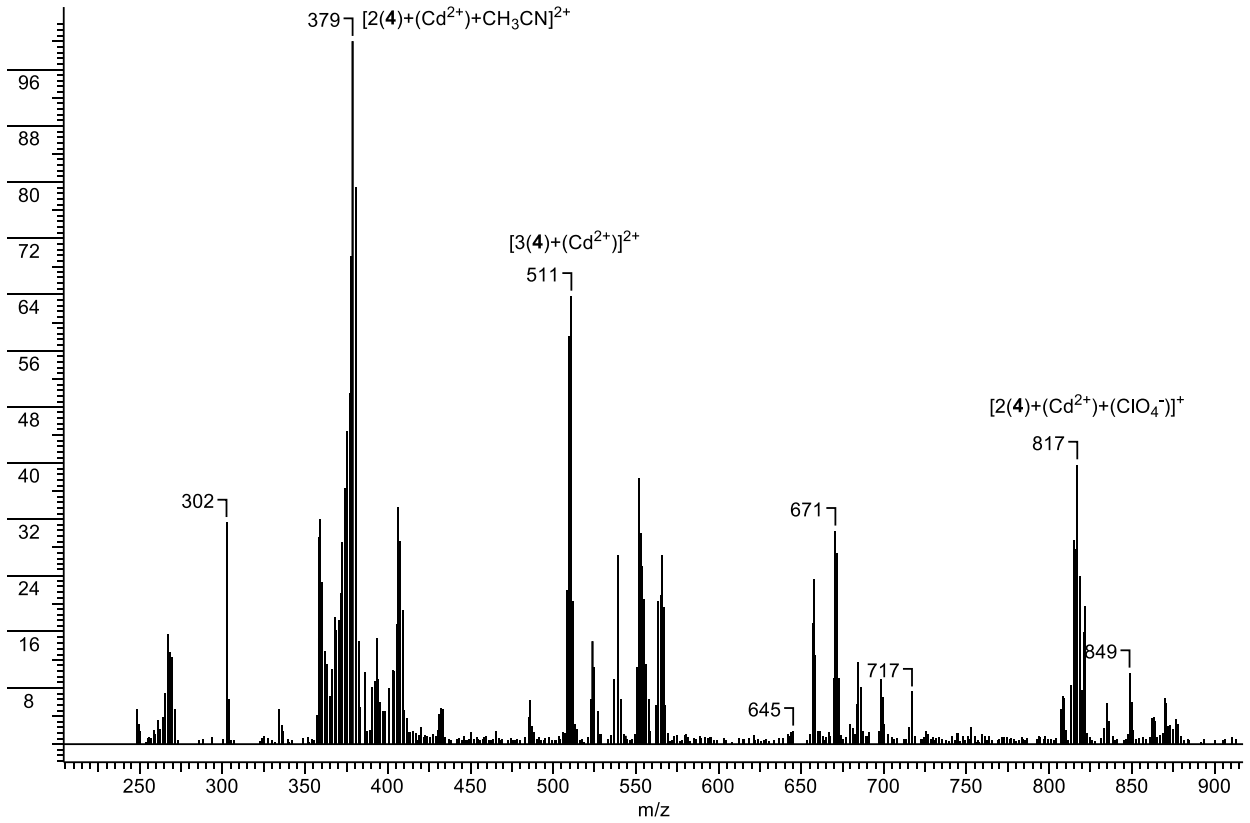


Figure S14. ESI-MS spectrum of mixture ligand **4** with Cd^{2+}, ratio 1:1.

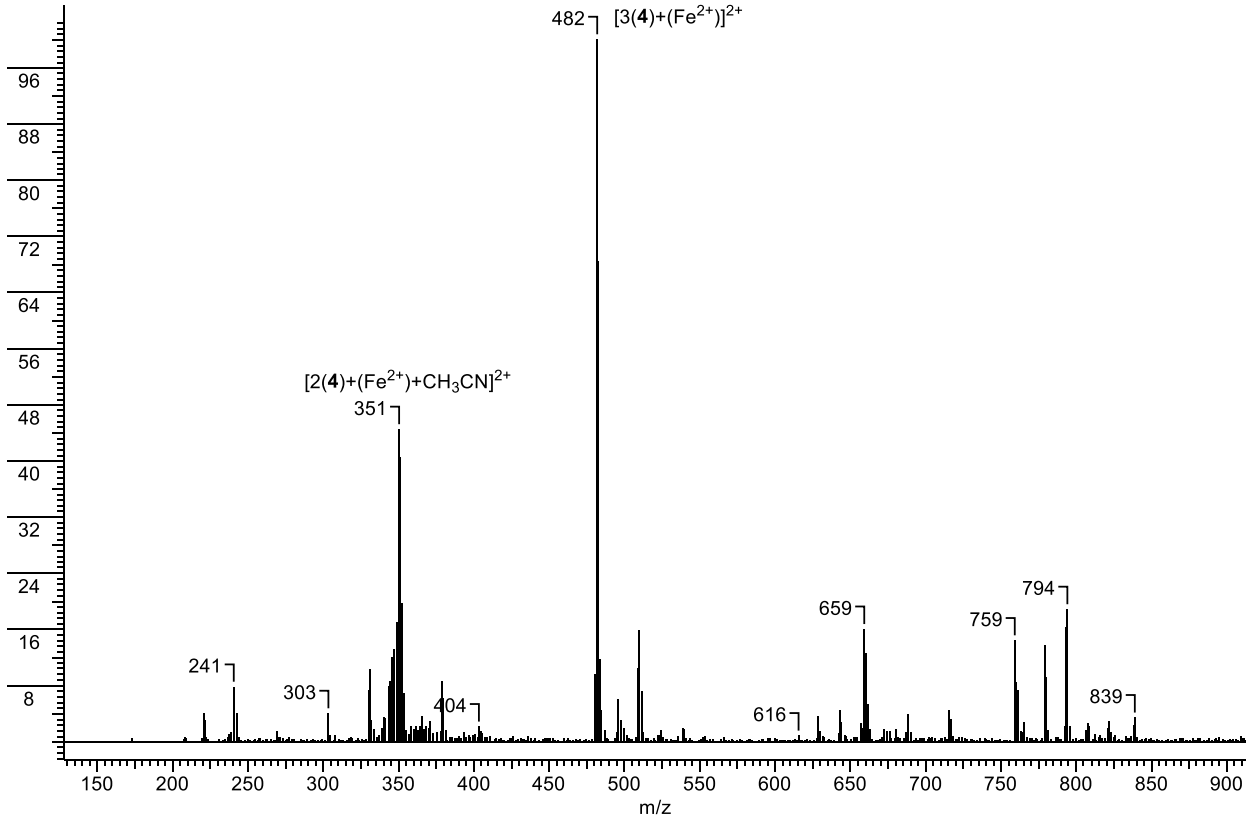


Figure S15. ESI-MS spectrum of mixture ligand **4** with Fe^{2+}, ratio 1:1.

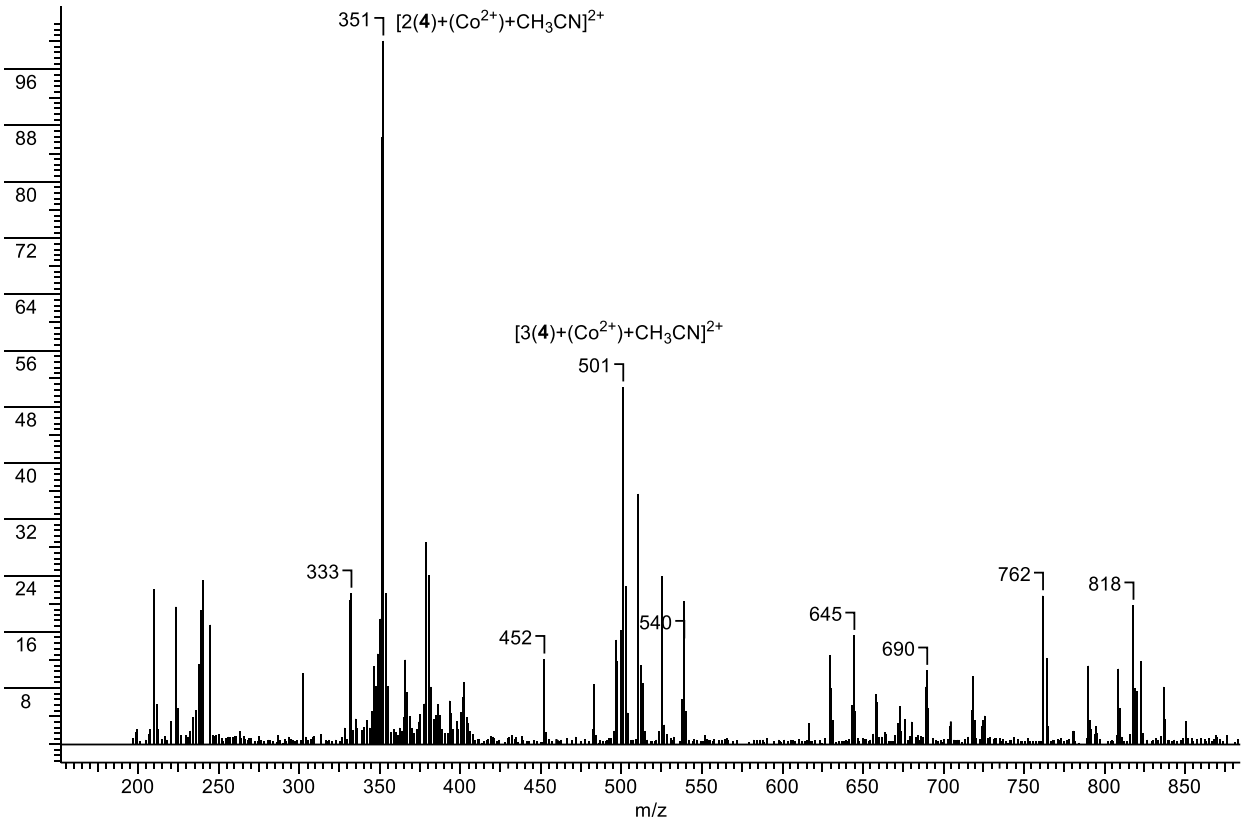


Figure S16. ESI-MS spectrum of mixture ligand **4** with Co^{2+}, ratio 1:1.

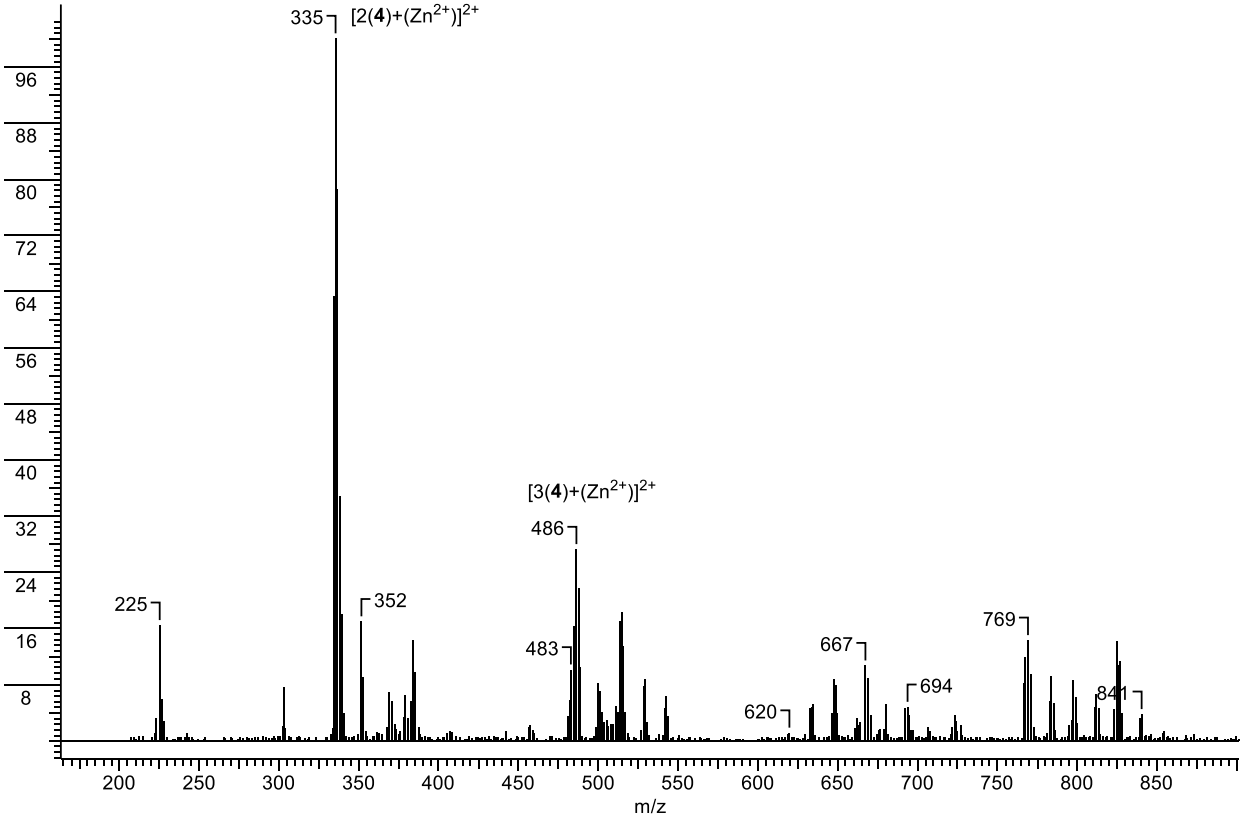


Figure S17. ESI-MS spectrum of mixture ligand **4** with Zn^{2+}, ratio 1:1.

Photophysical properties

Absorption and emission spectra

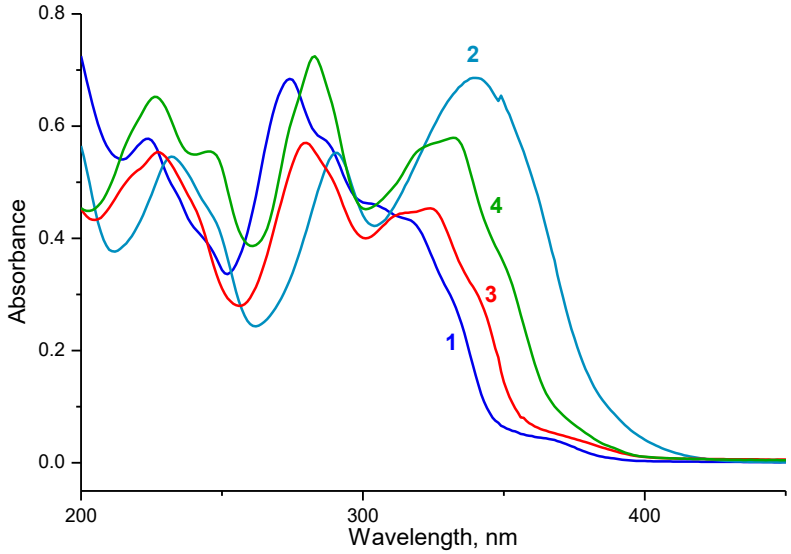


Figure S18. Electronic absorption spectra of **1-4** in acetonitrile, $C_{\mathbf{1\text{-}6}} = 2x10^{-5}$ M

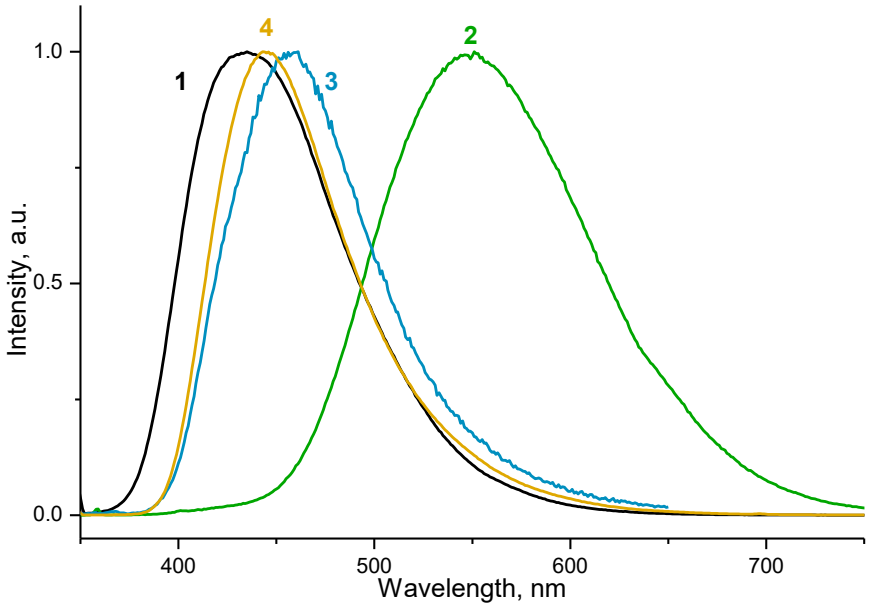


Figure S19. Normalized luminescence spectra **1-4** in acetonitrile. λ_{exc} 350 nm (**1**), 360 (**2**), 330 (**3**), 350 (**4**).

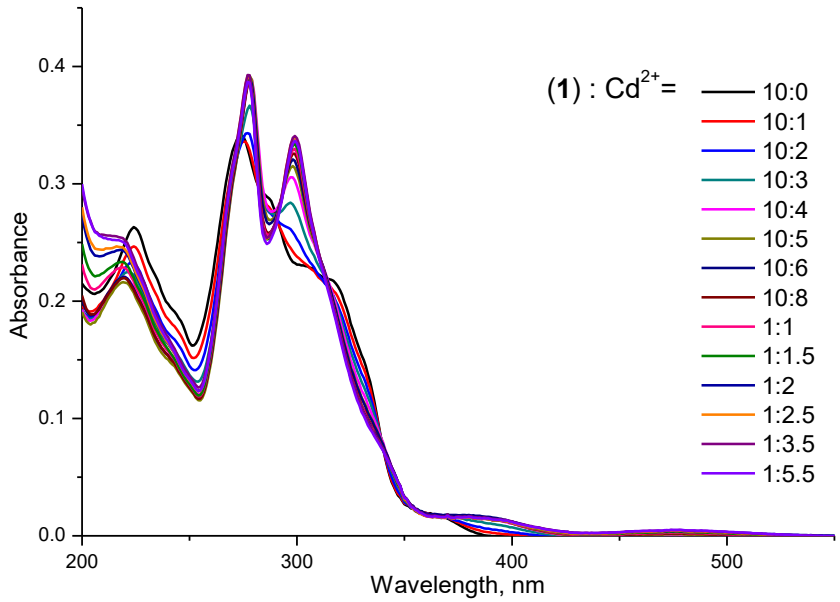


Figure S20. Electronic absorption spectra of a solution of ligand **1** in acetonitrile at various concentrations of cadmium(II) perchlorate. The initial concentration of the ligand $C_1=1x10^{-5}$ M, molar ratio ligand: metal indicated on the graph

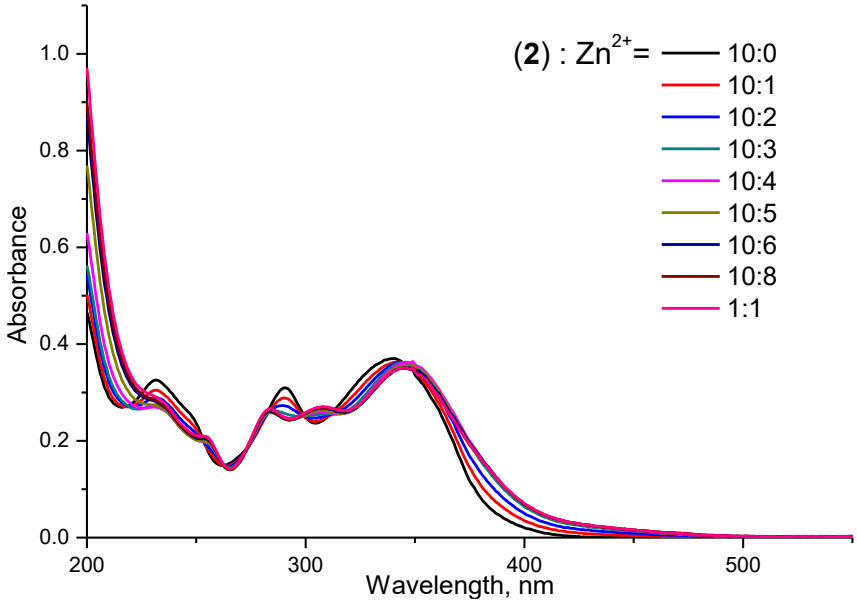


Figure S21. Electronic absorption spectra of a solution of ligand **2** in acetonitrile at various concentrations of zinc(II) perchlorate. The initial concentration of the ligand $C_2=1x10^{-5}$ M, molar ratio ligand: metal indicated on the graph

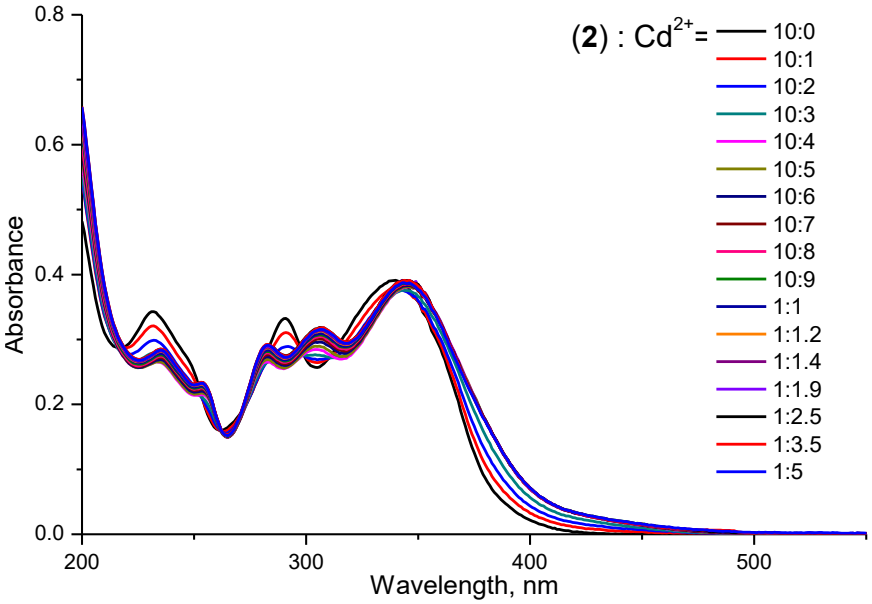


Figure S22. Electronic absorption spectra of a solution of ligand **2** in acetonitrile at various concentrations of cadmium (II) perchlorate. The initial concentration of the ligand $C_2=1x10^{-5}$ M, molar ratio ligand: metal indicated on the graph

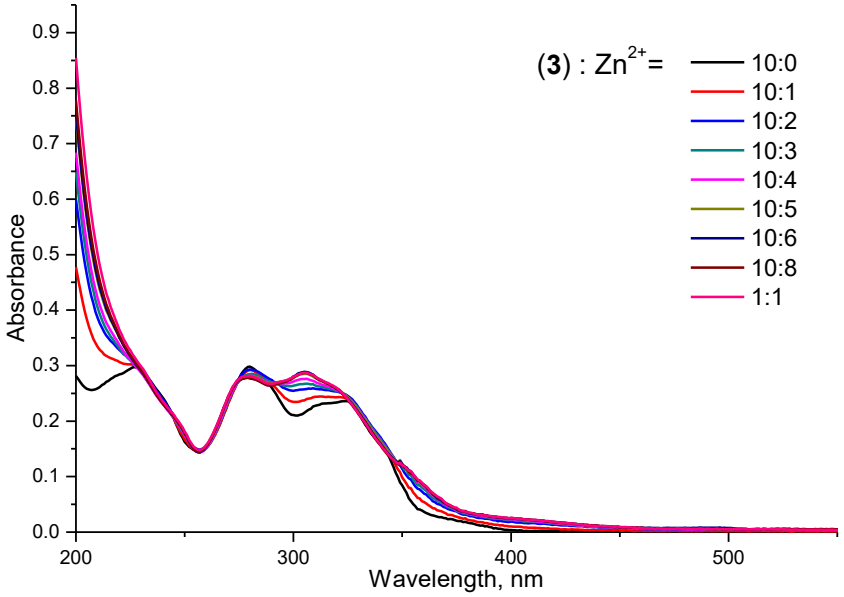


Figure S23. Electronic absorption spectra of a solution of ligand **3** in acetonitrile at various concentrations of zinc(II) perchlorate. The initial concentration of the ligand $C_3=1x10^{-5}$ M, molar ratio ligand: metal indicated on the graph

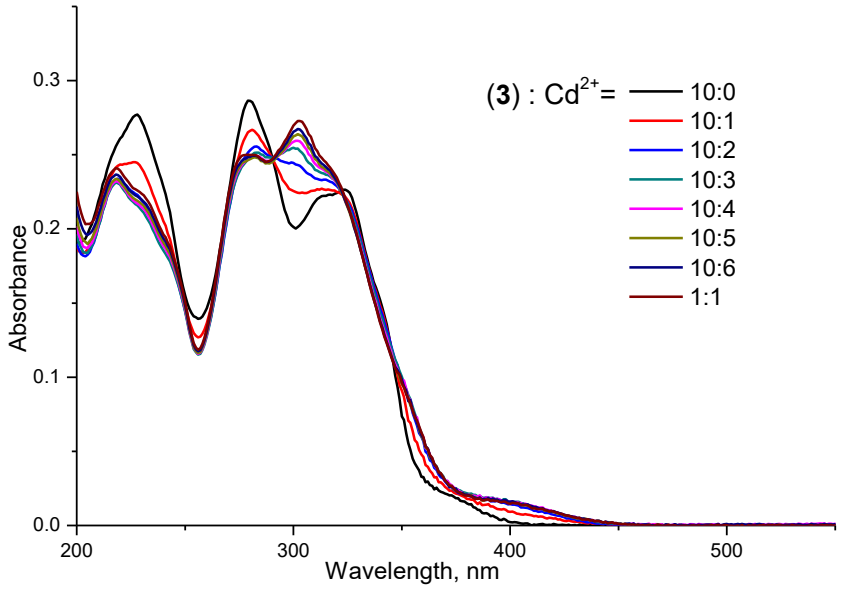


Figure S24. Electronic absorption spectra of a solution of ligand **3** in acetonitrile at various concentrations of cadmium(II) perchlorate. The initial concentration of the ligand $C_3=1x10^{-5}$ M, molar ratio ligand: metal indicated on the graph

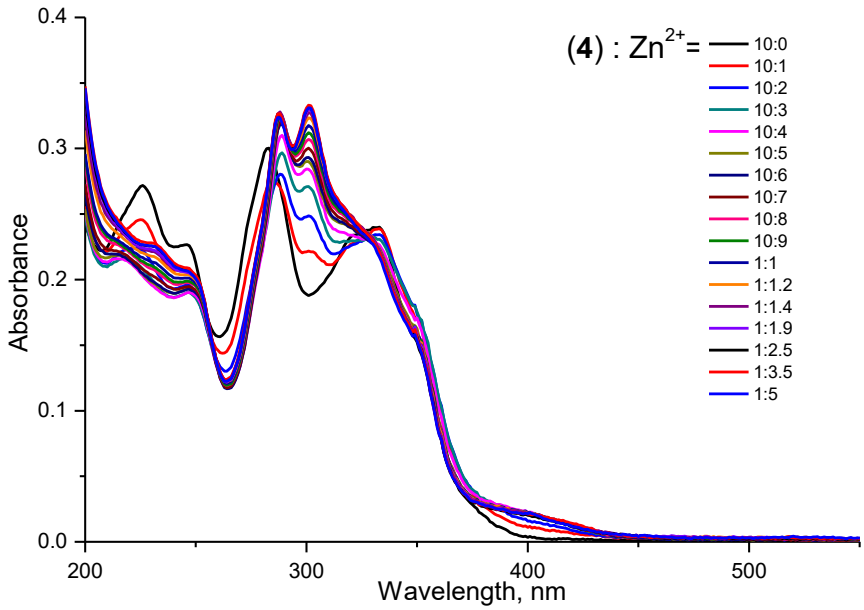


Figure S25. Electronic absorption spectra of a solution of ligand **4** in acetonitrile at various concentrations of zinc(II) perchlorate. The initial concentration of the ligand $C_4=1x10^{-5}$ M, molar ratio ligand: metal indicated on the graph

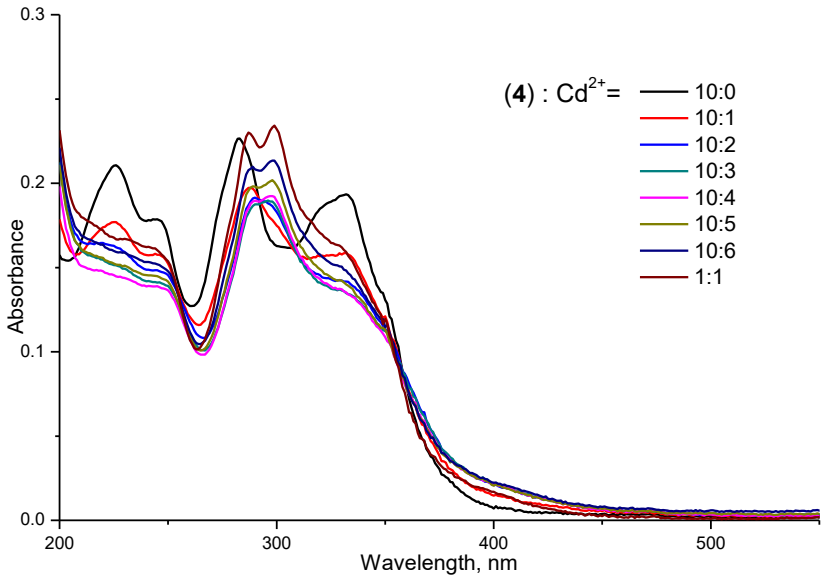


Figure S26. Electronic absorption spectra of a solution of ligand **4** in acetonitrile at various concentrations of cadmium(II) perchlorate. The initial concentration of the ligand $C_4=1x10^{-5}$ M, molar ratio ligand: metal indicated on the graph

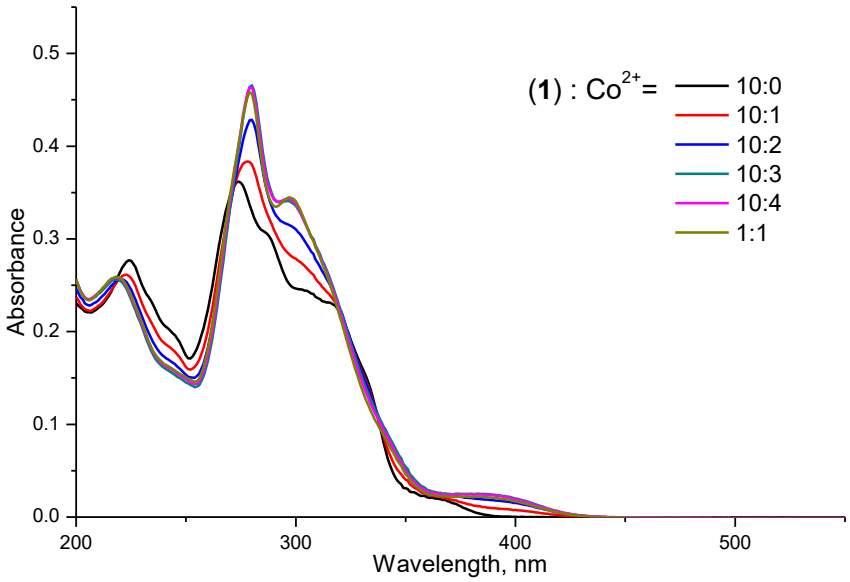


Figure S27. Electronic absorption spectra of a solution of ligand **1** in acetonitrile at various concentrations of cobalt(II) perchlorate. The initial concentration of the ligand $C_1=1x10^{-5}$ M, molar ratio ligand: metal indicated on the graph

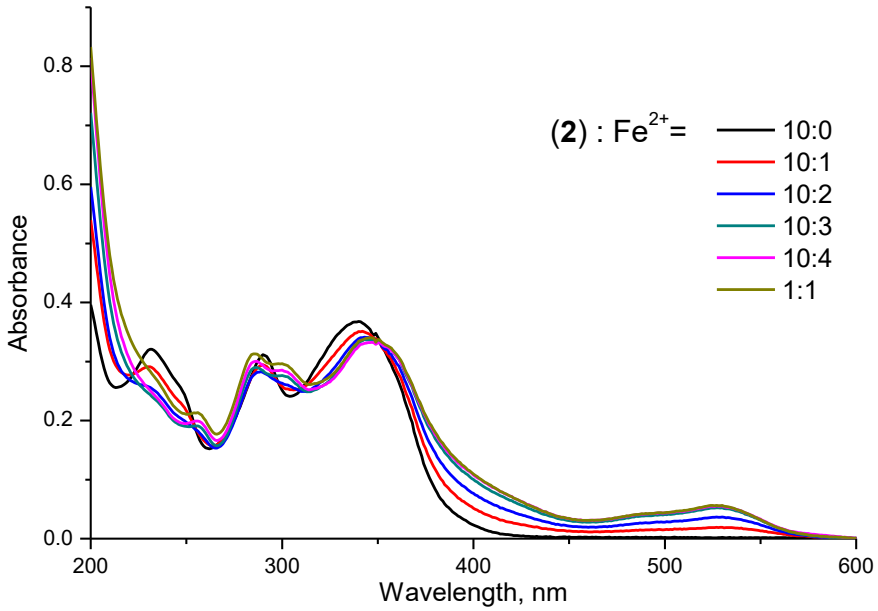


Figure S28. Electronic absorption spectra of a solution of ligand **2** in acetonitrile at various concentrations of iron(II) perchlorate. The initial concentration of the ligand $C_2=1x10^{-5}$ M, molar ratio ligand: metal indicated on the graph

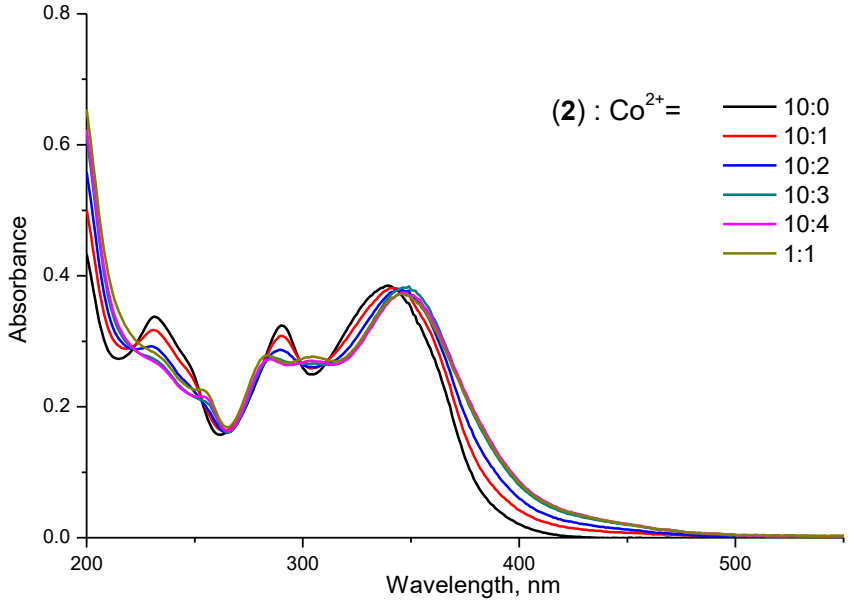


Figure S29. Electronic absorption spectra of a solution of ligand **2** in acetonitrile at various concentrations of cobalt(II) perchlorate. The initial concentration of the ligand $C_2=1x10^{-5}$ M, molar ratio ligand: metal indicated on the graph

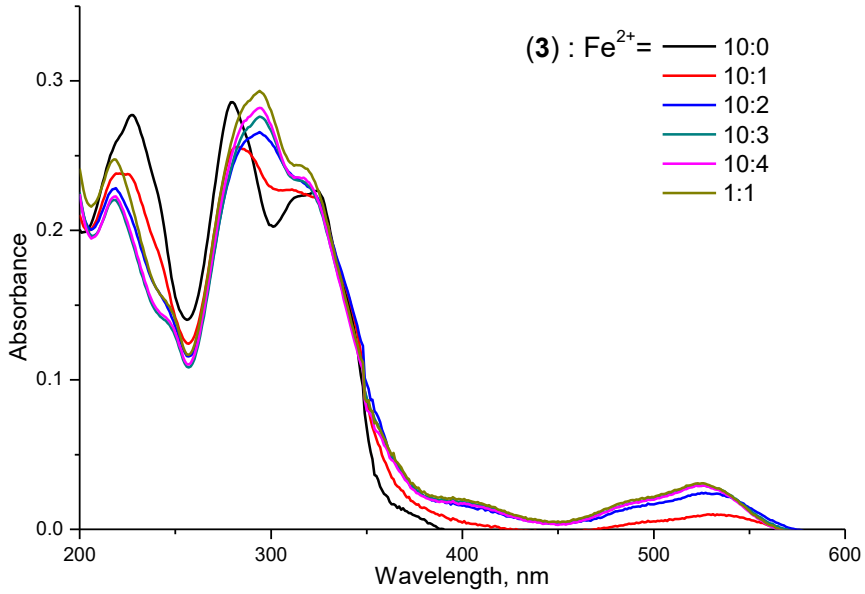


Figure S30. Electronic absorption spectra of a solution of ligand **3** in acetonitrile at various concentrations of iron(II) perchlorate. The initial concentration of the ligand $C_3=1x10^{-5}$ M, molar ratio ligand: metal indicated on the graph

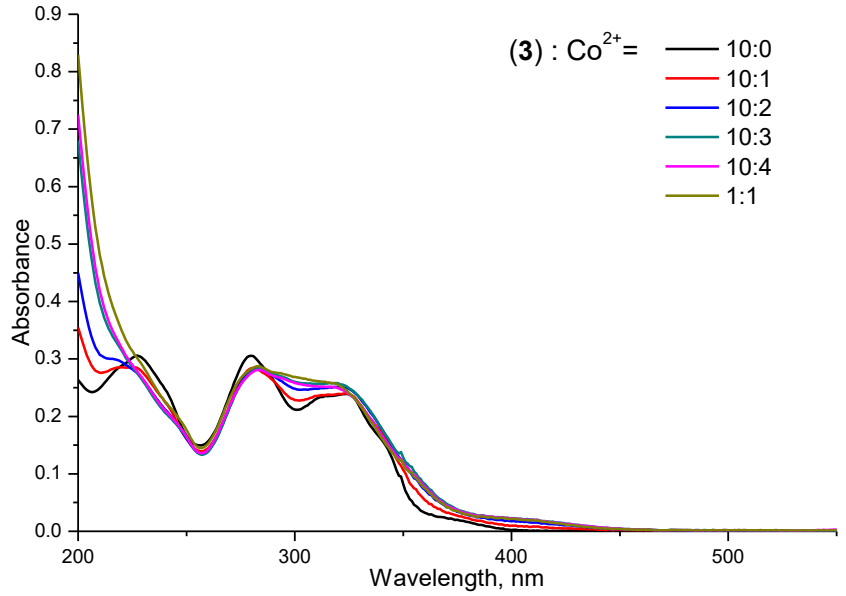


Figure S31. Electronic absorption spectra of a solution of ligand **3** in acetonitrile at various concentrations of cobalt(II) perchlorate. The initial concentration of the ligand $C_3=1x10^{-5}$ M, molar ratio ligand: metal indicated on the graph

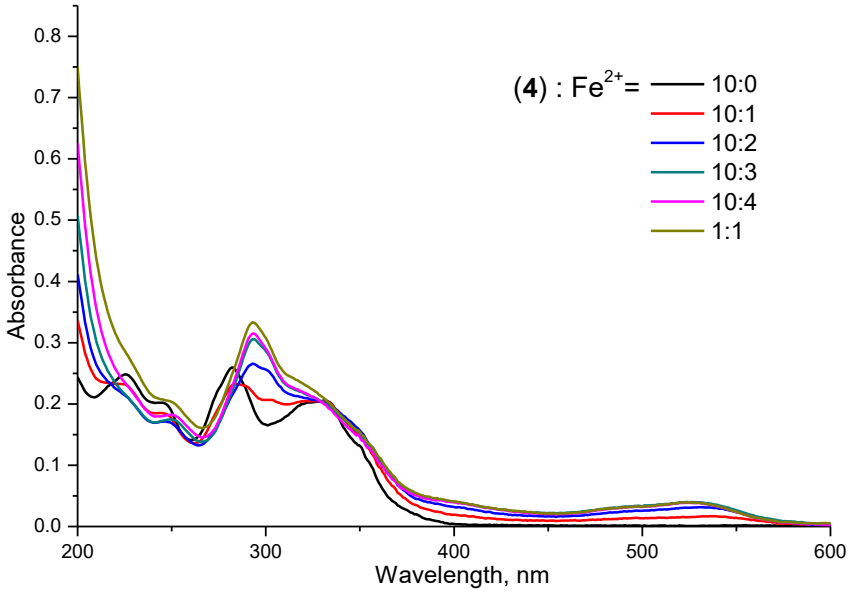


Figure S32. Electronic absorption spectra of a solution of ligand **4** in acetonitrile at various concentrations of iron(II) perchlorate. The initial concentration of the ligand $C_4=1x10^{-5}$ M, molar ratio ligand: metal indicated on the graph

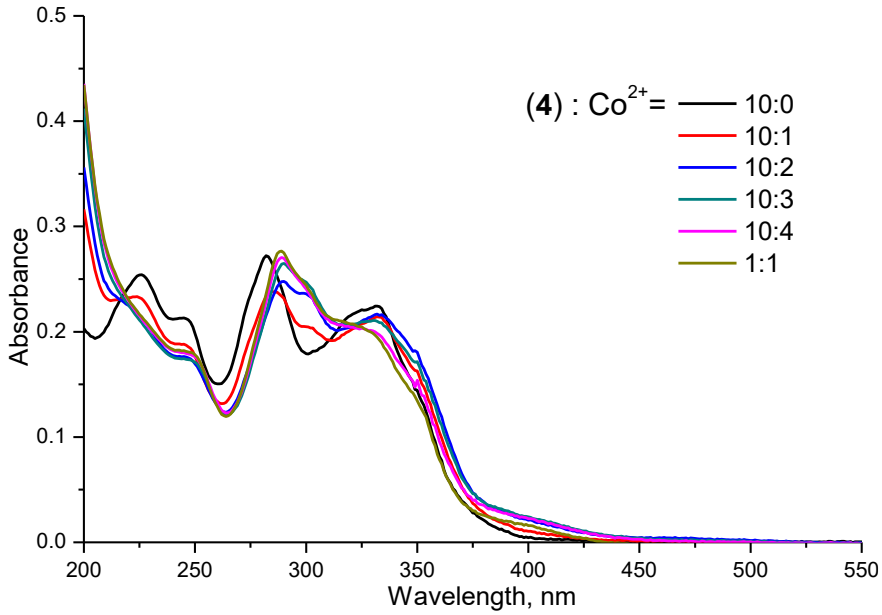


Figure S33. Electronic absorption spectra of a solution of ligand **4** in acetonitrile at various concentrations of cobalt(II) perchlorate. The initial concentration of the ligand $C_4=1x10^{-5}$ M, molar ratio ligand: metal indicated on the graph

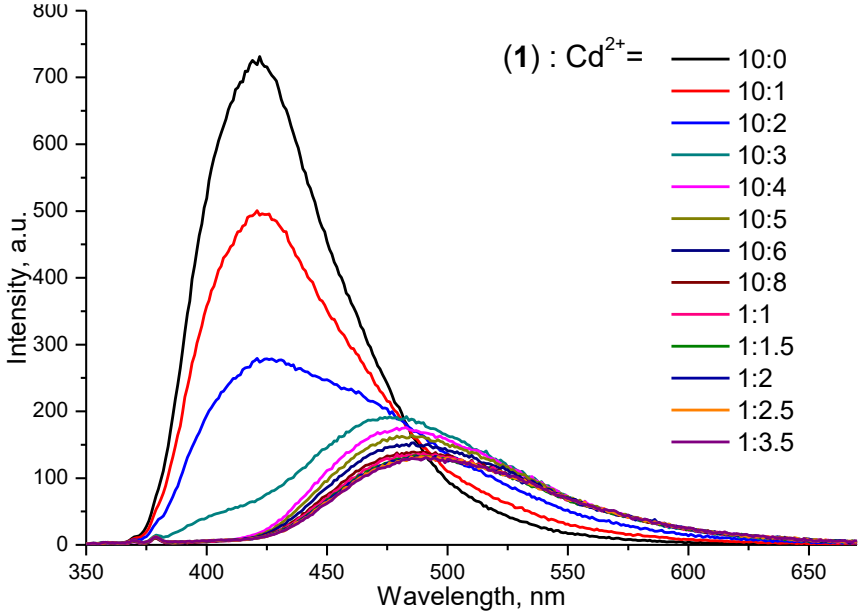


Figure S34. Emission spectra of a solution of ligand **1** in acetonitrile at various concentrations of cadmium(II) perchlorate.

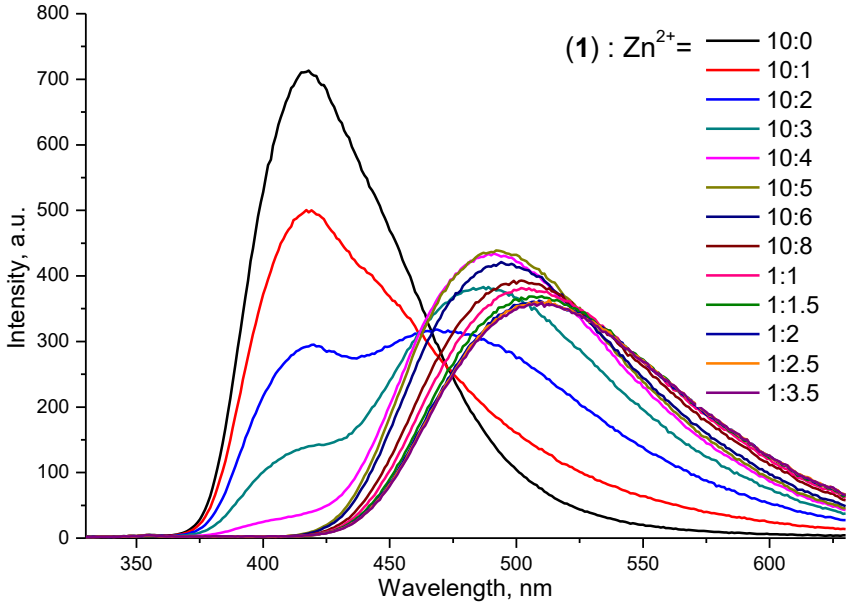


Figure S35. Emission spectra of a solution of ligand **1** in acetonitrile at various concentrations of zinc(II) perchlorate.

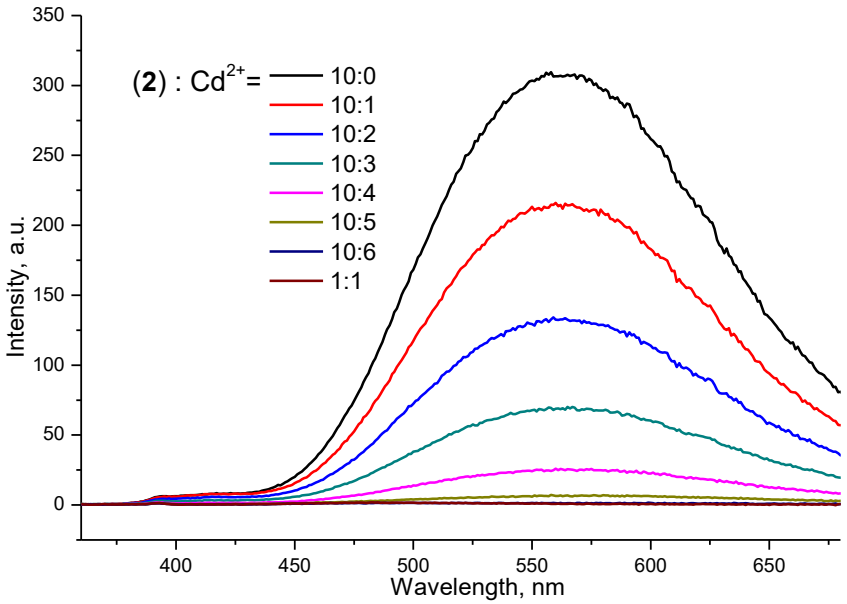


Figure S36. Emission spectra of a solution of ligand **2** in acetonitrile at various concentrations of cadmium(II) perchlorate.

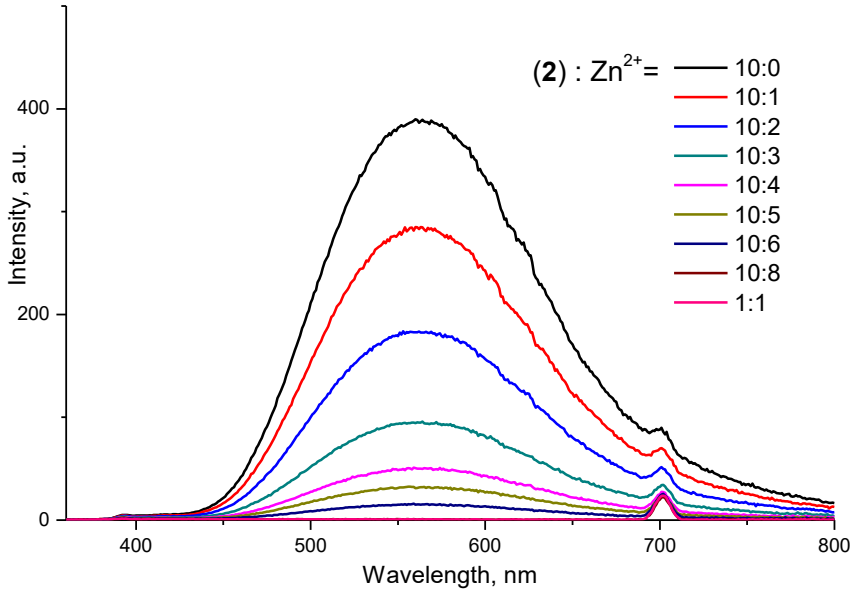


Figure S37. Emission spectra of a solution of ligand **2** in acetonitrile at various concentrations of zinc(II) perchlorate.

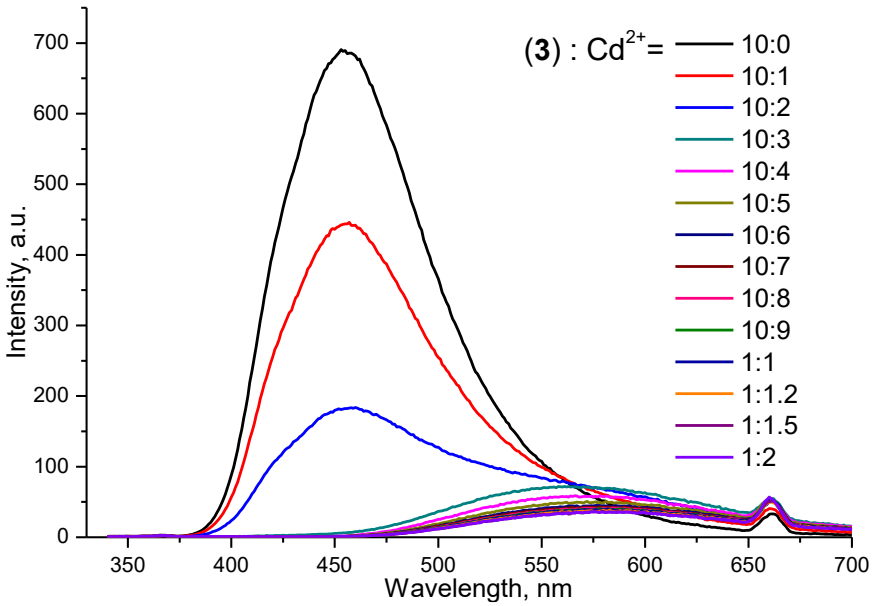


Figure S38. Emission spectra of a solution of ligand **3** in acetonitrile at various concentrations of cadmium(II) perchlorate.

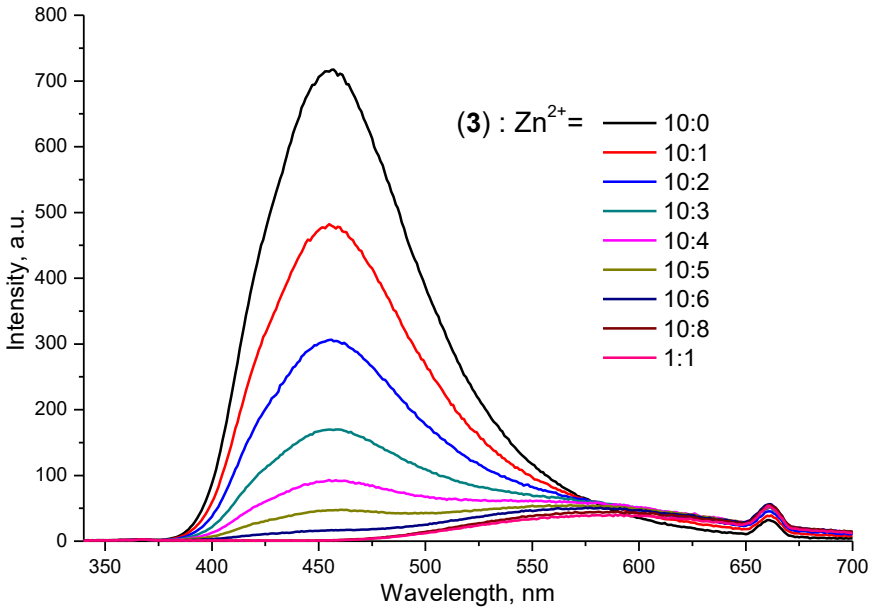


Figure S39. Emission spectra of a solution of ligand **3** in acetonitrile at various concentrations of zinc(II) perchlorate.

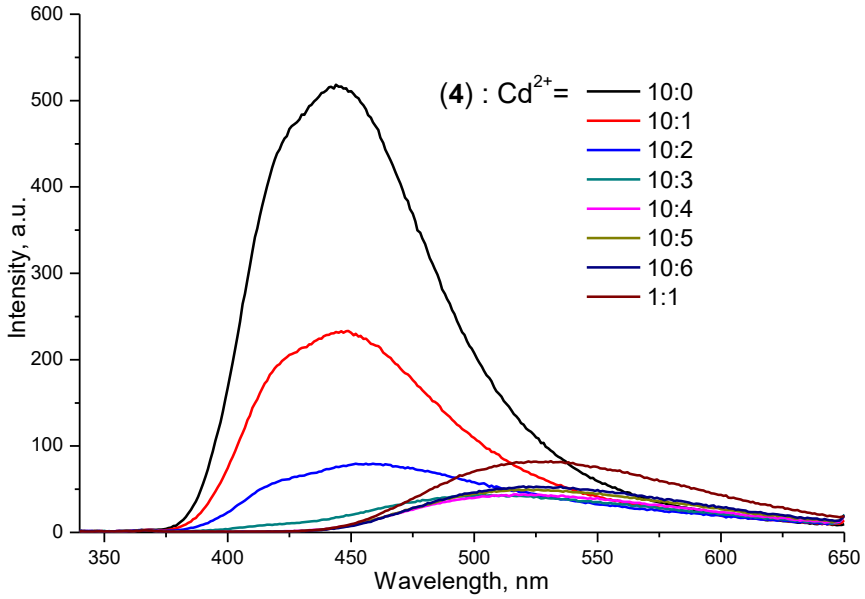


Figure S40. Emission spectra of a solution of ligand **4** in acetonitrile at various concentrations of cadmium(II) perchlorate.

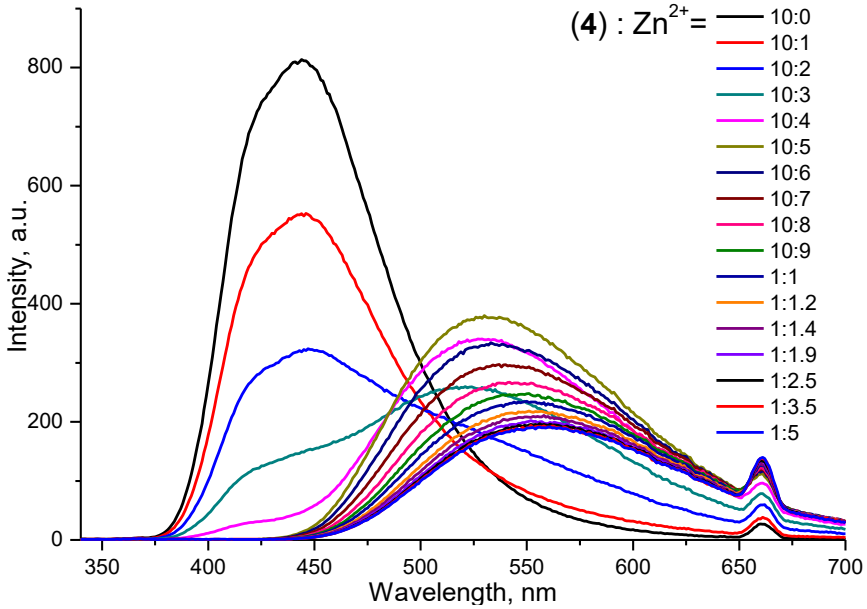


Figure S41. Emission spectra of a solution of ligand **4** in acetonitrile at various concentrations of zinc(II) perchlorate.

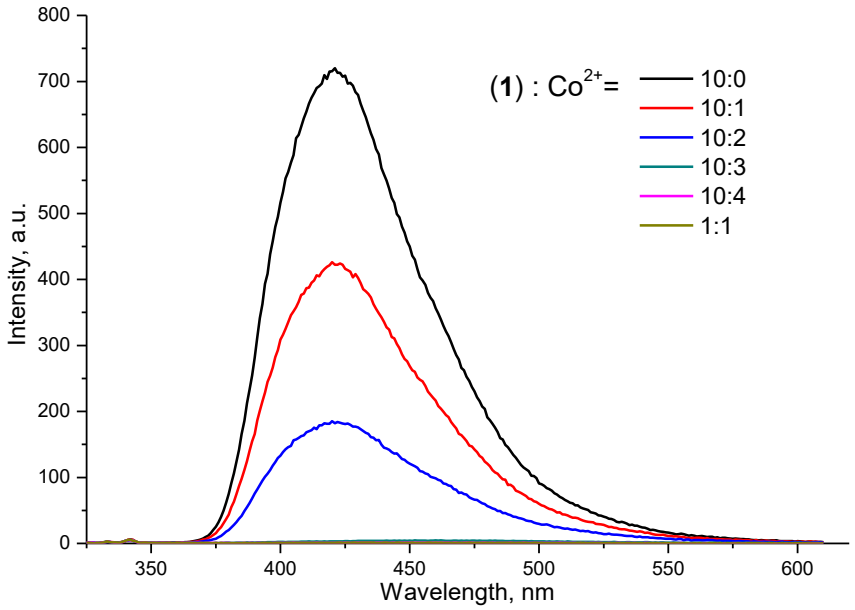


Figure S42. Emission spectra of a solution of ligand **1** in acetonitrile at various concentrations cobalt(II) perchlorate.

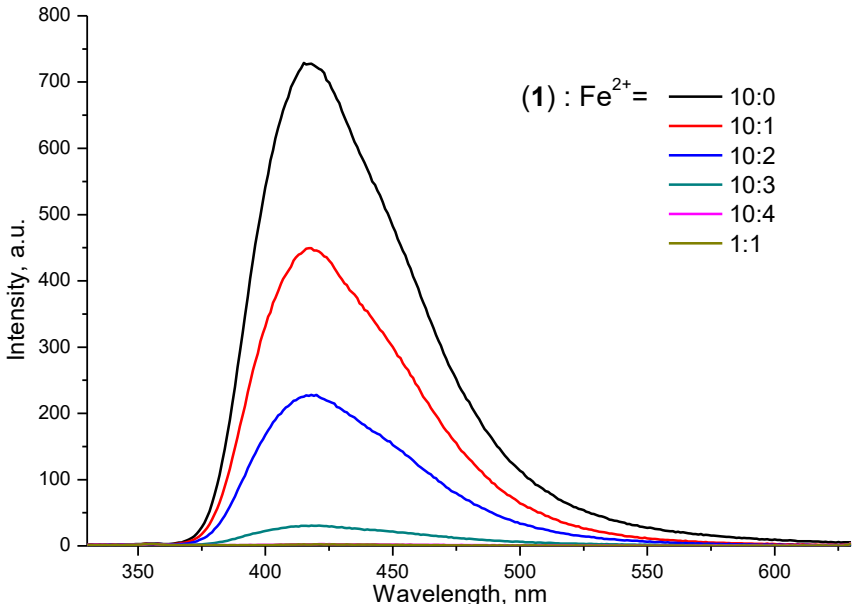


Figure S43. Emission spectra of a solution of ligand **1** in acetonitrile at various concentrations iron(II) perchlorate.

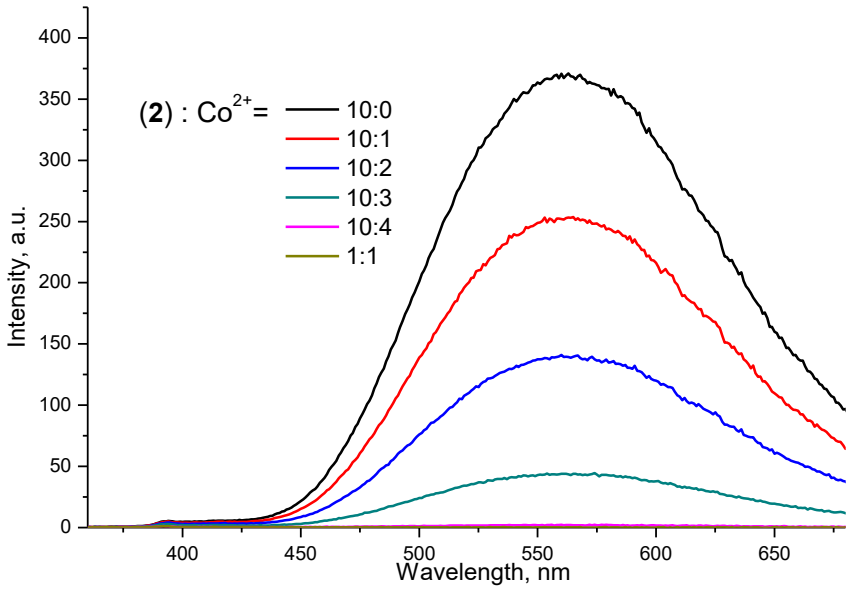


Figure S44. Emission spectra of a solution of ligand **2** in acetonitrile at various concentrations of cobalt(II) perchlorate.

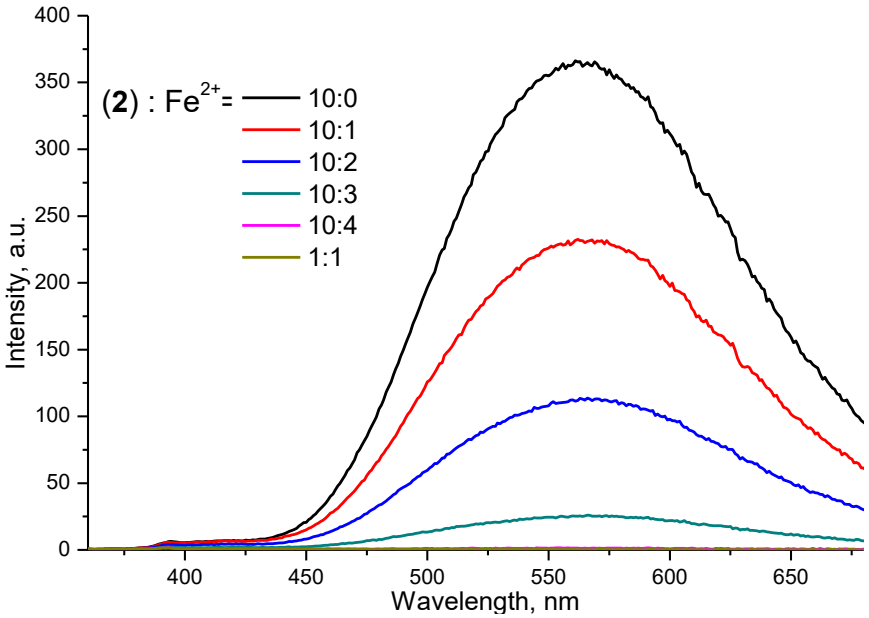


Figure S45. Emission spectra of a solution of ligand **2** in acetonitrile at various concentrations of iron(II) perchlorate.

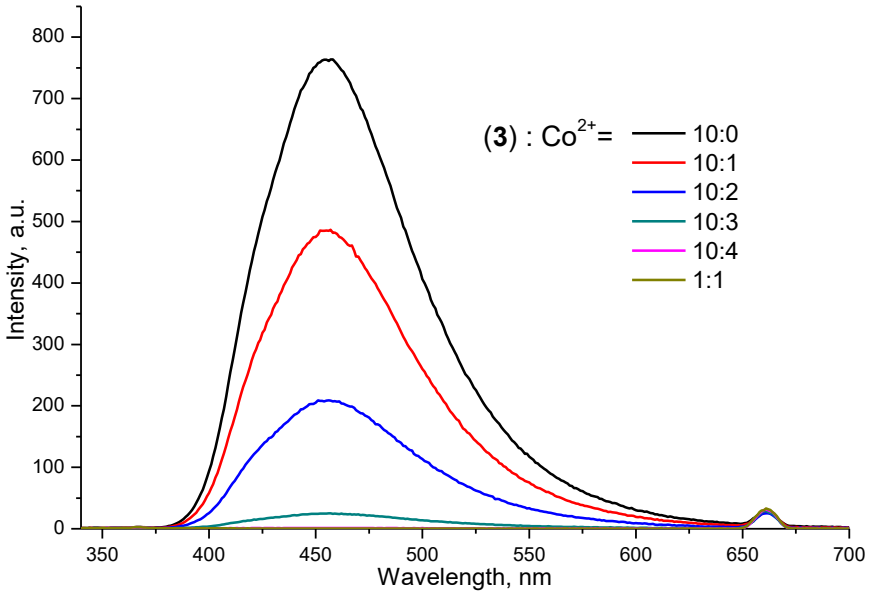


Figure S46. Emission spectra of a solution of ligand **3** in acetonitrile at various concentrations of cobalt(II) perchlorate.

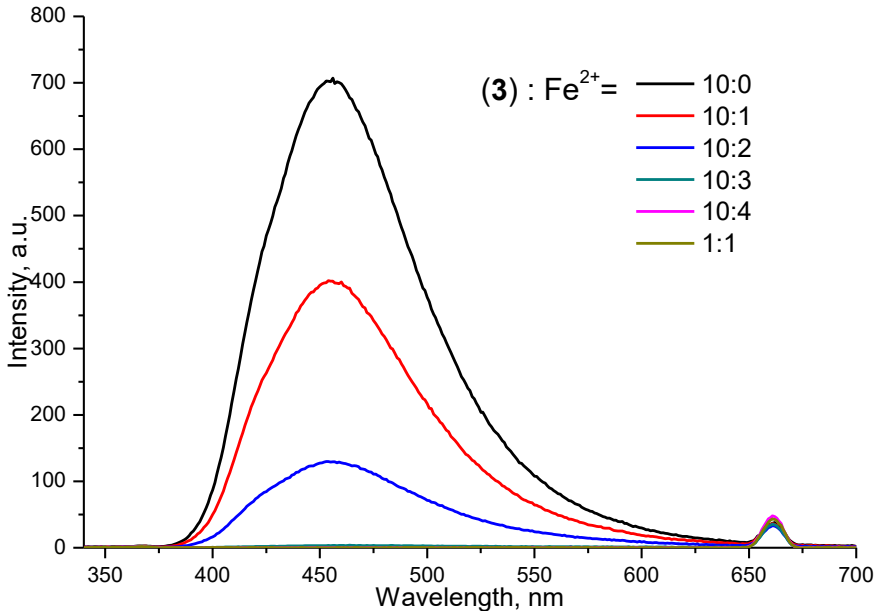


Figure S47. Emission spectra of a solution of ligand **3** in acetonitrile at various concentrations of iron(II) perchlorate.

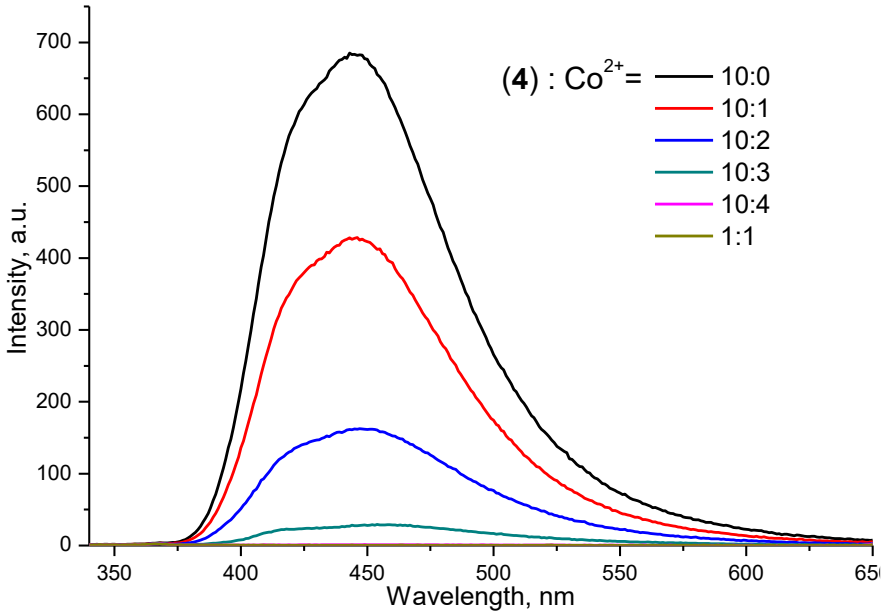


Figure S48. Emission spectra of a solution of ligand **4** in acetonitrile at various concentrations of cobalt(II) perchlorate.

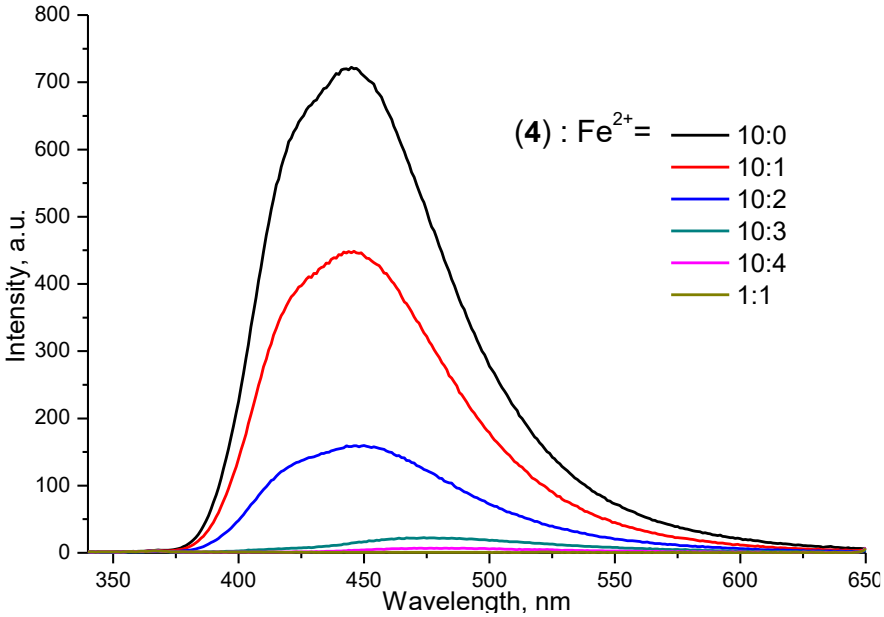


Figure S49. Emission spectra of a solution of ligand **4** in acetonitrile at various concentrations of iron(II) perchlorate.

Fluorescence quantum yield

All measured fluorescence spectra were corrected for nonuniformity of detector spectral sensitivity. Rhodamine 6G (φ_{fl} = 0.95) in ethanol and quinine sulfate in 0.5 M H_2SO_4 (φ_{fl} = 0.55) were used as a reference for the fluorescence quantum yield measurements. The fluorescence quantum yields were calculated using equation:

$$\varphi_i = \varphi_0 \frac{(1 - 10^{-A_0}) * S_i * {n_i}^2}{(1 - 10^{-A_i}) * S_0 * {n_0}^2},$$

where φ_i and φ_0 are the fluorescence quantum yields of the studied solution and the standard compound, respectively; A_i and A_0 are the absorptions of the studied solution and the standard, respectively; S_i and S_0 are the areas underneath the curves of the fluorescence spectra of the studied solution and the standard, respectively; and n_i and n_0 are the refractive indices of the solvents for the substance under study and the standard compound (n_i = 1.3404, acetonitrile; n_0 = 1.361, ethanol).

References

S1. A. R. Day and E. A. Steck, *J. Am. Chem. Soc.*, 1943, **65**, 452.
S2. R. H. Zheng, H. C. Guo, H. J. Jiang, K. H. Xu, B. B. Liu, W. L. Sun and Z. Q. Shen, *Chin. Chem. Lett.*, 2010, **21**, 1270.
S3. J.-Z. Wu, B.-H. Ye, L. Wang, L.-N. Ji, J.-Y. Zhou, R.-H. Li and Z.-Y. Zhou, *J. Chem. Soc., Dalton Trans.*, 1997, 1395.
S4. J. Bingwen, W. Tao, T. Chunhong, Z. Manhua and S. Tao., *Bull. Chem. Soc. Japan.*, 2000, **73**, 1749
S5. O. A. Fedorova, N. E. Shepel, S. D. Tokarev, E. V. Lukovskaya, Y. A. Sotnikova, A. A. Moiseeva and Y. V. Fedorov, *New J. Chem.*, 2019, **43**, 2817.
S6. R. M. F. Batista, S. P. G. Costa, M. Belsley, C. Lodeiro and M. M. M. Raposo, *Tetrahedron*, 2008, **64**, 9230.