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2,2′-Bipyridyl Chelated Ru(II)-Annulated NHC Complex of 1-Methyl-2-Pyridin-2-Yl-2H-Imidazo[1,5-a]Pyridin-4-Ylidene: Synthesis, Structure, Optical Properties, and DFT Interpretation

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Abstract

This article depicts the synthesis of Ru(II)-NHC complex, $[Ru(bpy)(NHC)(CH_3CN)_2][PF_6]_2$ (2); [NHC = 1-methyl-2-(pyridyl)imidazo[1,5-a]pyridine-2-yiledene, bpy = 2,2′-bipyridine] *via* Ag(I)-carbene trans-metallation process. X-ray diffraction studies of compound 2 elucidate the triclinic crystal system of a single crystal with a distorted octahedral geometry. To insight into the structure and optoelectronic properties, density functional theory (DFT) and time-dependent density functional theory (TDDFT) studies were performed, and the absorption spectra were of intra-ligand charge transfer transitions (ILCT) character along with the large contribution of (metal-ligand charge transfer (MLCT) transition in complexes. Compound 2 is fluorescent active and it is expected that the source of fluorescence is due to the presence of 2,2′-bipyridine fluorophore. Hirshfeld model studies were also performed of the crystal structure to illustrate the nature of intermolecular interactions present in the structure in the crystalline environment, and the molecule possesses several C-H…F^- weak H-bonding interactions. The molecule paves the way toward a new pro-apoptotic and antimicrobial compound against various cancer cells and is also a useful pre-catalyst for different types of hydrogenation reactions.

Keywords: Ru(II)-NHC complex, Optical Properties, DFT, TDDFT, Hirshfeld.
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1. Introduction

Ru(II)-complexes bearing polypyridine systems are still the area of intensive research[1-8] due to their photophysical properties. In the last three decades, attention has been given to intense applications starting from optoelectronic devices to targeted drug design. Ruthenium bipyridine complexes such as $[Ru(bpy)_3]^{2+}$ and its derivatives (Chart 1) have been extensively studied as active components in a variety of applications including supramolecular assembly, photoinduced electron-transfer reactions, and photochemistry. Several model complexes have been synthesized and compared with the most widely studied, $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine), an ideal photosensitizer.[9,10] This class of compounds shows excellent properties such as photosensitizers in dye-sensitized solar cells (DSSCs) and has thus been pivotal for advancing light-to-energy conversion technology.[11,12] Tremendous modifications in the polypyridine substitution pattern have been successfully applied for improving the metal-centered redox and excited-state properties.[13-17] Many groups have contributed to the improvement of the photophysical properties of such complexes, either by lowering the energy of the triplet metal-ligand charge transfer transitions (MLCT) excited state or by increasing the MC state energy, the common objective being to place the two states as far as possible from one another.[18-23]

Replacement of one or several pyridine ligand sites by N-heterocyclic carbenes (NHCs) has received surprisingly little attention.[24-27] To gain an insight into the photochemical reactions of carbene complexes, it is necessary to characterize the lowest-lying electronic excited states and their

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photophysical deactivation mechanisms. After the first successful isolation of N-heterocyclic carbene (NHC) by Arduengo *et al.*[28] in 1991, there has been immense growth in the field of chemical,[14,29-31] structural,[32-35] biomedical[36-39] and photophysical properties.[40-42] NHCs can form strong bonds with a broad spectrum of transition metals in various oxidation states and often afford stable complexes.[43-45] Efforts have been directed toward the development of novel NHC scaffolds. In this work, efforts are directed toward the synthesis, characterization, photophysical, DFT, TDDFT, and Hirshfeld model studies of bpy chelated Ru (II) complex supported by a known NHC, 1-methyl-2-pyridin-2-yl-2H-imidazo[1,5-a]pyridine-4-ylidene (1).[46]

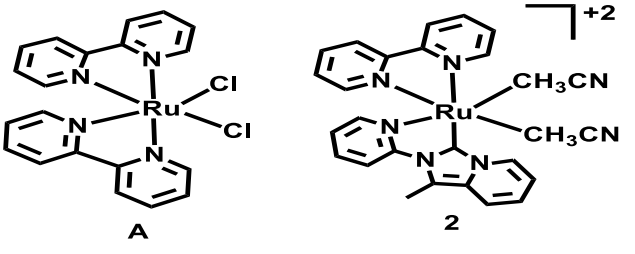
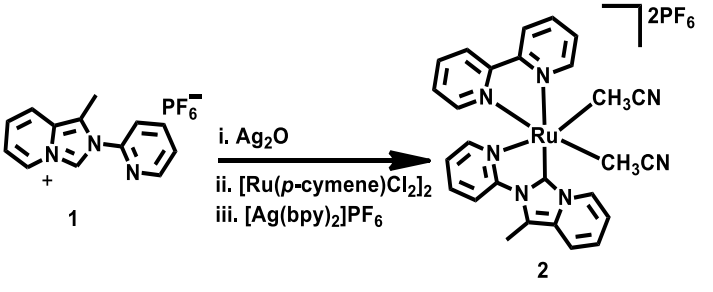


Chart 1. $Ru(bpy)_2]Cl_2$ complex A and studied complex 2.

2. Experimental Section

2.1. General procedures

All the reagents (*e.g.* 2-acetylpyridine, 2-aminopyridine, Ag_2O, $[Ru(p\text{-cymene})Cl_2]_2$, 2,2'-bipyridine, $AgPF_6$, paraformaldehyde, acetonitrile) were purchased from Sigma Aldrich and used without further purification. The complex $[Ag(bpy)_2]PF_6$ used for the preparation of the target complex 2 was prepared as a literature-reported procedure.[47] All manipulations were carried out under an open atmosphere otherwise stated. All solvents were distilled over appropriate drying agents and N_2-saturated prior to use. NMR spectra were measured on a Bruker 200 and 100.5 MHz spectrometer at 25 °C with tetramethylsilane as an internal standard. The J values were measured in Hz. The elemental analyses were performed using a Perkin-Elmer 2400 Series-II CHN analyzer. Electronic and emission spectra of the complex were obtained on a Shimadzu UV-1601 and Perkin-Elmer-LS 55 luminescence spectrometer respectively. Ligand 1 (Scheme-1) has been prepared as a slightly modified literature-reported procedure.[46,48,49] Molecular optimization and time-dependent DFT were done by adopting B3LYP/def2-TZVP basis set with Gaussian 09W software.[50] The number of imaginary frequencies of the molecule turned out to be zero, implying minimum energy structures on the potential energy surface.[51-55] The theoretical spectrum was studied in the acetonitrile solvent phase. To know the orbital information towards the UV-Vis transitions, TDDFT methodology was implemented in G09W, within the density functional theory framework. To know how the ligands and metal contribute towards the formation total frontier molecular orbital of the complex, Gauss Sum software was used to calculate the partial density of states (PDOS). Here, we have separated the whole complex into several fragments. Solvent medium (CH_3CN) calculation has been performed with the help of the polarizable continuum model (PCM) embedded in Gaussian09. Different electronic transitions within the FMOs were obtained using Gauss Sum software.[56] The intensity *vs* wavelength data obtained from computation was then plotted with the experimental data using ORIGIN software.[57] Different color code was used in ORIGIN to distinguish different spectra. The frontier molecular orbitals of the complex were generated in Gauss view using the same level of theory.



Scheme 1. Synthesis of $[Ru(bpy)(NHC)(CH_3CN)_2][PF_6]_2$.

Hirshfeld surface analysis is also done for complex 2. The molecular Hirshfeld surface is built on the basis of electron density distribution on the spherical atom.[58,59] The Hirshfeld surface is unique for a given crystal structure and a set of spherical atomic electron densities. It is this property that indicates the possibility of gaining additional insight into the intermolecular interaction of molecular crystals.[60] On the Hirshfeld surfaces, distances d_e and d_i show the distances from the surfaces to the external nucleus and the surface to the internal nucleus, respectively. The combination of d_e and d_i as a 2D fingerprint plot summarizes intermolecular contacts in the crystal.[61] The Hirshfeld surfaces d_{norm}, d_e, curvedness, shape index, and two-dimensional (2D) fingerprint plots were developed using the 'Crystal Explorer 17.5' application to visualize the intermolecular interaction in this molecule.[62]

2.2. Synthesis of proligand

The proligand 1-methyl-2-pyridin-2-yl-2H-imidazo[1,5-a] pyridin-4-ylidene (1) was prepared by the formulative cyclization reaction of corresponding Schiff base 2-pyridyl-N-(2-acetylpyridyl) methylamine (250 mg, 13.6 mmol) with crushed 91% paraformaldehyde powder (450 mg, 13.6 mmol) in 30 mL 1,4-dioxane, followed by adding 0.5 mL triethyl orthoformate, 2-3 drops of formic acid and 4 M HCl using slightly modified procedures.[46-49] The characterization data and yield were consistent with literature reports.

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2.3. Synthesis of $[Ru(bpy)(NHC)(CH_3CN)_2][PF_6]_2$

In 10 mL of acetonitrile, the ligand 1 (150 mg, 0.42 mmol) and Ag_2O (45 mg, 0.19 mmol) were stirred for 4 hrs in dark and then filtered through G-4 gouch plug with celite to get a clear solution of Ag(I)-NHC complex. $[Ru(p\text{-cymene})Cl_2]_2$ (150 mg, 0.25 mmol) was dissolved in the minimum amount of acetonitrile, in which the prepared Ag(I)-NHC complex solution was added dropwise. An immediate color change was observed from radish yellow to straw yellow. The solution was filtered to remove the AgCl. The resulting solution was evaporated to dryness under reduced pressure and recrystallized from acetonitrile/diethyl ether. An orange-yellowish microcrystalline product was separated by filtration and washed several times with petroleum ether to remove impurities. The yield was 87% (250 mg, 0.43 mmol). The prepared Ru (II)-NHC complex (140 mg, 0.25 mmol) was taken in 15 mL acetonitrile and the preprepared $[Ag(bpy)_2][PF_6]$ (190 mg, 0.32 mmol) in 5 mL acetonitrile was added dropwise to Ru(II)-NHC under the stirring condition at room temperature. White precipitation of AgCl was observed immediately, and the stirring was continued for another 4 hrs. After filtration of AgCl, a wine-red solution was obtained, the solvent was removed, and the target compound 2 was dried over silica. The compound was recrystallized from CH_3CN /Et_2O. The yield was 70% (120 mg, 0.18 mmol).

^{1}HNMR (DMSO-d_6, 25^{0}C, 200Mz) δ: 9.42 (d, J = 4.6 Hz, 2H, $H^{j,j'}$), 8.90 (d, J = 8.0 Hz,1H, H^a), 8.69 (d, J = 7.8 Hz, 2H, $H^{m,m'}$), 8.50-8.31(m, 2H, $H^{l,l'}$), 8.04-7.97 (d-t, 1H, H^d), 7.78-7.58 (m, 4H, $H^{c,e,f,h}$), 7.28-7.21 (m, 2H, $H^{k,k'}$), 7.03 (t, J = 16.0 Hz, 1H, H^g), 6.86 (t, J = 14.0 Hz, 1H, H^b), 2.40 (s, 3H, -CH_3 ^{i}). ^{13}CNMR (DMSO-d_6, 100.5 MHz, 25°C) δ: 150.4, 147.4, 144.5, 144.2, 142.2, 139.0, 138.6, 137.7, 130.5, 130.2, 129.9, 128.1, 127.6, 127.5, 127.4, 126.7, 125.3, 122.6, 122.0, 118.6, 116.0, 115.7, 115.4, 9.6. Anal. calcd. for $C_{27}H_{25}F_{12}N_7P_2RuC_{24}H_{20}AgN_4PF_6$, C, 38.67; H, 3.01; N, 11.69; Found C, 38.64; H, 3.00; N, 11.65%.

3. Results and discussions

3.1. Synthesis and characterization

The imidazolium salt precursor, 1-Methyl-2-pyridin-2-yl-2H-imidazo[1,5-a] pyridine-4-ylium hexafluorophosphate (1), was prepared by the formative cyclization reaction of the corresponding Schiff base 2-pyridyl-N-(2-acetylpyridyl) methylamine with paraformaldehyde, tri-ethyl ortho-formate, and 4 M HCl as previously reported procedures.[46] Ru(II) complex 2 is prepared *via* the silver carbene transfer method which is very common in NHC chemistry. Treatment of the proligand (1) with Ag_2O in acetonitrile at room temperature gives the silver complex $Ag(NHC)_2PF_6$. After isolation of the Ag-complex applying reported procedures,[63] it was treated with a stoichiometric amount of $[Ru(p\text{-cymene})Cl_2]_2$ in acetonitrile, stirring after some time, the solution changes from reddish yellow to straw yellow with the precipitation of AgCl. After filtration, the Ru(II)-NHC obtained in very good yield (87%). Finally, the treatment of complex Ru (II)-NHC with $[Ag(bpy)_2][PF_6]$ affords the targeted complex $[Ru(bpy)(NHC)(CH_3CN)_2]^{+2}$ (2), as shown in Scheme 1 with a very good yield of 75%. Complex 2 was characterized by the ^{1}HNMR and ^{13}CNMR spectroscopy. The formation of the $[Ru(bpy)(NHC)(CH_3CN)_2]^{+2}$ complex 2 was confirmed by the absence of the diagnostic imidazolium -NCHN peak in ^{1}HNMR signal associated with the imidazolium precursor (free ligand –NCHN; δ 10.12 ppm (s), in DMSO-d_6) and the downfield shift of α-pyridyl proton that observed at 8.90 ppm (free ligand 8.75 ppm). ^{13}CNMR spectroscopic analysis revealed that carbonic carbon appears at 174.6 ppm (free ligand at 150.4 ppm); a downfield shift suggested the $C_{carbene}$ atom coordinated to a Ru (II) center. The signals of 2,2'-bpy appear at 9.42, 8.69, and 8.50 ppm. Good execution of downfield shift for most of the aromatic protons was observed as compared to the analogous signals recorded in Ru (II)-complex 2. X-ray diffraction (XRD) studies, as shown in Fig. 1, confirmed the expected geometry of complex 2. The fine long needle-shaped crystals of 2 are crystallized as a 'triclinic crystal system' in the '*P*-1' space group. Additional structural support of complex 2 was obtained from spectroscopic studies, the absorbance maxima (λ_{max}) at 238 and 271 nm (with a hump of 420 nm) and photoluminescent maxima at 430 nm (Fig. 7) display that the absorption bands are red-shifted due to the presence of bipyridyl group.

3.2. X-ray crystal structure analysis of compound 2

Additional support for the proposed geometry of complex 2 was confirmed by single-crystal X-ray diffraction studies. Single crystals of 2 suitable for X-ray diffraction were grown by the slow diffusion of diethyl ether into a saturated acetonitrile solution of complex 2. The obtained crystallographic data and structure refinement details are listed in Table 1 and the corresponding bond parameters are listed in Table ST-1 of the supplementary information file. The lattice parameters are a = 12.5887(3)Å, b = 14.6129(3)Å, c = 18.9820(5)Å, α = 107.5648(9)°, β = 92.3910(8)°, γ = 91.9845(11)°, V = 3322.09(14) Å^3. The asymmetric unit of the title compound, drawn at 20% ellipsoidal probability, is depicted in Fig. 1. There are two molecules of the ruthenium complex and four molecules of the counter anion, PF_6^- in the asymmetric unit. In the presence of N∩C donor bidentate ligand in Ru (II)-NHC complex 2, the Ru-C_{carb} bond distance Ru(1A)-C(1A) = 1.988(6) Å is shorter than similar Ru-C_{carb} distance 2.033(3) Å reported in $[Ru(bpy)_2(NHC)]^{+2}$ complex bearing N∩C donor ligand.[64] Ru-N_{bpy} distances in present case Ru(1A)-N(4A) = 2.048(5) Å and Ru(1A)-N(5A) = 2.115(5) Å are comparable to the reported distances.[65,66] The Ru-N_{py} distance Ru(1A)-N(3A) = 2.061(5) Å distance is close to Ru-N_{bpy} distances in 2.

The complex displays the coordination geometry very close to a distorted octahedral geometry. The C(1a)-Ru(1a)-N(5a), N(3A)-Ru(1A)-N(6A) and N(4A)-Ru(1A)-N(7A), angles are 173.3(2), 176.6(2) and 174.1(2)° deviated from linearity; whereas the other angles C(1A)-Ru(1A)-N(3A),

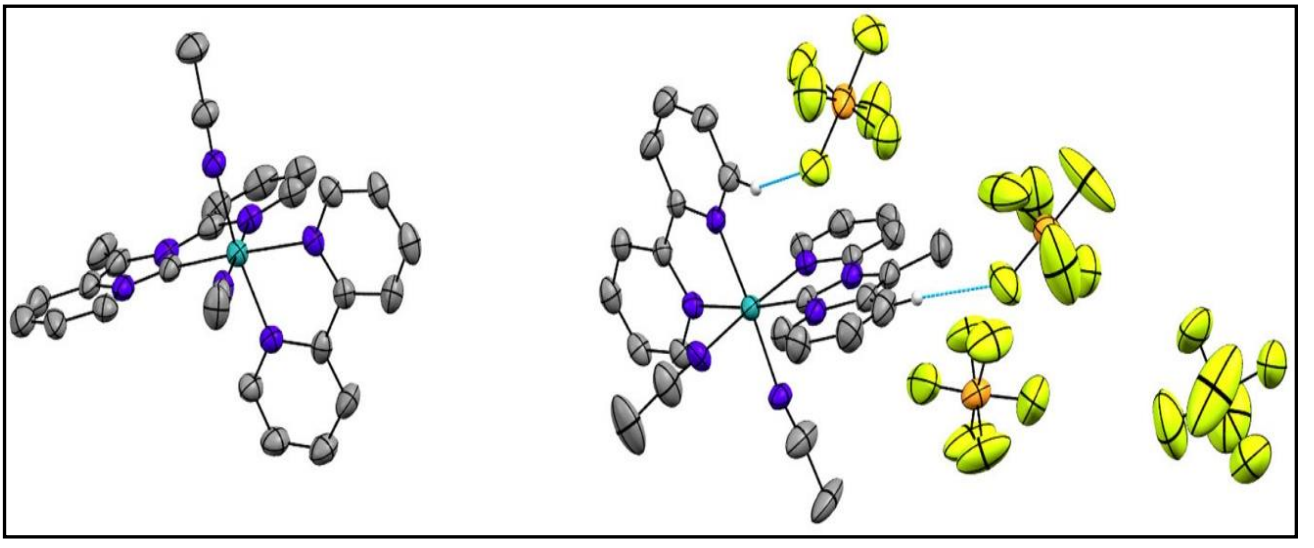

Fig. 1 The asymmetric unit of the complex drawn at 20% ellipsoidal probability. The dotted lines indicate intermolecular C-H…F- H-bonds.

Table 1. Crystallographic details of the complex 2.

Complex 2	Data
Formula	$C_{27}H_{25}F_{12}N_7P_2Ru$
Formula weight	838.55
Temperature/K	295
Wavelength(Å)	0.71073
Crystal system	Triclinic
Space group	*P-1*
a(Å)	12.5887(3)
b(Å)	14.6129(3)
c(Å)	18.9820(5)
α(˚)	107.5648(9)
β(˚)	92.3910(8)
γ(˚)	91.9845(11)
V (Å^3)	3322.09(14)
Z', Z	2, 4
Density (g cm^{-3})	1.677
μ (mm^{-1})	0.667
F (000)	1672
θ (min, max)	2.83, 25.00
$h_{min,\ max}$, $k_{min,\ max}$, $l_{min,\ max}$	-14, 14; -17, 17; -21, 22
No. of refl.	34135
No of unique ref./Obs. ref.	11653/7699
No. parameters	889
R_{all}, R_{obs}	0.1109, 0.0709
wR_{all},wR_{obs}	0.2229, 0.1932
$\Delta\rho_{max,\ min}$	0.922, -0.663
G.o.F.	1.040
CCDC No.	2008104

N(3A)-Ru(1A)-N(4A), N(4A)-Ru(1A)-N(5A), N(5A)-Ru(1A)-N(6A), N(3A)-Ru(1A)-N(7A), N(7A)-Ru(1A)-C(1A) are 78.4(3), 91.7(2), 77.81(19), 85.0(2), 88.5(2) and 88.4(2)° respectively indicate that complex 2 bears a distorted octahedral geometry (Fig. 2, Table ST-1).

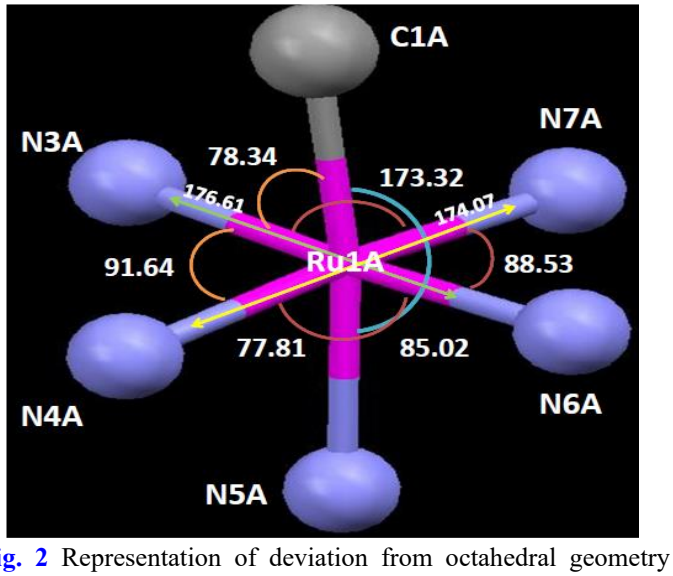

Fig. 2 Representation of deviation from octahedral geometry around Ru(II) in 2.

One such molecule of the metal complex is held with two different counterions via C-H···F- H-bonds, with the H···F distances in the asymmetric unit lying in the range of 2.42 ~ 2.47 Å. The crystal packing involves the formation of a complex network of C-H···F- H-bonds (Table ST-2) between different molecules of the asymmetric unit with the symmetry-related molecules in the crystal. It is of extreme importance to know that the distance between the donor hydrogen atoms and the acceptor fluorine atoms, lying in the range of 2.42 ~ 2.47 Å, is sufficiently short in comparison to the sum of the van der Waals radii of the participating atoms (the sum is 2.67 Å).[67] This may be on account of the favorable electrostatic contributions that govern interactions between the negatively charged fluorine atoms, of the anionic moiety, and the positively charged metal-ligand complex, that induces the electropositive character on the H-atoms of the ligand

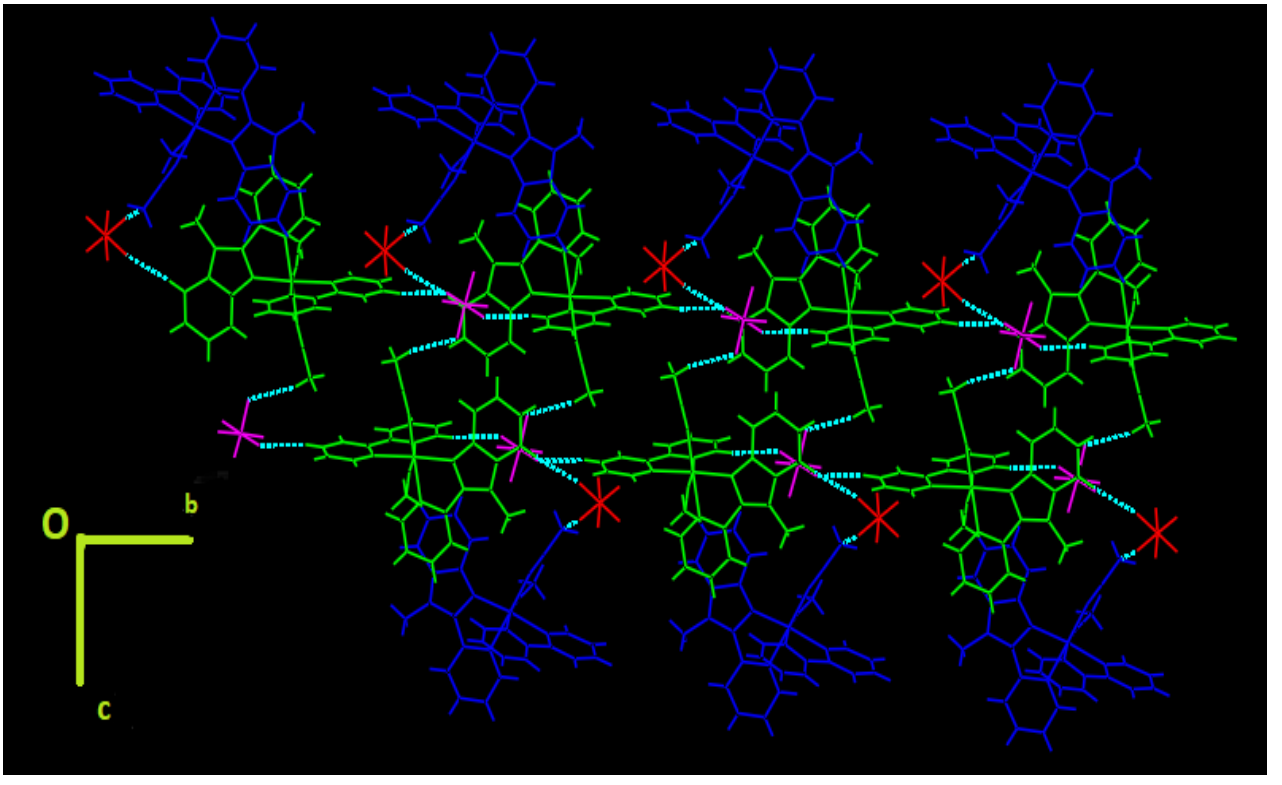

Fig. 3 The crystal packing with various C-H…F^- weak H-bonding interactions of the Ru-(bpy) complex down the bc-plane. Molecule A: Blue; Molecule B: Green; Molecule C and D: Red and Pink (two PF_6^-) ions in the vicinity of the complex. Dotted lines indicate intermolecular interactions.

backbone. Molecules of B-type (green in color) are connected via such H-bonds with two PF_6^- units, corresponding to molecule C (red in color) and D (pink in color). The supramolecular structure involving Molecule B (green in color) and one PF_6^- unit i.e., molecule D (pink in color) form a tetrameric R_4^4 (22) close ring motif,[68] which further propagates along the *bc*-plane (Fig. 3). Molecules of A-type (blue in color) are connected via similar H-bonds to a separate PF_6^- unit, corresponding to molecule C (red in color), as shown in Fig. 3.

3.3 Hirshfeld surface analysis

The Hirshfeld surfaces of the crystal structure were investigated to illustrate the nature of intermolecular interactions, which mapped over d_e, d_{norm}, shape index, and curvedness shown in Fig. 4. In the d_{norm} surfaces, the large red color spot shows the hydrogen bonding H···F contacts whereas the blue surface area represents the H···H contacts (Fig. 4b). The d_e surface features appear as a relatively flat green region where the contact distances are similar (Fig. 4a). The shape-index surfaces measure the donor-acceptor pair and curvedness surfaces measure how much shape effectively divides the surfaces into a set of patches. The absence of a triangle curved in both the shape-index surface and curvedness surface represents the absence of π···π contacts. The adjacent highlighted red and yellow regions on the shape index surface also show the strong hydrogen bonding interactions present in the molecule (Fig. 4c).

However, the blue curved and yellow regions on the curvedness surfaces shows the H···H interactions (Fig. 4d). The Hirshfeld surfaces show red spot due to C-H···F^- hydrogen bonding. The 2D fingerprint plot shows the sharp spike, which represents the strong hydrogen bonding present in the molecule (Fig. 5a). The fingerprint plot shows that the H···F contacts have a relatively higher contribution of 35% in comparison to other interactions. Further, the percentage contributions of other intermolecular interactions in this crystal structure are as follows: H···H (34.7%), C···H/H···C (18.8%), C···F/F···C (4.9%), N···H/ H···N (3.3%), C···C (2.4%) (Fig. 5b).

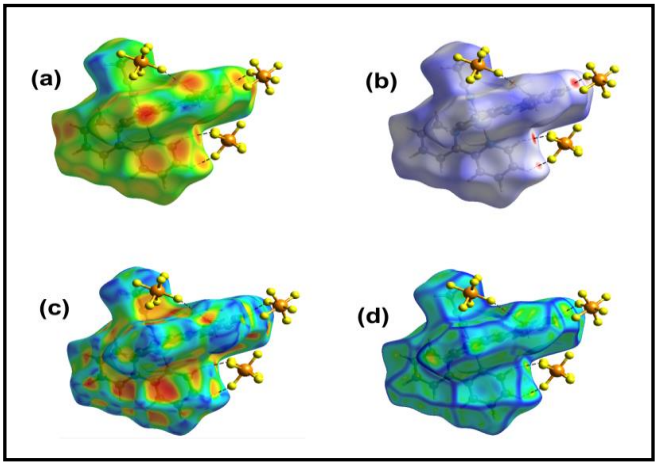

Fig. 4 Hirshfeld surfaces mapped with (a) d_e, (b) d_{norm}, (c) shape-index, and (d) curvedness for the compound.

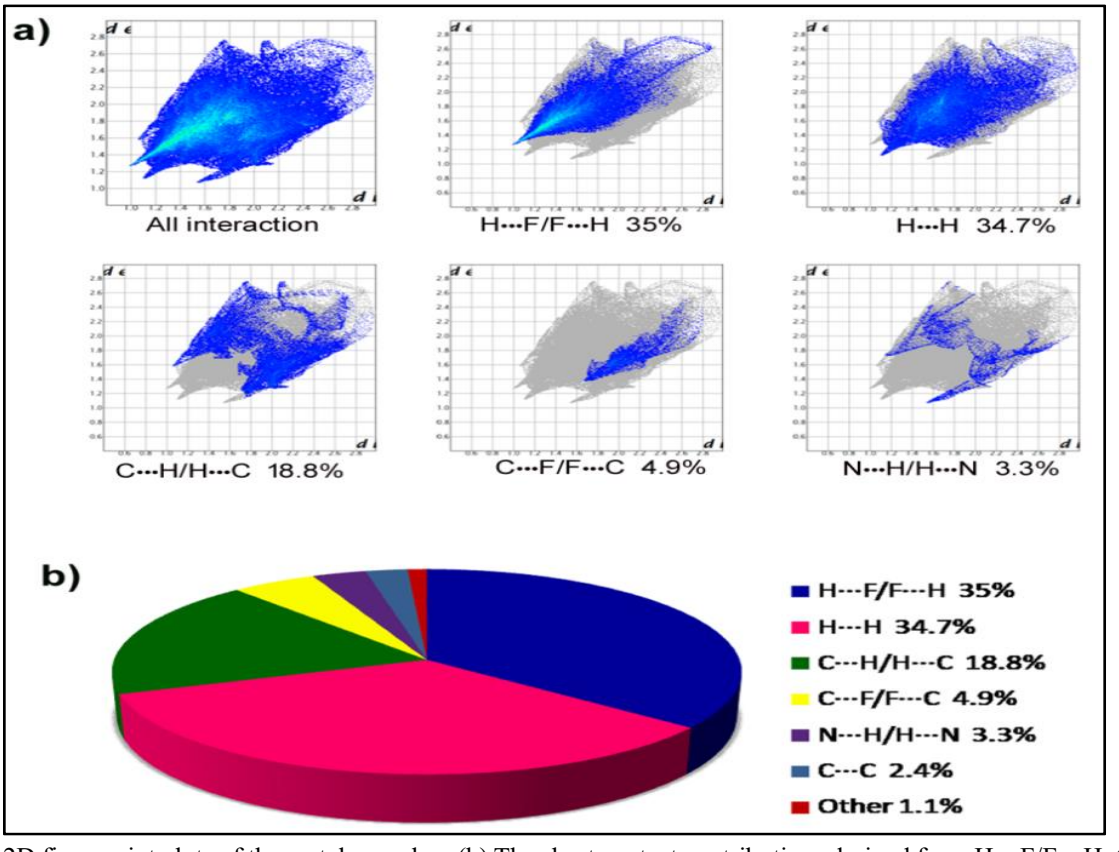

Fig. 5 (a) The 2D fingerprint plots of the metal complex; (b) The short contact contributions derived from H…F/F…H, C…H/H…C, C…F/F…C, N…H/H…N, C…C and H…H contacts.

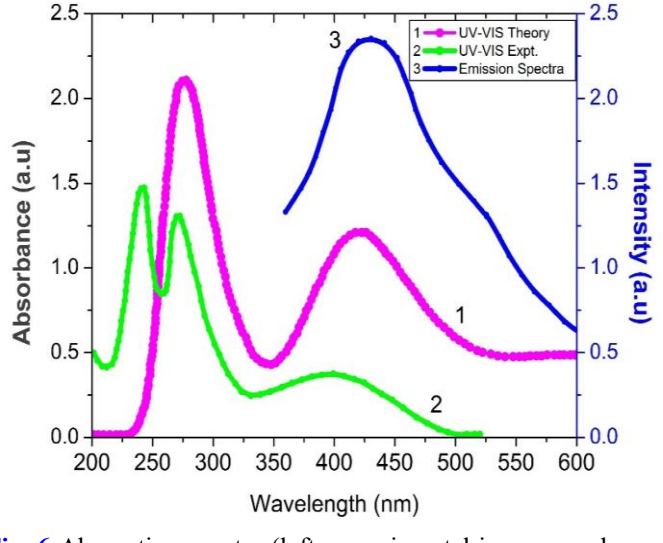

Fig. 6 Absorption spectra (left; experimental in green color and theoretical in pink color) and emission spectra (right, in blue color) of complex 2.

3.4. Spectroscopic studies

The UV-Vis absorption spectrum for complex 2 was recorded in acetonitrile solvent at room temperature shown in Fig. 6 (green). The mononuclear complex shows weak interaction bands at 235-420 nm due to the inter-ligand charge transfer (ILCT)bpy→NHC and metal-to-ligand charge transfer (MLCT) from t_{2g} to δ^*, whose energy varies with the nature of the ligand acting as an acceptor.[69,70] Complex 2 shows two sharp absorbance bands (λ_{max}) at 238 and 271 nm with a hump at 399 nm (the calculated transitions (pink) at 278-285 nm and 423 nm). The absorption bands at 238 and 271 nm have also been tentatively assigned to MLCT [Ru (II) → δ* arene]. The band in the region 399 nm may exhibit a small solvent effect or indication of luminescent spectra due to the presence of a bipyridyl group in the ligand. The photoluminescence property of complex 2 has been studied in acetonitrile at room temperature. Complex 2 shows strong luminescent spectra at 430 nm upon excitation at 400 nm due to the presence of a bipyridyl group. The emission spectrum of complex 2 is shown in Fig. 6 (blue).

Theoretical studies of absorption spectra of Ru (II)-NHC complex 2 in acetonitrile solvent are shown in Fig. 6 (pink), and significant transition values of absorption spectra are listed in Table 2. The moderately intense band at 238 -271 nm is owing to metal-ligand transitions. However, the absorption bands near 399 nm could have a substantial ligand contribution to the complex. The absorption maxima for complex 2 (λ_{max} = 285 nm) are found in between the reported complex.[71] The absorption maxima of 2 are due to the σ-donor and weak π-acceptor character of the NHC ligand compared to the bi-dentate 'bpy' ligand.[14] The MLCT-type transitions in the absorption spectra are supported by computational calculations [Fig. 6, Table 2] in the DFT platform.[72]

Table 2. Major transition values for absorption spectra of complex 2. (Experimental and theoretical data).

Wavelength (nm)		Osc.	Major Transitions
Expt.	Theory	Strength	
238	278	0.1357	HOMO-5->LUMO(12%), HOMO-3->LUMO+3(19%), HOMO-1->LUMO+6(47%)
271	285	0.0917	HOMO-3->LUMO+2(49%), HOMO-2->LUMO+3(24%)
399	423	0.1888	HOMO->LUMO+13 (87%)

The theoretical λ_{max} values 30~40 nm varied from experimental values. The calculated transitions at 278-285 nm (238-271 nm in expt.) involve a significant contribution from HOMO-1→LUMO+6 (47 %), HOMO-3→LUMO+2 (49 %), and HOMO-2→LUMO+3 (24%). Transitions at 423 nm (399 nm in expt.) involve HOMO→LUMO+13 (87%) (Table 2). To get an insight into the structure bonding correlation on the electronic transition of absorption spectra, the metal and ligand contributions to the formation of FMOs were also calculated[73-75] using the B3LYP/def2-TZVP level of theory (Fig. SF-1), and PDOS also analyzed (Fig. 7) using computational techniques.[76-79] The compositions of occupied FMOs show that these have significant ligand contributions both from NHC and bi-pyridine (47 ~ 49 %) and also Ru metal (25 ~ 77 %) from HOMO-1 to HOMO-3, and CH_3CN has a negligible contribution. The unoccupied MOs also exhibit a major share from NHC ligand (LUMO, 49%; LUMO+2, 72%), and *bi*-pyridine (LUMO, 45%; LUMO+4, 85%) and very less contribution from CH_3CN (Fig. 7, Table ST-3). Hence, instead of pure ligand characteristics (intra-ligand/inter-ligand) transitions, complex 2 bears a mixed mode of metal-ligand transitions. Under oxygen-free conditions, complex 2 is found to be emissive in CH_3CN at room temperature at 430 nm (Fig. 6). The emission is due to the presence of a bi-pyridine ligand present in the complex as compared to our previously reported complex.[69,71] Some selective FMOs are shown in Fig. SF-1.

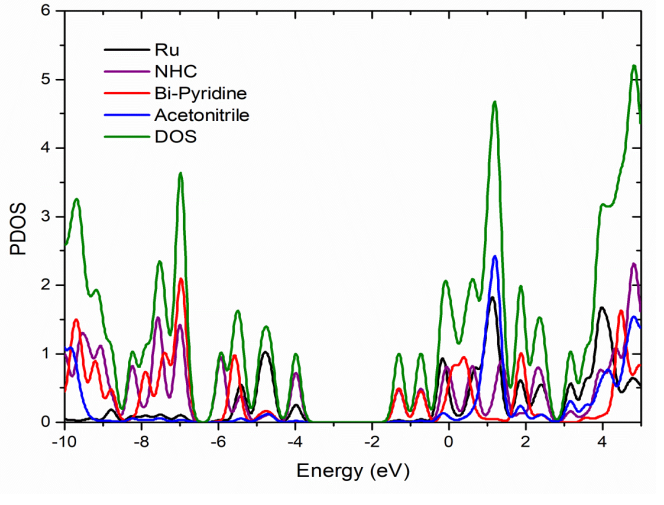

Fig. 7 Partial density of states (PDOS) for complex 2.

4. Conclusion

In this present work, we studied the coordination behavior of N-heterocyclic carbene and 2, 2′-bipyridyl ligand. The synthesis, structure, and luminescent properties of 2, 2′-bipyridyl Ru (II)-annulated NHC complex of 1-methyl-2-pyridin-2-yl-2H-imidazo[1,5-a] pyridin-4-ylidene are described. The distorted octahedral geometry of complex 2 has been confirmed by X-ray crystallographic studies. The molecules possess several C-H…F^- weak H-bonding interactions. Such interactions enrich the crystal engineering design parameters which are used to create higher-order structures. The photophysical properties of the complexes were also examined and found to depend on the ancillary ligands as well as the constituent metals. The peaks are due to ILCT character along with the maximum contribution of MLCT transition in complexes. Such features may find utility in materials used in contemporary electronics applications. Many of the abovementioned assignments were corroborated by a series of DFT and TDDFT calculations which were in good agreement with the experiment. The molecule will be useful for the pro-apoptotic and antimicrobial activity against various cancer cells[71,72,80] and also a useful pre-catalyst for the transfer hydrogenation of ketones[79-82] and also in asymmetric hydrogenation reactions.[83,84]

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Conflict of interest

There are no conflicts to declare.

Supporting information

Applicable.

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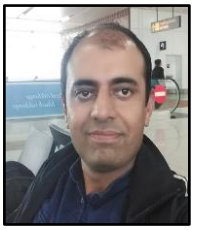

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