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Tuning the optoelectronic properties of Metallo-diphenyl-bipyridine coordination chloride complex

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Abstract
Studing metal complexes of organic molecules has attracted great attention to explore the mechanisms of charge transfer through organometallic single molecules. In this work, we investigate the optoelectronic properties of diphenyl-bipyridine coordination chloride transition metal complex. By varying the transition metal in the group of Co, Cu, Fe, Mg, Ru and Zn atoms, we demonstrate the ability to manipulate the optical and electronic properties of the system. Density function theory (DFT) calculations with B3LYP functional are used to determine electronic properties of the metallo-molecules, including ionization potential, electronic affinity, energy gap, electronegativity, hardness, softness, and dipole moment. To understand the optical performance of the systems, we consider their absorption spectra in the ultraviolet and infrared regions, in the framework of time-dependent DFT. We argue that the six metallic atoms have the ability to tune the optoelectronic properties of the complex molecules.

Keywords: diphenyl-bipyridine; complexes organic molecules; chloride complex metal; density functional theory calculations; absorption spectra; electronic properties

1. Introduction

The diphenyl - bipyridine conjugated organometallic complexes has been of great interest, particularly when the complexes are made with transition metals and coordinating to counter ions [1,2]. These complexes have applications in photovoltaic devices, chemical sensors, catalysis, and organometallic molecular devices [3-9]. The environmental and economic considerations also provide further motivations to develop such compounds for a variety of applications [10-13]. In these transition metal complexes, the photochemical properties can be dominated by the charge transfer in the low lying excited states [14,15].

These compounds provide the possibility to explore the effects of bonding on the binding properties of the central metal ion and coordination geometry. Diphenyl-bipyridine and its structural derivatives with abundant chemical coordination have been widely considered due to their strong affinity in binding a variety of transition metal ions, resulting in many supramolecular metal structures with remarkable photophysical and redox properties [16-20].

In what follows, our aim is to explore the potential optoelectronic properties of single-molecule metallo-diphenyl-bipyridine chloride complex by coordinating a different metallic ions [21]. In this regard, by varying the metal atom bonding between the two phenyl rings-bipyridine, we try to tune the energy levels and accordingly optoelectronic properties of these transition metal complexes, being dominated by the charge transfer coordinating of tetrachlorides [22]. We shall demonstrate the tenability of the optoelectronic properties of these molecules by varying the metallic atoms (X = Co, Cu, Fe, Mg, Ru, Zn) in the presence of four Cl^- counter ions.

2. Computational Method

For geometry optimization of our metallo-molecules, presented in figure 1a, we employed the Gaussian (09) package implementation of “density functional theory” DFT [23]. All DFT calculations were performed using the DFT/B3LYP hybrid functional in the ground state with LanL2DZ basis set [24,25].

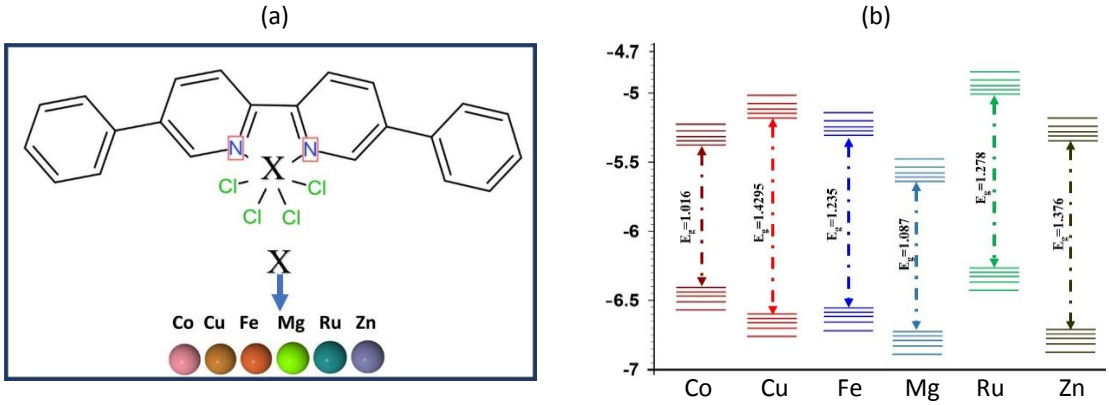

Figure 1. (a): Atomic configuration of the diphenyl-bipyridine coordination chloride complex metal X (X = Co, Cu, Fe, Mg, Ru, Zn) and (b): calculated electronic structure of the complexes within DFT/ B3LYP.

Table 1. Calculated HOMO, LUMO, ionization potential (IP), electron affinity (EA), energy gap (E_g), electronegativity (χ), chemical potential (μ), global hardness (η), and global softness (S) of metallic molecules in the presence of four Cl^- counter ions.

Metal atom (X)	HOMO (eV)	LUMO (eV)	IP (eV)	EA (eV)	E_g (eV)	χ	μ	η	S
Co	-6.400	-5.384	8.332	3.672	1.016	5.892	-5.892	0.508	1.969
Cu	-6.610	-5.181	8.166	2.716	1.429	5.896	-5.896	0.714	1.400
Fe	-6.553	-5.318	6.658	4.532	1.235	5.935	-5.935	0.617	1.620
Mg	-6.782	-5.695	7.471	3.931	1.087	6.238	-6.238	0.543	1.840
Ru	-6.279	-5.001	7.319	3.723	1.278	5.640	-5.640	0.639	1.564
Zn	-6.728	-5.352	7.425	3.616	1.376	6.040	-6.040	0.688	1.453

We calculated the electrical properties of the systems, including the highest occupied (HOMO) and the lowest unoccupied molecular orbital (LUMO), ionization potential (IP), electron affinity (EA), frontier molecular orbitals and dipole moments. The adiabatic Time-dependent (TD) DFT technique was used for calculating the optical properties of the molecules, including the UV and IR absorption spectra. The IP and EA parameters was calculated as follows [26,27]:

$$IP = E^{+} - E^{o}\,, \tag{1}$$

$$EA = E^{o} - E^{-}\,, \tag{2}$$

where E^{o} ($E^{\mp}$) is the ground state energy of the neutral (charged) molecule. Based on HOMO and LUMO, the energy gap (E_g), electronegativity (χ), chemical potential (μ), hardness (η), and softness (S) of the systems were calculated as follows [28-32]:

$$\chi = -(E_{LUMO} + E_{HOMO})/2\,, \tag{3}$$

$$\mu = -\chi\,, \tag{4}$$

$$\eta = (E_{LUMO} - E_{HOMO})/2\,, \tag{5}$$

$$S = 1/\eta\,. \tag{6}$$

The hardness and softness of a molecule are reliable indicators of the molecular chemical stability. It is clear that hardness is actually half of the energy gap, increasing the energy gap increase the hardness and decrease the softness of the molecule [33-35]. The chemical potential (μ) measures the ability of the system to cause a chemical or electrochemical reaction [36].

3. Results and Discussions

3. 1. DFT calculation of electronic properties

The obtained electronic properties of the investigated complexes within DFT-B3LYP are given in figure 1b and table 1. It is seen that a the largest ionization potential is obtained for Co atom (8.33 eV) while the smallest one happens for Fe (6.66 eV). On the other hand, the largest electron affinity appeared in the presence of Fe atom (4.53 eV) and the smallest one occurs for the Cu atom (2.72 eV). The highest and the lowest energy gaps were found for Cu and Co atoms (1.43 and 1.02 eV), respectively.

Table 1 demonstrates the effect of metallic atom on the electronic properties of the diphenyl-bipyridine coordination chloride. We found that the disparity is evident in the calculated electronic structures (figure 1b), ionization potentials, and the electron affinities, which indicates the tunable optical properties and chemical ability of the molecule to accept or donate an electron. The calculated electronegativities (table 1) are in the range of 5.64 (Ru) to 6.24 (Mg) while the hardness values are in the range 0.508 (Co) to 0.714 (Cu). As it was mentioned, these parameters play role to explore the electronic configuration and chemical stability of the molecules [37, 38].

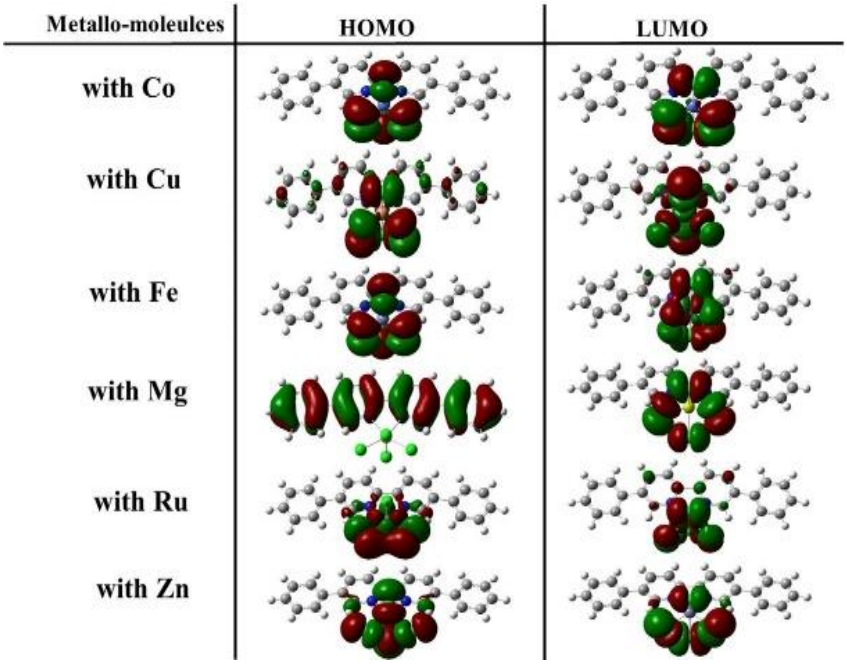

Figure 2. Frontier molecular orbitals (FMOs) for the metallo-molecules, obtained within DFT/ B3LYP.

3. 1. 1. Frontier molecular orbital (FMOs)

The iso-surfaces of frontier molecular orbitals (FMOs) of all structures are calculated and presented in figure 2. Red and green regions represent to positive and negative values of the wave functions, respectively. The plots show that, expect for HOMO of Mg complex, the FMOs, although delocalized, are distributed around the central metal atom.

3. 1. 2. Dipole moment effect:

The amount of polarity in the bonds is determined by the dipole moment of the molecule. A polarized molecule has a asymmetric distribution of charges, a net positive charge in one place and a net negative charge in another with a suitable distance, where the dipole moment is directly related to the separated charges and their distance. In different bonds, the degree of polarity can vary greatly [39-42]. In this study, the dipole moment of the molecules in the presence of all metal atoms were computed and shown in figure 3. The calculation shows that the highest dipole moment was at the Ru atom and the lowest one was at Zn.

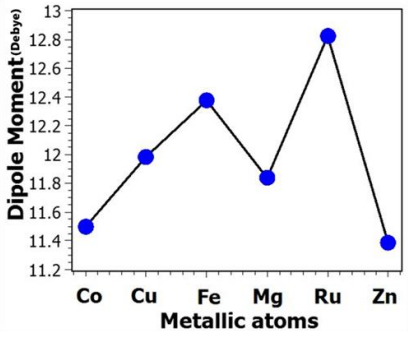

Figure 3. DFT calculation of dipole moment for each Metallo- diphenyl-bipyridine coordination chloride complex molecules.

3. 2. Optical properties

3. 2. 1. Ultraviolet spectrum:

The absorption spectrum in the UV region was calculated for the selected molecules using the (TD-DFT)/B3LYP with the basis set LanL2DZ (figure 4). The calculation shows the maximum absorption occurs for the Cu molecule at the energy of 3.8 eV, whereas for lowest UV absorption peak appears in the Fe complex at the energy 3.45 eV.

3. 2. 2. IR spectrum:

The infrared spectrum (IR) of the molecules were calculated using TD-DFT/B3LYP and the basis set LanL2DZ (figure 5). We found similar behavior in the absorption peaks of all metallo-molecules, the peaks are between 0.204 - 0.423 eV.

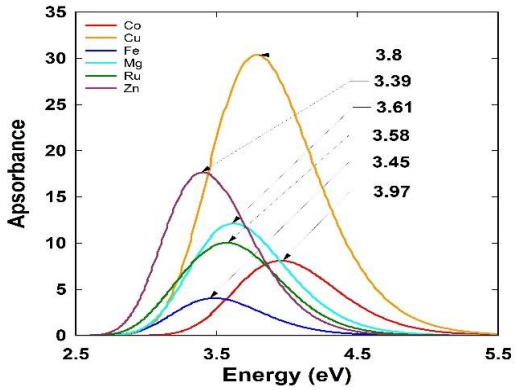

Figure 4. DFT/B3LYP calculation of UV spectrum vs the energy for each Metallo- diphenyl-bipyridine coordination chloride complex molecules.

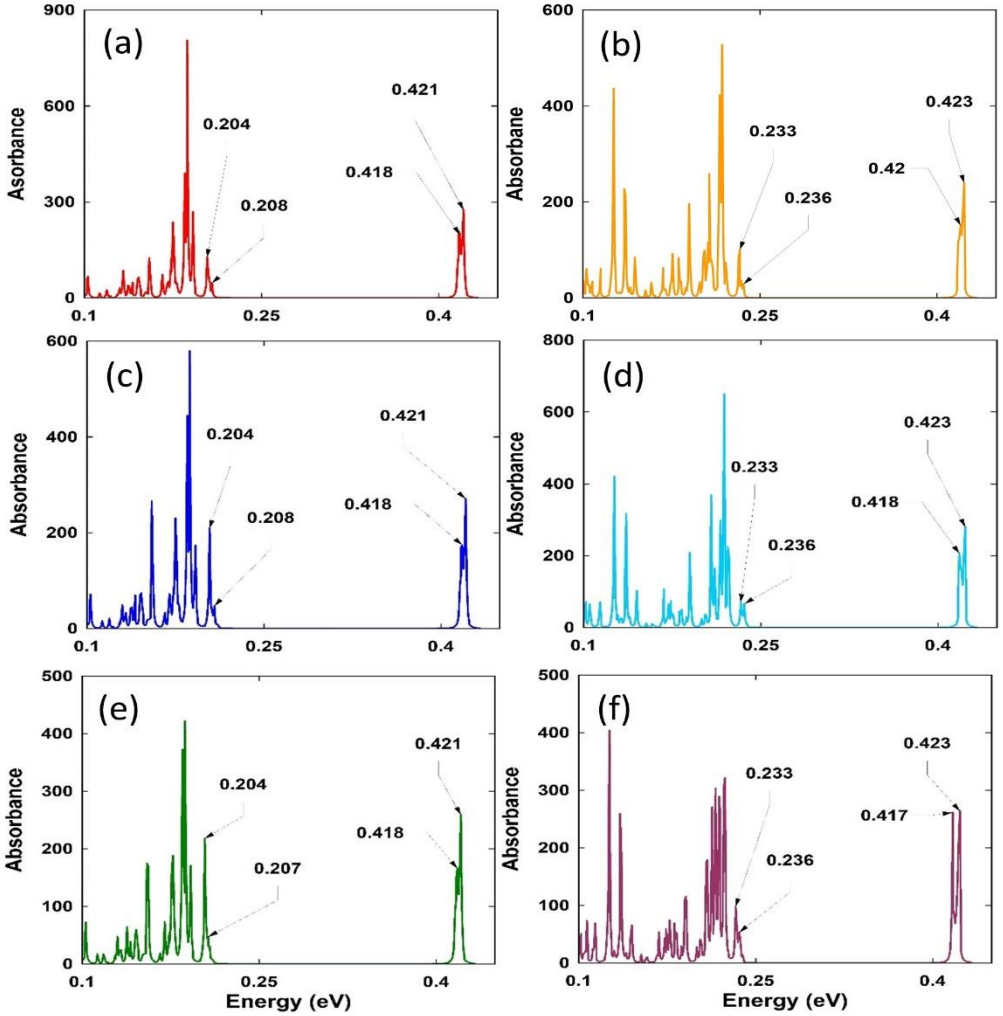

Figure 5. Computed IR absorbance spectrum of the Metallo - diphenyl - bipyridine coordination chloride complex molecules within DFT/B3LYP; (a) Co, (b) Cu, (c) Fe, (d) Mg, (e) Ru, and (f) Zn.

4. Conclusions

We have used the density functional theory (DFT-B3LYP) computations to study the electronic and optoelectronic properties of metallo - diphenyl - bipyridine coordination chloride complexes with a series of central metal atoms Co, Cu, Fe, Mg, Ru, and Zn. We found that the electronic and optical properties can be tuned by varying the metal atom, leading to a large ionization potential (IP = 8.33 eV) and low energy gap (Eg = 1.02 eV) in the Co complex, a large electron affinity (EA = 4.53 eV) in the Fe complex and a high electronegativity (X = 6.24) in the case of Mg atom. Furthermore, the most hardness appeared in the Cu complex and the most softness was recorded for the molecule with Co atom. We obtained the highest dipole moment of 12.85 Debye for Ru molecule and the lowest moment of 11.35 Debye for Zn based molecule. The optical performance of the systems was studied and it was found that the highest UV absorption happens in the Cu based molecule at the energy 3.8 eV, whereas the Fe complex at the energy 3.45 eV exhibits the lowest absorption peak. Similar IR absorption peaks was observed for all metal atoms based complex molecules.

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References

1. Z Ma, *et al., New Journal of Chemistry* **37**, 5 (2013) 1529.
2. M A Halcrow, *Coordination Chemistry Reviews* **249**, 24 (2005) 2880.
3. A Zucca, *et al., Journal of Organometallic Chemistry* **694**, 23 (2009) 3753.
4. J Dupont, C S Consorti, and J Spencer, *Chemical Reviews* **105**, 6 (2005) 2527.
5. D Saccone, *et al., Materials* **9**, 3 (2016) 137.
6. B Naidji, *et al., Synthetic Metals* **221** (2016) 214.
7. Q H Al Galiby, *et al., Nanoscale* **8**, 4 (2016) 2428.
8. R Papadakis, *Molecules* **25**, 1 (2020) 1.

9. M Noori, *et al., Scientific Reports* **6**, 1 (2016) 1.
10. E U Mughal, *et al., Royal Society Open Science* **7**, 11 (2020) 201208.
11. Z Ma, *et al., Dalton Transactions* **43**, 10 (2014) 4048.
12. M Mbarek, B Zaidi, and K Alimi, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **88** (2012) 23.
13. E Bednarova, *PhD Thesis*, Charles University (2018).
14. J Chapman, *et all., South African Journal of Science* **101**, 9 (2005) 454.
15. J V Caspar and T J J Meyer, *Phys. Chem.* **87** (1983) 952-957.
16. E C Constable, *Chemical Society Reviews* **36**, 2 (2007) 246.
17. U S Schubert and C Eschbaumer, *Angewandte Chemie International Edition* **41**, 16 (2002) 2892.
18. H Hofmeier and U S Schubert, *Chemical Society Reviews* **33**, 6 (2004) 373.
19. E A Medlycott and G S Hanan, *Chemical Society Reviews* **34**, 2 (2005) 133.
20. S C Yu, *et al., Advanced Materials* **15**, 19 (2003) 1643.
21. A V Malkov, *et al., Organometallics* **20**, 4 (2001) 673.
22. F Bodar Houillon, *et all., Inorganic Chemistry* **34**, 21 (1995) 5205.
23. C Lee, *et al., Macromolecules* **49**, 14 (2016) 5051.
24. O Ninis, *et al*., *Journal of Materials and Environmental Science* **8**, 7 (2017) 2572.
25. A D Becke, *The Journal of Chemical Physics* **98**, 7 (1993) 5648.
26. E Louis, *et al., Journal of Physical Chemistry Letters* **8**, 11 (2017) 2445.
27. R G Parr, *et al*., "*Absolute Electronegativity and Hardness: Applications to Organic Chemistry*," Academic Press (1989).
28. P Geerlings, F de Proft, and W Langenaeker, *Chemical Reviews* **103**, 5 (2003) 1793.
29. R G Parr, L V Szentpály, and S Liu, *Journal of the American Chemical Society* **121**, 9 (1999) 1922.
30. P K Chattaraj and S Giri, *Journal of Physical Chemistry* A **111**, 43 (2007) 11116.
31. S Kumar, "*Organic Chemistry*" University Amritsar (2006).
32. C G Zhan, J A Nichols, and D A Dixon, *Journal of Physical Chemistry* A **107**, 20 (2003) 4184.
33. M Oftadeh, S Naseh, and M Hamadanian, *Computational and Theoretical Chemistry* **966**, 1-3 (2011) 20.
34. G Job and F Herrmann, *European Journal of Physics* **27**, 2 (2006) 353.
35. R Hussain, *et al*., *Optical and Quantum Electronics* **52**, 8 (2020) 1.
36. M J Hoque, A Ahsan, and M B Hossain, *Biomedical Journal of Scientific & Technical Research* **9**, 5 (2018) 7360.
37. Y A Duan, *et al., Organic Electronics* **13**, 7 (2012) 1213.
38. J C Merlin and J P. Cornard, *Journal of Chemical Education* **83**, 9 (2006) 1393.
39. B D Joshi, *Journal of Institute of Science and Technology* **21**, 1 (2016) 1.
40. R P Smith and E M Mortensen, *Journal of the American Chemical Society* **78**, 16 (1956) 3932.
41. V Berezovsky, *Journal of the Optical Society of America* B **25**, 3 (2008) 458.
42. D G Trabada, *et al*., *ChemRxiv. Cambridge: Cambridge Open Engage;* (2020).