A DFT based assay for tailor-made terpyridine ligand - metal complexation properties

Krati Joshi, Sailaja Krishnamurty, Iksha Singh and Kaliaperumal Selvaraj

ABSTRACT

Electron-rich terpyridine ligand and its metal complexes have a potential to grow as responsive surfaces by adapting their physicochemical properties as a function of environment. The responsiveness is brought about by judicious molecular level designing that is currently hindered due to lack of information and control on terpyridine (TPy)–metal (M) interactions at single molecule level. So far there is no organised understanding on the binding of different metals with TPy ligand and ways to modulate it. Being a large conjugated pi system, TPy has a large scope to be functionalised with electron exchanging groups to alter its electronic structure and consequently its binding with metal atoms. In first report of such a kind, using density functional theory (DFT), we demonstrate that convenient modulation of TPy-M binding is possible through functionalisation of TPy for M = Co, Ru, Fe, Mo and Au. Electron donating groups viz., CH$_2$, OCH$_3$, C$_2$H$_5$, NH$_2$ and electron withdrawing groups viz., CF$_3$, COOH, CN and NO$_2$ are considered for functionalisation of TPy ligand. Significantly, the present work focuses on the functionalisation at 4 and 4’ positions of TPy molecule. The role of such a functionalisation in influencing the ligands structure–property correlation is missing in the literature to the best of our knowledge. The present investigation quantifies that by pertinent functionalisation of TPy, TPy-M binding energies can be modified up to $\sim$60 kcal/mol. Our results reveal that functionalisation leads to a considerable charge redistribution within the TPy-M complex with carbon atoms in pyridine rings functioning as major electron sink/source with a corresponding red/blue shift of $\epsilon_{\pi \pi}$. This modifies the red-ox, optical and other chemical properties of TPy-M complexes. In brief, the present report illustrates a way to design ligands such as TPy for diverse applications through tailor-made functionalisation using electronic structure methodology.

1. Introduction

Introduction of terpyridine (Tpy) ligand in device chemistry has expanded tremendously over the past few years owing to its switchable chemical and physical properties.[1] Its rich coordination chemistry provides various possibilities for functionalisation. The three different possible coordination sites in terpyridine ligand are: (i) 4’-position in the central ring (see Figure 1(a)) (ii) 4/4’, 5/5’ and 6/6’ positions in terminal rings [2,3] (see Figure 1(a)) and (iii) one widely known triple nitrogen poutch site. The 4’-position is substituted with leaving groups such as Cl, OH, etc.[2–6] which can be further readily functionalised giving rise to a plethora of ligands as components in metallo-polymers.[7] 4, 4’ and 4” positions when functionalised by various electron exchanging groups have a considerable impact on the catalytic activity and stability of the Tpy–metal (TPy-M) complexes.[2–4,8] In addition to it, maximum influence on physicochemical and luminescence properties of TPy-M complexes is observed in case of 4 and 4’ functionalisation.[9] The triple nitrogen poutch site is mostly utilised for coordination with metal atoms. Terpyridine binds to a number of metal ions at this site [10–23] resulting in a wide range of TPy–metal (TPy-M) complexes. The metal ion coordination with terpyridine introduces several dynamic features such as chelating effects, self-healing or responsive properties, functional properties including spin–crossover, electro-chromism and reactivity leading to applications in asymmetric catalysis, antitumor agents and biolabels depending on the choice of metal atom and functionalisation at 4/4’/4”-positions. Hence, by judicious choice of the metal ions and design of functionalised terpyridine ligands, the final structure and properties of the resulting metallo-polymers can be tailored at all length scales.

Few researchers have attempted to elucidate the structure–property correlation of functionalised TPy-M complexes for various metal atoms. In an experimental report, Henderson and Hayward [24] have demonstrated that ether functionalised Tpy-Co and TPy-Fe complexes, result in a labile complex, while amine functionalised TPy-Co complex is inert. Amine substitution in TPy-Fe complexes does not yield the oxidation-induced stability as observed in amine-TPy-Co complexes. Understandably, intramolecular interactions (molecular structures) play an important role in the property of a complex. For example, a theoretical report on trithiocyanato functionalised TPy-Ru black dye has shown that the interaction of metal with the TPy varies in different isomers (linkage isomers of thiocyanate groups). [25] In another DFT-based report on TPy-Ni complexes, it has been shown that replacement of methyl by a simple halide group alters the character of frontier orbitals, thereby affecting
applications requiring different degrees of metal binding strength can be constructed based on critical leads from theoretical calculations. For instance, to construct long-living and robust molecular assemblies on solid supports, a strong binding of M with TPy is needed. On the other hand, for applications such as chemical sensors, a loose binding is needed. These varied situations of binding demand highly tailor-made material design. Thus, altering the electronic structure of the ligand such as TPy by functional group of choice would yield more promising novel materials.

In the present report, we systematically study the TPy-M binding energy for various metals using DFT-based calculations. The digression in the binding as a consequence of functionalisation of TPy with appropriate electron donating and electron withdrawing groups is evaluated. The less studied 4 and 4′ positions are considered for functionalisation in TPy-M complexes. Structure–property relationship is investigated and variations in molecular and electronic structure of TPy-M complexes are compared for unfunctionalised and functionalised TPy ligand. Parameters such as atomic charges, Fukui functions and molecular orbitals are used to understand the electron redistribution that influences the TPy-M interaction. In short, a generalised understanding of the coordination chemistry of TPy ligand with different transition metal atoms at molecular level is attempted. To the best of our knowledge, such an information is not available in the literature and this study is the first step towards understanding the role of functionalisation on structure–property relationship of TPy-M complexes.

2. Computational details

All calculations are performed in the framework of density functional theory (DFT), using a linear combination of Gaussian orbitals as implemented in Gaussian 09 software package. Geometries in the present investigation are optimised using its red-ox properties. There is also a theoretical investigation elucidating the electronic structure of TPy complex with metals such as Cr, Fe, Ir, etc. Interestingly, all these functionalisation studies concentrate on the 4′-position in the central ring. There are no detailed experimental or theoretical studies so far elucidating the role of functionalisation at various positions (such as 4 and 4′) in the terminal rings of TPy ligand.

Most importantly, though the importance of a rational design of TPy-M complexes is established, fundamental knowledge of TPy-M binding chemistry remains elusive. In particular, the role of metal ions involved and functionalisation of terpyridine ligands in modulating the TPy to M binding energies and thereby its electronic properties is yet unknown. Hence, the development or refinement of these advanced materials based on TPy-M complexes is hampered. Few scanty reports attempt to evaluate TPy-M binding constants as a function of rate of dissociation, thermodynamics and kinetics and role of functionalisation. An interesting report recently published demonstrates the importance and possibility of quantifying the binding of TPy ligand with transition metals experimentally.

In the above work, the researchers have practically decoded single molecular coordination forces in the TPy-M complexes. However, even though recent growth in the branches such as electron transfer processes and probing them through ultra fast spectroscopy and advanced electro chemical techniques made it possible to understand highly impressive electron delocalisation at molecular level, it is still a very difficult problem experimentally and hence application of theoretical methodologies to understand and decode various molecular forces in these complexes is more viable at this juncture. Not only theoretical methodologies can predict the variation in the TPy-M binding energies, they also reveal the extent of electronic structure modification, thereby giving leads to synthesis and application chemists.

In summary, interesting futuristic materials such as TPy-M-based red-ox systems with enormous scope in several advanced
Perdew–Burke–Ernzerhof (PBE) \[37\] exchange and correlation functional with Stuttgart–Dresden (SDD) Relativistic Effective Core Potentials (RECP) \[38,39\] as basis sets for Co, Fe, Ru and Au atoms. The properties of the systems with these atoms are seen to be substantially affected by relativistic effects.\[40–44\] Los Alamos Effective Core Potentials (LanL2) with Double Zeta (DZ) \[45\] polarisation are used for Mo atom. Triple Zeta Valence Basis Sets for C, H, N, Cl, O and F atoms.

The TPy molecule is considered to be in its neutral state. All the metal atoms are considered to be in their +III oxidation state. Hence, the metals are neutralised with three chlorine atoms. In short, all the TPy-M complexes are in neutral state. Co-TPy and Au-TPy complexes with even number of electrons have a spin multiplicity of 1 and the calculations for the same are carried out using unrestricted Kohn–Sham formalism. On the other hand, Ru-TPy, Fe-TPy and Mo-TPy complexes have odd number of electrons and the calculations on these complexes are carried out using unrestricted Kohn–Sham formalism.

The gradient and displacement for convergence of a geometry is considered with a threshold value of 10\(^{-5}\) au.\[47–50\] The criterion for convergence of SCF cycles is 10\(^{-6}\) au. Unfunctionalised (bare ligand with no functional group) TPy-M complexes are designed and optimised first followed by the optimisation of TPy with few electron donating groups (EDGs) or electron withdrawing groups (EWGs). Functionalisation is done at 4 and 4’ positions of terminal rings (see Figure 1(a)) as there is practically no understanding on the role of functionalisation at these positions in establishing structure–property relationship in TPy-M complexes as mentioned in the earlier section. Functional groups such as CH\(_3\), OCH\(_3\), C\(_6\)H\(_5\) and NH\(_2\) are considered for EDGs and CF\(_3\), COOH, CN and NO\(_2\) are considered for EWGs. It may be noted that in this text, bare ligand, TPy with no functional EDGs or EWGs is referred as ‘unfunctionalised TPy’ and TPy attached with any of the functional groups is referred as ‘functionalised TPy’. For the metal (M) complexed with unfunctionalised TPy ligand is referred as ‘TPy-M’, while the metal complexed with a functional group as ‘EDG/EWG-TPy-M’. Similarly, the Cl atom attached to 4’ carbon of the central pyridine ring is referred as TPy-chlorine and that attached to the metal atom as ‘M-chlorine’.

Our analysis of the molecular orbital energies and orbital occupation numbers (see Table 1) shows that all the optimised complexes are in their lowest spin state. Following the geometry optimisation, harmonic vibrational frequencies are computed for various complexes. All frequencies are found to be real, indicating all TPy-M conformations are local minima. BSSE corrected binding energy between the metal and TPy is calculated using the following formula:

$$BE = E_{CI} - (E_L + E_M)$$  \[1\]

where BE is the binding energy of metal with TPy. \(E_C\) is the energy of functionalised or unfunctionalised TPy-M complex and \(E_L\) is the energy of ligand TPy. \(E_M\) is the energy of metal (MCI\(_2\), M = Co, Ru, Fe, Mo and Au). Basis set superposition error (BSSE) is included while calculating binding energies using counterpoise correction method. Charges on atoms in various complexes are calculated using the Hirshfeld partitioning scheme. Hirshfeld population analysis (HPA) is reported to be superior to other partitioning schemes probably due to its stockholder nature.\[51\] According to Parr and Nalewajski \[52\], when atoms combine together to form molecules, information loss is at a minimum when charges are partitioned according to HPA. However, in order to validate the results and conclusions based on HPA charge analysis, we have calculated natural population analysis (NPA) charges for NO\(_2\) functionalised TPy-M complexes and compared the results with that of HPA charges.

3. Results and discussion

3.1. Structure and electronic properties of unfunctionalised TPy-M complexes

Figure 1(a) illustrates the atomic positions and the nomenclature for different nitrogen atoms in the unfunctionalised TPy ligand. N and N’ are nitrogen atoms in terminal (side) pyridine rings
(together referred as N_{terminal}), while N′ is the nitrogen atom in central pyridine ring (referred as N_{central}). Atomic positions of 4 and 4′ carbon atoms are sites for functionalisation with EDGs and EWGs as already discussed. 4′ site is functionalised by CI atom. This site is generally used for extended architectures or anchoring on surfaces. Optimised conformations of unfunctionalised terpyridine–metal (TPy–M) complexes are shown in Figure 1(b)–(f). The corresponding structural and electronic properties are given in Table 1. Detailed structural analysis reveals that (see Table 1) in Co–TPy, Ru–TPy and Fe–TPy complexes two of the N–M–N angles are around 81° and the third N–M–N angle is around 163° indicating a nearly octahedral complex. In contrast, the N–M–N angles in TPy-Mo complex are 72°, 72° and 140° indicating it to be a distorted octahedral complex. Thus, metal atoms in TPy-Co, TPy-Ru and TPy-Fe complexes are sterically more viable (due to larger N–M–N angles) for an attack by a second ligand molecule as compared to that in TPy-Mo. Being closer to octahedral complex, the M–N– bond length (metal–nitrogen from central pyridine ring) in Co, Ru and Fe is shorter than the M–N and M–N′ (metal–nitrogen from terminal pyridine rings) bond distances. This is consistent with earlier reports, where M–N′ distances are found to be shorter than the M–N and M–N″ bond distances in Ru-Tpy complexes.[53–55] Mo is equidistant from all three nitrogen atoms in the TPy ligand. Au bonds with only central nitrogen atom (N′) resulting in a distorted square planar complex. The presence of a single Au–N bond is also clearly observed from Au–N bond distances. Interestingly, the N–M–N, N–M–N′ and N′–M–N″ bond angles in Au are nearly identical to those of Mo. We note that in all above five cases (Co, Ru, Fe, Mo and Au), M-chlorine coordination of the TPy–M complex retains a near octahedral orientation with all Cl–M–Cl at right angles (90° ± 5°).

Analysis of charge distribution among various TPy–M complexes shows that Ru, Mo and Au are positively charged centres, while Co and Fe hold a small negative charge. From Table 2, it is seen that the charges on nitrogen atoms of TPy ligand with which Co and Fe are attached have much lower charge (~0.033 and ~0.017, respectively) as compared to those with which Ru and Mo are attached (~0.107 and ~0.188). This implies that there is a possibility of strong π-back bonding in case of TPy-Ru and TPy-Mo complexes, as a result Ru and Mo acquire high positive charge. However, this effect is either not present or less in case of TPy-Co and TPy-Fe complexes resulting in negatively charged Co and Fe metal atoms. Au is bonded to only one nitrogen out of the three nitrogen atoms of TPy ligand. As a result, interacting N atom acquires some electrons from Au atom leading to a more positive Au centre. Consequently, carbon atoms in the pyridine rings are the only positive centres in TPy-Co and TPy-Fe complexes and rest of the atoms (metal, Cl and N atoms) draw electrons from them. Accordingly, highest occupied molecular orbitals (HOMO) in these two complexes (see Supporting Information, Supp-Figure 1) is localised on negatively charged Cl and metal atoms. HOMO is polarised by the presence of positively charged carbon atoms. Lowest unoccupied molecular orbital (LUMO) is predominantly contributed by the carbon atoms in pyridine rings. Ru is least positively charged among the other three metal atoms. The positive charge (0.1 e) on the Ru in combination with the larger N–M–N bond angles makes Ru to be a nucleophilic centre. Mo and Au metal atoms in TPy–M complexes carry significant positive charge. HOMO as well as LUMO orbitals in TPy–Ru, TPy–Mo and TPy–Au complexes are predominantly contributed by d orbitals of metal atoms making them strong red-ox centres. The order of positive charge held by metal centre is as follows: Au > Mo > Ru > Fe > Co. The charge distribution on N and N′ (N_{terminal}) are more negative as compared to N′ (N_{central}) in all the complexes. Negative charge localisation on N atoms is in the following order: Au > Mo > Ru > Co > Fe. Thus, the trend in negative charge held by nitrogen atoms is in line with that of the positive charge held by the metal centres indicating the charge transfer is essentially from N atom to M. Interestingly, in TPy–Au complexes, the ratio of N_{terminal}/N_{central} charges is higher as compared to that in other complexes due to no interaction between Au and N_{terminal} atoms.

Chlorine atom in 4′ position (TPy–chlorine atom) plays a very important role in building of supramolecular assemblies. Substituents anchored at this position determine the directionality of TPy–M complexes. Mono layers of TPy–metal complexes are also anchored on various substrates through this position. On the other hand, reactivity of chlorine atoms attached to metal centre (M–chlorine) determines the rate of formation of bis-TPy–M complexes. Hence, charge on all chlorine atoms influences the reaction chemistry of TPy–M complexes such as dimerisation, anchoring on substrate and functionalisation, etc. It is seen that metal–chlorine is nearly in an ionic state from Hirshfield charges. The negative charge on metal chlorine decreases in the following order Au > Mo > Co > Ru > Fe. Indeed, it is more difficult to have monomer complexes of TPy–Au, TPy–Mo and TPy–Co as compared to TPy–Ru and TPy–Fe monomer complexes.[29] More reactive metal chlorine atoms in TPy–Au, TPy–Mo and TPy–Co-based complexes ease the formation of bis-terpyridine complexes. Tpy-Chlorine hold 0.01 (e) to 0.05 (e) depending on the metal centre. Well-known local reactivity descriptors, Fukui functions are used to evaluate the ease of anchoring of TPy–M units on a substrate for TPy-chlorine.[56,57] Cl atoms in all TPy–M complexes have higher relative electrophilicity as compared to relative nucleophilicity and hence are most likely to be attacked by nucleophile. Cl atom attached to Au metal are the most negative one in comparison to those from the other metal complexes, indicating it as the most vulnerable site for a nucleophilic attack. Interestingly, analysis of relative reactivity indices shows that TPy–Mo has both the indices close to each other. In other words, its relative nucleophilicity is nearly equal to that of relative electrophilicity. This trend is also corroborated by lower HOMO–LUMO gap (particularly alpha gap) for TPy–Mo complex as compared to other TPy–M complexes. Thus, TPy–Mo complex is more viable for both electrophilic and nucleophilic reactions making it more active. On the other hand, we could not establish a clear correlation between Fukui functions and HOMO–LUMO energy gap for other TPy–M systems.

Binding energies of M with TPy are as follows: Ru > Mo > Co > Fe > Au. In short, TPy–Ru complexes with the highest binding energy are most stable among all the TPy–metal complexes. This promotes the formation of highly stable TPy–Ru supramolecular architectures as seen in earlier experimental studies.[11–13] A combined DFT and experimental study reports similar metal binding order but for pyridine: Os > Ir > Pt > Ru > Rh > Ni > Co > Fe > Pd > Cu > Au > Ag.[58] Interestingly, another experimental study by Shubert et.al. reported metal binding order between TPy–M as, Co > Ru > Fe > Ni > Cu > Mn > Cd.[59] In all cases
including the present one, binding energy of Au with TPy is the least among metals. This is attributed to the fact that Au coordinates uniquely through a single Au–N bond.

### 3.2. Structure and electronic properties of EDG functionalised TPy-M complexes

Structural and electronic properties of EDG functionalised TPy-M complexes (EDGs are CH₃, C₆H₅, OCH₃ and NH₂ groups) are discussed below. The structural and electronic modifications due to functionalisation are analysed and presented in Supporting Information, Supp-Figure 2, Supp-Tables 1 and 2, respectively. Though the structure is more or less retained with respect to bond lengths and bond angles, (see Supporting Information, Supp-Table 1) functionalisation sterically strains the complex from its original molecular plane. This is quantified by a change in the 4–N–N'–4' dihedral angle as seen from Supp-Table 1 and Supp-Figure 3 (see Supporting Information). The loss of molecular planarity in large \(pi\) systems such as TPy plays a predominant role in deciding its properties based on electronic excitations.

The charge redistribution in EDG-TPy-M complexes is given in the Table 2. EDGs donate 0.1–0.3 electrons to the TPy-M. CH₃ and NH₂ are the most EDGs and OCH₃ is the least EDG for all TPy-M complexes. The charge gained by TPy-M from EDG varies depending upon both metal centre and EDG. The electrons gained by TPY-M (M = Co, Ru, Fe, Mo and Au) are predominantly (50–70%) shared by the carbon atoms in three pyridine rings. Rest of the charge (50–30%) gets redistributed among metal centre, chlorine atoms and \(N_{\text{central}}\) terminal atoms. The electron gained by M-chlorine in all cases indicates that the Cl predominantly (50–70%) plays a predominant role in deciding its properties based on electronic excitations. The charge redistribution in EDG-TPy-M complexes is given in the Table 2. EDGs donate 0.1–0.3 electrons to the TPy-M. CH₃ and NH₂ are the most EDGs and OCH₃ is the least EDG for all TPy-M complexes. The charge gained by TPy-M from EDG varies depending upon both metal centre and EDG. The electrons gained by TPY-M (M = Co, Ru, Fe, Mo and Au) are predominantly (50–70%) shared by the carbon atoms in three pyridine rings. Rest of the charge (50–30%) gets redistributed among metal centre, chlorine atoms and \(N_{\text{central}}\) terminal atoms. The electron gained by M-chlorine in all cases indicates that the Cl predominantly (50–70%) plays a predominant role in deciding its properties based on electronic excitations.

### Table 2. Hirshfeld charges (e) on various atoms in unfunctionalised and functionalised TPy-M complexes. Gain/loss of charge by tpy carbon atoms after functionalisation is highlighted. Summary of NPA(N) charges (highlighted in red) lost by TPy-carbon-atoms/gained-by-EWG is included for NO₂ functionalised TPy-M complexes.

| Metals/atom centre | TPy-M | CH₃ | C₆H₅ | OCH₃ | NH₂ | CF₃ | CN | COOH | NO₂ |
|-------------------|-------|-----|------|------|-----|-----|----|------|------|
| Co                |       |     |      |      |     |     |    |      |      |
| M                 | 0.443 | 0.440 | 0.437 | 0.429 | 0.431 | 0.449 | 0.418 | 0.418 | 0.445 |
| N                 | -0.055 | -0.057 | -0.063 | -0.068 | -0.072 | -0.052 | -0.062 | -0.063 | -0.063 |
| N'                | -0.056 | -0.056 | -0.066 | -0.070 | -0.076 | -0.053 | -0.062 | -0.063 | -0.063 |
| Cl(M)             | -0.863 | -0.863 | -0.863 | -0.863 | -0.863 | -0.863 | -0.863 | -0.863 | -0.863 |
| Cl(TPy)           | -0.026 | -0.027 | -0.026 | -0.028 | -0.035 | -0.012 | -0.021 | -0.015 | -0.019 |
| Net charge gained/lost on functionalisation |        |     |      |      |     |     |    |      |      |
| TPy C-atoms       |       |     |      |      |     |     |    |      |      |
| M                 | -0.106 | -0.102 | -0.100 | -0.101 | -0.171 | -0.069 | 0.168 | -0.012 | (H)-0.140 |
| N                 | -0.004 | -0.007 | -0.008 | -0.012 | -0.020 | 0.001 | -0.005 | -0.001 | -0.004 |
| N'                | -0.009 | -0.014 | -0.017 | -0.023 | -0.032 | -0.032 | -0.032 | -0.032 | -0.032 |
| Cl(M)             | -0.875 | -0.876 | -0.876 | -0.880 | -0.882 | -0.736 | -0.873 | -0.741 | -0.865 |
| Cl(TPy)           | -0.023 | -0.027 | -0.026 | -0.028 | -0.035 | -0.012 | -0.021 | -0.015 | -0.019 |
| Net charge gained/lost on functionalisation |        |     |      |      |     |     |    |      |      |
| TPy C-atoms       |       |     |      |      |     |     |    |      |      |
| M                 | 0.276 | 0.105 | 0.114 | 0.266 | 0.005 | -0.209 | -0.047 | (H)-0.210 | (N)-0.195 |
| N                 | -0.007 | -0.135 | -0.095 | -0.238 | -0.072 | 0.133 | 0.024 | (H)-0.055 | (N)-0.257 |
| N'                | -0.091 | -0.158 | -0.156 | -0.153 | -0.173 | -0.145 | -0.144 | -0.143 | -0.143 |
| Cl(M)             | -1.112 | -1.072 | -1.069 | -1.114 | -1.084 | -1.040 | -1.036 | -1.036 | -1.028 |
| Cl(TPy)           | -0.021 | -0.019 | -0.018 | -0.024 | -0.025 | -0.004 | 0.001 | -0.007 | 0.003 |
| Net charge gained/lost on functionalisation |        |     |      |      |     |     |    |      |      |
| TPy C-atoms       |       |     |      |      |     |     |    |      |      |
| M                 | 0.133 | 0.110 | 0.089 | 0.253 | -0.001 | -0.204 | -0.059 | (H)-0.219 | (N) 0.340 |
| N                 | 0.113 | -0.111 | -0.052 | -0.195 | 0.067 | 0.116 | -0.012 | (H)0.115 | (N)0.562 |
blue shift is observed for the C=C bond stretch as illustrated in the Figure 2. Hence, the electron-rich pyridine skeleton EDG-TPy-M complexes are more likely to be attacked by electrophiles with potential application in electrophilic substitution reactions.

The highest metal binding energy is seen in case of NH₂-TPy-Ru complex (−97.26 kcal/mol) and the smallest metal binding energy is observed for OCH₃-TPy-Au complex (−24.03 kcal/mol). Figure 3 gives a graphical illustration of variation in binding energies for EDG-TPy-M complexes with respect to their unfunctionalised counterparts. EDGs affect metal to TPy the charge gained by M, N, N’, N”, M-chlorine and TPy-chlorine atoms are summed up and compared with the total charge lost by various EDGs for TPy-Co and TPy-Ru cases in (see Figure 2) which confirms that the largest share of electrons donated by EDGs gets delocalised within the TPy carbon atoms. Thus, the three pyridine rings act as a sink for flow of electrons. This observation suggests that the optical and red-ox properties of the resulting TPy-M complexes can be altered by attaching appropriate groups to the TPy. There is a change in the interatomic distances (0.01–0.02 Å) of the carbon atoms in pyridine rings due to accumulation of charge on them. Consequently, a blue shift is observed for the C=C bond stretch as illustrated in the Figure 2. Hence, the electron-rich pyridine skeleton EDG-TPy-M complexes are more likely to be attacked by electrophiles with potential application in electrophilic substitution reactions.

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binding in distinctive ways. We summarise the stability of various EDG-TPy-M complexes below:

\[
\begin{align*}
\text{NH}_2\text{-TPy-Co} & \rightarrow \text{CH}_3\text{-TPy-Co} > \text{C}_6\text{H}_5\text{-TPy-Co} > \text{OCH}_3\text{-TPy-Co} \\
\text{NH}_2\text{-TPy-Ru} & > \text{C}_6\text{H}_5\text{-TPy-Ru} > \text{CH}_3\text{-TPy-Ru} > \text{OCH}_3\text{-TPy-Ru} \\
\text{C}_6\text{H}_5\text{-TPy-Fe} & > \text{NH}_2\text{-TPy-Fe} > \text{CH}_3\text{-TPy-Fe} > \text{OCH}_3\text{-TPy-Fe} \\
\text{NH}_2\text{-TPy-Mo} & \geq \text{C}_6\text{H}_5\text{-TPy-Mo} > \text{CH}_3\text{-TPy-Mo} > \text{OCH}_3\text{-TPy-Mo} \\
\text{NH}_2\text{-TPy-Au} & \geq \text{CH}_3\text{-TPy-Au} \geq \text{C}_6\text{H}_5\text{-TPy-Au} \geq \text{OCH}_3\text{-TPy-Au}
\end{align*}
\]

Thus, NH2 is seen to increase the binding between metal and TPy in all cases by 2–10 kcal/mol making the complex more stable. An exception to this is TPy-Fe complex, where C6H5 group is showing maximum increase in binding energy as compared to NH2 group. OCH3 functional group reduces the TPy to metal binding energy by 13–60 kcal/mol with respect to unfunctionalised complex. (see Supporting Information, Supp-Table 2, for precise variations in the TPy to metal binding energies on EDG functionalisation of TPy molecule). From Figure 3, it is that for all TPy-M complexes, CH3 group increases the binding energy of the metals with TPy by 2–6 kcal/mol. In the presence C6H5 group binding energy of metals such as Fe, Mo and Au is increases by 5–10 kcal/mol. On the other hand, the presence of same group in Ru and Co TPy-M complexes lowers their binding energy.

To understand the trends observed in the metal to TPy binding energy, a thorough analysis of molecular orbitals is performed. As a case study, molecular orbitals of EDG functionalised TPy-Co complexes are presented in the Supp-Figure 4 of Supporting Information. The HOMO of the complex with the highest Co to TPy binding energy, i.e. NH2-TPy-Co shows
a strong overlap between p-orbitals of Cl and d-orbitals of Co. It implies that there is a strong delocalisation of electrons from Cl to Co and finally to TPy and vice versa. This gives the complex an overall stability which is higher in comparison to other EDG functionalised complexes. Such kind of electron delocalisation effect is not seen in the HOMO of the complex OCH₃-TPy-Co, where Co to TPy binding energy is lower. This effect can be correlated with electrostatic potentials (ESPs). The ESPs are plotted for TPy-Co complexes with the highest and lowest binding energy, i.e. NH₃-TPy-M and OCH₃-TPy-Co, and compared with that of unfunctionalised TPy-Co complex. The ESPs plot are given in Supp-Figure 5 of supporting information. In case of complex with the lowest Co to TPy binding energy, it is observed that accumulation of negative potential is more on Cl atoms as compared to bare TPy-Co complex. This implies that delocalisation of electrons is weak between Cl-Co-TPy leading to lower binding energy of Co with TPy. On the other hand, complex with the highest binding energy, i.e. NH₃-TPy-Co shows negligible negative potential on Cl atoms as compared to bare TPy-Co complex, which in turn shows that there is a strong delocalisation of electrons between Cl to Co and finally to TPy and vice versa. This leads to a strong binding of Co to TPy. This effect is consistently seen in other EDG-TPy-M complexes with different metal atoms. Similar analogy is seen in EWG functionalised TPy-M complexes (Pictures are not shown).

The above observation suggests that complexes such as NH₃-TPy-M (or C₆H₅-TPy-Fe) with higher binding energy facilitate formation of stable supramolecular constructs better. Results further suggest that terpyridine ligand functionalised with groups such as OCH₃ that lowers the binding energies have potential to form responsive surfaces in applications such as chemical sensing (for example Au). Binding energy results indicate in general that TPy to M binding can be conveniently fine tuned by functionalising it with appropriate groups so as to facilitate their exploitation in a number of applications.

3.3. Structure and electronic properties of EWG functionalised TPy-M complexes

As in case of EDG-TPy-M complexes, the geometrical parameters in EWG-TPy-M complexes show subtle variations in EWG-TPy complexes with a small change in the planarity of the overall complex. The charge redistribution in EWG-TPy-M complexes is given in Table 2. EWGs withdraw electrons from TPy-M complex. CN and COOH are the most EWGs. Once again the charge lost by TPy-M to EWG varies depending upon both metal centre and EWG. The electrons are predominantly (50–70%) lost from the carbon atoms in three pyridine rings. Rest of the charge is withdrawn from the metal centre, chlorine atoms and N_terminus atoms. Interestingly, metal centres gain some electrons in COOH-TPy-Co, NO₂-TPy-Co and NO₂-TPy-Ru complexes. The charge lost by M, N, N', N'', M-chlorine and TPy-chlorine atoms are all summed up and compared with the total charge gained by various EWGs for TPy-Co and TPy-Ru cases in Figure 2 which confirms that major share of lost to EWGs are from the TPy carbon atoms. Thus, the three pyridine rings act as a source for electron flow. Interestingly, this observation is consistent in both HPA and NPA charge partitioning schemes. To elaborate it, we have presented the summary of charge lost/gained by TPy carbon atoms and EWG group for NO₂-TPy-M complexes using NPA partitioning schemes in Table 2 in red. Thus, this observation is seen to be independent of choice of charges. Charges on various atoms using both HPA and NPA partitioning scheme is elaborated in Supp-Table 3 of Supporting Information. Similar to the case of EDG-TPy complexes, there is a change in the interatomic distances (0.01 Å) within the carbon atoms of pyridine rings. A red shift is observed accordingly for C - C bond stretch as illustrated in Figure 2. Thus, importantly, the charge redistribution observed in the TPy molecule can be corroborated by a shift in IR stretch frequency of C - C bonds.

In contrast to EDGs, EWGs are showing marginal changes on the binding of metal to TPy ligand. In TPy-M complexes, functionalisation by all the EWGs lower the binding energy by 2–10 kcal/mol. An exception to this is TPy-Mo complex, where EWGs such as COOH and NO₂ groups increase the binding energy by 5–6 kcal/mol (see Supporting Information, Supp-Table 2, for precise variations in the TPy to metal binding energies on EWG functionalisation of TPy molecule). This may be understood from the fact that in large x systems such as TPy where unsaturated pyridine rings exist with electron-rich hetero atoms such as N, withdrawal of electrons becomes more difficult compared to addition. It is the hallmark of such electron-rich systems as the conjugation retains a strong intramolecular electron delocalisation within itself through resonance.

4. Conclusions

The present investigation using DFT calculations elucidates that functionalisation of TPy-M complexes does not influence the structural integrity in terms of bond lengths and bond angles. However, some bulky functional groups perturb the planarity of the conjugate TPy molecule. In contrast to this, functionalisation does influence the binding behaviour of TPy ligand with metals.

Charge redistribution is observed in TPy-M complex on functionalisation with EDGs and EWGs affecting its molecular reactivity. Substantial quantum of charge is donated to/withdrawn from carbon atoms in pyridine by electron exchanging functional groups as seen from HPA and NPA partitioning schemes. Both HPA and NPA partitioning schemes are in well agreement with each other. This is largely attributed to the pyridine rings that act as electron sink reflecting alteration in C - C interatomic distances. However, this electron distribution significantly alters red-ox, optical and other interesting properties of this popular system. A systematic observation of blue and red shift due to donating and withdrawing groups, respectively, clearly supports this. OCH₃ group is seen to impair the stability of TPy-M complexes. The binding energy of metal to TPy is witnessed to be altered as much as 60 kcal/mol depending on the functional group attached to TPy. The variations in binding energy are found to be specific to the metal ions and functional groups bonded to TPy. It is also established from both frontier molecular orbitals as well as ESPs that after functionalisation, delocalisation of electrons between Cl-M-TPy or vice versa is playing a pivotal role in the binding of a metal to the TPy ligand.

In short, findings during the present investigation demonstrate the possibility of a convenient design of ligand by functionalisation for applications that demand characteristic binding
of ligand with specific metal and also to construct large supramolecular assemblies.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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