

# SOLVENT-INDUCED AGGREGATION THROUGH Pt...Pt INTERACTIONS: THEORETICAL STUDY OF THE LUMINESCENT ORGANOPLATINUM(II) TERPYRIDYL COMPLEXES

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## ABSTRACT

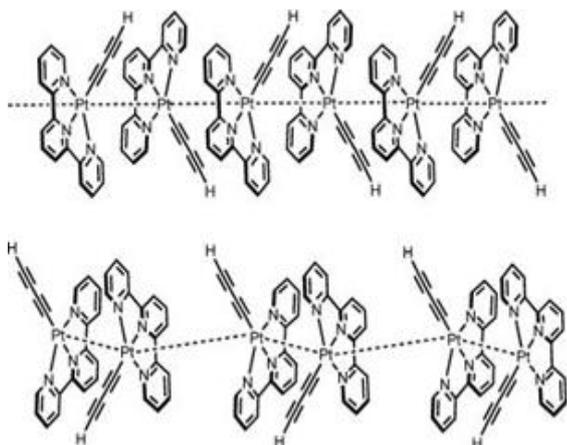
We report a theoretical study of both the structural and optical properties of phosphorescent square-planar Pt(II) terpyridine complexes, namely [Pt(tpy)(C≡C-C≡CH)]OTf that exhibit, at high concentrations, an additional emission band at longer wavelength. The complex [Pt(tpy)(C≡C-C≡CH)]OTf 1 has been found to exist in two forms, a dark-green and a red form; both of which have been structurally characterized and shown to exhibit different crystal-packing arrangements. The geometry optimizations of both the ground state of the considered monomer and different possible trimers have been performed in solution using several density functional theory (DFT) functionals. The UV-visible absorption spectra of the complexes are well rationalized using a vertical time-dependent DFT (TD-DFT) protocol relying on a global hybrid exchange-correlation functional. Le changement remarquable des caractéristiques d'absorption UV-vis induites par des changements dans la composition du solvant peut être considéré comme un type spécial de solvatochromisme.

**KEYWORDS:** Square-planar; DFT; absorption; TDDFT; UV-visible.

## 1 INTRODUCTION

The photophysics of alkynylplatinum(II) terpyridyl complexes represent an important emergent area of research and development [1-4]. The present review exclusively deals with photophysical processes in square planar platinum(II) complexes of the general formulae: [Pt(N<sup>^</sup>N<sup>^</sup>N<sup>^</sup>)(C≡CR)]<sup>+</sup>, where N<sup>^</sup>N<sup>^</sup>N<sup>^</sup> is a tridentate polypyridines (terpyridine) [5]. In recent years, square planar platinum complexes have attracted much attention from the hundreds of transition metal complexes. Square-planar platinum(II) complexes are one of the important classes of metal complexes that have been extensively explored due to their capability to exhibit Pt(II)...Pt(II) interactions and to display rich photophysical properties [6,7]. Pt...Pt interactions in platinum(II) polypyridyl systems have been mainly studied in the solid state and soluble complexes have enabled detailed spectroscopic examinations in solution [8-10]. In this Account,

we describe our development of these alkynylplatinum(II) terpyridyl complexes and their unique spectral properties. The formation of Pt...Pt and π-π stacking interactions is usually associated with obvious color changes. In particular, Yam and co-workers have reported as a result of different intermolecular interactions [10]. Complex [Pt(tpy)(C≡C-C≡CH)]OTf 1 has been found to exist in two forms, a dark-green form and a red form; both of which have been structurally characterized and shown to exhibit different crystal-packing arrangements. The crystal packing of the complex cation of 1 in dark-green form and red form are depicted in Figure 1. The molecular structures coordinated to the platinum atom in a square-planar geometry. The dark-green form of 1 exists as a linear chain with the platinum atoms equally spaced, with short intermolecular Pt...Pt contacts of 3.388 Å. The red form, on the other hand, shows dimeric structure with alternating Pt...Pt distances of 3.394 and 3.648 Å [10].



**Figure 01:** Perspective view of complex cation of 1 in dark-green form (top) and in red form (bottom)

The geometry optimizations of both the ground of 1the considered monomer and different possible trimers have been performed in solution using several density functional theory (DFT) functionals. For the trimers which are shown to exhibit a head-to-tail configuration, a significant shortening of the Pt...Pt distance, compared to that in the ground state. The UV-visible absorption spectra of the complexes are well rationalized using a vertical time-dependent DFT (TD-DFT).

## 2 COMPUTATIONAL DETAILS

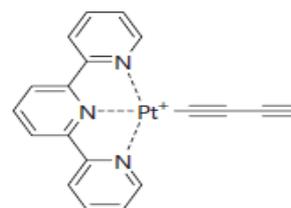
The optimized geometries of trimers were used to perform DFT calculations at the PBE0 [11] level using the LANL2DZ [12] basis set augmented with polarization functions (D exponent for C, N, and S, i.e., 0.5870, 0.7360, and 0.4960, respectively, and F exponent for Pt, i.e., 0.8018, the new basis set being denoted LANL2DZP) on all atoms, except hydrogen ones, with the Gaussian09 program [13]. In the TD-DFT [14] calculations, the solvent effects were taken into account by means of the polarizable continuum model (PCM) [15]. Drawings of molecular structures were done using the Mercury software [16], and

molecular orbitals using GaussView program [17], whereas theoretical absorption spectra were plotted using Swizard [18].

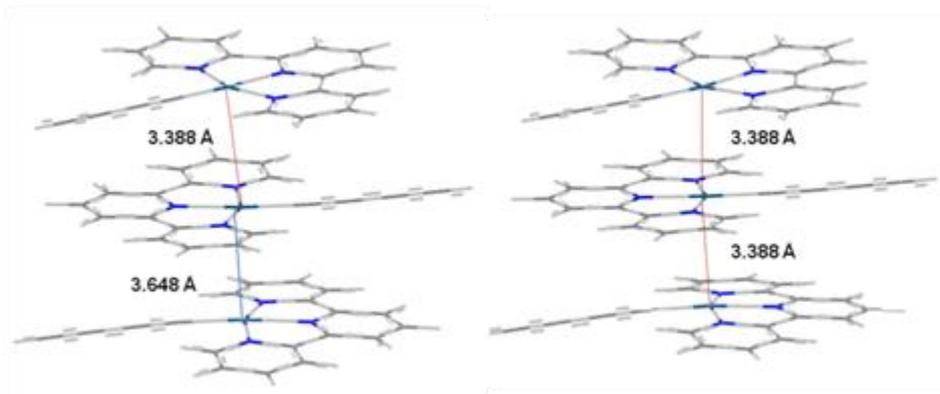
## 3 RESULTS AND DISCUSSION

### 3.1 Structures and geometries

Complex  $[Pt(tpy)(C\equiv C-C\equiv CH)]OTf$  1 under consideration are depicted in Scheme Figure 2. The optimized structure of the trimer was shown in Figure 3. The two molecules packed neither head-to-tail nor head-to-head, trimers structures of the this complex has been built starting from the ground-state optimized geometries, considering both the dark-green form of 1 exists as a linear chain with the platinum atoms equally spaced, with short intermolecular Pt...Pt contacts of 3.388 Å and the red form, on the other hand, shows dimeric structure with alternating Pt...Pt distances of 3.388 and 3.648 Å (see Figure 1). At the same level of theory, we fully optimized the geometries of the trimers 1-D-g and 1-R in both their S0 state. The optimized S0 structure of the trimers is presented in Figures 3. In addition, selected structural and energetic parameters are listed in Table 1



**Figure 02:** Structure of the  $[Pt(tpy)(C\equiv C-C\equiv CH)]$



**Figure 03:** PBE0 / LANL2DZ optimized ground-state (S0) geometries with Pt...Pt distances of the  $[Pt(tpy)(C\equiv C-C\equiv CH)]$  trimers. 1-D-g (Pt...Pt contacts of 3.388) and 1-R (Pt...Pt distances of 3.388 and 3.648 Å)

The obtained results indicate that the energies of the two trimers are almost the same (energy difference equal to ca. 0.05 eV). Note that in our computational study we considered the most stable. Considering optimized geometries of trimers of complex 1, it can be seen that both the bond lengths and the valence angles remain close to their monomeric values. For example, the Pt1–N2 bond of complex 1 is calculated to be equal to 2.022 Å for the monomer and equal to 2.037 Å for 1-D-g and 2.037, 2.035 Å in the unit trimer 1-R (Table 1). Considering the acetylide part of the ligands, which can be affected by

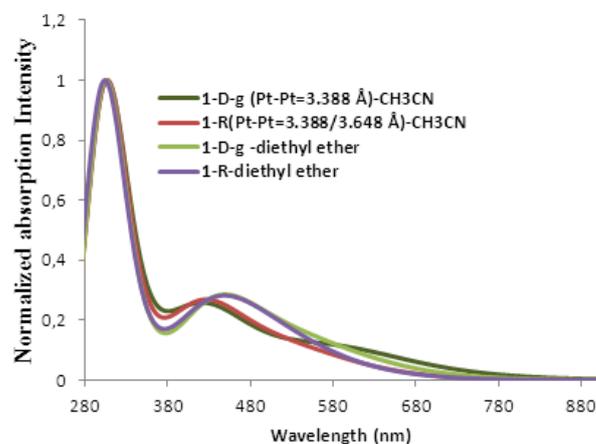
dimerization, we note that the Pt1–C $\alpha$ , C $\alpha$ –C $\beta$ , and C $\beta$ –C $\gamma$  distances in the monomer and in the two units trimers in complex 1 are the same (up to 0.01 Å) that is 1.96, 1.24, and 1.37 Å, respectively. The calculated bond angles in the acetylide part of the complex 1 are weakly affected by aggregation. Indeed, from Table 1 we can note that the Pt1–C $\alpha$ –C $\beta$  angle is equal to 180° in the monomer, 176–178° in the trimers. These geometric deformations arise from the interplay between Pt...Pt bimetallic interactions and the interligand  $\pi$ ... $\pi$  interactions [19-21].

**Table 01: Selected S0 Optimized Geometric Parameters and Energies of the Considered trimers 1-D-g and 1-R**

	RX <sub>1-D-g</sub> [10]	RX <sub>1-R</sub> [10]	Complex 1-D-g	Complex 1-R
energy (eV) *	/	/	-82720.498	-82720.547
d(Pt1...Pt2) (Å)	3.388	3.394	3.388	3.388
d(Pt2...Pt3) (Å)	3.388	3.648	3.388	3.648
dPt1–N2	2.027	2.027	2.037/2.035	2.037/2.035
dPt1–C $\alpha$	2.00	2.00	1.963	1.962
dC $\alpha$ –C $\beta$	1.17	1.17	1.242	1.242
dC $\beta$ –C $\gamma$	1.28	1.28	1.374	1.374
(Pt–Pt–Pt)(deg)	179.2°	154.3°	179.225	175.552
(Pt1C $\alpha$ C $\beta$ )(deg)	177.2	177.6	176-178	176-178
*Total binding energy				

### 3.2 Photophysical studies of the complexes: UV–Visible Absorption.

Starting from the optimized geometries obtained at the TD-PBE0/LANL2DZP level has been performed to simulate the UV–visible spectra of complexes 1-D-g and 1-R in acetonitrile and diethyl ether. The computed vertical absorption spectra of the trimers 1-D-g and 1-R are displayed in Figure 4, and the calculated absorption wavelengths are reported in Table 2. In addition, the MOs involved in the related electronic transitions are shown in Figure 5. The simulated UV-vis spectra of the trimers 1-D-g and 1-R of complex 1 display a low-energy absorption in the visible region assigned to a mixture of LLCT [ $\pi(\text{alkynyl}) \rightarrow \pi^*(\text{N}^{\wedge}\text{N}^{\wedge}\text{N})$ ] and of metal-to ligand charge transfer (MLCT) [ $d\pi(\text{Pt}) \rightarrow \pi^*(\text{N}^{\wedge}\text{N}^{\wedge}\text{N})$ ]. The observed absorption spectra of complexes 1-D-g and 1-R exhibit an intense absorption band in the UV region ( $\lambda = 300\text{--}380\text{ nm}$ ) and an absorption band at ca. 591 and 542 nm. Compared to the case for 1-D-g, a blue shift of 49 nm of the low-energy absorption band is therefore observed for 1-R. Interestingly, the 1-D-g exhibits an additional lower energy absorption band at 591 nm, blue-shifted by 187, compared to the case of the corresponding monomer (416 nm [9])

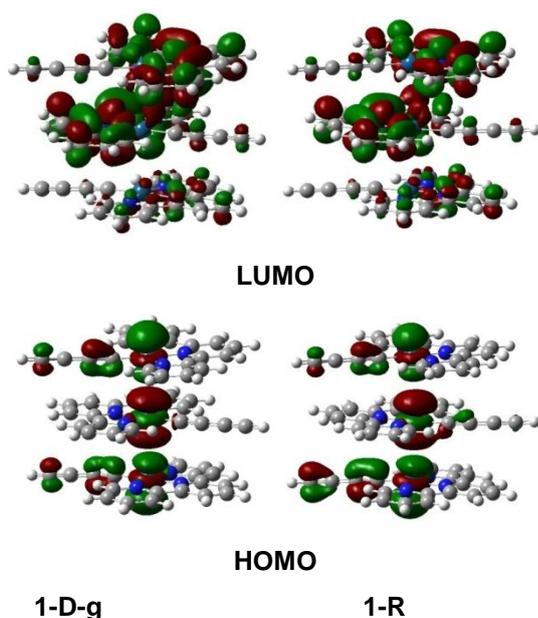


**Figure 04: Simulated UV–visible spectra of complexes 1-D-g (green line) and 1-R (red line), at the PBE0/LANL2DZP level in CH<sub>3</sub>CN and diethyl ether**

**Table 02: Calculated Absorption Spectra ( $\lambda_{\text{cal}}$  in nm and Oscillator Strengths in au) at the PBE0/LANL2DZP Level in  $\text{CH}_3\text{CN}$  and diethyl**

ether				
compound	$\lambda_{\text{cal}}$ (nm)	<i>f</i>	Main contributions (weight)	assignment
1-D-g- $\text{CH}_3\text{CN}$	685	0.09	HOMO→LUMO(+68%)	LLCT/MLCT
			HOMO →LUMO+2(+10%)	LLCT/MLCT
1-R- $\text{CH}_3\text{CN}$	510	0.09	HOMO→LUMO(+67%)	LCT/MLCT
			HOMO →LUMO+2(+15%)	LLCT/MLCT
1-D-g-diethyl ether	562	0.09	HOMO→LUMO(+67%)	LLCT/MLCT
1-R-diethyl ether	539	0.08	HOMO→LUMO(+67%)	LLCT/MLCT

As depicted in Figure 05, the HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) of trimers exhibit considerable similarities. The HOMOs of the trimers are combinations of the Pt(II)  $d_{yz}$  orbital and the  $\pi(\text{C}\equiv\text{C})$  orbital. The LUMOs are mainly localized part of the terpyridinemoiety. Therefore, lowest-lying absorptions can be attributed to combined  $[\pi(\text{C}\equiv\text{C})\rightarrow\pi^*(\text{trpy})]$  ligand-to-ligand charge-transfer (LLCT) and  $[d\pi(\text{Pt})\rightarrow\pi^*(\text{trpy})]$  metal to-ligand charge transfer (MLCT) transitions, if these HOMO to LUMO transitions are allowed.



**Figure 05: Frontier MOs at the Isovalue of 0.02 au for the 1-D-g and 1-R. Considering the Optimized Geometries**

#### 4 CONCLUSION

In this work we have reported the results of theoretical investigations on complex  $[\text{Pt}(\text{trpy})(\text{C}\equiv\text{C}-\text{C}\equiv\text{CH})]\text{OTf}$ . The ground-state DFT geometry optimizations for the two considered complexes 1-D-g and 1-R indicate that considering the formation of trimeric specie play an important role. The UV-vis absorption changes with various solvent compositions. The drastic color changes displayed by solutions of 1 are believed to arise from the

formation of aggregates in solution. It is anticipated that such drastic solvent-induced sensitive changes in color via aggregation of metal-metal bonded (Probes of environmental changes and may find potential applications in materials science and sensor technology). The calculated new low energy absorption band for the trimers are assigned to a combination of LLCT and MLCT from the HOMO localized on the Pt-acetylide to the LUMO delocalized on the N<sup>^</sup>N<sup>^</sup>N ligand.

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