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[Mn(CO)$_3$(bpy)(N-2-chlorobenzylbenzimidazole)]OTf complex as a new photoactivatable CO-releasing molecule

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Metal carbonyl complexes have been accepted major for storage and transportation of carbon monoxide which is an important gasotransmitter. We synthesized novel manganese(I)carbonyl complex with general formula [Mn(CO)$_3$(bpy)L]OTf (bpy =2,2'-bipyridyl, L= N-(2-chlorobenzyl)benzimidazole, OTf = SO_3CF_3). The complex was characterized by LC-MS, ^{1}H NMR, 2D-COSY NMR, ^{13}C NMR, IR and elemental analysis. The CO-releasing properties of the complex were investigated. The DFT/TDDFT analyses were also made by ORCA package program.

Key words: CORM, carbonyl complexes, manganese

INTRODUCTION

Carbon monoxide (CO) is a tasteless, odorless, and colorless gas that often referred to as "silent killer" due to its well established toxicity. CO which binds to hemoglobin to form carboxyhemoglobin (COHb) blocks the oxygen transport in the bloodstream whereas COHb levels of up to 10% caused by CO inhalation are asymptomatic. Furthermore, CO which is a byproduct of heme catabolism has been recognized as an important gasotransmitter in mammals and plays versatile roles in tissue protection [1-5]. Although the mechanism of action has not been understood yet, the researches have pointed out that CO could take part in heme oxygenase equilibrium of hemoglobin degradation process [6]. Many papers about anti-inflammatory, antiapoptotic, antiprofilerative, antioxidant, and anticancer activities have supported the therapeutic characteristic of CO [7-9]. The studies about the CO have divided into two ways: (1) analysis of the bioactivities and the mechanism of action [5, 10-13] and (2) transport the CO with controllable amount and speed to the tissue. Transition metal carbonyl complexes have considered as promising candidates to provide certain amount of CO to biological systems within a certain time [14, 15]. CO-releasing molecules (CORMs) can provide CO with ligand substitution [16, 17], enzyme-triggered [18, 19] and photo-activation [20-23] reactions. Photoactivatable CO-releasing molecules (PhotoCORMs) have to be sensitive to certain wavelength of UV/Vis light but stable in dark within used solvent or solvent systems. It is well-known that penetration depth of light into tissue depends on wavelength and ideal PhotoCORM must release CO by long wavelength within steady times.

Irradiation into the low-lying metal-to-ligand charge transfer (MLCT) bands, which belong to transitions from the metal to the lowest π* orbital of the ligand, may give rise to photo-dissociation of carbonyl ligand and this is, in fact, the main mechanism of CO release with UV-light. An understanding of photochemistry of transition metal compounds requires knowledge of the properties of molecular orbitals, and appropriate excited states. Density functional theory (DFT) and time-dependent DFT approach (TDDFT) plays a crucial role in characterization of the excited states coordination complexes [24-29]. Furthermore, applications of TDDFT approaches have recently been reported on transition metal complexes and got good results. Structures and electronic transitions predicted with the popular BP86 functional are no worse or in many cases are even slightly better than those predicted by the hybrid B3LYP functional [30-35].

In this study, novel [Mn(CO)$_3$(bpy)(N-2-chlorobenzylbenzimidazole]OTf (bpy: 2,2'-bipyridyl; OTf: SO_3CF_3) were synthesized as a CORM. The structures of ligand and compound were elucidated by ^{1}H NMR, 2D-COSY NMR, ^{13}C NMR, IR, LC-MS, and elemental analysis. CO-releasing properties of the compound were investigated. Also DFT/TDDFT analysis of complex was made with ORCA package program by both BP86 and B3LYP functionals for obtaining the optimized geometries, MO electron densities and having insights electronic transitions that promote CO-release.

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EXPERIMENTAL

Materials and methods

All reactions were carried out under argon using standard Schlenk and vacuum techniques. Solvents were freshly distilled after refluxing over metallic sodium or phosphorous pentoxide for 3-4 days [36]. IR spectra were recorded on solid samples with a Shimadzu IRAffinity-1 ATR spectrometer. Band intensities are marked as strong (s), medium (m), weak (w), or shoulder (sh). NMR spectra were recorded on a Bruker Ultra Shield 300 MHz spectrometer. Chemical shifts δ in ppm indicate a downfield shift relative to tetramethylsilane (TMS) and were referenced relative to the solvent signals. Coupling constants J are given in Hertz. Absorption spectra were measured using a Shimadzu UV-1800 spectrophotometer equipped with quartz cuvettes (d=1 cm). Elemental analysis (C, H, and N) were obtained using a CHNS-932 (LECO) instrument. LC-MS was carried out on an Agilent 1100 Series instrument. All chemicals were purchased from Sigma Aldrich and used without further purification.

Synthesis of ligand

Small pieces of lithium (45 mmol, 312 mg) were added slowly to ethylene diamine at 110 °C. The solution was allowed to reach room temperature after stirring for 1 hour and n-alkylbenzylchloride (50 mmol) and toluene (40 mL) were added. Precipitated lithium chloride was filtered and the N-(n-alkyl benzyl)ethylene diamine was isolated by distillation from the oily mixture (120 °C/0.01 mmHg) after solvents were removed under vacuum. N-(n-alkylbenzyl)ethylenediamine (35 mmol) and N,N-dimethylformamide dimethylacetal (40 mmol) were stirred for 2 hours at 100 °C and methanol and dimethyl amine were separated at 120 °C by distillation. The last product was isolated from yellow oily residual by distillation under vacuum (124 °C/0.01 mmHg). Yield:1.96 g (81%). ^{1}H NMR (399.9 MHz, $CDCl_3$) δ (ppm) = 8.05 (s, 1H, NC*H*N), 7.86-7.89 (m, 1H, NC_6H_4N), 7.45-7.48 (m, 1H, NC_6H_4N), 7.26-7.37 (m, 4H, $CH_2C_6H_4$Cl), 7.17-7.22 (m, 1H, NC_6H_4N), 6.89-6.92 (m, 1H, NC_6H_4N), 5.49 (s, 2H, $CH_2C_6H_4$Cl). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm) = 143.8 (N*C*HN), 133.7, 133.1, 133.0, 130.0, 129.7, 128.7, 127.5, 123.4, 122.6, 120.4, 110.0 (NC_6H_4N ve $CH_2C_6H_4$Cl), 46.5 ($CH_2C_6H_4$CI). Anal. Calc. for $C_{14}H_{11}N_2Cl$ (242.70 gmol-1): C, 69.28; H. 4.57; N, 11.54. Found: C, 69.32, H, 4.60, N, 11.50. M.P:80-82 °C.

Synthesis of complex

$Mn(CO)_3$(bpy)Br was prepared according to literature methods by Staal [37]. $Mn(CO)_3$(bpy)Br (100 mg, 0.267 mmol) were added into the solution of AgOTf (82.2 mg, 0.320 mmol) in acetone (10 mL). Precipitated AgBr was filtrated by Celite and the ligand was added after stirring for a day in room temperature. Acetone was evaporated under vacuum. Precipitated orange product was filtered and washed with 5 mL cold methanol and 10 mL cold diethyl ether. Yield: 152.2 mg (83.1%). ^{1}H NMR (300 MHz, DMSO-D_6) δ (ppm) = 5.456 (s, 2H, $NCH_2C_6H_4Cl$), 7.784 (s, 1H, NCHN), 9.453 (d, J=5.0, 2H, $N_2C_{10}H_8$, 6/6'), 8.637 (d, J=3.0, 2H, $N_2C_{10}H_8$, 3/3'), 8.305 (t, J=8.0, 2H, $N_2C_{10}H_8$, 4/4'), 7.821 (t, J=7.0, 2H, $N_2C_{10}H_8$, 5/5'), 7.901 (d, J=8.0, 1H, $NCH_2C_6H_4Cl$), 7.015 (d, J=7.5, 1H, $NCH_2C_6H_4Cl$), 7.518 (d, J=8.0, 1H, NC_6H_4N),7.25-7.4 (m, 5H, $NCH_2C_6H_4Cl$ ve NC_6H_4N). ^{13}C NMR (300 MHz, DMSO-D_6) δ (ppm) = 46.86 ($NCH_2C_6H_4Cl$), 165.39 (NCHN), 155.02, 154.72, 140.44, 127.84, 124.06 ($N_2C_{10}H_8$), 146.60, 141.31, 133.12, 132.55, 132.14, 121.69 ($NCH_2C_6H_4Cl$), 130.27, 130.16, 129.89, 129.67, 127.62, 124.34 (NC_6H_4N), 190.58 (CO). LCMS: m/z 452.1 [M-OTf-3CO]$^{+}$. IR (cm^{-1}, ATR): 1444.75, 1475.61 (s, C-H), 1603.88 (s, C-N), 2035.95, 1944.33, 1930.83 (s, CO)

Myoglobin assay

Stock solutions of the complexes for myoglobin assays were prepared in DMSO. PBS (0.1 M, pH=7.4), 100 mM sodium dithionite (100 µL), 15 µM carbonyl complex and 60 µM myoglobin were combined in a cuvette to give a total volume of 1000 µL. Solutions were degassed by bubbling with argon at each step of the procedure. Horse muscle myoglobin solution prepared in PBS (0.1 M, pH = 7.4) was reduced to deoxymyoglobin by addition of a solution sodium dithionite in PBS (0.1 M, pH = 7.4). Irradiation was made with a 365 nm CAMAG UV Lamp at 1 min intervals during the initial 20 min, then continued at 5 min intervals until no further difference in MbCO concentration was observed. The final solution was placed 5 cm front of the UV lamp. All irradiation experiments were carried out in triplicate. Solutions were freshly prepared for the dark stability and photo-activation experiments. Dark stability spectra were collected automatically for the required period of time by the spectrometer software.

THEORY/CALCULATION

DFT calculations were carried out with ORCA version 2.8 using the BP86 and B3LYP functional with the resolution-of-the-identity (RI) approximation, a def2-TZVP/ def2-TZVP/J basis set, the tightscf and grid4 options, and the COSMO solvation model with water as the solvent for geometry optimizations [30, 31].

RESULTS AND DISCUSSION

Novel ligand of complex was synthesized by adding 2-chlorobenzylchloride to benzimidazole and characterized by ^{1}H NMR, ^{13}C NMR, IR and elemental analysis as detailed in the experimental section. NCHN hydrogen of free ligand shows a singlet at 8.05 ppm in ^{1}H NMR and the NCHN carbon of free ligand shows resonance at 143.8 ppm in ^{13}C NMR. Also, benzyl CH_2 hydrogens are seen at 5.49 ppm as a singlet at ^{1}H NMR and at 46.5 ppm in ^{13}C NMR. IR spectroscopy and elemental analysis were used for confirmation the characterization of free ligand.

The complex was synthesized by stepwise ligand addition to pre-synthesized Mn(CO)$_3$(bpy)Br. The characterization of the complex was performed with ^{1}H NMR, ^{13}C NMR, IR, and LC-MS. NMR signals at 9.45 ppm (t), 8.64 ppm (d), 8.31 ppm (t) and 7.82 ppm (t) with good splitting and integration are assigned to bpy moiety of the complex. Single signal at 7.78 ppm also indicates the hydrogen atom between nitrogens of benzimidazole moiety. All the assignments of the ^{1}H NMR spectrum was confirmed by 2D-COSY NMR spectrum. The signal at 165.4 ppm of the ^{13}C NMR of complex is attributed to NCHN carbon of the benzimidazole moiety. The benzyl CH_2 of benzimidazole moiety shows signal at 46.9 ppm ^{13}C NMR.

IR spectra must have three C-O bands due to the Cs point group and the C-O bands were recorded 2035.9, 1944.3 and 1930.8 cm^{-1}. The band at 1603.8 cm^{-1} is assigned to C-N. Also remarkable 1261.4, 1228.9, 1145.6, and 1030.0 cm^{-1} bands are labeled as OTf that used as precipitant of the complex. LCMS analysis of complex is consistent with expectations. The strongest band of LCMS is attributed to M-OTf-3CO form of the compound. The complex displayed broad maximum on 380 nm and two shoulders on 325 and 276 nm, the extinction coefficients were calculated 2834.4, 5972.5, and 17171.2 M^{-1}cm^{-1} according to Lambert-Beer law, respectively.

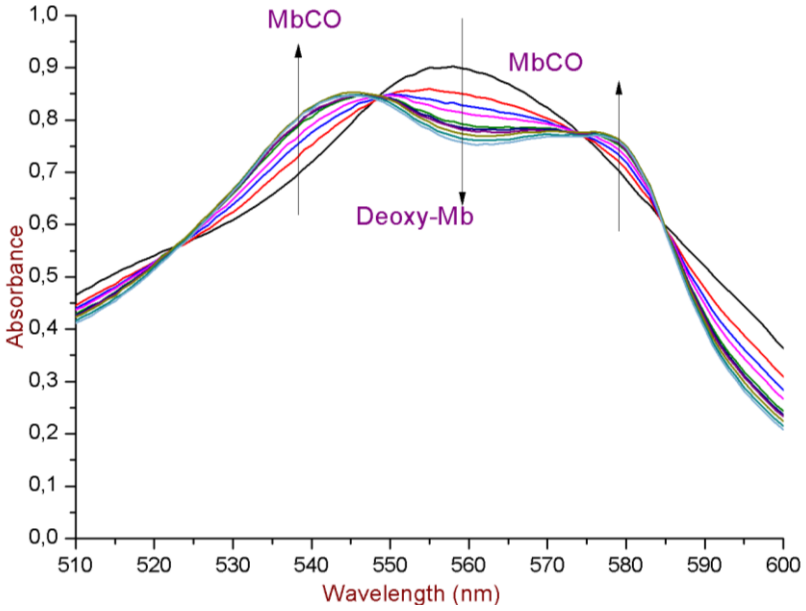
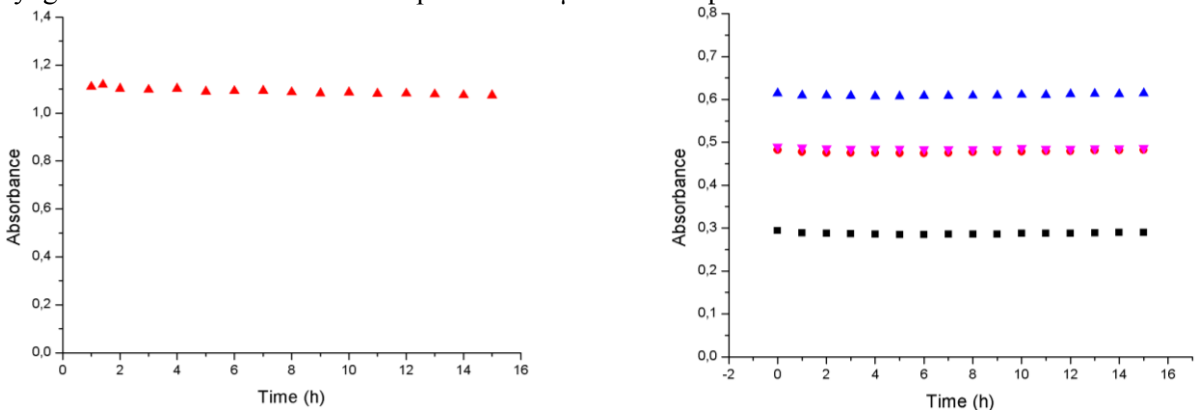


Figure 1. Change of absorption of myoglobin with the irradiation at 365 nm UV light for a solution of complex (15 μM) in 0.1 M PBS (pH=7.4) in the presence of myoglobin (60 μM) and sodium dithionite (10 mM) under argon atmosphere as monitored by UV/Vis spectroscopy.

CO-releasing properties of the complex was identified by myoglobin-assay as detailed above. The absorption of the complex in DMSO for 380 nm (the main maximum of the complex) and myoglobin assay solution for 510, 540, 557 and 577 nm (510 nm: isobestic point; 540 nm: Mb-CO; 557 nm: deoxy-Mb; 577 nm: Mb-CO) was measured in the dark in 16 h. The compound has showed good dark stability with only negligible spectral fluctuations (Figure 2). Then the complex was irradiated with 366 nm UV-lamp for confirmation the light sensitivity (Figure 3). The light sensitivity and CO-releasing of the complex were also confirmed with IR (Figure 4). In myoglobin assay, due to binding of released CO with myoglobin, the reaction is forced towards product side. Carbonmonoxy myoglobin concentration [MbCO] and equivalence CO (eq. CO) which become fixed after a while have indicated total released CO. Total released CO, CO equivalents, and half-life ($t_{1/2}$) were determined with UV-Vis Spectrophotometer at 1 minute intervals with 366 and 410 nm UV-lamps (Figure 1). The $t_{1/2}$

in this study is defined as the time taken to release 50% of the total CO ligands present per molecule. Carbonmonoxy myoglobin concentration of the complex is 34.8 µM while the equivalence CO is 2.32 with 366 nm UV-lamp. But carbonmonoxy myoglobin concentration of the complex is 23.6 µM while the equivalence CO is 1.9 with 410 nm UV-lamp. Half-life of the complex can be used for kinetic analysis. The complex has released half of its CO in 20.8 min with 366 nm UV-lamp while the half-life is calculated 69.2 min with 410 nm UV-lamp.



a b

Figure 2. a) Change of absorption spectra of complex with in dark in DMSO **b)** Change of absorption at selected wavelengths (510 nm: isobestic point ,black; 540 nm: Mb-CO, red; 557 nm: deoxy-Mb, blue; 577 nm: Mb-CO, pink) with increasing incubation time in the dark (0 to 16 h) for a solution of complex (15 µM) in 0.1 M PBS at pH 7.4 in the presence of myoglobin (60 µM) and sodium dithionite (10 mM) under a dinitrogen atmosphere as monitored by UV/vis spectroscopy.

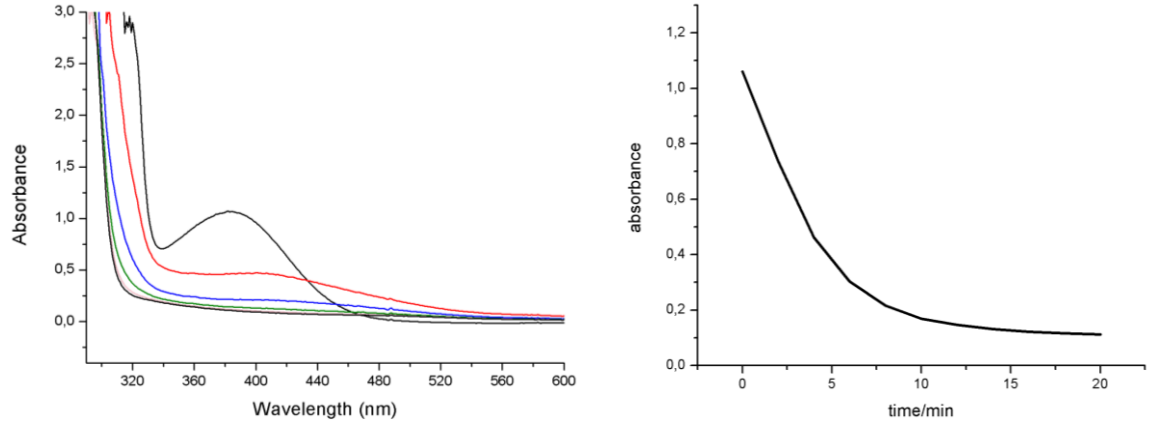


Figure 3. Change of absorption of the complex with 366 nm light in DMSO.

If the CO releasing occurs as observed in the myoglobin assay, the reactions must result with the formation of di- or mono-carbonyl complexes of manganese. Typical IR spectra for fac-manganese (I) tricarbonyl complex is detailed the experimental section. During excitations, strong IR bands of parent complex have disappeared that indicates the dissociation of $[Mn^{I}(CO)_3]$-units of complex. On the other hand new IR bands have emerged in the region around 1975 cm^{-1} and 1860 cm^{-1}. These bands could be attributed to cis-manganese (I) dicarbonyl complexes [38, 39]. The new IR bands around 1850 cm^{-1} and 1875 cm^{-1} might be considered as monocarbonyl manganese (I) complexes [40] (Figure 4).

The complex was structurally optimized by DFT with ORCA package program with COSMO model in water. Manganese compounds containing aromatic ligands usually exhibit intense metal-to-ligand charge transfer (MLCT) transitions in UV-Vis spectrum. Electronic transitions and molecular orbitals which have contribution to electronic transitions were analyzed. Only strong transitions with an oscillator strength >0.01 are reported and contributions >20% are listed in Table 1. HOMO of molecule intensively The HOMO-LUMO transition is a kind of MLCT which is expected to occur in 584.5 nm theoretically, but this transition could not be observed in UV-spectrum of the complex practically because of weak oscillation strength.

Electronic states with highest oscillating force in 376.6 nm is state 11 in which electrons flow from manganese to 2,2'-bipyridyl. This state mostly includes HOMO-1→LUMO+2 transition and is in excellent agreement with experimental maximum in 380 nm. However, state 18 in which electrons flow from metal to benzimidazole by HOMO-1→LUMO+3 in 336.6 nm and state 22 in which electrons flow from benzimidazole to 2,2'-bipyridyl by HOMO-5→LUMO+2 in 327.4 nm are also agree with the shoulders on the UV-Vis spectrum in 325 nm. These three states can be considered as broadness of the maximum of the complex (Table 1).

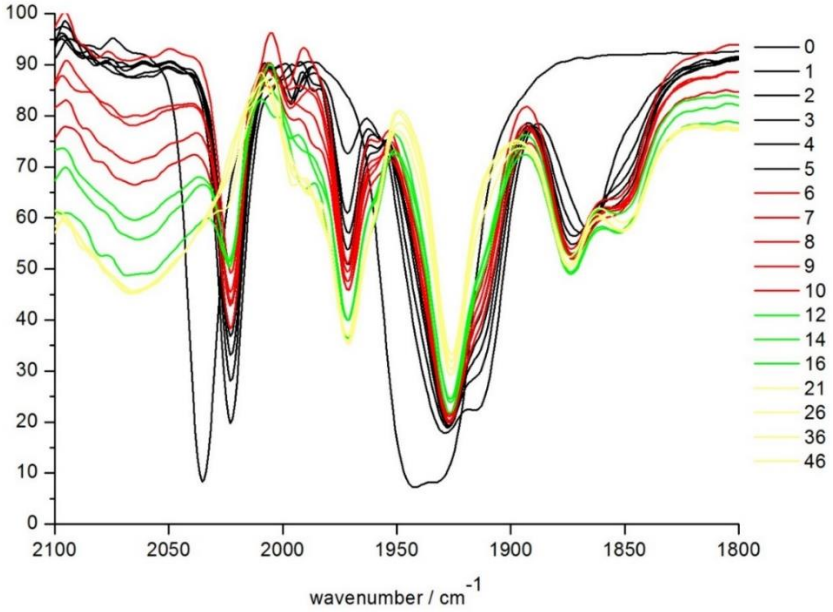
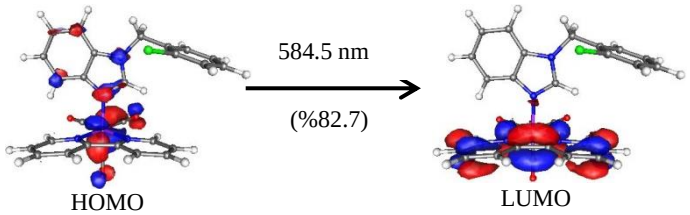
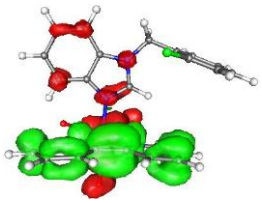
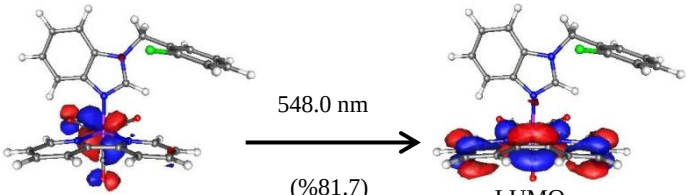
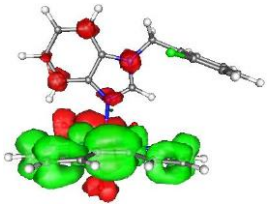
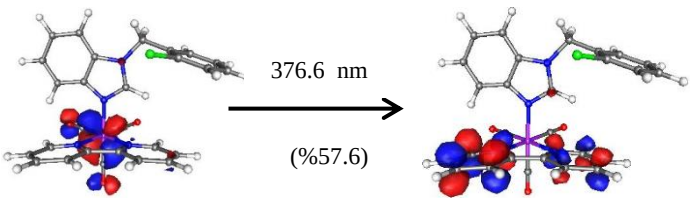
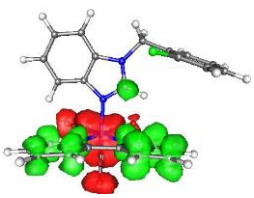
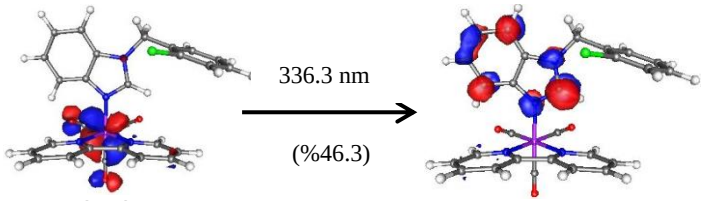
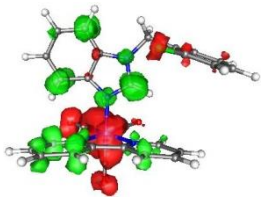
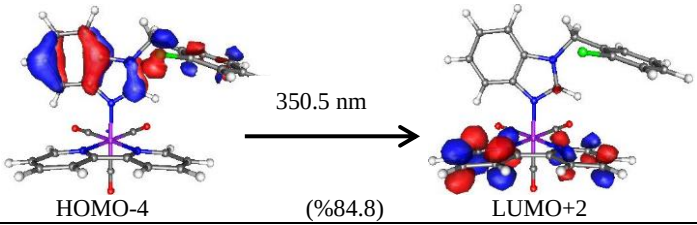
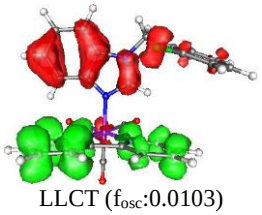
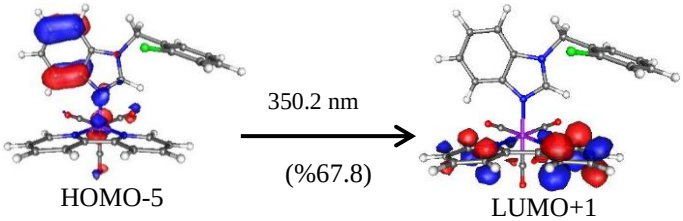
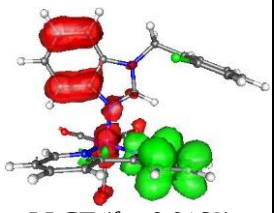
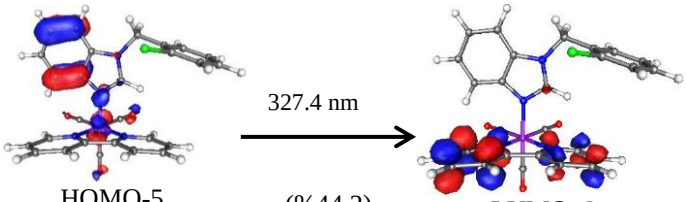
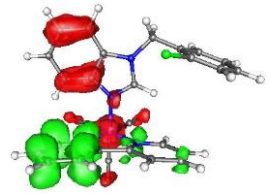
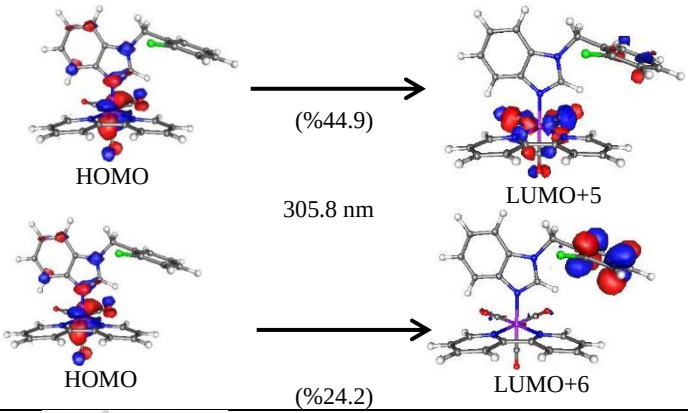
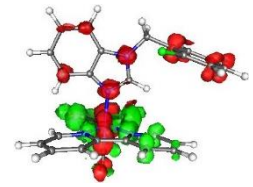
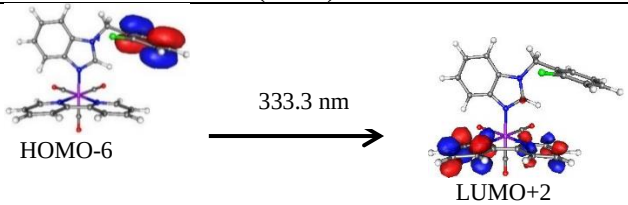
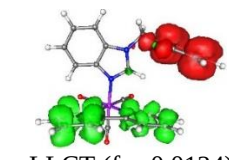
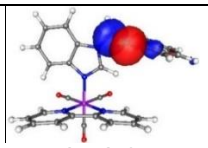
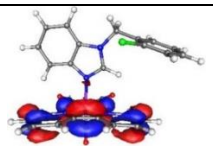


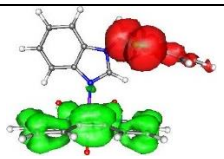
Figure 4. Time-dependent changes in the IR spectra of the complex consists of transition metal orbitals while LUMO is formed completely from 2,2'-bipyridyl orbitals.

Table 1. Energies (in nm), Oscillator Strength (f_{osc}), Main Orbital Contributions, and Type of Transition Involved in the Most Important Singlet Excitations of the complex Calculated with TDDFT/BP86

State	Molecular Orbitals	Main Transitions
1		 MLCT (f_{osc}:0.0157)
2		 MLCT (f_{osc}:0.0192)
11		

		MLCT (f_{osc}:0.0605)
18		
19		
20		
22		
26		
30		

31	 HOMO-8	338.2 nm →	 LUMO


LLCT (f_{osc}:0.0113)

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