

Supplementary information

Control of metal-directed self-assembly by metal-amine interactions

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NMR and MS data

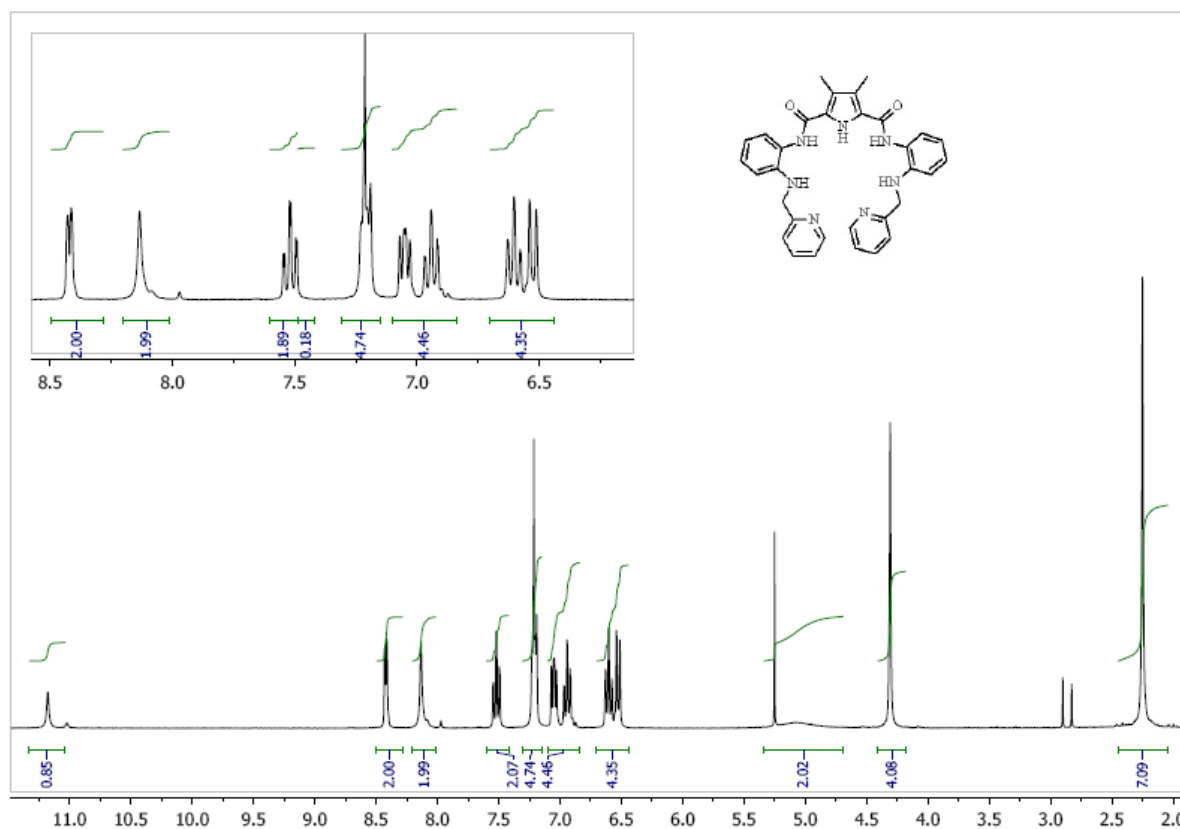


Figure S1. ¹H NMR of L in CDCl₃.

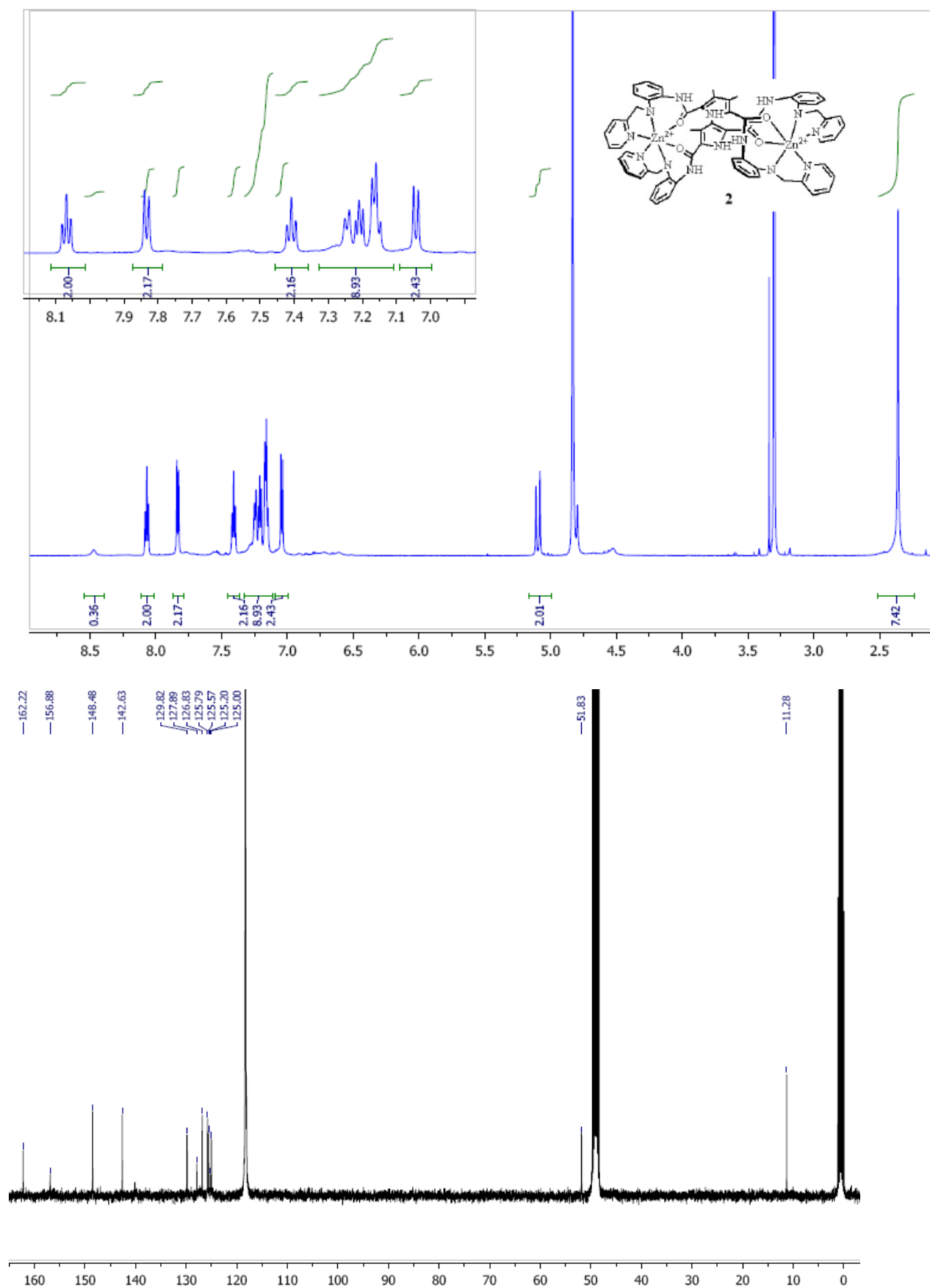


Figure S2. 1H and ^{13}C NMR of $L_2Zn_2(ClO_4)_4$ in CD_3OD and mixture of CD_3OD and CD_3CN respectively.

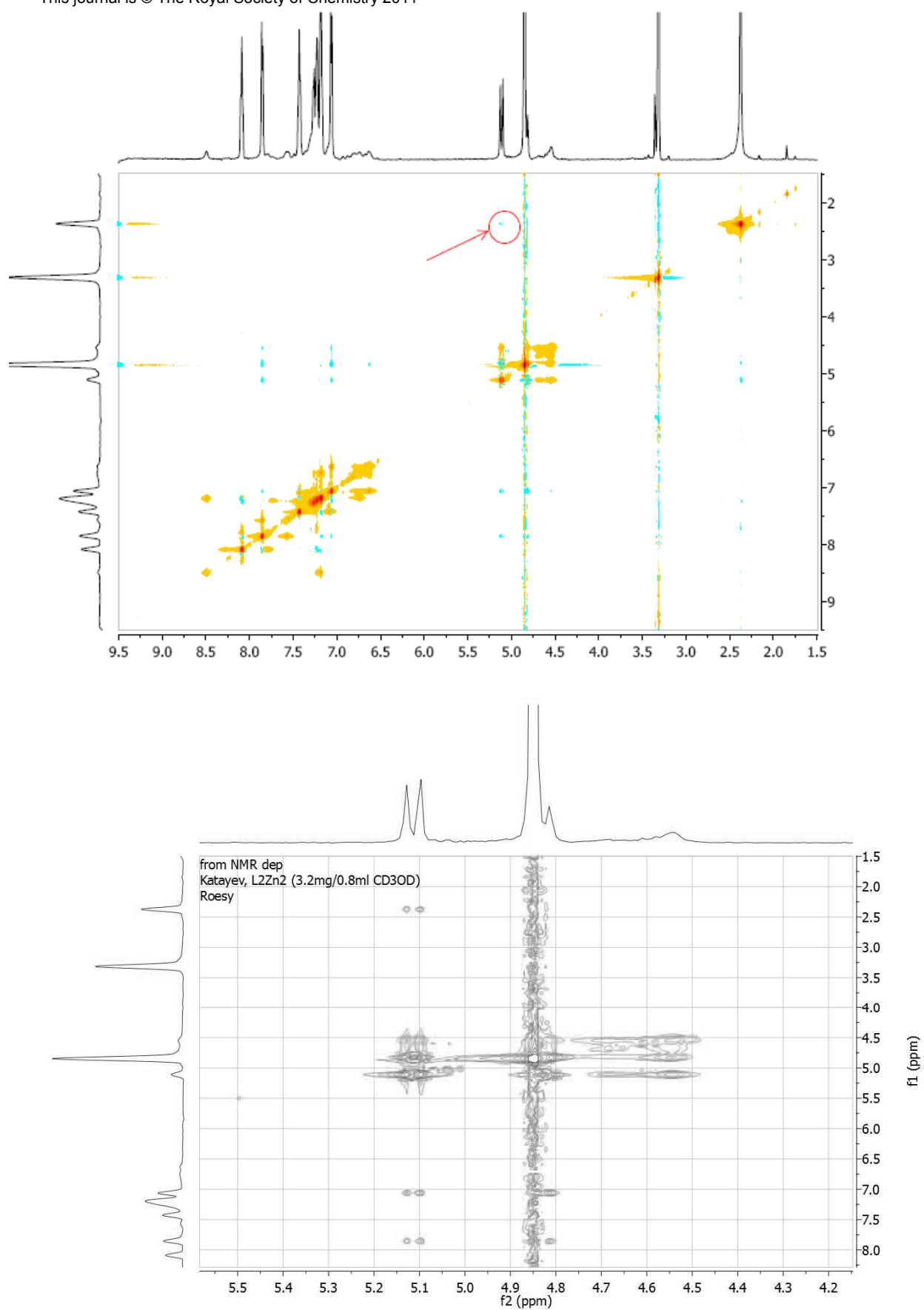


Figure S3. 2D-ROESY of **2** in CD_3OD , the cross peak between methylene and methyl signals is shown with the arrow. The expansion of the respective region is shown in black and white.

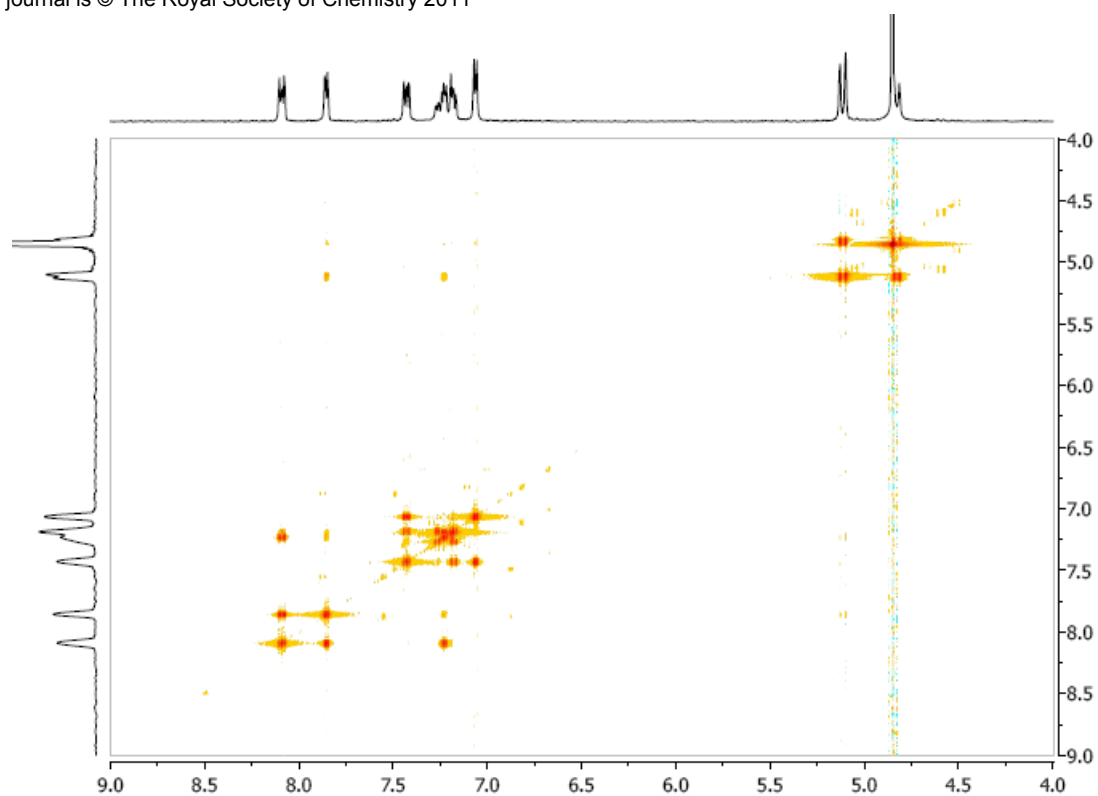


Figure S4. 2D-COSY of **2** in CD₃OD.

Study of complexes with *n*-propylamine and 1,5-diaminopentane (PDA)

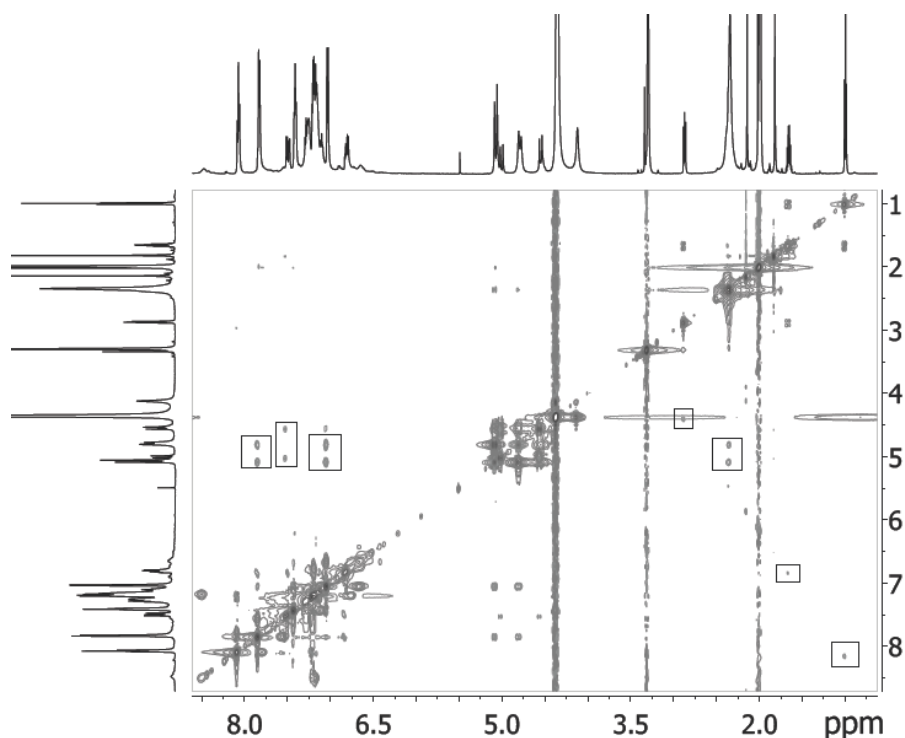


Figure S5. 2D-ROESY of the complex $L_2Zn_2(n\text{-propylamine})(ClO_4)_4$. Key cross peaks are marked with squares.

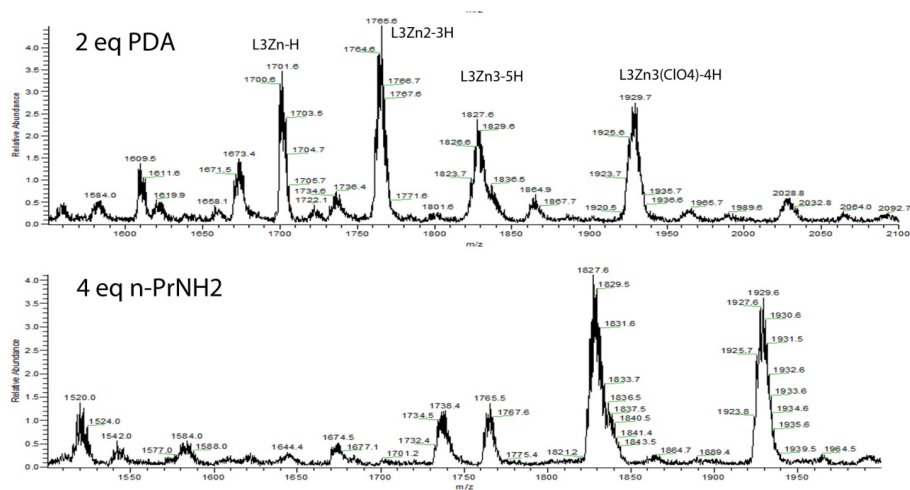


Figure S6. ESI-MS of the solutions prepared by the addition of certain equivalents of amines to the $L_2Zn_2(ClO_4)_4$ complex $c=10^{-3}M$ in methanol.

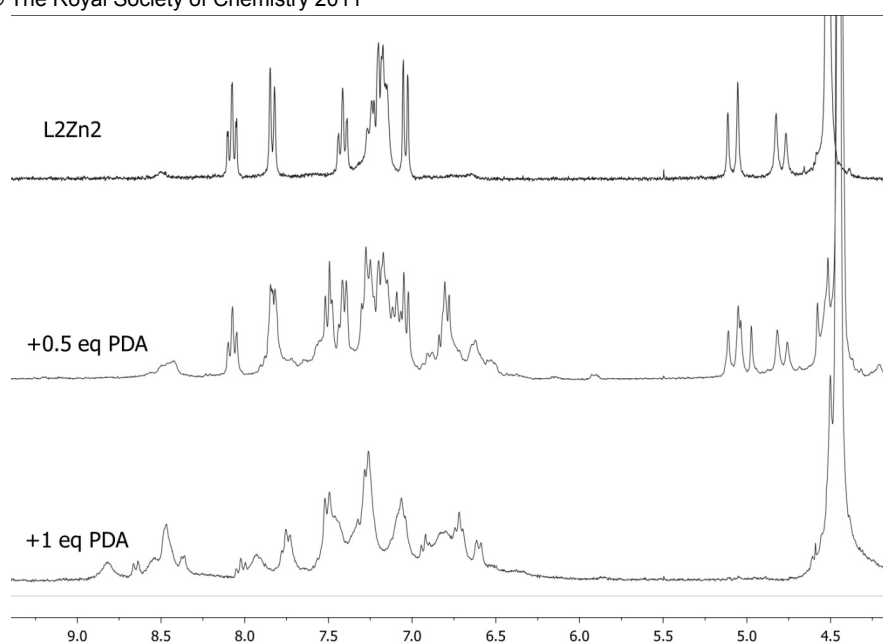


Figure S7. Addition of 0.5 equiv. of 1,5-pentanediamine to the solution of complex $L_2Zn_2(ClO_4)_4$ ($c=10^{-3}$) in CD_3OD .

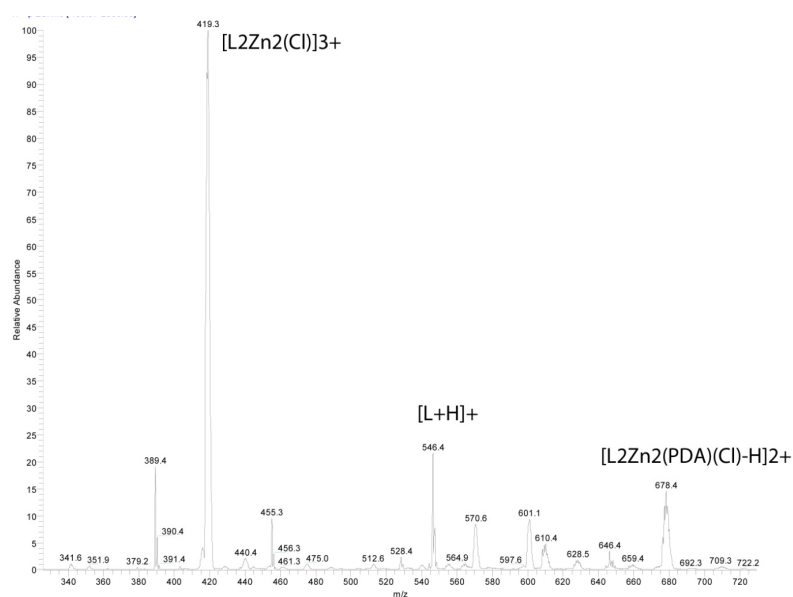


Figure S8. ESI-MS of the solution prepared by mixing of complex $L_2Zn_2(ClO_4)_4$ (1 mmol, $c=10^{-5}M$) and 1,5-pentanediamine (1 mmol) in methanol-acetonitrile. The assignment of the peaks has been done according to the isotope distribution modeling.

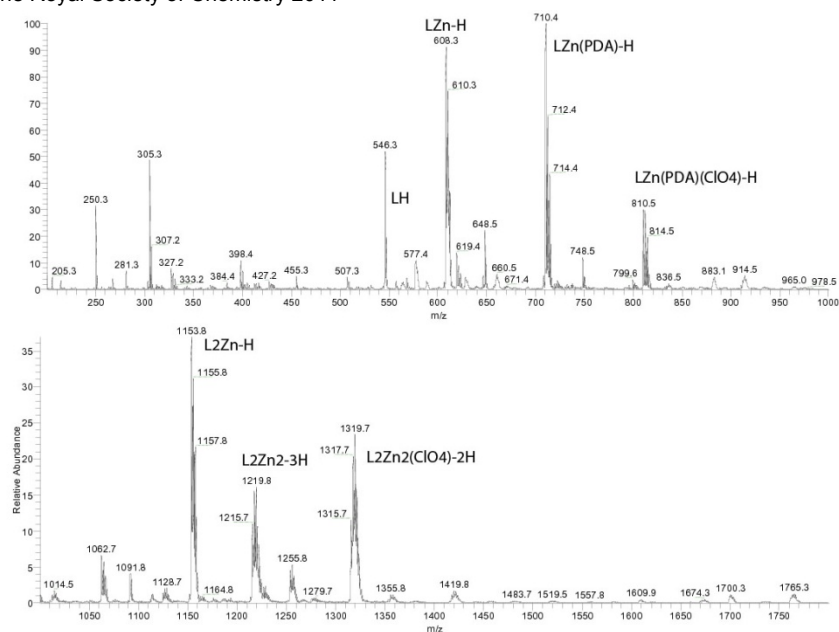


Figure S9. ESI-MS of the methanol solution prepared by the addition of zinc perchlorate in one portion to the mixture of the ligand and 1,5-pentanediamine ($c=10^{-3}$ M).

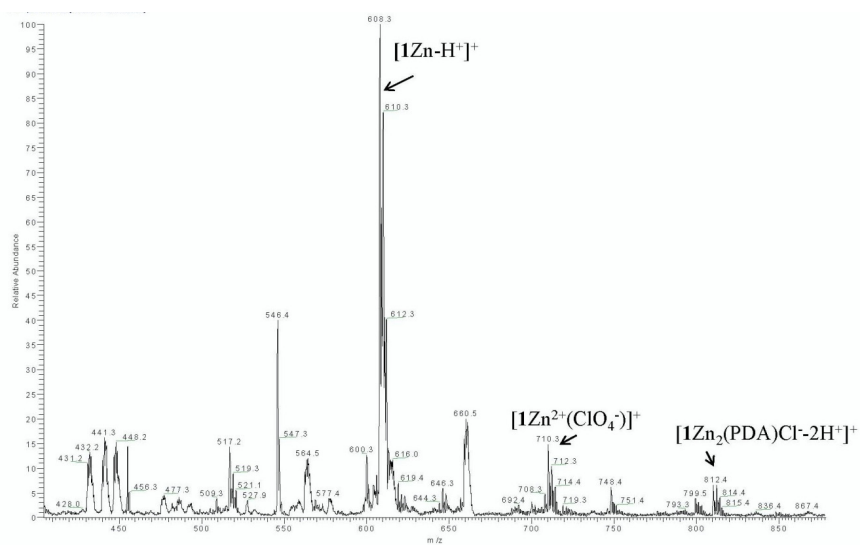


Figure S10. ESI-MS of the solution prepared by mixing the ligand (1 mmol, $c=10^{-3}$) and 1,5-pentanediamine (4 mmol), followed by slow addition of zinc perchlorate in methanol.

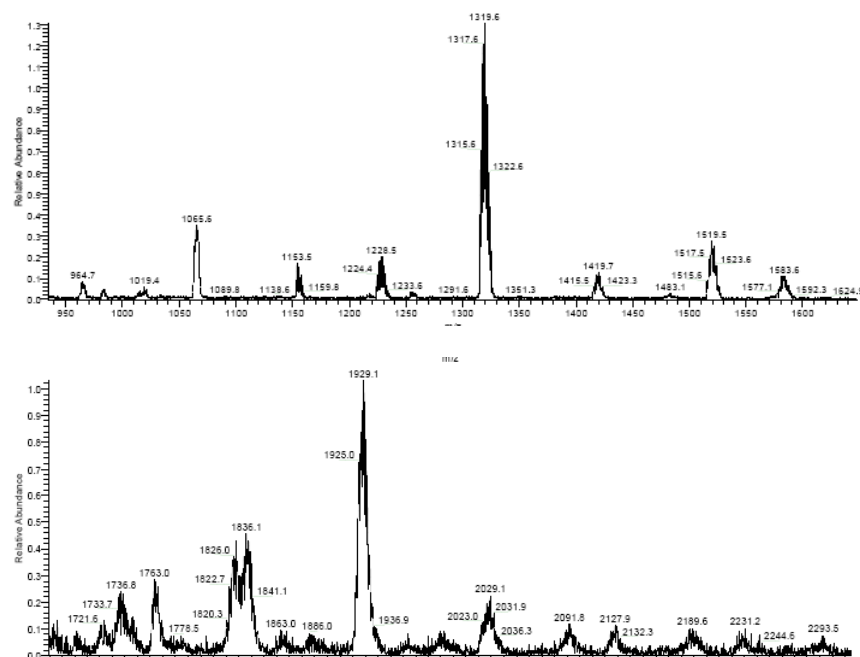


Figure S11. ESI-MS of the solution prepared by mixing the ligand and 1,5-pentanediamine (1 mmol, 10^{-5} M), followed by slow addition of zinc perchlorate (1 mmol) in methanol.

Titration data

The following graphs are exported from HYPQUAD 2006 program and show fitting curves (red dashed lines) to the experimental points (blue rhombuses). The other red and blue lines correspond to the calculated relative amount of corresponding species present in solution, and their calculated absorbance spectra.

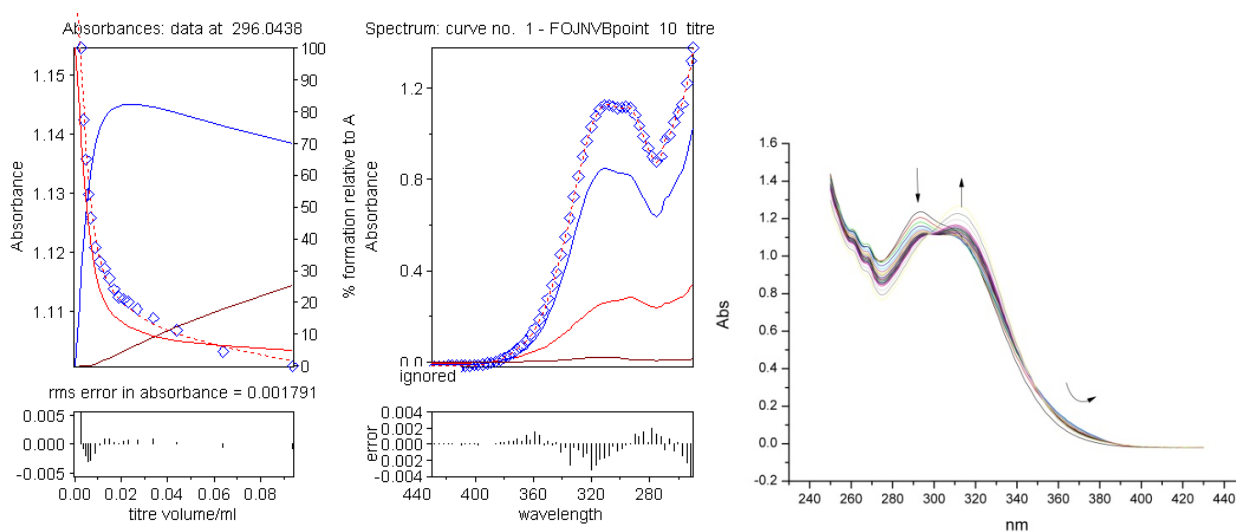


Figure S9. Titration of ligand **1** with zinc perchlorate hexahydrate.

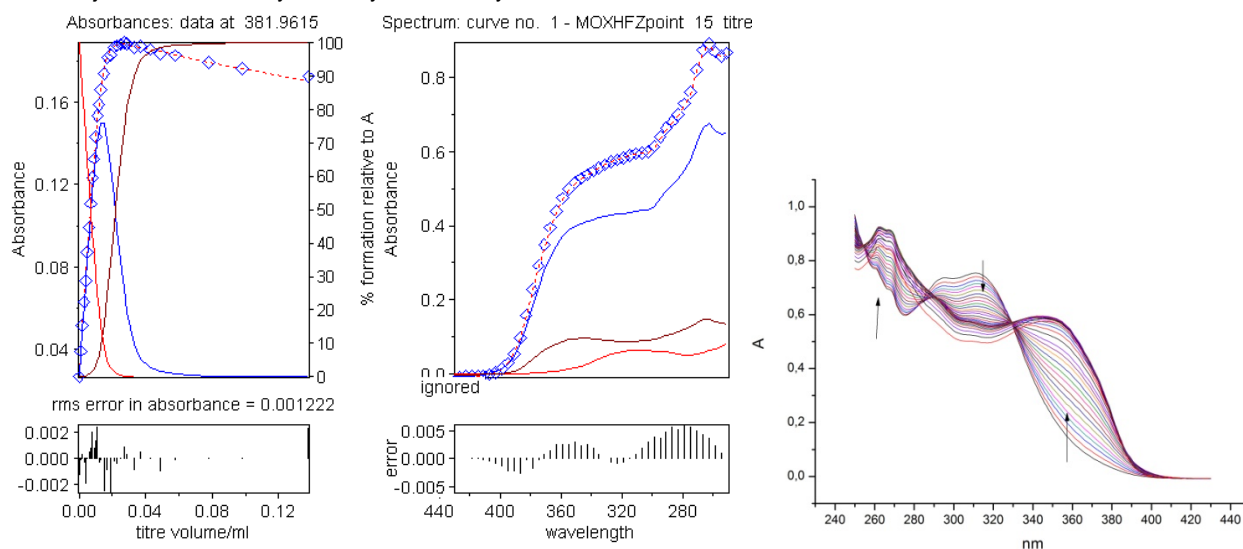


Figure S10. Titration of **2** with *n*-propylamine.

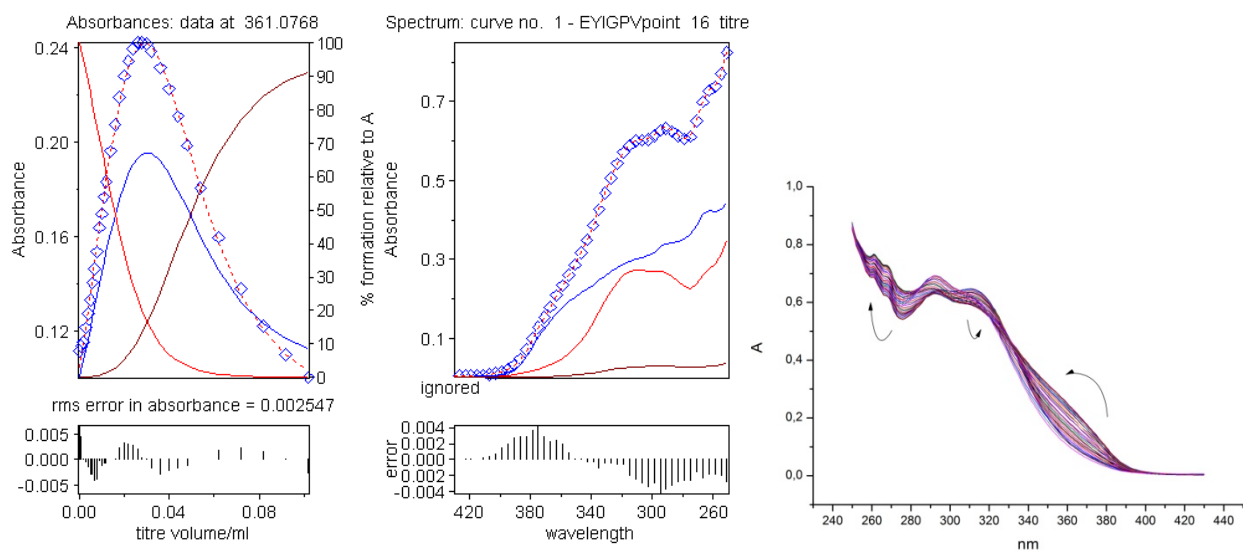


Figure S11. Titration of **2** with 1,2-ethylenediamine

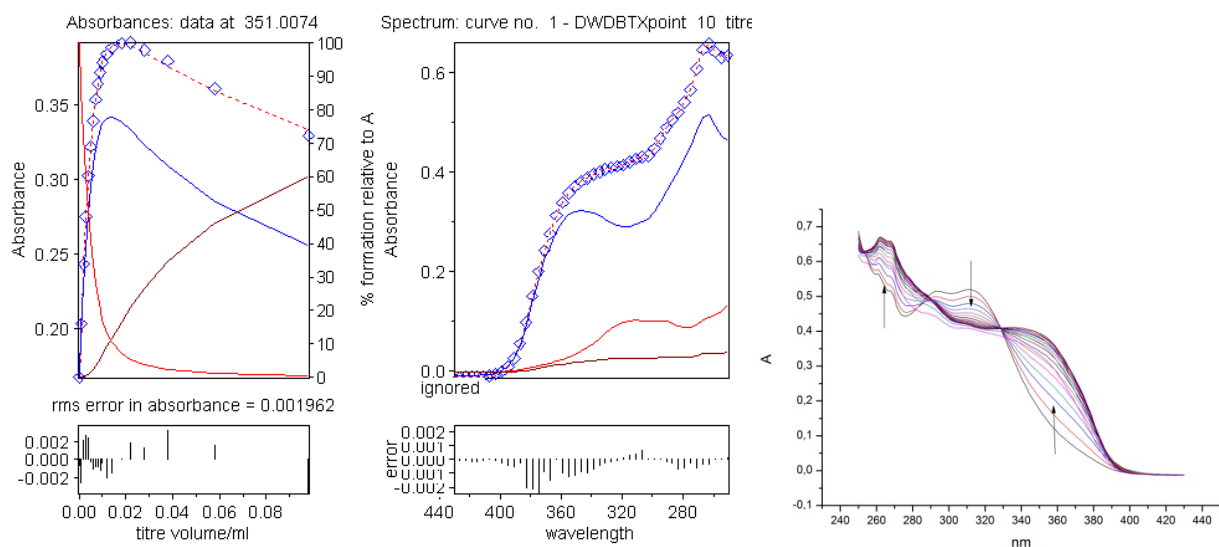


Figure S12. Titration of **2** with 1,3-propanediamine.

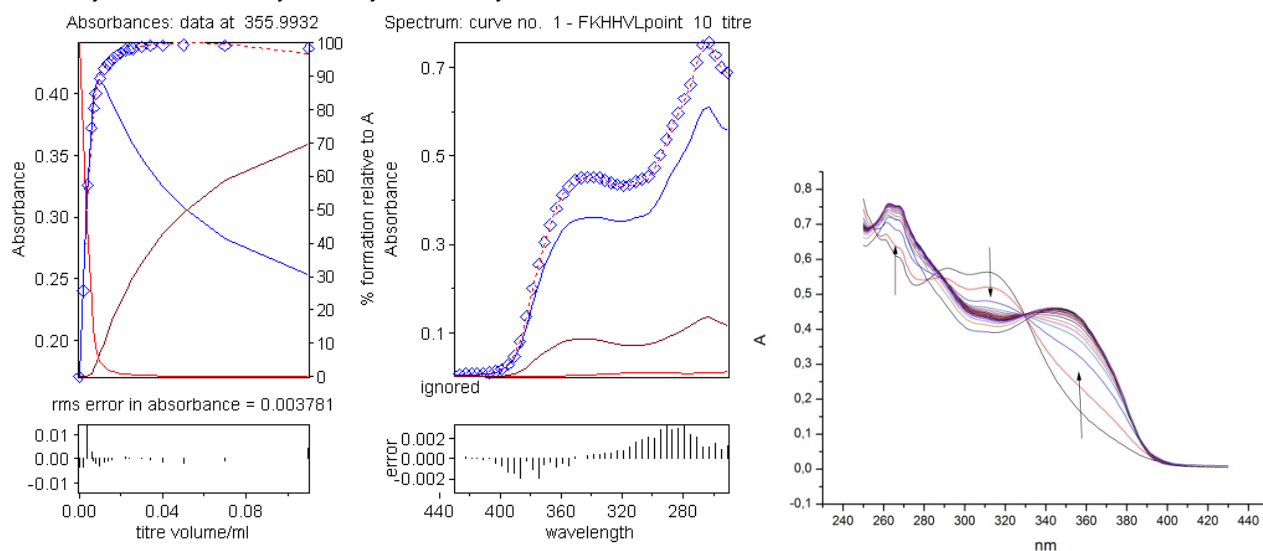


Figure S13. Titration of **2** with 1,4-butanediamine.

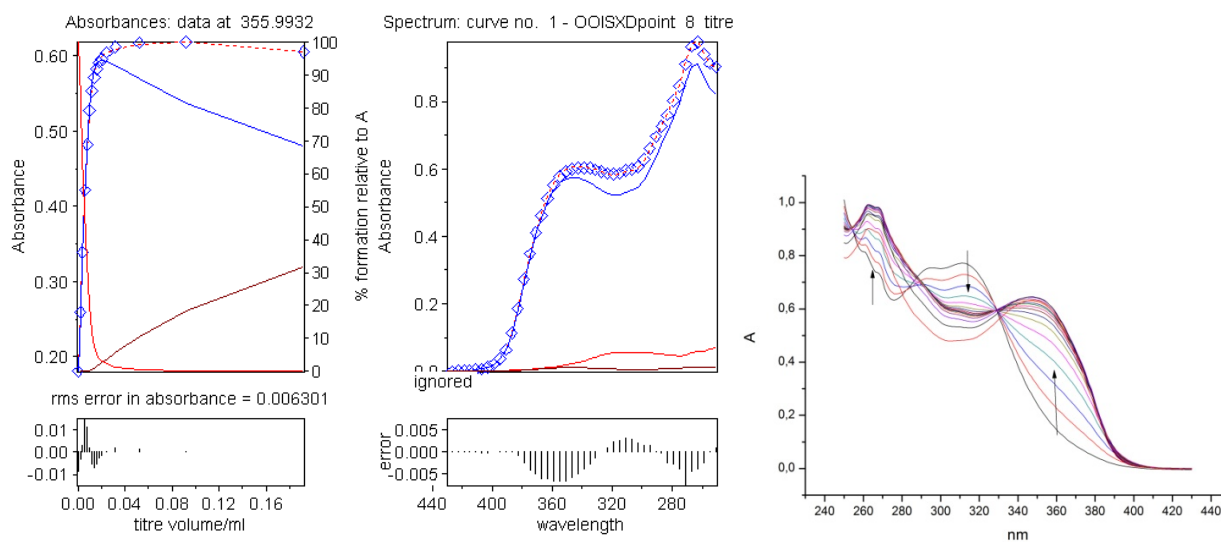


Figure S14. Titration of **2** with 1,5-pentanediamine.

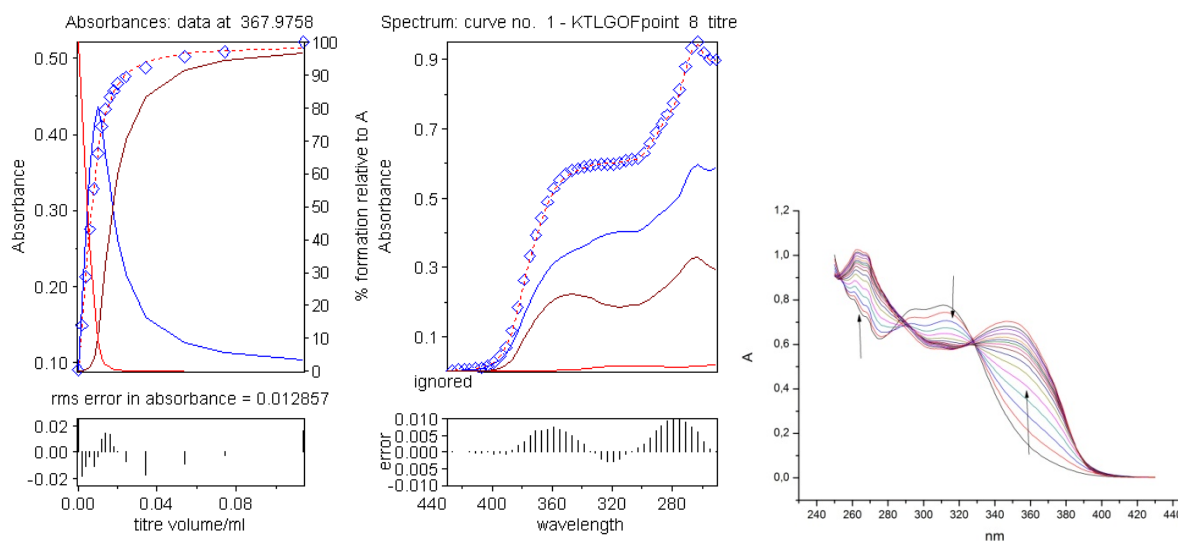


Figure S15. Titration of **2** with 1,6-hexanediamine.

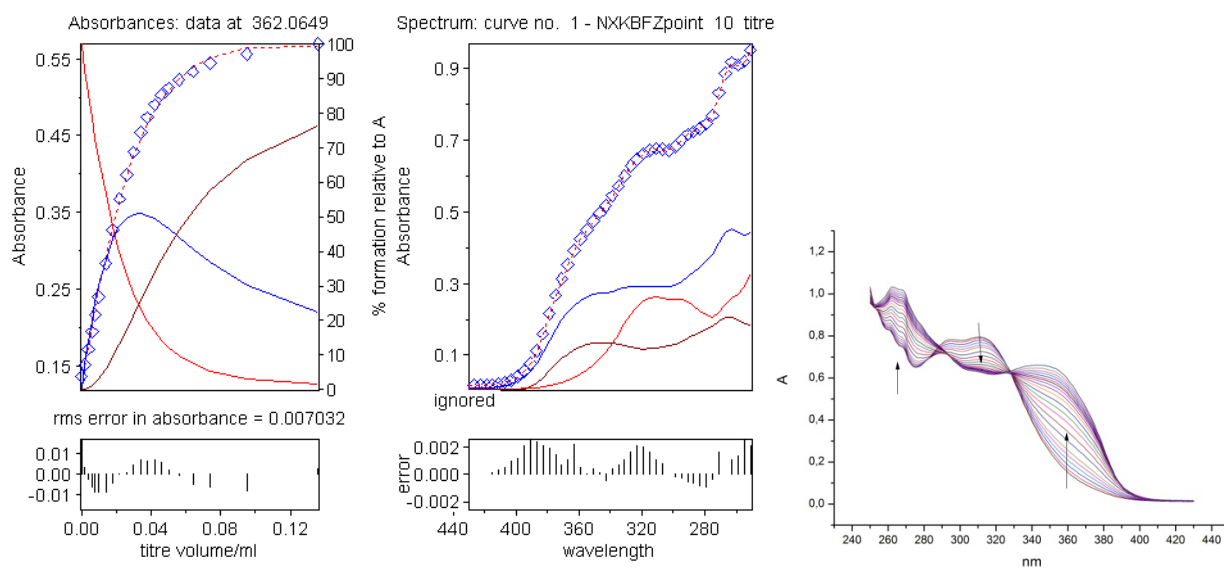


Figure S16. Titration of **2** with 1,8-octanediamine.

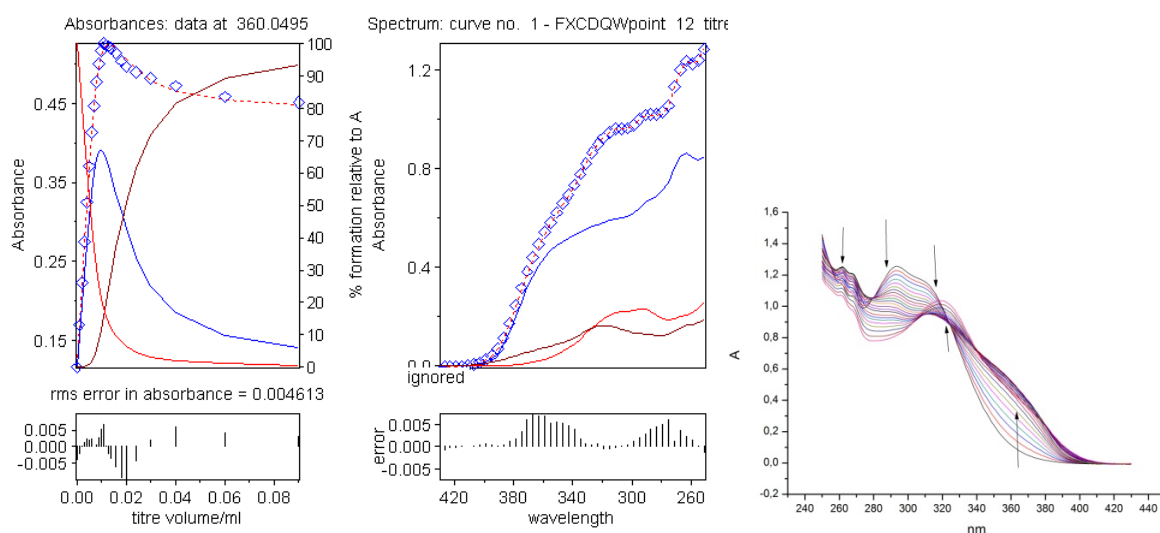


Figure S17. Titration of **1** with zinc perchlorate in the presence of 1 eq. of *n*-propylamine.

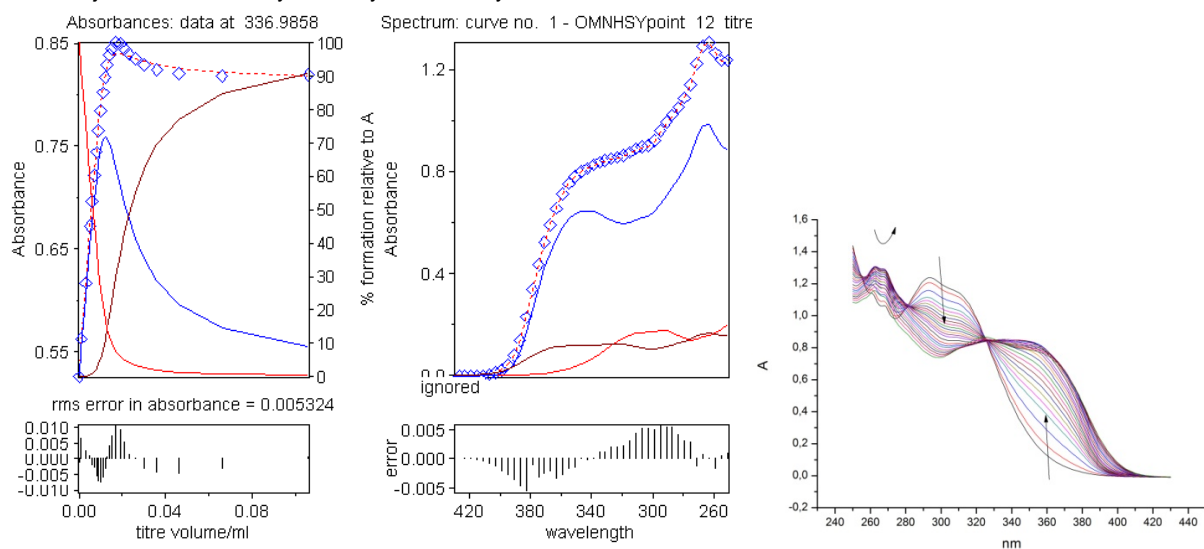


Figure S18. Titration of **1** with zinc perchlorate in the presence of 2 eq. of *n*-propylamine.

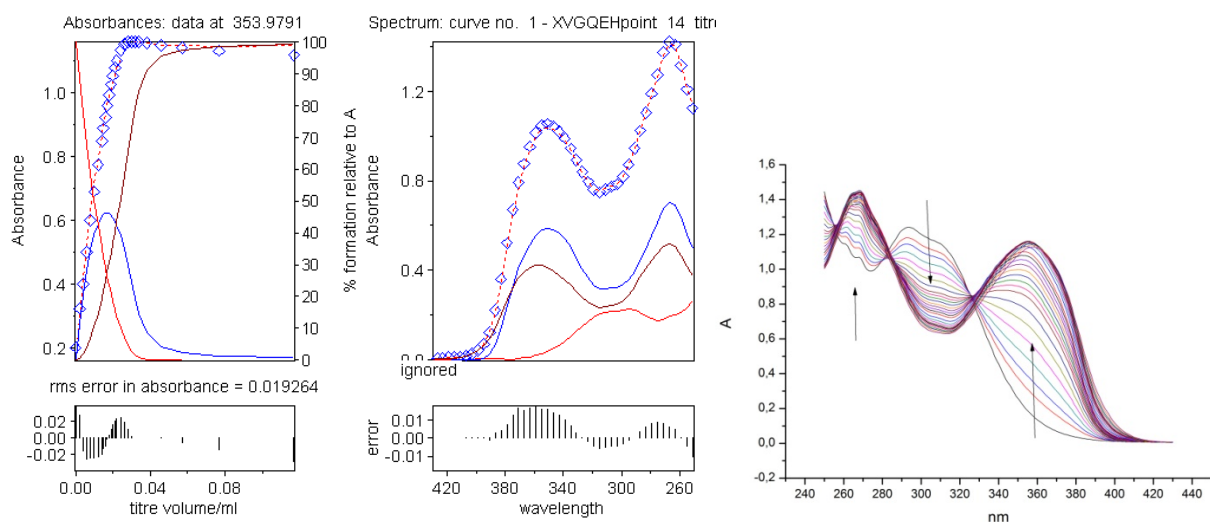


Figure S19. Titration of **1** with zinc perchlorate in the presence of 4.1 eq. of *n*-propylamine.

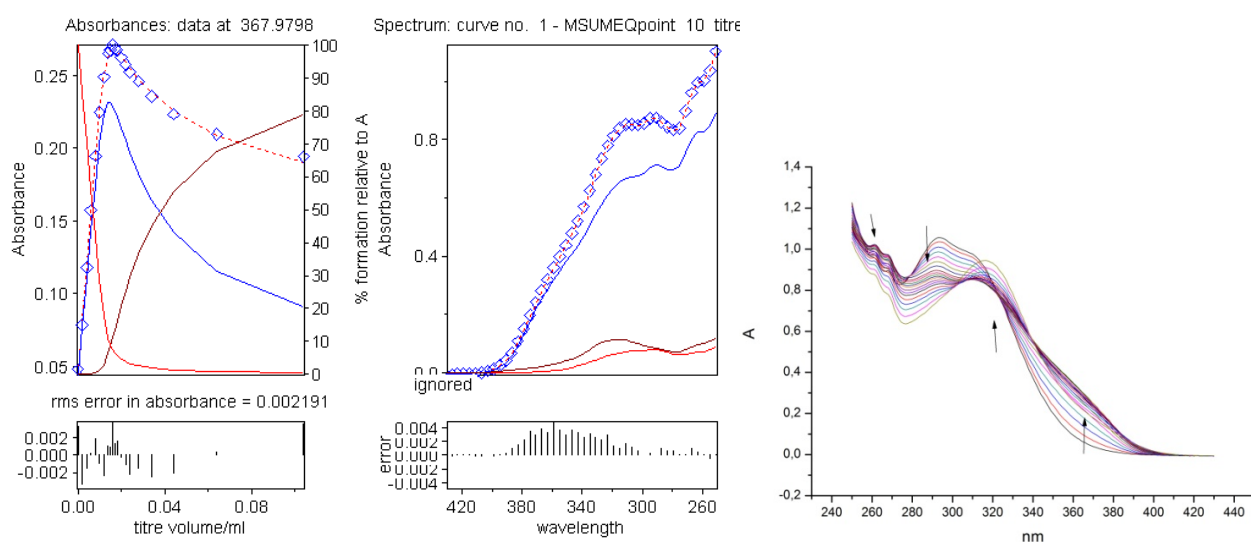


Figure S20. Titration of **1** with zinc perchlorate in the presence of 1 eq. of 1,2-diaminoethane.

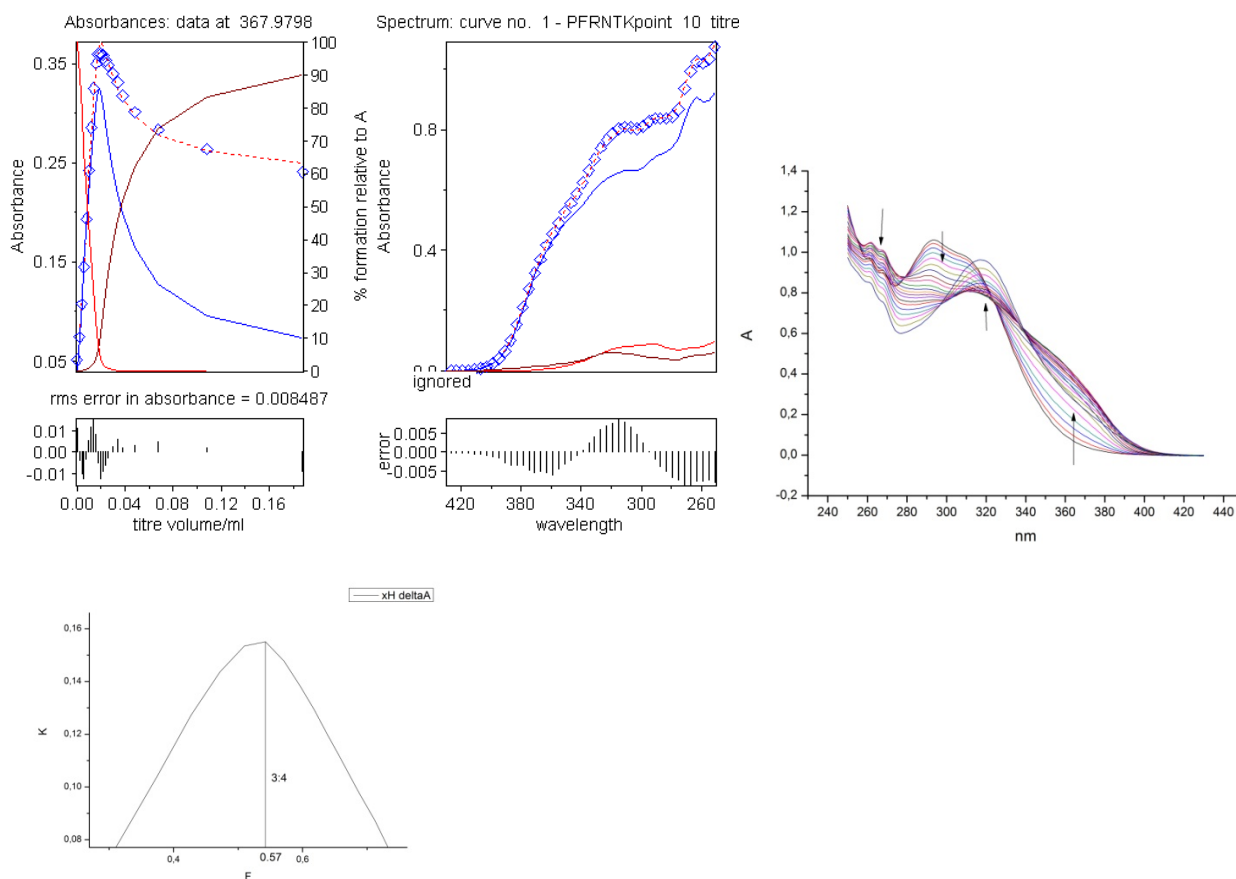


Figure S21. Titration of **1** with zinc perchlorate in the presence of 2 eq. of 1,2-diaminoethane.

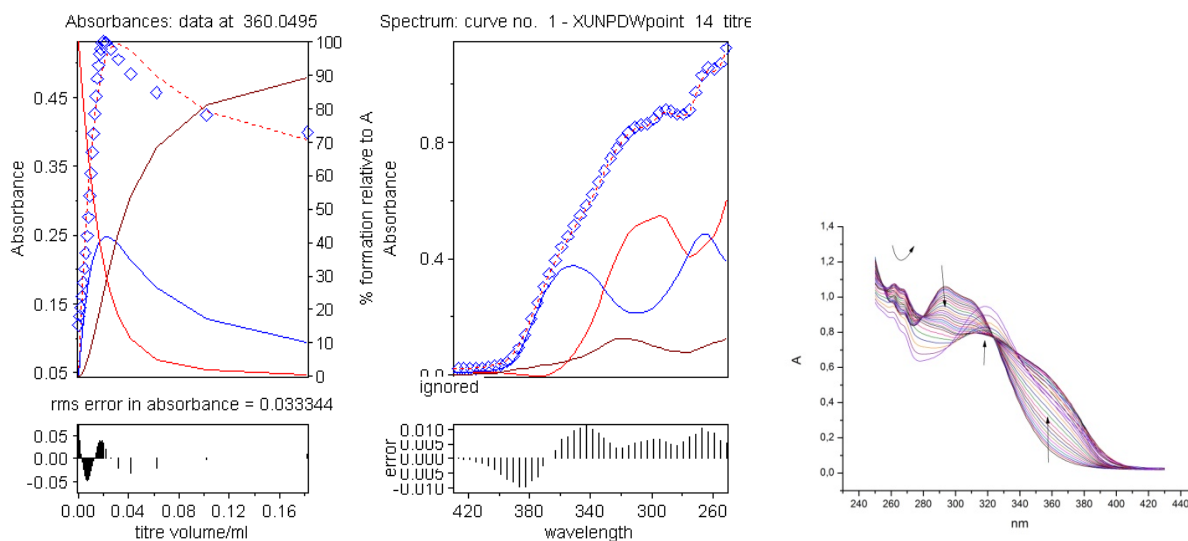
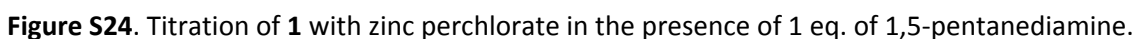
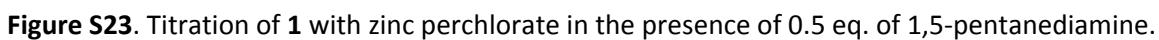


Figure S22. Titration of **1** with zinc perchlorate in the presence of 3 eq. of 1,2-diaminoethane.



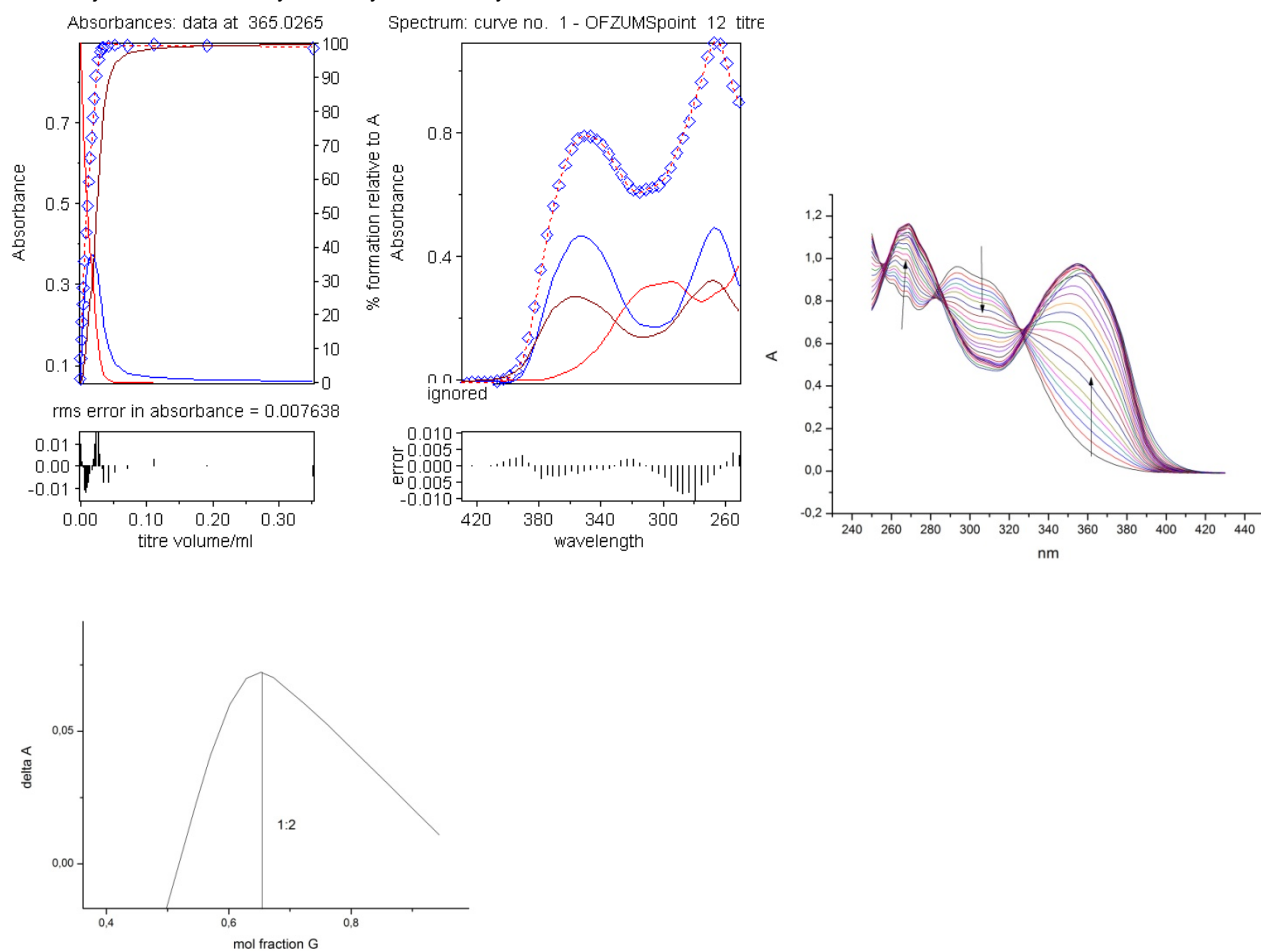


Figure S24. Titration of **1** with zinc perchlorate in the presence of 2.1 eq. of 1,5-pentanediamine