

Understanding the solid-state phosphorescence of a new class of Tellurophenes compounds

Inara de Aguiar^a (PQ), Eric Rivard^b (PQ), Alex Brown^b (PQ) and Gabriel L. C. de Souza^a (PQ)

^a Federal University of Mato Grosso, Department of Chemistry, 78060-900 Cuiabá-MT, Brazil

^b University of Alberta, Department of Chemistry, T6G 2R3 Edmonton, AB, Canada

Keywords: Tellurophenes, Phosphorescence, DFT, ADF, Excited States

INTRODUCTION

In the last year, the first phosphorescent Tellurophenes compounds and their polymeric analogues in solid state were discovered.¹ These species can be applied in light-emitting diode technologies. Although Te compounds are generally non-emissive, these Te compounds containing pinacolboronate (BPin) showed long-lived triplet states in solid state, at room temperature and in the presence of water and oxygen. Several new Te, Se, and S containing compounds with similar spectroscopic features were synthesized and almost none of them exhibited phosphorescence. In order to better understand the excited states and the phosphorescence pathways of these molecules aiming to enhance the emissive properties of this new class of compound, computations studies using a variety of functional and basis sets were performed.

METHODS

Computations were carried out with Gaussian 09 and ADF suite of codes.^{2,3} The ground state structures of the Te compounds were determined at B3LYP, CAM-B3LYP and M06 functional with the cc-pVDZ basis set (in Gaussian 09) and at the B3LYP/TZ2P level of theory in gas-phase (in the case of ADF). Using the ADF, the relativistic calculations with the Zero Order Regular Approximation (ZORA) formalism including scalar relativistic (SR) and spin-orbit relativistic (SO) methods were performed.

Using all the functional and basis sets referred before, the twenty low-lying excited states were probed using TD-DFT in Gaussian 09 while the forty low-lying excited states were determined using Self-Consistent Spin-Orbit Coupling Time-Dependent Density Functional Theory in ADF.

RESULTS AND DISCUSSION

Results obtained using the B3LYP functional showed one striking difference for the Te-BPin compound (emissive) compared to the Se-BPin and the S-BPin compounds (non-emissive). In the Te heterocycle, there is a triplet state (T_3) which is nearly degenerated with the singlet state (S_1), while in the S and Se analogues, the T_3 state is about 1 eV higher in energy suggesting that the Te compound has energetically well-matched states to enable efficient singlet-triplet crossing to occur; once T_3 is populated, relaxation through the triplet manifold to the T_1 state is possible, followed by emission. The investigation was extended on the entire series of Te containing compounds synthesized by Rivard *et al.*¹

For all the functional and basis set used in the present work, the tendency reported by the previous study¹ was not observed anymore. No linear correlation between the singlet and triplet states were observed for the emissive and non-emissive compounds. The first results using the spin-orbit considerations through ADF were more consistent and the emission is correlated to the energy gap required to reach the first S_1 state.

CONCLUSIONS

The studies revealed that theoretical emissive properties of this type of compounds cannot be evaluated without spin-orbit coupling considerations.

ACKNOWLEDGMENTS

The authors thank CNPq and CAPES.

¹ E. Rivard *et al.*, *Angew. Chem. Int. Ed.*, 53, 4587, (2014).

² M. J. Frisch *et al.*, *Gaussian 09 D.01*, (2009).

³ G. Velde *et al.*, *J. Comp. Chem.*, 22, 931, (2001).