



Green-emitting Zn(II) halide complexes with *N,N,N',N'*-tetramethyl-*P*-indol-1-ylphosphonic diamide as ligand

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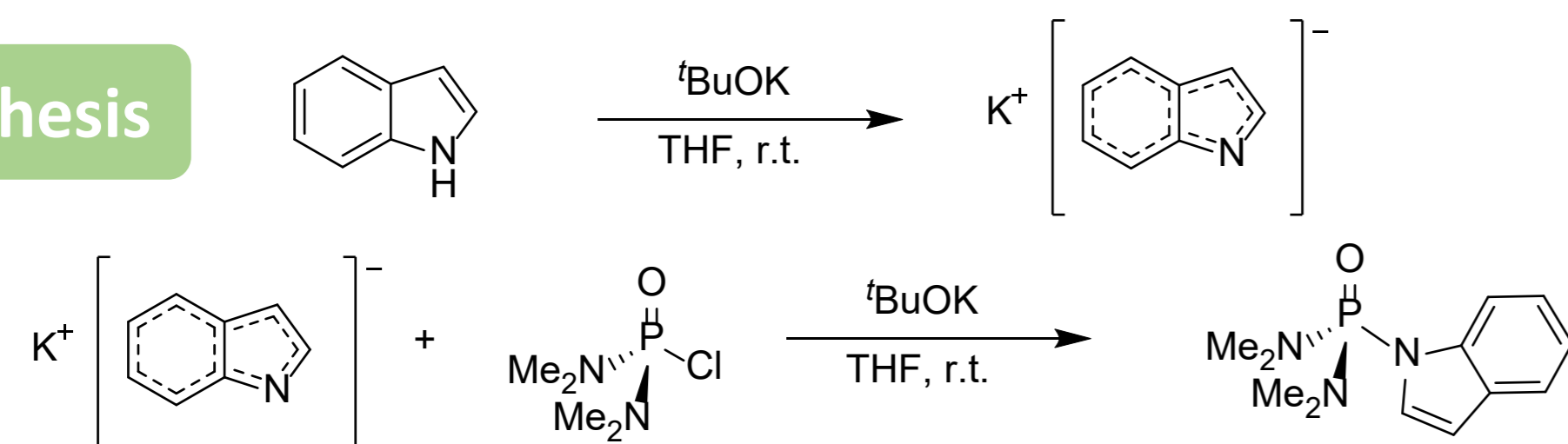
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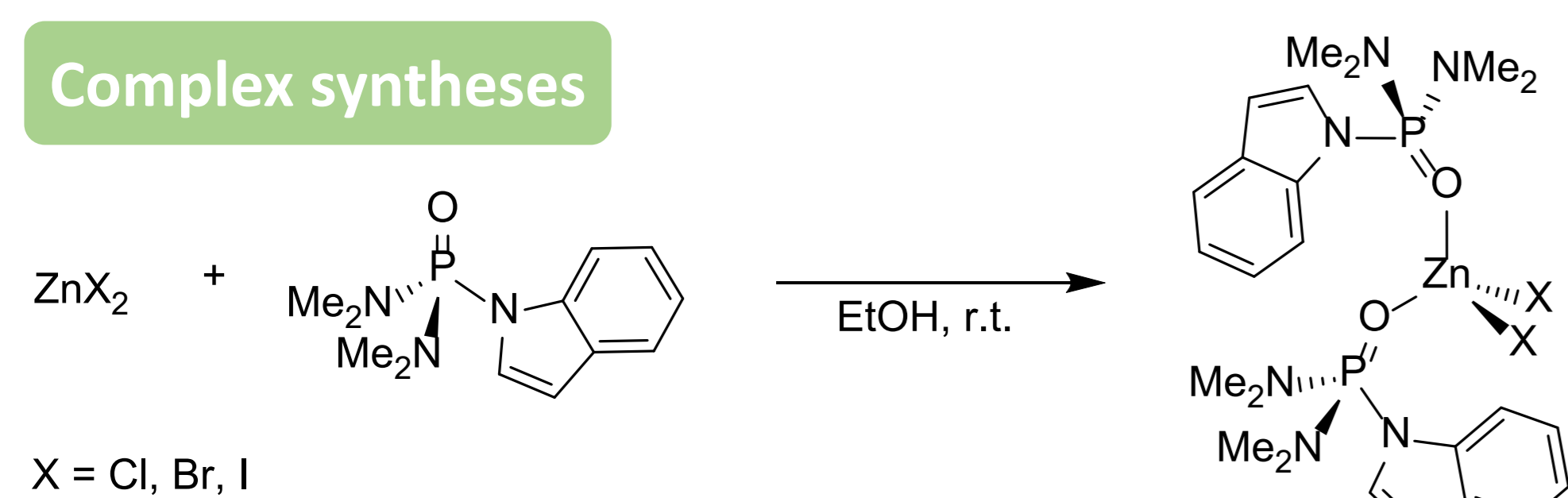
Introduction

Luminescent earth-abundant transition metal complexes are nowadays extremely appealing for applications such as OLEDs (organic light emitting diodes) [1]. Encouraging results were achieved with manganese(II) and copper(I) as metal centres but much less attention was devoted to zinc(II) derivatives [2-3]. In fact, in the majority of cases the emission is related to the fluorescence of the ligands enhanced by coordination, because the high oxidation state prevents metal-to-ligand charge transfer mechanisms [4]. However, phosphorescence can be detected when the low lying *s* and *p* orbitals of the metal centre are involved [5]. Despite the complexes having general formulae $[ZnX_2\{O=PPh_3\}_2]$ (*X* = Cl, Br, I) are known since the Eighties [6], the investigation on other [O=P]-donor ligands is limited and their luminescence was never deeply studied. Herein, we report the synthesis and characterization of luminescent zinc(II) halide complexes having *N,N,N',N'*-tetramethyl-*P*-indol-1-ylphosphonic diamide as ligand. Green phosphorescence was observed with the bromo- and the iodo-derivatives.

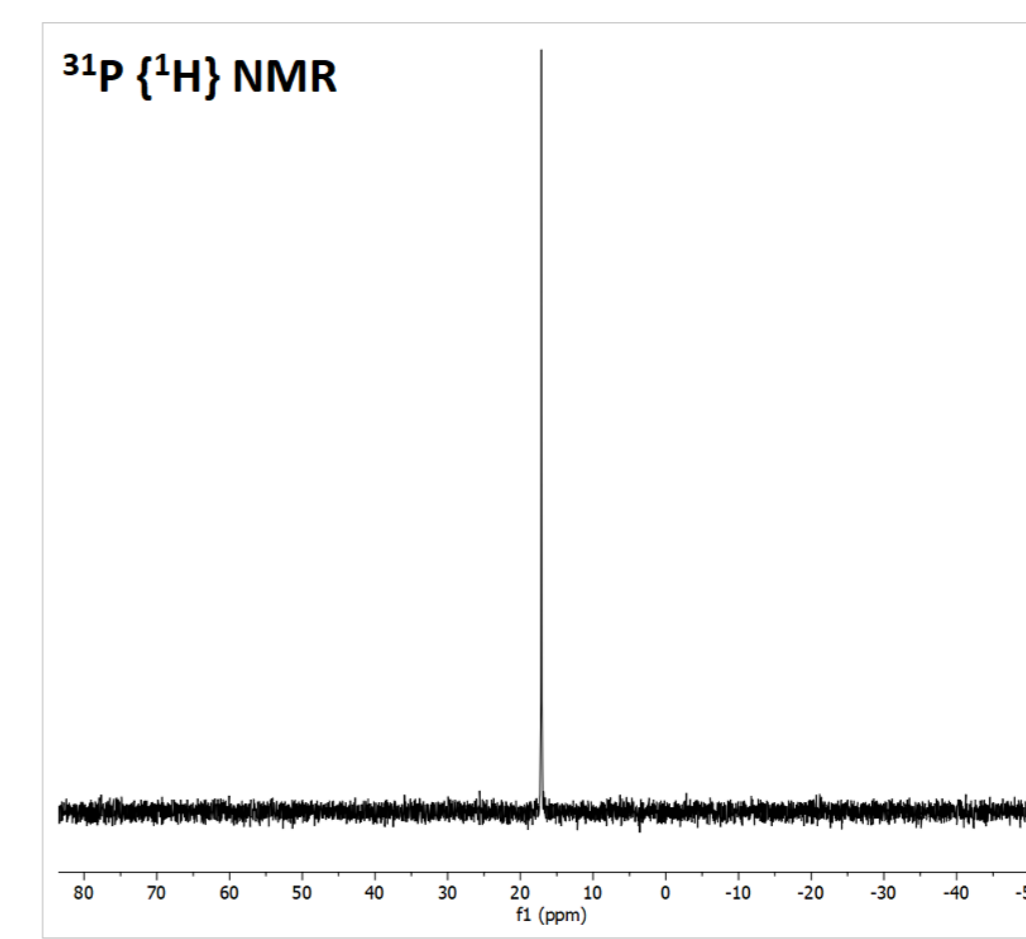
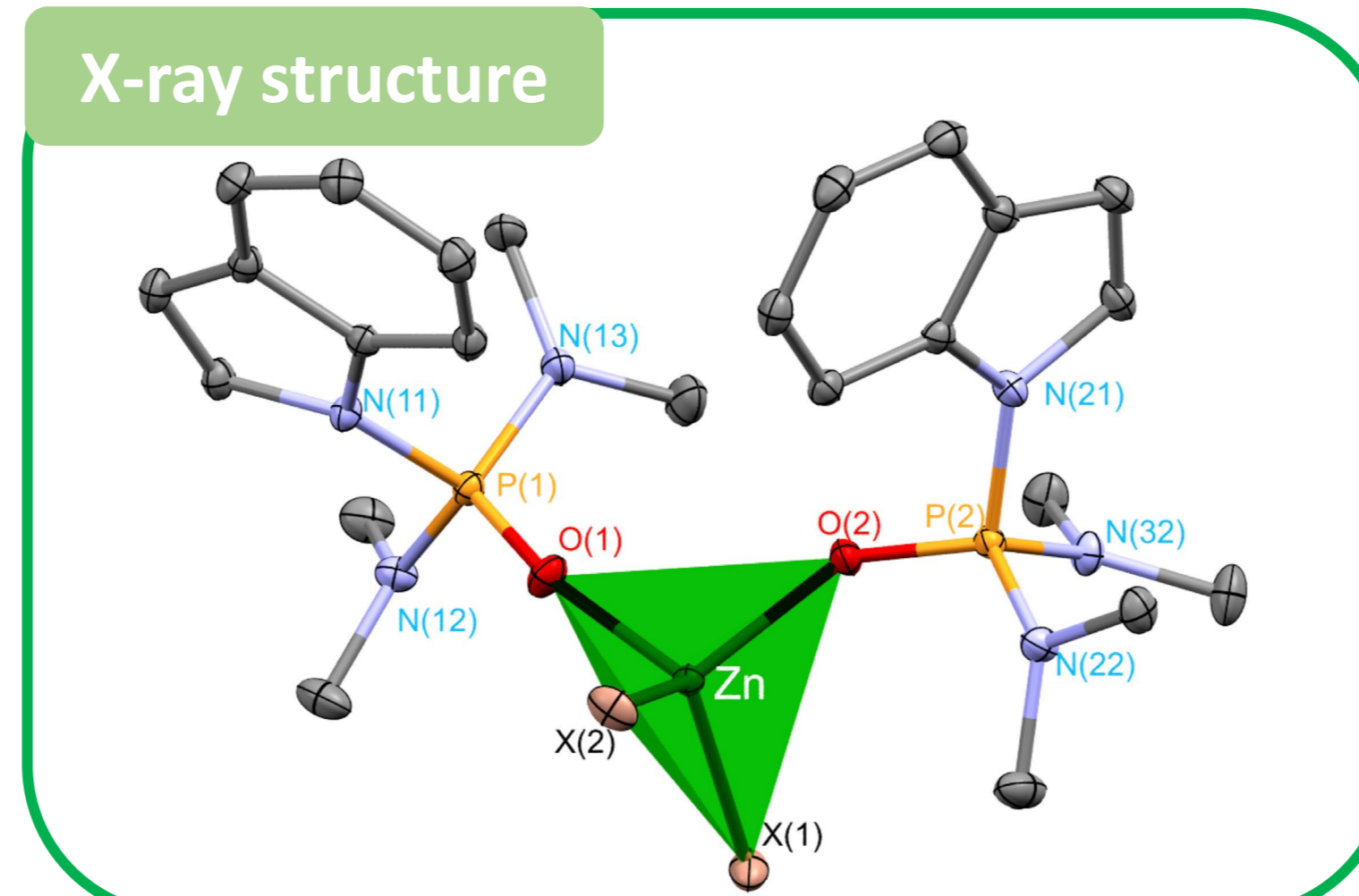
Ligand synthesis



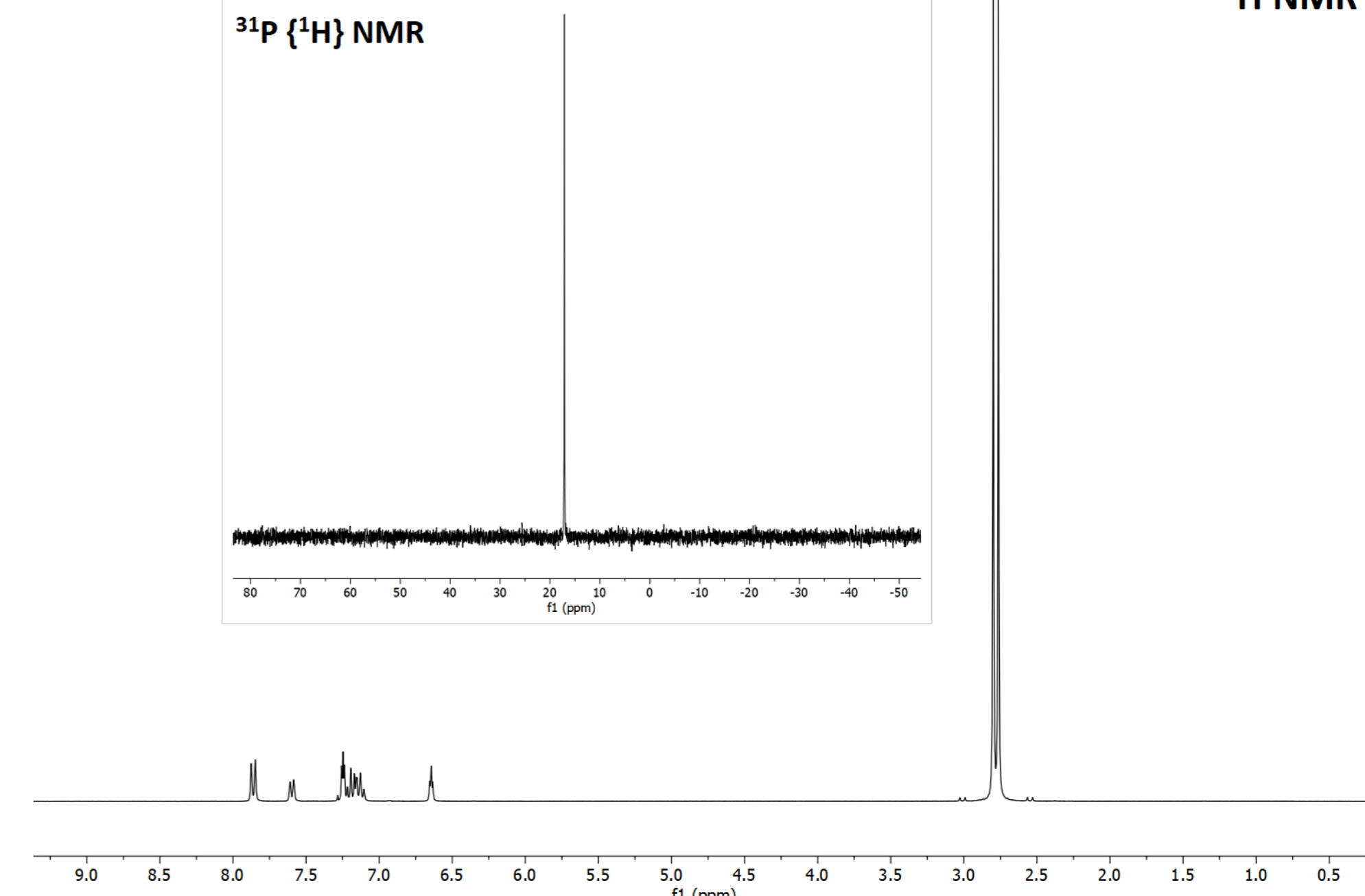
Complex syntheses



X-ray structure

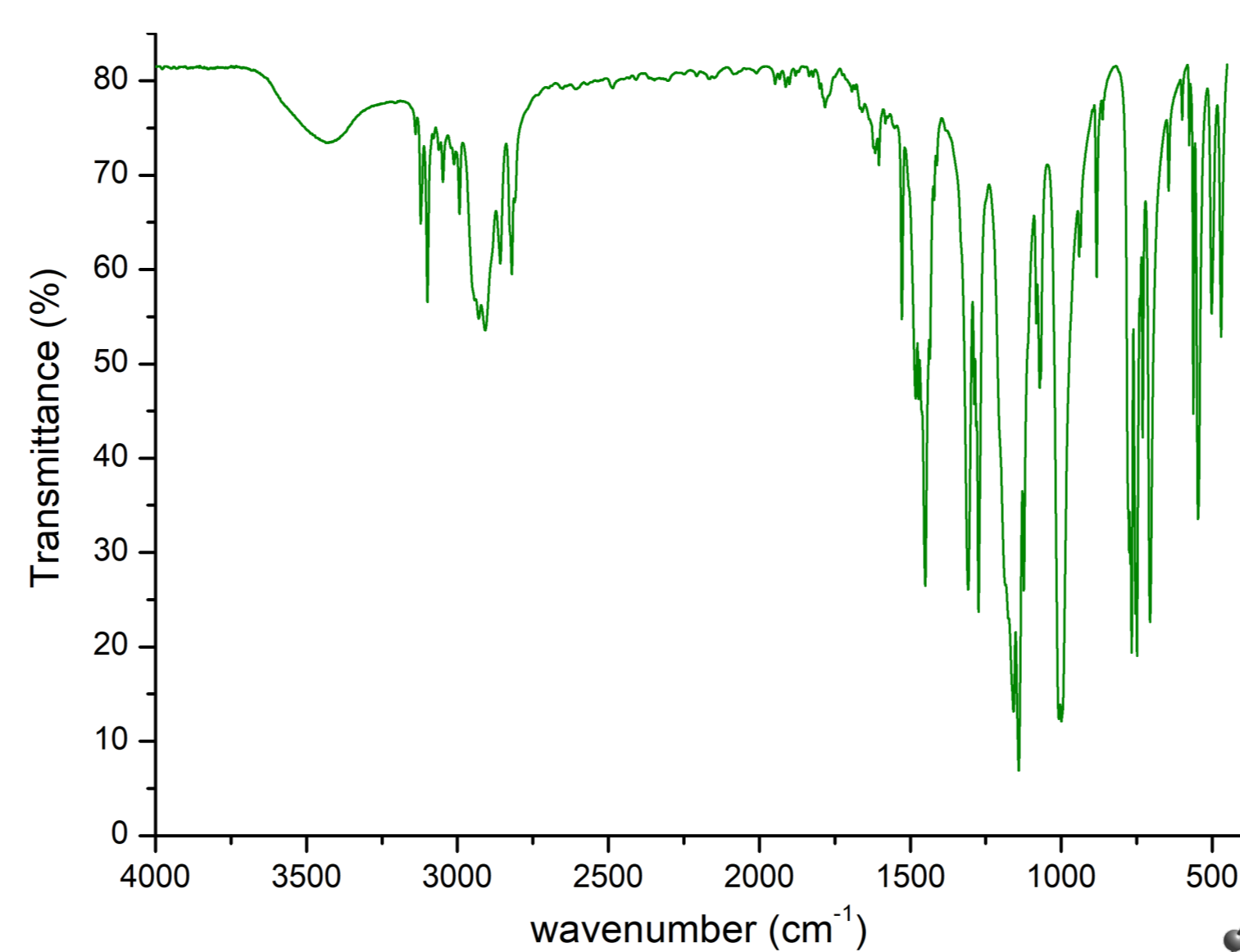


¹H NMR



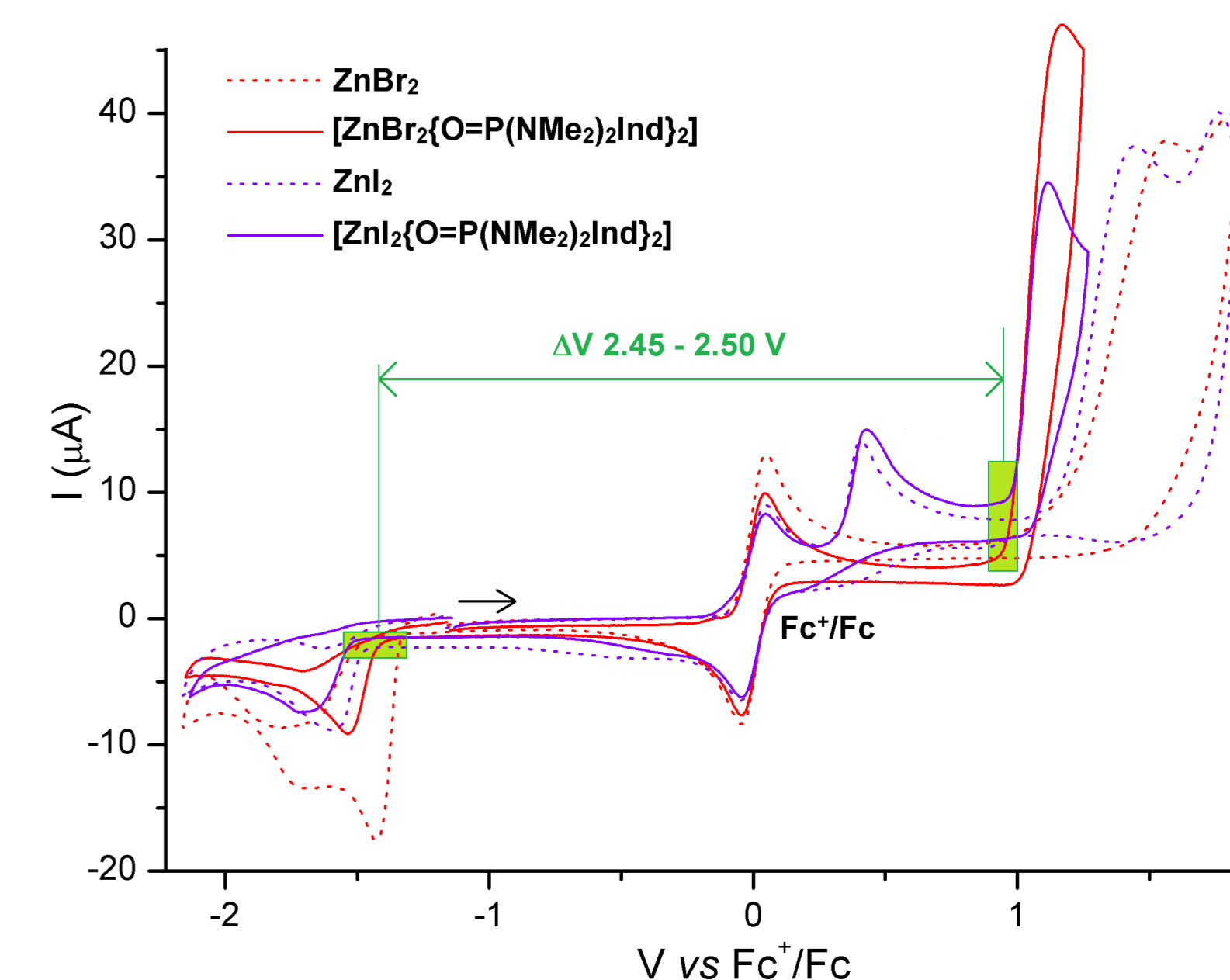
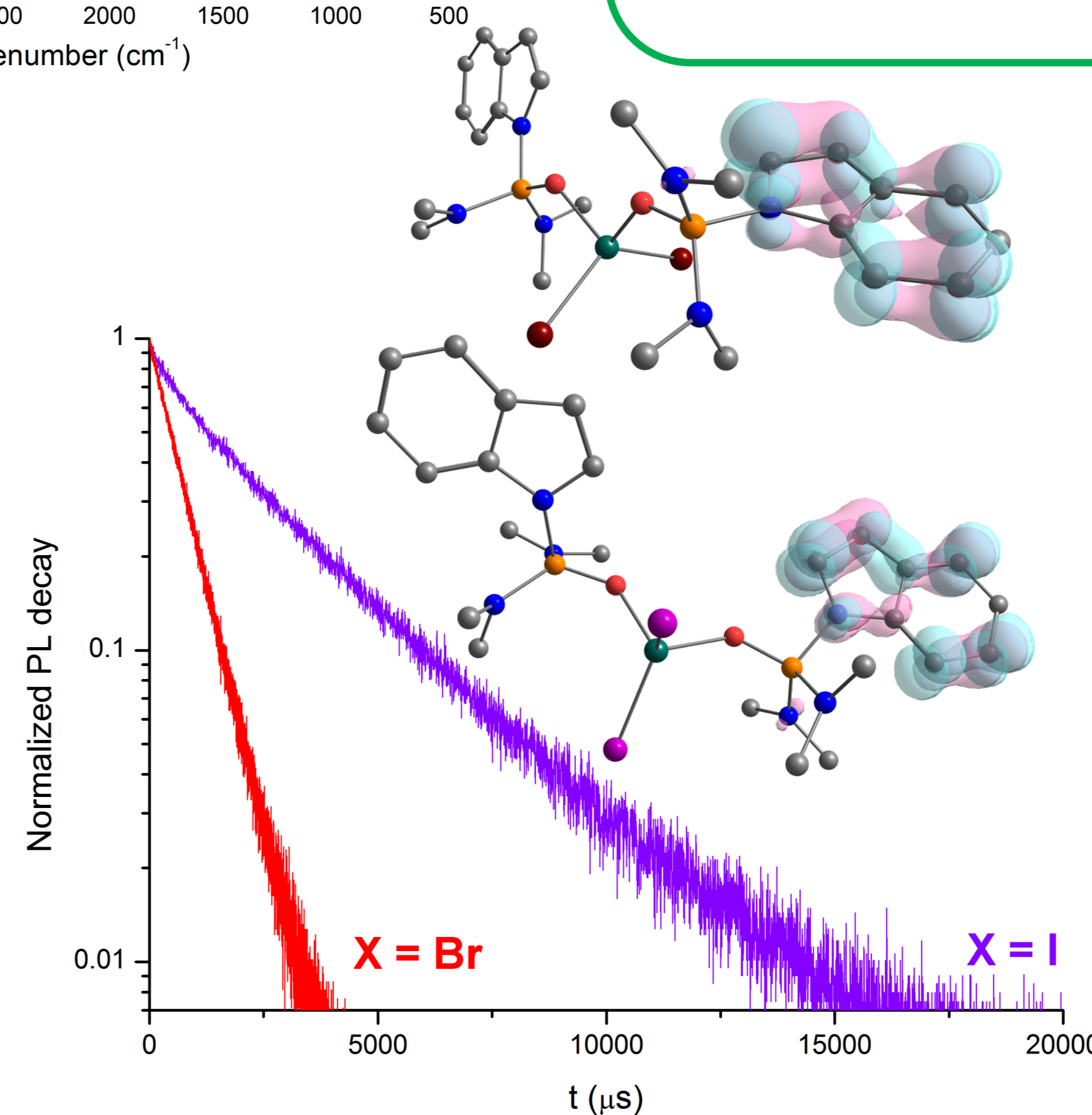
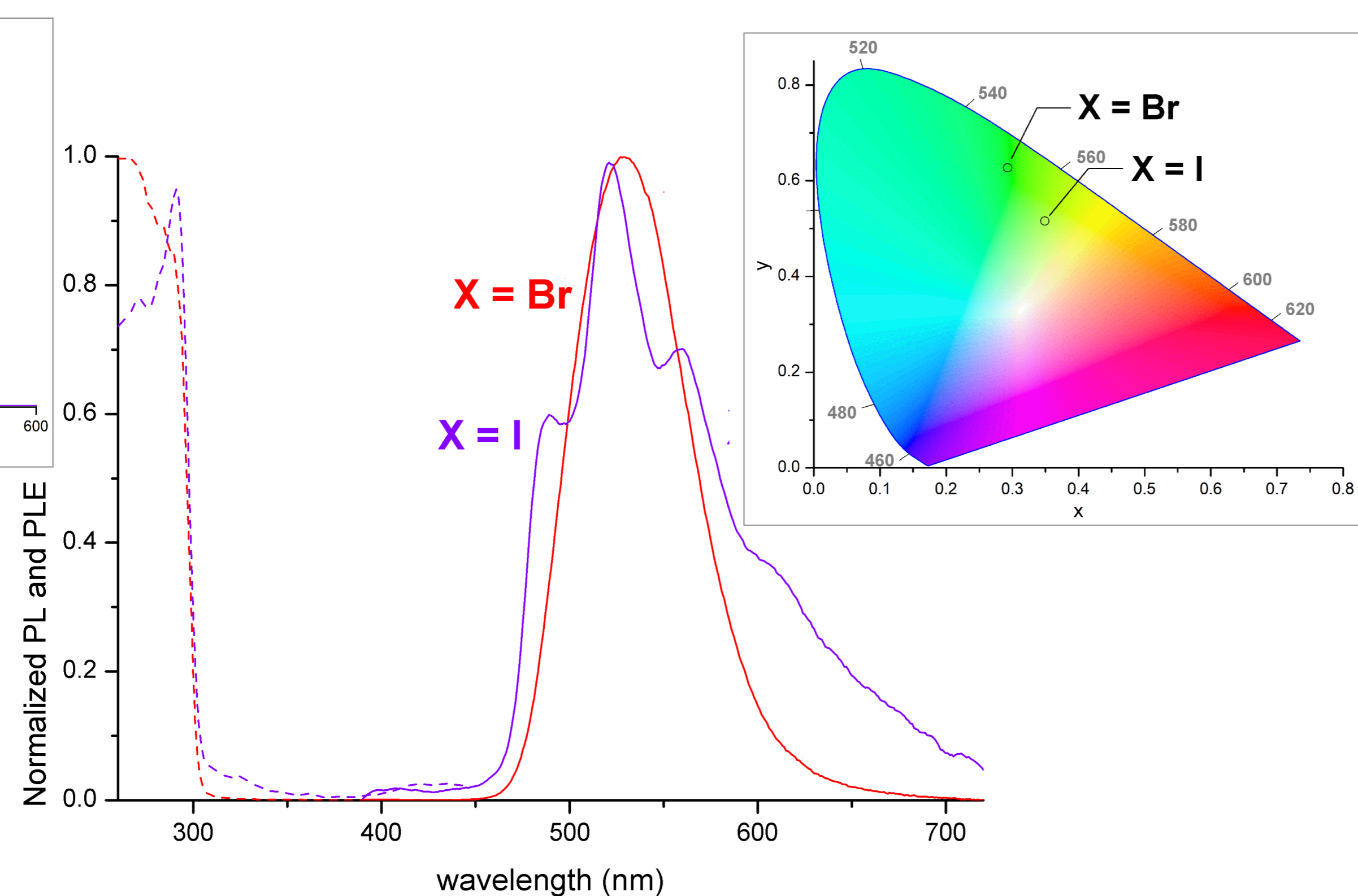
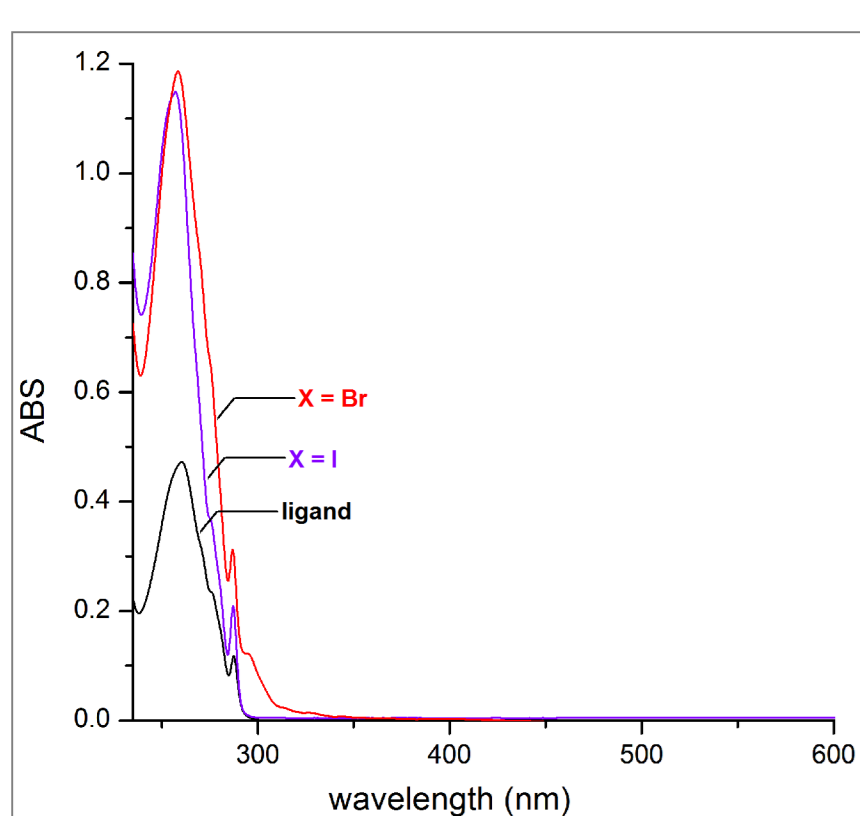
Photoluminescence

- The chloro-derivative does not exhibit any luminescent property.
- $[ZnX_2\{O=P(NMe_2)_2Ind\}_2]$ (*X* = Br, I) exhibits intense emission in the green region with lifetimes around 0.7 ms (*X* = Br) and 2.6 ms (*X* = I).



Photoluminescence

- On the basis of DFT calculations and experimental outcomes (*i.e.* cyclic voltammetry), the mechanism responsible of the emission is related to ³LC (ligand-centred) transitions.
- The onsets of the ligand-centred oxidation and metal-centred reduction processes are separated by 2.45 - 2.50 V, corresponding to an energy difference in the same range of the emission.



Acknowledgments

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