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Superalkali Ligands as a Building block for Aromatic Trinuclear Cu(I)-NHC Complexes

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Imidazole and benz-imidazole based different NHC ligands have been designed to make Cu(I)@NHC complex. Calculated vertical electron affinity suggests that all the ligands are belongs to a special type of molecule, superalkali and have very good non linear activity. All of them form Cu(I)@NHC complexes which have a trinuclear Cu_3 core. Canonical Molecular Orbital contribution towards Nucleus-independent chemical shift values suggest that the Cu_3 ring is both σ- and π-aromatic. Changes of aromaticity and other reactivity parameters like electrophilicity, hardness are changing with different ligand environment. It has been found that pyrazine based NHC makes a more reactive complex than pyridine. Natural localized molecular orbitals of these complexes suggest that they have sp^2 hybridization like BH_3.

1. Introduction

In development of new molecules and materials, chemistry plays a pivotal role in advancing the world where we live in. The history started with the breakthrough in the isolation of crystalline Zeise's salt[1], and then after organometallic compounds shows major contribution in this advancement due to its wide range of applications. Isolation of stable N-Heterocyclic Carbene (NHC) by Arduengo[2] opened a new window to researchers in developing NHC based metal complexes (M-NHC)[3] due to their potential and versatile applications and most remarkably NHC can be bottleable for future use. NHCs, the 'phosphine mimic'[4], form stable bonds to transition metals through the 'push–pull' mechanism[5-7] and thus remain as centre of inquisitiveness during new molecular scheming. Though most catalyst studies revolved around Pt-NHC complexes[8], other groups of metals also offer ample scopes. Copper is relatively less expensive than platinum and has a long history in catalysis[9,10]. Beyond catalysis, many researchers in this field are focusing on the

development of novel NHC ligands[11,12], NHCs as fluorescent materials[13-17], and compounds in biomedical applications[18-20]. NHCs having fluorescence properties has profuse scope as photosensitizers in dye-sensitized solar cells and have thus played an essential role in escalating technology of light-to-energy conversion[21]. In materials science, Ir(III), Ru(II), Os(II), Au(I), Au(III), Ag(I) complexes supported by 2-phenylpyridine[22] have received a lot of attention as these are promising luminescent materials for new light emitting devices such as mobile phones, PCs, and TVs[21]. Even if researchers have synthesized a broad range of M-NHC complexes[23-35], Cu(I)-NHC complexes are comparatively fewer[36-42] in this range, while it has a huge catalytic[43] and medicinal application[44]. Catalyst morphology has a strong influence in the catalyst effectiveness and its recovery[45,46]. So, tuning to structural versatility is a curiosity for every researcher. Invention of Basket-Shaped dinuclear Cu(I)–NHC is a remarkable report to science[47] and most interestingly, only two articles on trinuclear Cu(I)–NHC complexes came in to account[48,49]. "Chemistry is all about connecting and disconnecting atoms to form new molecular or supramolecular objects. So understanding the ways in which atoms and molecules can be held together should play an important role in developing new chemistries"[50]. Concept of aromaticity introduced by Hofmann[51] in 1855, to explain the structure, stability and reactivity of a wide range of organic molecules has a dictating role on explaining the nature of connectivity between two atoms and the geometry of the molecule. In 1931, Huckel proposed a generalized definition of aromaticity [(4n+2) π -electron rule] which is widely accepted[52] by the scientific community even today. Aromaticity criterion then becomes a popular qualitative tool to account for stability of a particular class of organic molecules. But, further progression of ideas along with the development of computation shows that the given term can be expanded into several dimensions and term "Aromaticity"

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cannot be a monopoly of the organic chemistry but can be used for inorganic and metal-organic hybrid molecules. Boldyrev et al. in their breakthrough effort presented both theoretical and experimental evidences of aromaticity in an all-metal system Al_4^{2-} [53,54]. The Al_4^{2-} ring has been shown to be of perfect square planar geometry with two π-electrons delocalized through the entire skeleton of the all-metal framework and they launched a new term, 'all-metal aromaticity'. The initial π-aromaticity concept is now long-drawn-out to σ-, δ- and three-dimensional aromaticity [55-59]. In our recent study, on the designing of new class of organometallic superalkali [60-62] complexes, it is found that the trinuclear $Au_3(IMD)_3$ [IMD=Imidazole] complex become aromatic [63]. These results triggered us to propose new aromatic organometallic all-metal core complexes coupled with NHC ligands. In this manuscript, We have made an attempt to design new aromatic tri nuclear Cu(I) complexes coupled with pyridine(Py), pyrimidine(Pym), pyrazine(Pyz) and pyridazine(Pyd) based imidazole/benzimidazole NHC ligands.

2. Theoretical Methods

The stability, reactivity and aromaticity of all the cluster compounds are judged under the paradigm of conceptual density functional theory based global reactivity descriptors like ionization energy (IE), electron affinity (EA), hardness (η), electronegativity (χ), and electrophilicity index (ω) [8,64-67]. The aromaticity of the complexes is analyzed through calculation of the nucleus independent chemical shift (NICS) values of the metallic rings by adopting the standard procedure as prescribed by Schleyer et al. [68,69]

To understand the stability, reactivity and aromaticity of these complexes geometry optimization has been performed at the B3LYP/LANL2DZ level of theory in the G09 suite program [70]. To get the stable ground state geometry, the frequency calculation has also been performed at the same level of theory. The zero imaginary frequency value confirms their existence in the minima on the potential energy surface. The ionization energy (IE) and electron affinity (EA) have been calculated by ΔSCF method in and B3LYP/Def2SVP// B3LYP/LANL2DZ level of theory. After obtaining the IE and EA, all conceptual density functional theory (DFT) based global and local reactivity descriptors like electronegativity (χ), hardness (η), electrophilicity (ω) have been obtained by standard techniques. Dissected NICS were computed at the Cu3 ring centres for all complexes at the B3LYP/LANL2DZ level. [71,72] NBO 7.0 [73] was employed to dissect the computed NICS values into individual σ and π canonical molecular orbital (CMO) contributions. The CMO-NICS procedure employed here allows one to extract specific CMO contributions relevant to σ- and π-aromaticity. Three σ orbitals and three π orbitals relevant for σ- and π-aromaticity in the Cu complexes were considered (see molecular orbitals for Cu_3^+ ring in Fig. 7).The computed NICS(0)σzz and NICS(0)πzz values include only contributions from the out-of-plane "zz" tensor component (i.e., direction perpendicular to the ring plane) of

selected σ and π molecular orbitals. Frontier molecular orbitals (FMO), Density of state (DOS) and partial DOS have been generated to analyse the bonding pattern of all the studied complexes. Natural localized molecular orbitals (NLMO) are also obtained to find the hybridization of the complexes. Time dependent density functional theory (TD-DFT) methodology has been employed for the generation of UV-Vis (ultra violet visible) spectra.

3. Results and discussion

3.1 Geometry

Experimentally it has been observed that the ligands [BzNHC-$(CH_2Py)_2$]+ and [NHC-$(CH_2Py)_2$]+ are stabilized by a counter ion PF_6^- / BF_4^-, we have taken only cationic part for our calculation. For the designing of trinuclear Cu(I)@NHC complexes we have taken two different sets of ligands [NHC-R_2]+ (R= CH_2Py, CH_2Pyd, CH_2Pym and CH_2Pyz) and [BzNHC-R_2]+ (R= CH_2Py, CH_2Pyd, CH_2Pym and CH_2Pyz). Figure 1 depicts the optimized geometries
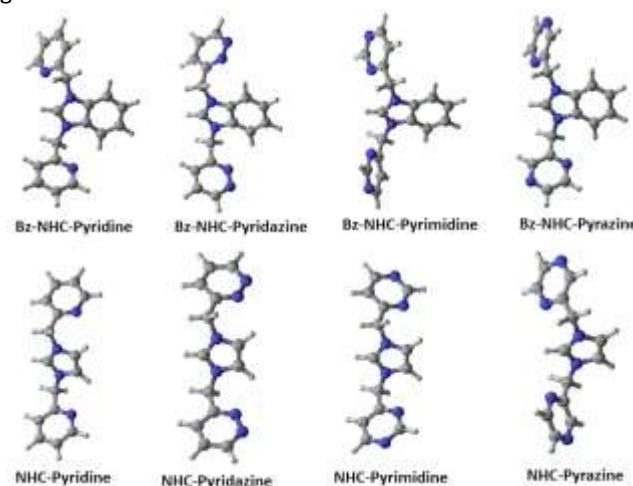
Fig 1. Optimized geometries of [BzNHC-R_2]+ (R= CH_2Py, CH_2Pyd, CH_2Pym and CH_2Pyz) and [NHC-R_2]+ (R= CH_2Py, CH_2Pyd, CH_2Pym and CH_2Pyz).

of all ligands. The Cartesian coordinates of such ligands with Cu_3 core are given in supporting information T5 and T6. It has been found that upon changing the R1 group, the geometries remain same. The natural population analysis (NPA) charge calculation reveals that all the carbene centers are electrophilic in nature. In between NHC-pyridine and Bz-NHC-pyridine, the latter is more electrophilic. The electron deficiency on carbene center is also increasing if we start from pyridazine to pyrazine for [NHC-R_2]+ complex. As all the ligands are in cationic form, stabilized by one counter anion PF6-, we have calculated the vertical electron affinity (VEA) which is an indirect method to measure the ionization energy of the system. The calculated VEA values of the all the ligands are varying from 3.03 eV to 3.86 eV which suggests that they are in fact superalkali in nature. Most of the cases, NHC is more superalkali nature than Bz-NHC. If we take an example of [(μ-NHC-$(CH_2Py)_2)_3Cu_3$]$^{3+}$ and [(μ-BzNHC-$(CH_2Py)_2)_3Cu_3$]$^{3+}$, [(μ-NHC-$(CH_2Py)_2)_3Cu_3$]$^{3+}$ tend to release electron more

Table 1. Calculated NPA charge on C center, VEA, Dipolemoment and First order hyperpolarizability of the studied Ligands.

Molecules	NPA Charge on C center	VEA (eV)	Dipole moment (Debye)	First order static hyperpolarizability (esu)
BzNHC-(CH$_2$Py)$_2$	0.319	3.43	2.13	2.23×10-30
BzNHC-(CH$_2$Pyd)$_2$	0.289	3.82	8.03	2.82×10-30
BzNHC-(CH$_2$Pym)$_2$	0.348	3.75	2.68	3.27×10-30
BzNHC-(CH$_2$Pyz)$_2$	0.315	3.86	0.28	2.63×10-30
NHC-(CH$_2$Py)$_2$	0.255	3.03	3.33	0.24×10-30
NHC-(CH$_2$Pyd)$_2$	0.254	3.58	8.39	1.36×10-30
NHC-(CH$_2$Pym)$_2$	0.259	3.53	4.19	0.25×10-30
NHC-(CH$_2$Pyz)$_2$	0.300	3.64	1.67	0.76×10-30

Table 2. Some important distances and angles of the studied Cu(I)@NHC complexes. Available experimental data has been provided in first parenthesis.

Molecule	Distances (Å)	Angle (º)		
	(M-M) M=Cu, Ag, Au	(M-M-M) M=Cu,Ag, Au	(M-C$_{nhc}$- M) M=Cu, Ag, Au	
[(μ-NHC(CH$_2$Py)$_2$)$_3$Cu$_3$]$^{3+}$ (*exp parameter*)	2.71, 2.71, 2.68 *(2.51, 2.52, 2.51)*	60.28, 59.39, 60.33 *(60.1, 59.9, 59.9)*	79.67, 79.61, 81.81 *(76.13, 76.31, 75.96)*	
[(μ-BzNHC(CH$_2$Py)$_2$)$_3$Cu$_3$]$^{3+}$	2.47,2.50, 2.52	58.99, 60.85, 60.16	75.97, 75.32, 76.95	
[(μ-NHC(CH$_2$Py)$_2$)$_3$Ag$_3$]$^{3+}$	2.93, 2.93, 2.94	59.89, 60.21, 59.89	77.82, 77.43, 77.43	
[(μ-BzNHC(CH$_2$Py)$_2$)$_3$Ag$_3$]$^{3+}$	2.94 2.94 2.94	50.98, 50.97, 60.01	77.86, 77.90, 77.98	
[(μ-NHC(CH$_2$Py)$_2$)$_3$Au$_3$]$^{3+}$	2.84, 5.28, 5.25	31.33, 73.81, 74.86	80.01, 101.22, 101.17	
[(μ-BzNHC(CH$_2$Py)$_2$)$_3$Au$_3$]$^{3+}$	2.85, 2.85, 2.85	59.99, 59.99, 60.02	77.19, 77.23, 77.17	
[(μ-NHC(CH$_2$Pyz)$_2$)$_3$Cu$_3$]$^{3+}$	2.68, 2.68, 2.69,	59.99, 60.04, 59.97	78.72, 78.74, 78.78	
[(μ-NHC(CH$_2$Pyz)$_2$)$_3$Ag$_3$]$^{3+}$	2.94, 2.94, 2.94	60.00, 60.00, 60.01	77.45, 77.47, 77.40,	
[(μ-NHC(CH$_2$Pyz)$_2$)$_3$Au$_3$]$^{3+}$	2.96, 3.36, 3.27	64.94, 61.92, 53.13	86.34, 69.81, 70.08	

efficiently because of low ionization energy. This confirms that all the ligands want to release electron to form carbene ligands which are responsible for the formation of trinuclear Cu(I)@NHC complexes. We have also calculated the nonlinear optical properties (NLO) of these ligands because it is established that superalkali complexes possess large NLO property. The calculated values suggest that they have a very good NLO nature as most of them have higher NLO than urea (0.373 × 10^{-30} esu) which is considered to be a standard molecule for the prediction of NLO property. All the NPA charges on C center along with their NLO values are given in Table 1. The optimized geometries of the Cu$_3$-complexes are given in Figure 2. It depicts, all eight ligands form trinuclear complex. The bond parameters of the Cu-NHC complexes are reported in Table-2. In all complexes, Cu(I) center form hexa-coordinating geometry with a triangular Cu$_3$ core bridged by three NHCs ligands (imidazolidene/benzimidazolylidene). Each Cu(I) is coordinated to two Cnhc centers and two 'Npy' centers (pyridine/pyrimidien/pyrazine/pyridazine) of two different ligands followed by two adjacent Cu(I) center forming a distorted tetrahedral geometry. The connectivity of Cu–Cu lies between 2.620 –2.710 Å displaying slightly weak metal–metal interactions, than those of other similar trinuclear Cu-NHC complexes (2.46–2.52 Å)[74-84]. For each complex three Cu-Cu bond distances are almost equal forming Cu$_3$ core an equilateral triangle ranging the Cu-Cu-Cu angle 59.58-60.21°. The Cu–N bond distances fall in the range of 2.200-2.230 Å, slightly greater than the reported value 2.085(4)–2.111(4) Å [73-83].
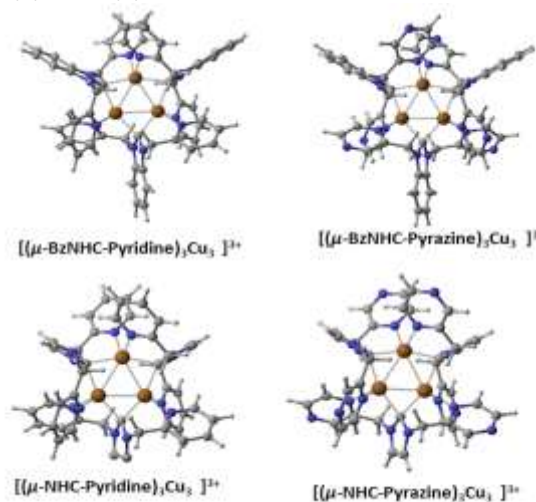
Fig 2. Optimized geometry of [(μ-BzNHC-R$_2$)$_3$Cu$_3$]$^{3+}$ (R= CH$_2$Py and CH$_2$Pyz) and [(μ-NHC-R$_2$)$_3$Cu$_3$]$^{3+}$ (R= CH$_2$Py and CH$_2$Pyz).

Each NHC forms the 3c–2e bond with two copper ions with Cu–C$_{NHC}$ bond distances of 2.050-2.214 Å, which are within the normal range of Cu–C$_{NHC}$ bonds (1.80–2.20 Å). The NHC frame (Imidazole/Benzimmidazole) lies perpendicular to the trinuclear Cu$_3$ core plane. So to satisfy the coordination geometry, ligands form a chair form and thus Npy- Cu-Npy angles are in the range of 94.27-97.10 ° and Cu-Cnhc- Cu angles are in the range of 76.30-81.81°. Notably, the N-C-N (NHC) angles in Benzimmidazole derivatives are very close to that found in saturated imidazolylidenes and

benzimidazolylidenes (~105°), but in Imidazole derivatives these are 2~3 ° distorted. The geometries of all the complexes are also in good agreement with the available experimental data. So it is evident that all the ligands can efficiently form a tri nuclear complex with Cu. Since all the complexes contain Cu_3 unit, we wanted to study the bonding and aromaticity pattern in detail. From Table 2, it is evident that irrespective of the ligand, the geometrical parameters are quite similar. To check the role of ligands in their trinuclear arrangement, we have taken a different imidazole based ligand with electron donating -CH_3 and withdrawing -CN groups. The optimized geometries of Cu trinuclear complexes are given in Figure 3. Further we have extended this calculation for Ag and Au trinuclear complexes.
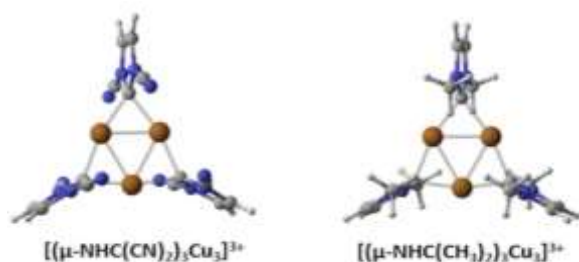

$[(\mu\text{-NHC(CN)}_2)_3Cu_3]^{3+}$ $[(\mu\text{-NHC(CH}_3)_2)_3Cu_3]^{3+}$

Fig 3. Optimized geometry of $[(\mu\text{-NHC-R}_2)_3Cu_3]^{3+}$ (R= CN and CH_3).

The optimized geometries and their geometrical parameters are given in supporting information (Table T3 and Figure S1). We have observed that for all coinage metal complexes, the ligand supports to form equilateral M_3 (M=Cu, Ag and Au) complex. We have also examined the role of our studied ligands with Ag and Au. Some interesting findings we have observed for Ag and Au trinuclear complexes with BzNHC-$(CH_2Py)_2$ and NHC-$(CH_2Py)_2$ ligands. While both the ligands from equilateral Ag_3 complexes, NHC-$(CH_2Py)_2$ fails to make for Au. Equilateral Au_3 is observed for BzNHC-$(CH_2Py)_2$ ligand. For $[(\mu\text{-NHC(CH}_2Py)_2)_3Au_3]^{3+}$ complex an isoscale triangle is formed with a bond distance of 2.84, 5.28, and 5.25 Å. To check further, NHC-$(CH_2Pyz)_2$ ligand has been taken to form Au_3 complex. We have found that the Au-Au distance has substantially decreased from 5.28 Å to 3.36 Å. These finding suggests that the ligands play an important role in the formation of M_3 (M=Cu, Ag and Au) core. All the optimized geometries are given in Figure 4 and geometrical parameters are given in Table T4.

3.2 Bonding and Reactivity:

In order to know the bonding pattern, we first calculate the hybridization of the following tri nuclear complexes. The hybridization has been calculated from the natural localized molecular orbital (NLMO) which gives the information about a Lewis structure in terms of orbital overlap. Since all of the complexes have three ligands and there is Cu_3 core, we assumed that the hybridization of these complexes will be like BH_3. From the Figure 5 it is evident that the NLMO of Cu-NHC complexes are similar to the BH_3 molecule. This concludes that the hybridization is of sp^2

$[(\mu\text{-NHC(CH}_2Py)_2)_3Ag_3]^{3+}$ $[(\mu\text{-NHC(CH}_2Pyz)_2)_3Ag_3]^{3+}$

$[(\mu\text{-NHC(CH}_2Py)_2)_3Au_3]^{3+}$ $[(\mu\text{-NHC(CH}_2Pyz)_2)_3Au_3]^{3+}$

$[(\mu\text{-BzNHC(CH}_2Py)_2)_3Ag_3]^{3+}$ $[(\mu\text{-BzNHC(CH}_2Py)_2)_3Au_3]^{3+}$
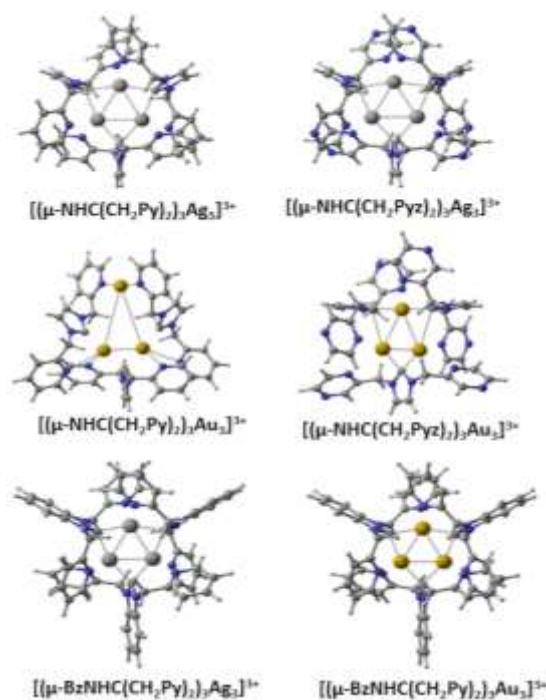
Fig 4. Optimized geometry of $[(\mu\text{-BzNHC-R}_2)_3M_3]^{3+}$ (R= CH_2Py, M=Ag and Au) and $[(\mu\text{-NHC-R}_2)_3M_3]^{3+}$ (R= CH_2Py, CH_2Pyz, M=Ag and Au).

nature. To study the bonding in detail, we have also calculate the density of states(DOS) and partial density of states(PDOS). The corresponding plots are given in Figure 6. The PDOS of $[(\mu\text{-NHC-(CH}_2Pyz)_2)_3Cu_3]^{3+}$ depict that the contribution of Ligand is more than the Cu_3 core in unoccupied frontier orbitals whereas almost same contribution has observed in HOMO. This signifies that the HOMO of the molecule is generated through the intermolecular overlap of

BH_3

$[(\mu\text{-BzNHC(CH}_2Py)_2)_3Cu_3]^{3+}$

$[(\mu\text{-NHC(CH}_2Py)_2)_3Cu_3]^{3+}$

Fig 5. Hybridization of Cu_3-trinuclear complexes of $[(\mu\text{-BzNHC-(CH}_2Py)_2)_3Cu_3]^{3+}$ and $[(\mu\text{-NHC-(CH}_2Py)_2)_3Cu_3]^{3+}$.

Fig 6. Density of states(DOS) and Partial density of states(PDOS) of [(μ-NHC-(CH$_2$Pyz)$_2$)$_3$Cu$_3$]$^{3+}$ and [(μ-BzNHC-(CH$_2$Pyz)$_2$)$_3$Cu$_3$]$^{3+}$.

Table 3. Calculated hardness (η) and electrophilicity (ω) values for the Cu(I)@NHC complexes.

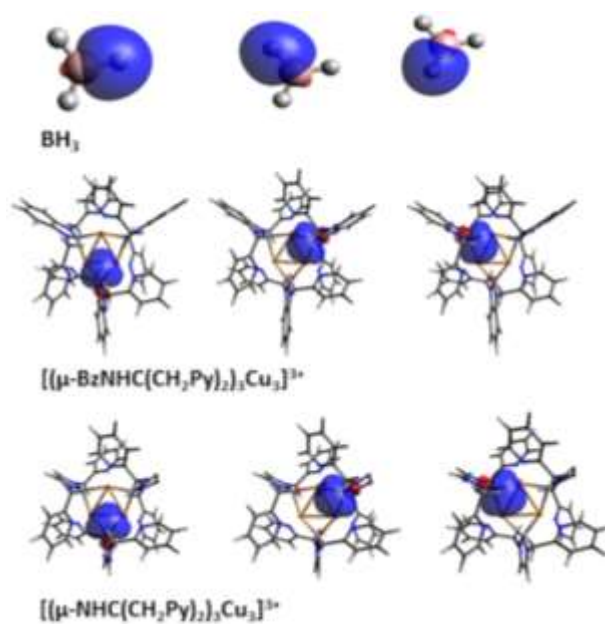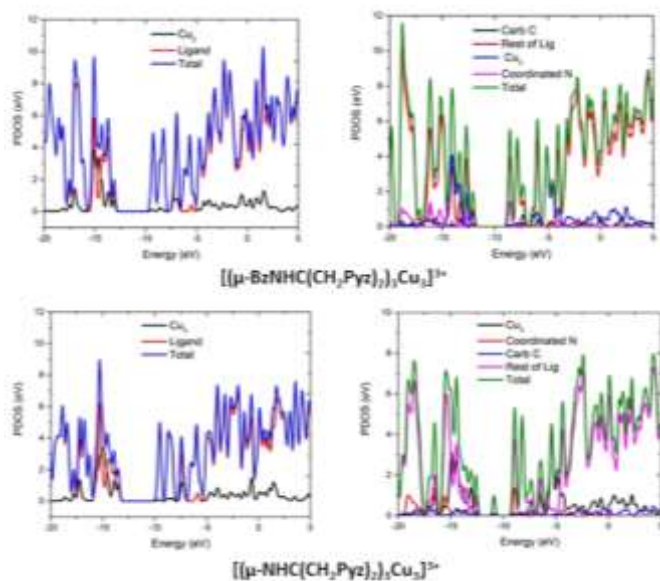| Molecules	η, eV	ω, eV
[(μ-BzNHC-(CH$_2$Py)$_2$)$_3$Cu$_3$]$^{3+}$	5.68	9.64
[(μ-BzNHC-(CH$_2$Pyd)$_2$)$_3$Cu$_3$]$^{3+}$	5.28	10.36
[(μ-BzNHC-(CH$_2$Pym)$_2$)$_3$Cu$_3$]$^{3+}$	5.57	10.87
[(μ-BzNHC-(CH$_2$Pyz)$_2$)$_3$Cu$_3$]$^{3+}$	5.49	11.51
[(μ-NHC-(CH$_2$Py)$_2$)$_3$Cu$_3$]$^{3+}$	6.01	9.40
[(μ-NHC-(CH$_2$Pyd)$_2$)$_3$Cu$_3$]$^{3+}$	5.47	10.31
[(μ-NHC-(CH$_2$Pym)$_2$)$_3$Cu$_3$]$^{3+}$	6.03	10.68
[(μ-NHC-(CH$_2$Pyz)$_2$)$_3$Cu$_3$]$^{3+}$	8.83	11.45

both core and ligand orbitals. The pattern of DOS and PDOS are same for [(μ-BzNHC-(CH$_2$Pyz)$_2$)$_3$Cu$_3$]$^{3+}$ complex. The plots of rest of the complexes are given in supporting information. To find the reactivity pattern of these complexes, we have calculated different conceptual density functional theory based global reactivity descriptors like hard ness, electronegativity and electrophilicity. The calculated electrophilicity for [(μ-BzNHC-(CH$_2$Py)$_2$)$_3$Cu$_3$]$^{3+}$ is found to be 9.64 eV. Change of the ligand from pyridine to pyridazine, pyrimidine and pyrazine increases the electrophilicity of the complex. This suggest that the complex becomes more reactive by changing the position of N to ortho, meta and para with respect to pyridine-N. Similar trend is also observed for NHC cases. These results suggest that among the three isomer pyrazine complex is the most reactive and the least stable. To see the aromaticity of the core Cu$_3$ of the studied complexes, we have adopted CMO-NICS (canonical molecular orbital-NICS) calculation, which is strictly focuses on the canonical molecular orbital to calculate the dissected NICS. Although, normal NICS calculation gives good aromaticity value for organic system, for inorganic ring system it is difficult to apply due to

the huge effects of sigma bonds. Computed NICS(0)$_{\sigma zz}$ (three σ orbitals) and NICS(0)$_{\pi zz}$ (three π orbitals) indicates that the Cu$_3$$^+$ core is doubly aromatic, but becomes less upon complexation to ligands (see Table 4). Plots of molecular orbitals relevant to σ-aromaticity and π-aromaticity in the Cu$_3$$^+$ core are shown in Figure 7 (molecular orbital plots for complexes are included in the Supporting Information, Figure S6-S8).
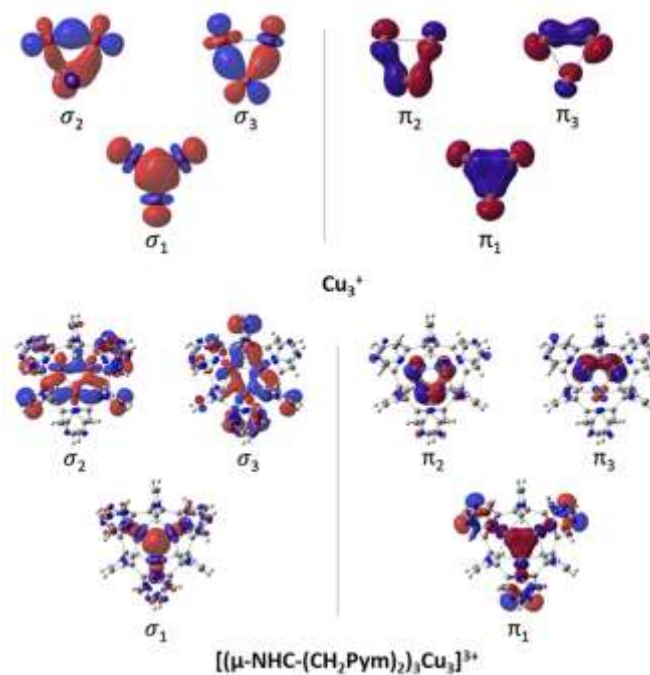
Fig 7. Molecular orbitals relevant to σ and π aromaticity in the Cu$_3$$^+$ ring and [(μ-BzNHC-(CH$_2$Pym)$_2$)$_3$Cu$_3$]$^{3+}$.

Table 4. CMO-NICS(0)σzz and CMO-NICS(0)πzz values computed for the trinuclear Cu(I)-NHC complexes at the B3LYP/lanl2dz level.

Complex	σ_1	σ_2	σ_3	NICS(0)$_{\sigma zz}$
[(μ-BzNHC-(CH$_2$Py)$_2$)$_3$Cu$_3$]$^{3+}$	−2.2	−1.2	−1.3	**−4.6**
[(μ-BzNHC-(CH$_2$Pyd)$_2$)$_3$Cu$_3$]$^{3+}$	−2.6	+1.0	+1.0	**−0.7**
[(μ-BzNHC-(CH$_2$Pym)$_2$)$_3$Cu$_3$]$^{3+}$	−2.5	−1.7	−1.6	**−5.8**
[(μ-BzNHC-(CH$_2$Pyz)$_2$)$_3$Cu$_3$]$^{3+}$	−2.8	−1.6	−1.6	**−6.1**
[(μ-NHC-(CH$_2$Py)$_2$)$_3$Cu$_3$]$^{3+}$	−2.3	−0.4	−0.4	**−3.2**
[(μ-NHC-(CH$_2$Pyd)$_2$)$_3$Cu$_3$]$^{3+}$	−2.5	+0.3	+0.3	**−2.0**
[(μ-NHC-(CH$_2$Pym)$_2$)$_3$Cu$_3$]$^{3+}$	−2.6	−0.4	−0.4	**−3.4**
[(μ-NHC-(CH$_2$Pyz)$_2$)$_3$Cu$_3$]$^{3+}$	−2.9	−0.6	−0.6	**−4.0**
Cu$_3$$^+$	−7.3	−3.6	−3.6	**−14.6**
Complex	π_1	π_2	π_3	NICS(0)$_{\pi zz}$
[(μ-BzNHC-(CH$_2$Py)$_2$)$_3$Cu$_3$]$^{3+}$	−1.1	−0.9	−0.9	**−2.9**
[(μ-BzNHC-(CH$_2$Pyd)$_2$)$_3$Cu$_3$]$^{3+}$	+1.4	+0.1	+0.2	**+1.8**
[(μ-BzNHC-(CH$_2$Pym)$_2$)$_3$Cu$_3$]$^{3+}$	0.2	−0.9	−0.9	**−1.7**
[(μ-BzNHC-(CH$_2$Pyz)$_2$)$_3$Cu$_3$]$^{3+}$	−3.6	0.0	+0.1	**−3.5**
[(μ-NHC-(CH$_2$Py)$_2$)$_3$Cu$_3$]$^{3+}$	−1.6	−0.3	−0.3	**−2.2**
[(μ-NHC-(CH$_2$Pyd)$_2$)$_3$Cu$_3$]$^{3+}$	+1.1	−0.1	−0.1	**+0.9**
[(μ-NHC-(CH$_2$Pym)$_2$)$_3$Cu$_3$]$^{3+}$	+0.2	−0.9	−0.9	**−1.6**
[(μ-NHC-(CH$_2$Pyz)$_2$)$_3$Cu$_3$]$^{3+}$	−0.6	−0.2	−0.2	**−1.0**
Cu$_3$$^+$	−1.2	−2.5	−2.5	**−6.2**

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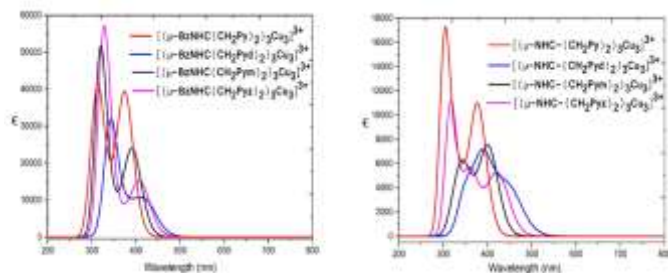
Fig 8. UV Vis spectra of $[(\mu\text{-BzNHC-R}_2)_3Cu_3]^{3+}$ (R= CH$_2$Py, CH$_2$Pyd, CH$_2$Pym and CH$_2$Pyz) and $[(\mu\text{-NHC-R}_2)_3Cu_3]^{3+}$ (R= CH$_2$Py, CH$_2$Pyd, CH$_2$Pym and CH$_2$Pyz).

To know the photo physical property of these Cu(I)@NHC complexes, electronic spectra of the compounds in the wavelength range 200–800 nm were screened in CH$_3$CN solution and the transitions have been assigned based on TD-DFT calculations. The corresponding spectra are depicted in Figure 6. In Table 4, we have tabulated some important transitions along with their oscillator strength and frontier molecular orbitals involvement. The appearance of peaks is observed in between 300 − 500 nm in all the cases. The complexes exhibit transitions within 303 nm ~ 328 nm corresponding to intra-ligand charge transfer transitions (ILCT), L(π) →L(π*) and that in the range of 341 nm to 378 nm is due to the admixture of MLCT (metal-ligand and charge transfer) and LLCT (ligand-ligand charge transfer) transitions [Cu(dπ)/L(π)→L(π*)] which is a characteristic feature of copper complexes bonded with conjugated organic chromophore.

The transitions in the range of 391 nm to 426 nm to the MLCT (metal-ligand charge transfer); Cu(dπ)→L(π*) as compared with the reported complexes.[78] Looking at the Figure 6, we have found that for both the cases slight blue shift has been observed if we change the ligand from pyridazine to pyrazine. pyrazine complex is found to be more blue shifted that the other isomers. This can be explained from the aromaticity values of these complexes. As we know the disturbance in conjugation leads to blue shift, pyrazine complex being less aromatic than pyrimidine and pyridazine, it is more blue shifted.

Conclusions

In conclusion, we have successfully designed six different NHC ligands based on pyridazine, pyrimidine, pyrazine and demonstrated their reactivity and stability in terms of conceptual density functional theory based reactivity descriptors and aromaticity. First principle calculation on such ligands show that all of them are superalkali with very good nonlinear optical properties. They can form Cu(I)@NHC complexes with an aromatic Cu$_3$ core. All the Cu$_3$ core possesses high sigma and low pi aromaticity. Among pyridazine, pyrimidine and pyrazine, pyrazine make more reactive and less aromatic complexes. The superatomic clusters have *sp²* hybridization. Blue shift has been found in UV-Vis spectra calculated in acetonitrile solvent. We hope

that these designed complexes can be easily synthesized and they have potential applications in modern synthetic chemistry as catalyst.

Table 4. The major transitions with Osc. Strength and $\lambda_{excitation}$ of Tri nuclear cluster.

Molecules	λexc (nm)	Osc. Strengt (f)	Major transition
$[(\mu\text{-Bz-NHC-(CH}_2\text{Py)}_2)_3Cu_3]^{3+}$	375	0.26	H→L (95%)
	317	0.10	H-1→L+8 (13%), H→L+6 (36%), H→L+7 (12%)
$[(\mu\text{-BzNHC-(CH}_2\text{Pyd)}_2)_3Cu_3]^{3+}$	426	0.05	H→L (72%)
	344	0.20	H→L+6 (88%)
$[(\mu\text{-Bz-NHC-(CH}_2\text{Pym)}_2)_3Cu_3]^{3+}$	392	0.16	H→L (87%)
	319	0.15	H-2→L+5 (30%), H→L+8 (14%)
$[(\mu\text{-Bz-NHC-(CH}_2\text{Pyz)}_2)_3Cu_3]^{3+}$	409	0.10	H-1→L (36%), H →L (53%)
	328	0.20	H-4→L+1 (11%), H-3→L+2 (10%), H-1→L+6 (45%)
$[(\mu\text{-NHC-(CH}_2\text{Py)}_2)_3Cu_3]^{3+}$	378	0.07	H-1→L (93%)
	303	0.08	H-1→L+9 (56%)
$[(\mu\text{-NHC-(CH}_2\text{Pyd)}_2)_3Cu_3]^{3+}$	391	0.06	H-4→L+2 (16%), H-3→L+4 (17%), H-2→L+1 (34%)
	353	0.02	H-1→L+7 (74%)
$[(\mu\text{-NHC-(CH}_2\text{Pym)}_2)_3Cu_3]^{3+}$	403	0.05	H-1→L (62%), H→L (29%)
	341	0.04	H-4→L+2 (31%), H-3→L+3 (31%)
$[(\mu\text{-NHC-(CH}_2\text{Pyz)}_2)_3Cu_3]^{3+}$	425	0.03	H→L (85%)
	360	0.04	H-4→L+2 (26%), H-3→L+3 (26%), H-2→L (40%)
	316	0.06	H→L+9 (79%)

Conflicts of interest

"There are no conflicts to declare".

Acknowledgements

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