SYNTHESIS, CHARACTERIZATION AND DENSITY FUNCTIONAL THEORY OF COPPER(II) COMPLEX AND COBALT(II) COORDINATION POLYMER FOR DETECTION OF NITROAROMATIC EXPLOSIVES

Adedibu C. Tella^{a*}, Victoria T. Olayemi^{a,b}, Folahan A. Adekola^a, Adetola C. Oladipo^{a,c}, Vincent O. Adimula^a, Joseph O.Ogar^c, Eric C. Hosten^d, Adeniyi S. Ogunlaja^d Stephen P. Argent^e and Robert Mokaya^e

^a Department of Chemistry, University of Ilorin, P.M. B 1515, Ilorin, Kwara State, Nigeria. E-mail: ac_tella@yahoo.co.uk Phone: +2348035019197

^b Department of Chemistry, College of Pure and Applied Sciences, Kwara State University, P.M. B 1530, Malete, Nigeria.

^c Department of Physical Sciences, Landmark University, Omu-Aran, Kwara State, Nigeria

^d Department of Chemistry, Nelson Mandela University, PO Box 77000, Port Elizabeth, 6031, South Africa.

^e School of Chemistry, University of Nottingham, NG7 2RD, University Park, Nottingham, United Kingdom.

Abstract

In recent years there has been a significant interest to design luminescent materials to detect explosives with a great degree of selectivity, sensitivity, and fast response time. Two new luminescent compounds, [Cu(Biphen)(Meim)(H₂O)] **1** and [Co(BDC)(Meim)₂]_n **2** (where HBiphen = biphenyl-4-carboxylic acid, H₂BDC = 1,4-benzenedicarboxylic acid and Meim = 1-methylimidazole) were synthesized under solvothermal and reflux conditions. The compounds were characterized by elemental analysis, FT-IR, thermogravimetric analysis, and electronic spectroscopy. Single Crystal X-ray Diffraction (SC-XRD) was used to determine their crystal structures. **1** crystallizes in the monoclinic space group *I2/a*, and the geometry around the metal center is square pyramidal connected by two (μ-N)₂ of Meim and two (μ-O)₂ of Biphen and a coordinated water molecule. **2** exhibits tetrahedral geometry connected by two (μ-N)₂ of Meim and two (μ-O)₂ halves of BDC in the triclinic space group *P-1*. Photophysical properties of the solid-state complexes were analyzed using fluorescence spectroscopy. **1** displayed high emissions at 430 nm (λ_{ex} = 264 nm) and **2** at 384 nm (λ_{ex} = 265 nm) which could be assigned to ligand to metal charge transfer (LMCT) due to the ligand's extended π-conjugation. Compounds **1** and **2** display selective nitroaromatic quenching response over other organic molecules having detection limits ranging between 1.66 ppm and 13.07 ppm, respectively. Density Functional Theory (DFT) revealed that potential interactions leading to the formation of adducts result from the transfer of electrons by hydrogen bonding and π-π stacking. Compound **2** was found to have greater ability to quench nitro analytes.

Keywords Coordination Polymers, Fluorescence, Nitroaromatics, Solvothermal, Quenching

1. Introduction

Coordination polymers (CPs) are a class of compounds constructed from metal ions bonded to organic ligands to form 1D, 2D and 3D structures. The structural properties of the compounds are explored by considering the functionality of the ligand and the geometry of the metal via crystal engineering leading to self-assembly of inorganic metal nodes and organic moieties [1]. Coordination polymers are of great interest owing to their promising applications in gas adsorption, catalysis, sensors, and drug delivery. The detection of nitro compounds has been of great concern in the past two decades due to its significance in global security and environmental protection [2]. While several methods for detecting nitro compounds have been developed, these methods of identification are restricted by equipment requirements and cost [3]. Recently, some researchers have reported the quenching of luminescence intensities of coordination polymers in the presence of nitro aromatic molecules [4]. Tehrani *et al* [5] investigated two novel sensing probes of metal coordination polymer for the sensing of nitro compounds. These two MOFs were suspended in a solution of different nitro compounds for sensing. The quenching efficiency of the MOFs for nitro-containing compounds revealed that 2,4,6-trinitrotoluene (TNT) has the highest quenching percentage as compared to the other nitroaromatic compounds, and that possible interactions between the MOFs and the nitro analytes arise from hydrogen bonds from the Urea groups in the MOF cavity and π – stacking interactions. It was also observed that these interactions, and the orientation of the urea group within the pores of the MOFs, are vital for the sensing of nitro compounds. The luminescent MOFs can be designed for use in explosive detection in such a way that there will be a direct target between the framework and the guest resulting in guest-induced interactions. Bu *et al*, [6] also used another 3D MOF to examine the sensing ability of electron-withdrawing nitroaromatic explosives in solution or vapour. The electron rich ligand of the coordination polymer was advantageous to its sensitivity. The results showed that the limit of detection (LOD) of nitrobenzene was very low (0.135 ppm) and its emission intensity was drastically

quenched. Recently, Li and co-workers designed three multidimensional luminescent Cu(II) coordination polymers for selective detection of acetylacetone, benzaldehyde and $\text{Cr}_2\text{O}_7^{2-}$ [7]. The quenching effect was ascribed to electron-transfer transitions of the analytes decreasing the energy transfer between the π and π^* orbitals of the bis(benzimidazole) N-ligands. Yang *et al* [8] reported the dual-responsive detection of acetylacetone and $\text{Cr}_2\text{O}_7^{2-}$ in aqueous solution using a water-stable Cd(II) MOF. The quenching effect was attributed to resonance energy transfer from the excited MOF to the acetylacetone and $\text{Cr}_2\text{O}_7^{2-}$. This was clearly observed from the large overlaps with the excitation band of the MOF. Following our studies on the synthesis and application of coordination polymers in environmental remediation [9,10], luminescence [11] and chemical sensing [12], we report the synthesis of copper(II) complex and cobalt(II) coordination polymers assembled from carboxylate and 1-methylimidazole ligands for the detection of nitroaromatic explosives.

2. Experimental

2.1. Materials and methods

All reagents and chemicals are of analytical grade and were used as received without further purification. 1,4-Benzenedicarboxylic acid, Biphenyl-4-carboxylic acid, 1-methylimidazole (s.g. 1.03) were purchased from Sigma Aldrich, Germany. $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were supplied by Alfa Aesar, UK. Solvents: Ethanol (98.8%), *N,N*-Dimethyl formamide (99.0%) were obtained from Central Drug House (P) Ltd New Delhi India.

2.2. Instrumentation and characterization

The samples were characterized by elemental analysis using an Exeter Analytical CE-440 Elemental Analyser. The infrared spectra were recorded using a Bruker Alpha diamond module FT-IR spectrometer with attenuated total reflectance (ATR) attachment for solid samples. Powder X-ray diffraction (PXRD) patterns were measured on a PANalytical X'Pert PRO

diffractometer with a Cu-K α light source (40 kV, 40 mA) with a step size of 0.02 ° and a 50 s time step. UV-Vis absorption spectra were measured in the solid-state in the range 200 to 800 nm using an Agilent Cary Spectrophotometer with a slit width of 2 nm. The fluorescence emission spectra were recorded on an Agilent Cary Eclipse Spectrophotometer set at 2 nm slit width for both the excitation and emission. TGA was performed using an SDT-Q600 TA instrument. The samples were heated in air with a heating rate of 10 °C min⁻¹ and the scan was recorded within the temperature range of 30-600 °C.

2.3. Synthesis of the compounds

Cu(Biphen)(Meim)(H₂O) 1

1 was synthesized by dissolving 0.249 g of CuSO₄·5H₂O (1 mmol) in 10 mL distilled water and was mixed carefully with 0.198 g (1 mmol) of Biphenyl-4-carboxylic acid previously dissolved in 10 mL ethanol solution. 0.1 mL of 1-methylimidazole in 5 mL ethanol was added while stirring gently. The blue suspension formed was heated at 80 °C in the oven for 4 h under atmospheric condition. Blue spherical crystals were harvested by filtration after 24 h. Yield = 83%, M.P = 228 °C, C₃₄H₃₂N₄O₅Cu (640.19 g mol⁻¹). Anal. found: C; 63.74, H; 4.93, N; 8.78%. Calcd: C; 63.79, H; 5.04, N; 8.75%. IR (ATR cm⁻¹): 3373, 3124, 1600, 1241, 1375, 652, 473.

Scheme 1: Reaction pathway of [Cu(Biphen)(Meim)(H₂O)]

[Co(BDC)(Meim)₂]_n 2

2 was synthesised by dissolving 0.237 g (1 mmol) of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ in 10 mL distilled water and carefully layering it over 0.166 g (1 mmol) of 1,4-benzenedicarboxylic acid (BDC) in 10 mL *N,N*-dimethylformamide in a 100 mL Pyrex beaker. 0.08 mL (1 mmol) of 1-methylimidazole (Meim) in 10 mL *N,N*-dimethylformamide was gently added to the solution while stirring. A clear purple-coloured solution was formed and was refluxed at 120 °C for 2 h. Purple crystals of **2** were harvested by filtration after 3 days with a yield of 79%. M.P = 373 °C, $\text{C}_{16}\text{H}_{16}\text{N}_4\text{O}_4\text{Co}$ (387.26 g mol^{-1}). Anal. found: C; 49.52, H; 3.99, N; 14.24%. Calcd: C; 49.50, H; 4.41, N; 14.43%. IR (ATR cm^{-1}): 3123, 1580, 1235, 1360, 552, 495.

Scheme 2: Reaction pathway of $[\text{Co}(\text{BDC})(\text{Meim})_2]_n$

2.4. Fluorescence Experiment

The method described by Wang *et al*; 2013 was modified and adopted for the fluorescence experiment [13]. 3 mg of finely ground samples were dispersed in 1 mM of three different aromatic nitro compounds (nitrobenzene, 4-nitroaniline and 4-nitrophenol) and then ultrasonicated for 30 min. to form stable suspensions which was allowed to age for 24 h before fluorescence studies. To examine the selectivity of the compounds (CPs) towards the nitro analytes, the compounds were used to probe other organic molecules (ethanol, DMF, methanol, benzene).

2.5. Computational Details

Single crystal X-ray diffraction structures of [Cu(Biphen)(Meim)₂(H₂O)] and [Co(BDC)(Meim)₂]_n were used for geometry optimization. Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) energies were generated with the Gaussian09 quantum chemistry package [14] at the DFT (Density Functional Theory) B3LYP/6-311++G**(d,p) level [15, 16]. Optimized molecules were obtained with the Avogadro and Chemcraft visualization program.

2.6. X-ray Crystallography

Single crystal X-ray data for **1** was collected at 200 K on a Bruker Kappa Apex II diffractometer, and **2** at 120 K on a GV1000, Atlas S2 diffractometer. The Olex2 suite was used as a graphic user interface (GUI) and as imaging software [17]. The structures were solved with the ShelXT [18] structure solution program using Intrinsic Phasing and refined with the ShelXL [19] refinement package using Least Squares minimisation. All non-hydrogen atoms were refined with anisotropic displacement parameters and images were prepared via Mercury 4.1.0.

Table 1a: Crystal data and structure Refinement Details for 1 and 2

Details	1	2
Empirical formula	C ₃₄ H ₃₂ CuN ₄ O ₅	C ₁₆ H ₁₆ CoN ₄ O ₄
Formula weight	640.19	387.26
T (K)	200	120
Wavelength (Å)	0.71073	1.542
Crystal system	Monoclinic	Triclinic
Space group	I2/a	P-1
Crystal size (nm)	0.23 x 0.28 x 0.38	0.86 x 0.34 x 0.32
a (Å)	16.8401(9)	7.5184(4)
b (Å)	6.0328(4)	8.8257(4)

c (Å)	30.0546(16)	13.1889(6)
α (°)	90	81.377(4)
β (°)	101.509(3)	77.441(4)
γ (°)	90	72.717(4)
V (Å ³)	2991.9(3)	812.28(7)
Z	4	2
ρ_{calc} (g/cm ³)	1.421	1.583
F(0 0 0)	1332	398
2 θ range for data collection (°)	4.938 - 56.71	6.894 - 145.88
Radiation type	MoK α	CuK α
Reflections collected	3718	5599
R indices R1/wR2	0.0289, 0.0835	0.0414, 0.1094
Largest peak (e Å ³)	0.49	0.74
Deepest hole (e Å ³)	-0.44	-0.85

3. Results and discussion

3.1. Structural description

The molecular structure of **1** showing atom numbering is given in Fig. 1a. Detailed crystallographic data and structure refinement parameters are summarized in Table 1a, while selected bond lengths and bond angles are presented in Table 1b. **1** crystallizes in the monoclinic crystal system ($a = 16.840$, $b = 6.032$, $c = 30.054$) with space group $I2/a$. The square pyramidal Cu(II) ion is coordinated by two (μ -N)₂ of Meim and two (μ -O)₂ of Biphen symmetrical around a 2-fold rotational axis in the basal plane, with the apical position occupied by a coordinated water molecule. The complex revealed a slightly distorted square-pyramidal geometry with a distortion parameter τ of 0.19 [20, 21]. The Biphen is completely deprotonated and the coordination mode of the carboxylic acid groups around the Cu(II) ion is monodentate. The Cu1-O21 distances is 1.957(9) Å (Table 1b) which compares favourably with the range

1.930-1.990 Å [22] usually observed for copper complexes. The bond length of the two Cu1-N11 bonds is 1.992(12) Å which agrees favourably with the reported range of 1.974-2.008 Å [23]. The bond angle between the imidazolyl nitrogen (N11), copper and oxygen of carboxylates (N-Cu1-O) is in the range of 87.9(5)-97.5(4) °. The O–H···O type of intermolecular hydrogen bonds exist between the bound water molecule and O22 of the carboxylate group linking adjacent molecules along the b-axis. The bond distances and angles for the hydrogen bonding interaction are O3–H3 = 0.88 Å, H3···O22 = 2.754 Å, O3–O22 = 1.88 Å and O3–H3···O22 = 170 ° (Fig.1b). The crystal packing is depicted in Fig. S1 consisting of layers mutually interacting by weak π - π stacking via the imidazolyl ring, thereby stabilizing the crystal structure.

Fig. 1a: ORTEP view of [Cu(Biphen)(Meim)(H₂O)] (1) drawn at 50% ellipsoid.

Fig. 1b: Hydrogen bonding interaction in [Cu(Biphen)(Meim)(H₂O)] (1)

2 is a centrosymmetric entity that crystallizes as a four-coordinate mononuclear polymer with a tetrahedral geometry (distortion parameter $\tau = 0.81$). The Co(II) ion is surrounded by two Meim molecule and half a molecule of BDC ligand. The ORTEP diagram with atom numbering is shown in Fig. 2a. The average bond length of Co1-O is 2.001 Å while that of Co1-N is 2.035 Å and are within the reported average bond lengths of Co-O and Co-N [24]. The bond angles O-Co1-N range from 106.0(8) ° to 123.8(7) °, while that of O-Co1-O is 100.3 °. These compare favourably with those reported in literature for Co(II) polymers [25]. Table 1a presents the selected interatomic bond lengths and bond angles. The completely deprotonated BDC ligand shows a monodentate coordination environment around the Co²⁺ ion, while the Meim adopts a *cis*-conformation. The Co(II) cations are bridged by BDC to form a 1D zigzag chain with the Meim ligands serving as pendant, as shown in Fig. 2b. The C-H $\cdots\pi$ interaction observed between the aromatic ring of BDC ligand and CH group of imidazole ring has a distance of 3.620 Å as shown in Fig. S2.

Fig. 2a: ORTEP view of $[\text{Co}(\text{BDC})(\text{Meim})_2]_n$ (**2**) drawn at 50% ellipsoid.

Fig. 2b: 1D zigzag chain of $[\text{Co}(\text{BDC})(\text{Meim})_2]_n$ (**2**)

Table 1b: Observed and calculated interatomic bond lengths (Å) and bond angles (°) of the compounds

1			2		
Parameters	exp.	calcd	Parameters	exp.	calcd
Bond lengths	-	-	Bond lengths	-	-
Cu1 – O3	2.241(18)	2.24243	Co1 – O1	1.999(15)	1.99907
Cu1 – O21_a	1.957(9)	1.95121	Co1 – O3	1.975(17)	1.97483
Cu1 – N11	1.992(12)	1.98701	Co1 – N1	2.057(19)	2.05679
Cu1 – O21	1.957(9)	1.95157	Co1 – N3	2.022(19)	2.02193
Cu1 – N11_a	1.992(12)	1.98701	-	-	-
Bond angles	-	-	Bond angles	-	-
O3 – Cu1 – O21_a	88.5(3)	88.426	O1 – Co1 – N1	101.9(7)	101.880
O3 – Cu1 – N11	97.5(4)	97.572	O1 – Co1 – N3	121.5(7)	121.427
O3 – Cu1 – O21	88.5(3)	88.426	O3 – Co1 – O1	99.1(7)	99.975
O3 – Cu1 – N11_a	97.5(4)	97.572	O3 – Co1 – N1	106.0(8)	106.019
O21 – Cu1 – O21_a	176.1(4)	176.852	O3 – Co1 – N3	123.8(7)	123.851
O21 – Cu1 – N11_a	87.9(5)	86.629	N3 – Co1 – N1	100.9(8)	100.871
N11 – Cu1 – O21_a	87.9(5)	86.629	-	-	-
N11 – Cu1 – N11_a	165.0(5)	164.856	-	-	-

Symmetry codes; **1**: 1/2-x,+y,1-z, **2**: -x,1-y,1-z; 1-x,-y,-z

3.2 Spectroscopic Studies

3.2.1. FT-IR

The spectra of the compounds were compared with those of the ligands (Table S1). Some new bands were found while some were shifted in the FTIR spectra of the compounds as shown in Figs. 3a and 3b. This shows the existence of coordination of the metal to the ligands. For **1**, the broad absorption band at 3373 cm⁻¹ is assigned to $\nu(\text{O-H})$ coordinated water. The free Biphenyl-4-carboxylic acid showed a broadband from 2979 cm⁻¹ to 2546 cm⁻¹ which was assigned to the $\nu(\text{O-H})$ of carboxylic acid present. This was shifted to 2091 cm⁻¹ in the

spectrum of **1** as a result of deprotonation and coordination of the Biphen ion to the metal [26]. $\Delta\nu$ of the anti-symmetric and symmetric stretching of the COO^- bonded to Cu is 225 cm^{-1} confirming a monodentate coordination mode [27]. Weak peaks at 652 cm^{-1} and 473 cm^{-1} are characteristic of Cu-N and Cu-O respectively. For **2**, the sharp peaks at 1580 and 1360 cm^{-1} correspond to the anti-symmetric and symmetric stretching of the COO^- bonded to Co respectively. Smaller peaks in the range of $1294\text{--}889\text{ cm}^{-1}$ and $889\text{--}552\text{ cm}^{-1}$ correspond to the in- plane and out of plane bending of the C-H group of the benzene ring of the BDC linker. Peaks around 552 cm^{-1} and 495 cm^{-1} are characteristic of Co-N and Co-O respectively. The sharp narrow peak at 3123 cm^{-1} is assigned to aromatic C-H stretching vibration of the ligands (Fig. 3b).

Figure 3a: FTIR spectra of **1** and its ligands

Figure 3b: FTIR spectra of **2** and its ligands

3.2.2. UV-Vis Spectroscopy

The electronic data of the compounds were recorded in solid-state and at room temperature (Table 1c.) In the UV region of the spectrum of **1**, intra-ligand transition results in absorption maxima at 266 nm assigned to $\pi \rightarrow \pi^*/n \rightarrow \pi^*$ transitions and a near visible band 351 nm assigned to LMCT (Fig. S3). The broad band in the visible region suggests the donation of electrons by the ligands to the Cu^{2+} ion with absorption maxima at 552 nm assigned to d-d transitions (${}^2\text{E}_g - {}^2\text{T}_{2g}$) [28]. In **2** the absorption band observed at 225 nm is assigned to $\pi \rightarrow \pi^*/n \rightarrow \pi^*$ transitions while the two broad bands in the visible region (Fig. S4). The band at 431 nm is as a result of ligand-metal charge transfer (LMCT) while the band at 617 nm indicates the transition of spin-allowed tetrahedral Co^{2+} , ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{F})$ [29].

Table 1c: Electronic data of ligands and compounds

Compounds	Wavelength, λ_{max} , nm (E, cm^{-1})	Assignment
Biphen	225 (44,449)	$\pi - \pi^*$
	285 (35,092)	$\pi - \pi^*/n - \pi^*$
BDC	211 (47,399)	$\pi - \pi^*$
	324 (30,868)	$\pi - \pi^*/n - \pi^*$
Meim	223 (44,848)	$\pi - \pi^*$
1	266 (37,598)	$\pi - \pi^*/n - \pi^*$
	351 (28,494)	LMCT
	552 (18,118)	${}^2E_g - {}^2T_{2g}$
2	225 (44,449)	$\pi - \pi^*/n - \pi^*$
	431 (23,204)	${}^4A_2(F) - {}^4T_1(F)$
	617 (16,209)	${}^4A_2(F) - {}^4T_1(P)$

3.2.3. Photoluminescence Spectra

Luminescent measurements were carried out on the compounds as prepared in the solid state and at room temperature. The photoluminescent (PL) spectra of the compounds and their free ligands are shown in Fig. 3c & 3d. **1** emits strongly at 430 nm upon excitation at 297 nm. The emission spectrum of the free ligand shows a main peak at 431 nm assigned to $n - \pi^* / \pi^* - \pi$ transitions of the ligand [30]. The similar emission bands exhibited by the compound and the ligand suggests that the emission of **1** could be attributed to ligand-centered electronic transitions perturbed by the coordinated metal ions, leading to ligand to metal charge transfer (LMCT). The free BDC ligand displays one main fluorescent emission at 366 nm which is assigned to $n - \pi^* / \pi^* - \pi$ transitions of the ligand. The emission band of **2** is slightly red shifted (about 19 nm) with reduced intensity ($\lambda_{\text{em}} = 384$ nm). This may be assigned to ligand to metal charge transfer (LMCT) because of chelation to the metal [31].

Fig. 3c: PL Spectra of [Cu(Biphen)(Meim)(H₂O)] and its ligand in solid state ($\lambda_{\text{ex}} = 297$ nm)

Fig. 3d: PL Spectra of [Co(BDC)(Meim)₂]_n and its ligand in solid state ($\lambda_{\text{ex}} = 265$ nm)

3.3. Thermal Analysis

Fig. 3e showed the thermal decomposition patterns of the compounds. The TGA curve of **1** shows the first decomposition stage having a percentage weight loss of 1.71% (2.80%) (exp. (calcd.)). This corresponds to the loss of a molecule of coordinated water at around 137 °C. The second stage of the decomposition between 216 – 357 °C is attributed to gradual loss of the ligands (two molecules of Meim and one molecule of Biphen) with percentage weight loss of 41.62% (40.64%) (exp. (calcd.)) and a collapse of the framework between 415 – 540 °C leaving a residue of CuO with a total weight of 12.53% (9.7%) (exp. (calcd.)). The TGA curve of **2** shows three decomposition steps. There was no weight loss until decomposition at 200 °C, indicating that no guest molecules are present in the pores of the framework. A weight loss of 70.12% exp., calcd. 68.2% is ascribed to the loss of the methylimidazole ligand and a total collapse of the framework at 410 °C is the loss of the BDC ligand. The final residue of CoO has a total weight of 19.25 % (26.5%) (exp. (calcd.)).

Fig. 3e: TGA Curve of 1 and 2

3.4. Fluorescence Sensing

Compound **1** displayed a clear response sensitivity to the nitroaromatics examined in the order 4NP > 4NA > NB as shown in Fig. 4a. The emission bands were reduced rapidly following incremental addition of nitroaromatic compounds up to 3 mM (Fig. 4b, Fig. 4d & Fig. 4f). The quenching capacities are 96.8 % for 4NP, 85.9% for 4NA and 63.10% for NB respectively (Fig. S5). The quenching efficiency of the nitro analytes were evaluated using the Stern-Volmer (S-V) equation, $I_0/I = K_{SV}[M] + 1$ [32], in which I_0 and I are the emission intensities of maximum emission band before and after the addition of nitroaromatic compounds, $[M]$ represents the molar concentration of the nitro analytes (mM), and K_{SV} is the S-V constant (M^{-1}). Good linear correlations were obtained ($R^2 > 0.9$) and presented in Fig. 4c, Fig. 4e & 4g. Furthermore, the limits of detection were calculated based on $3\sigma/k$ (σ = standard deviation;

k = slope of emission intensity versus concentration plot) for the three nitro analytes (Table 1d). Compound **2** was also found to be highly selective towards nitroaromatic compounds with significant quenching of its luminescent intensities. The luminescent quenching towards nitroaromatics is in the order 4NA > 4NP > NB as shown in Fig. 5a. The quenching capacities are 96.6%, 88.7% and 85.7% for 4NA, 4NP and NB respectively (Fig. S6). To further investigate the selectivity of **2** towards nitroaromatic compounds, a batch of suspensions of **2** in DMF was dispersed in the nitro analytes with gradual increment in concentration. The emission band was found to reduce as the concentration of nitro analytes increased up to 3 mM (Fig. 5b, Fig. 5d & Fig. 5f). The dose-response curves (S-V plot) showed good linearity ($R^2 > 0.9$) and high quenching constants (K_{sv}) as shown in Fig 5c, Fig. 5e & Fig. 5g. The limits of detection are low and in the range 1.66 – 2.93 ppm (Table 1d).

Fig. 4a: Luminescence intensities of **1** when immersed in different nitro analytes.

Fig. 4b: Emission spectra of **1** dispersed in DMF with incremental addition of 4NP

Fig. 4c: Stern-Volmer plot of **1** in 4-nitrophenol

Fig. 4d: Emission spectra of **1** dispersed in DMF with incremental addition of 4NA

Fig. 4e: Stern-Volmer plot of **1** in 4-nitroaniline

Fig. 4f: Emission spectra of **1** dispersed in DMF with incremental addition of NB

Fig. 4g: Stern-Volmer plot of **1** in nitrobenzene

Fig. 5a: Luminescence intensities of **2** when immersed in different nitro analytes

Fig. 5b: Emission spectra of **2** dispersed in DMF with incremental addition of 4NA

Fig. 5c: Stern-Volmer plot of **2** in 4-nitroaniline

Fig. 5d: Emission spectra of **2** dispersed in DMF with incremental addition of 4NP

Fig. 5e: Stern-Volmer plot of **2** in 4-nitrophenol

Fig. 5d: Emission spectra of **2** dispersed in DMF with incremental addition of NB

Fig. 5g: Stern-Volmer plot of **2** in nitrobenzene

Table 1d: K_{SV} and LOD values of nitroaromatic compounds using **1** and **2** as sensors

Nitroaromatic compounds	$K_{sv} (M^{-1})$	LOD (ppm)
1		
4NA	7.7×10^4	2.67
4NP	1.79×10^5	13.07
NB	1.76×10^4	1.84
2		
4NA	7.9×10^4	1.66
4NP	3.49×10^4	2.93
NB	1.76×10^4	1.95

Fig. 5h: Photographs of **1** before and after immersion in different nitro analytes under UV light

Fig. 5i: Photographs of **2** before and after immersion in different nitro analytes under UV light

3.4.1. Quenching mechanism

The possible quenching mechanism by nitroaromatic compounds was further examined. Firstly, the PXRD patterns of **1** and **2** were collected after immersion in the nitro-analytes to monitor the stability of the compounds. The PXRD patterns of the compounds were observed to be consistent with the simulated patterns which indicates high structural integrity and stability (Fig. 6a & 6b). Thus, the luminescence quenching is not caused by the collapse of the structure. Secondly, from the structural characterization of the compounds, the ligands of the CPs are π -electron rich. The quenching effect may result from Photoinduced Electron Transfer (PET) attributable to donor-acceptor electron transfer mechanism [33, 34] because the nitro-

group is a characteristic electron withdrawing substituent. Therefore, upon excitation, the excited electrons of the CPs could transfer to the LUMO of the nitroaromatic compounds, which causes the quenching effect. To further understand the quenching phenomena by electron transfer, competition experiment was carried out by CP immersion in aniline, comprising an electron donor substituent. Results revealed that there was no significant reduction in the luminescent intensity of the compounds when treated with aniline and incremental addition of aniline up to 3 mM enhanced the fluorescent intensities (Fig. S7 & S8). This observation agrees with literature report [35].

Fig. 6a: PXRD patterns of **1** before and after immersion in 4-nitrophenol

Fig. 6b: PXRD patterns of **2** before and after immersion in 4-nitroaniline

2 was found to perform better than **1** in the sensing of the nitro analytes studied, having higher quenching percent towards the nitroaromatic compounds (Fig. 6c). The mechanism of the sensing and superiority of **2** over **1** was further investigated by DFT studies.

Fig. 6c: Quenching capacity of the compounds in the different nitro analytes

3.5. Recyclability

The recyclability of the compounds in the nitro-analytes (4-NP and 4-NA) was investigated by washing in DMF several times. The intensities of **1** and **2** did not change significantly after three-fold use (Fig. 6d & 6e).

Fig. 6d: Changes in emission intensities of **1** after three recycles in 1mM 4-NP

Fig. 6e: Changes in emission intensities of **2** after three recycles in 1mM 4-NA

3.6 Comparison with other organic solvents

To confirm the selectivity of **1** and **2** towards nitroaromatic analytes, the compounds were used to probe other organic solvents. The fluorescence responses of **1** and **2** to various organics show significant quenching by nitroaromatics including nitrobenzene (NB), 4-nitrophenol (4NP) and 4-nitroaniline (4NA) compared to other organics including alcohols (methanol, ethanol), aromatic (benzene), amine (aniline) and amide (*N,N*-dimethylformamide) whose effect on the emission of **1** and **2** is negligible under the same experimental condition (Fig. S9 and S10). The high selectivity was further validated by the fluorescence responses of **1** and **2** towards 4-nitrophenol (4NP) and 4-nitroaniline (4NA) respectively. Moreover, competition experiments of **1** and **2** in a mixture containing nitroaromatics indicated that luminescent intensities of nitro analytes were unaffected by the presence of other interfering organic solvents (Fig. S9a-c and Fig. S10a-c).

3.7. Density Functional Theory (DFT) studies

3.7.1 Geometry optimization

The optimized structures of the compounds (CPs) are shown in Fig. S11 and S12, respectively. The optimized structures are similar to that obtained in the experiment. Full optimization of **1** and **2** led to the final structure bond lengths and angles slightly different from the experimental (Table 1b). Some slightly overestimated and underestimated calculated bond distances and angles between Cu and Co with surrounding atoms are due to movement of electronic density within the compounds.

Frontier molecular orbitals help with predicting reactivity, stability, and resistance of molecules by forecasting their electrical transport properties. HOMO has the ability to donate electrons, while LUMO withdraws electrons [36]. For **1**, HOMO originates (Fig. S13a) from the aromatic ring of biphenyl-4-carboxylic acid, while carboxylic groups, copper atom and imidazolyl ring

contributed to LUMO energies (Fig. S13b). For **2**, the metal ion contributes to the HOMO energies (Fig. S14a), while carboxylic groups and imidazolyl ring contributes to the LUMO energies (Fig. S14b). The HOMO–LUMO gap are in the order of **2** (7.036 eV) > **1** (8.390 eV). Generally, **2** provide a much higher electrical transport properties compared to **1**. Table 1e, presents the HOMO, LUMO and Band Gap of [Cu(Biphen)(Meim)(H₂O)] and [Co(BDC)(Meim)₂]_n.

3.7.2. CP-nitro analyte interactions

Orbital Energy Gap

Wide HOMO–LUMO gap implies high stability, charging resistance, and changes in the number and distribution of electrons. Hence hard molecules have a significant HOMO–LUMO gap. Meanwhile, small HOMO–LUMO gap is indicative of highly polarizable soft molecules, as they need only small amounts of energy to get them to the excited states.

HOMO–LUMO gap

Looking at the three nitro-compounds, 4-nitroaniline and 4-nitrophenol showed a small HOMO–LUMO energy gap which results in better polarization and reactivity as observed in the fluorescence studies. Conversely, when compared with 4-nitrophenol and 4-nitroaniline, nitrobenzene provided the largest HOMO–LUMO energy gap indicating a hard molecule with low reactivity (Table 1e). The HOMO–LUMO gap energies of nitro compounds are in the order: Nitrobenzene (4.679 eV) > Nitrophenol (4.558 eV) > Nitroaniline (3.763 eV) (Table 1e).

Adducts formed between **1** and nitro compounds suggested that HOMO was derived from nitro compounds and **1** (around Biphen) while LUMO was derived from **1** (Fig. 7). This obviously confirmed that the interaction between the **1** and the nitro compounds is through the HOMO donation of electrons to the LUMO [37]. Therefore, potential interactions resulting from adduct

formation are mediated by the hydrogen bonding between (4-nitrophenol and 4-nitroaniline) and the π face of **1** [38].

Nitro compounds showed that the HOMO and LUMO centers on **2**, resulting in an interaction (π - π stacking) between the **2** and the Nitro compounds (nitrobenzene, 4-nitrophenol, 4-nitroaniline) (Fig. 8). However, the calculated LUMO energies for the molecules of the nitro analytes lie lower than that of **1** and **2** which means that excited electrons can be transferred from the conduction band of the frameworks to the LUMOs of the nitro analytes (Fig. 9) [39].

LUMO energies with lower energy values are more important in evaluating favourable interaction between compounds (CPs) and nitro-molecules, because the LUMO sites contribute to the overlapping of incoming HOMO orbitals. The energy gaps of adducts formed between **1** with Nitrobenzene, Nitrophenol and Nitroaniline are 9.196, 9.138 and 9.016 eV, respectively, while **2** with nitrobenzene, nitrophenol and nitroaniline are 7.099, 7.125 and 6.936 eV, respectively. Based on the reported LUMO energy values of adducts, 4-nitroaniline is the most favourable molecule for the quenching of **2** while the LUMO energy values of **1** adducts do not adhere to the experimental order of decrease in photoluminescent intensity, which indicates that charge transfer may not be the only phenomenon responsible for quenching [40].

Fig. 7: Frontier orbitals showing (a) HOMO and (b) LUMO positions of **1**-nitrobenzene, (c) HOMO and (d) LUMO positions of **1**-nitrophenol and (e) HOMO and (f) LUMO positions of **1**-nitroaniline.

Fig. 8: Frontier orbitals showing (a) HOMO and (b) LUMO positions of **2**-nitrobenzene, (c) HOMO and (d) LUMO positions of **2**-nitrophenol and (e) HOMO and (f) LUMO positions of **2**-nitroaniline.

Fig. 9: HOMO-LUMO energy profiles of compounds and nitro analytes

Table 1e: HOMO, LUMO and Band Gap of 1, 2, CPs-nitroanalytes and nitroaromatic molecules

	HOMO (eV)	LUMO (eV)	Band Gap (eV)
1	-8.281	0.109	8.390
2	-6.700	0.336	7.036
1-nitrobenzene	-8.425	0.771	9.196
1-nitrophenol	-8.381	0.757	9.138
1-nitroaniline	-8.373	0.643	9.016
2-nitrobenzene	-6.287	0.812	7.099
2- nitrophenol	-6.308	0.817	7.125
2- nitroaniline	-6.465	0.47	6.936
Nitrobenzene	-8.080	-3.401	4.679
Nitrophenol	-7.957	-3.399	4.558
Nitroaniline	-6.668	-2.905	3.763

Preliminary theoretical studies was conducted to compare the energy gap of the 4-nitrophenol adducts when metal centers are swapped (Co for Cu in **1** and Cu for Co in **2**). This resulted in a slight increase in energy band gaps (Table 1f), hence, lowering the quenching ability. The optimized structure and HOMO-LUMO position for the interaction of 4-nitrophenol with swapped metal center is reported in the supplementary data section (Figures S15-S16). From the theoretical studies, it is obvious that band gaps of synthesized compounds **1** and **2** play significant role in influencing quenching ability.

Table 1f: HOMO, LUMO and Band Gaps of swapped metal centers

	Current Study			Metal center swapped (Co for Cu in 1 and Cu for Co in 2)		
	HOMO (eV)	LUMO (eV)	Band Gap (eV)	HOMO (eV)	LUMO (eV)	Band Gap (eV)
1-nitrophenol	-8.381	0.757	9.138	-8.307	0.732	9.039
2-nitrophenol	-6.308	0.817	7.125	-6.688	2.222	8.910

4. Conclusions

Two new coordination compounds were successfully synthesized using flexible carboxylate and imidazolyl ligands. The compounds show excellent luminescent response by virtue of their photophysical properties. The luminescence intensities of the **1** and **2** were found to be quenched drastically by nitroaromatic analytes and upon incremental concentrations of the nitro analytes. **2** was found to have superior sensitivity towards the nitro analytes compared to **1**. All experimental results indicate that the selectivity of the CPs relates to both the structures and electronic properties of the CPs and the nitro-analytes, as well as to the essence of their interactions. Computational studies have also shown that interactions between the structures and the nitro analytes could result from strong intermolecular hydrogen bonding, π - π stackings

and photo-induced electron transfer. The fast response time, sensitivity and recyclability make them potential materials for commercial grade sensors.

Conflict of Interest

There are no conflicts to declare.

Supplementary data

CCDC 2016804 and 1999492 contains the crystallographic data of [Cu(Biphen)(Meim)(H₂O)] **1** and [Co(BDC)(Meim)₂]_n **2**, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures

Acknowledgements

We are grateful to Royal Society of Chemistry (RSC) for funding and also to the School of Chemistry, University of Nottingham for X-ray crystallography analysis of the compounds. The authors thank Redeemer's University, Ede, Nigeria for the fluorescence studies and the Center for High Performance Computing (CHPC), Capetown, South Africa for providing the platform to carry out molecular modelling studies using the Gaussian09 software.

References

1. S.R. Batten, N. R. Champness, X-M. Chen, G-M. Javier, S. Kitagawa, L. Ohrstrom, M. O'Keeffe, M. K. Suh, J. Reedijk
CrystEngComm, 14 (2012) p. 3001-3004.
2. D. T. McQuade, A. E. Pullen, T. M. Swager
Chem. Rev. 100 (2000) p. 2537–2574.
3. D. S. Moore
Rev. Sci. Instrum. 75 (2004) p. 2499–2512.

4. Y.W. Li, J.R Li, L.F. Wang, B.Y. Zhou, Q. Chen, X.H. Bu,
J. Mater. Chem. A 1 (2013) p. 495–499.
5. A.A. Tehrani, L. Esrafilifili, S. Abedi, A. Morsali, L. Carlucci, D.M. Proserpio, J. Wang,
P.C. Junk, T.F. Liu
Inorg. Chem. 56 (2017) p. 1446–1454.
6. D. Tian, Y. Li, R.Y. Chen, Z. Chang, G-Y Wang, X-H Bu
J. Mater Chem A 2 (2014) p. 1465–1470.
7. A-L. Li, Y-H. Qu, L. Fu, C. Han, G-H. Cui
CrystEngComm, 22 (2020) p. 2656-2666.
8. Y-J. Yang, Y-H Li, D. Liu, G-H. Cui
CrystEngComm, 22 (2020) p. 1166-1175.
9. A.C. Tella, M.D. Olawale, M. Neuburger, J.A. Obaleye
Journal of Solid-State Chemistry 255 (2017) p. 157-166.
10. A.C. Tella, A.C. Oladipo, V.O. Adimula, O.A. Ameen, S.A. Bourne, A.S. Ogunlaja,
New Journal of Chemistry 43 (2019) p.14343-14354.
11. A.C. Tella, S.O. Owalude, M.F. Omotoso, S.J. Olatunji, A.S. Ogunlaja, L.O. Alimi,
O.K. Popoola, S.A. Bourne Journal of Molecular Structure 157 (2018) p. 450 - 455.
12. A.C. Tella, G. Mehlana, L.O. Alimi, S.A. Bourne
Zeitschrift fur anorganische und allgemeine chemie (ZAAC) 64 (2017) p. 523–530.
13. G-Y. Wang, L-L. Yang, L. Yue, H. Song, W-J. Ruan, Z. Chang, X-H. Bu
Dalton Trans 42 (2013) p.12865-12868.
14. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R.
Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato,
X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M.
Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H.

- Nakai, T. Vreven, J. A. Montgomery Jr, J. E. Peralta, F. Ogliaro, M. Bearpark, J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J.V. Ortiz, J. Cioslowski, D. J. Fox,
- (2016), GAUSSIAN 16, Revision D.01, Gaussian Inc., Wallingford, CT.
15. A. D. Becke
J. Chem. Phys, 98 (1993) p. 5648-5652.
 16. C. Lee, W. Yang, R.G. Parr Phys. Rev. B, 37 (1988) p. 785-789.
 17. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K Howard, H. Puschmann
J. Appl. Cryst. 42 (2009) p. 339-341.
 18. G. M. Sheldrick
Acta Cryst. A71 (2015) p. 3-8.
 19. G. M. Sheldrick
Acta Cryst C71 (2015) p. 3-8.
 20. A. W. Addison, T. N. Rao, J. Reedijk, J. Van Rijn, G. C. Verschoor
J. Chem. Soc., 7 (1984) p. 1349-1356.
 21. K. Das, S. Dolai, P. Vojtisek, S.C. Manna
Polyhedron 149 (2018) p. 7-16.
 22. A.C. Tella, S.O. Owalude, S.J. Olatunji, S.O. Oloyede, A.S. Ogunlaja, S.A. Bourne
J Sulfur Chem 39 (2018) p. 588–606.
 23. D.F. Shriver, P.W. Atkins
Inorganic chemistry 3rd edn (1999) p. 235–236.

24. Z-X. Li, X. Chu, G-H. Cui, Y. Liu, L. Li, G-L. Xue
CrystEngComm 13 (2011) p. 1984-1989.
25. H. Zhou, G.X. Liu, X.F. Wang, Y. Wang
CrystEngComm 15 (2013) p. 1377-1388.
26. S. S. Prasad, M.R. Sudarsanakumar, V.S. Dhanya, S. Suma, Prathapachandra Kurup
M.R.
Journal of Molecular Structure 1173 (2018) p. 196-204.
27. N. Hojnik, M. Kristl, A. Golobic, Z. Jaglic, M. Drofenik
Central Eur J Chem 12 (2014) p. 320-6.
28. S. M. Sheta, M. E. Said, M. M. Abd-Elzaher
Dalton Trans., 47 (2018) p. 4847–4855.
29. R. A. Ahmadi, F. Hasanvand, G. Bruno, H. A Rudbari, S. Amani
Inorganic Chemistry (2013) p. 1-7.
30. G.Y. Wang, C. Song, D.M. Kong, W.J. Ruan, Z. Chang, Y. Li J.
Mater. Chem. A 2 (2014) p. 2213–2220.
31. L.H. Cao, H.Y. Li, S.Q. Zang, H.W. Hou, T.C.W. Mak
Cryst. Growth Des. 12 (2012) p. 4299–4301.
32. G. F. Ji, J. J. Liu, X. C. Gao, W. Sun, J. Z. Wang, S. L. Zhao, Z. L. Liu
J. Mater. Chem. A 5 (2017) 10200.
33. S. Pramanik, C. Zheng, X. Zhang, T. J. Emge, J. Li
J. Am. Chem. Soc 133 (2011) p. 4153–4155.
34. H. Sohn, M. J. Sailor, D. Magde, W. C. Trogler
J. Am. Chem. Soc 125 (2003) p. 3821–3830.
35. Q. Tu, L. Ren, Y. Cui, A. Cheng, E. Gao
CrystEngComm. (2020) p. 21-24.

36. Y. Ji1, X. Liu, G. Fu, Y. Chen, F. Wang, J. Zhao
Materials Science and Engineering 87 (2015) p. 012104
37. J.H. Qin, H.R. Wang, M.L. Han, X.H. Chang, L.F. Ma
Dalton Trans 46 (2017) p. 15434–15442.
38. S. Kumar, N. Venkatramaiah, S. Patil
J. Phys. Chem. C, 117 (2013) p. 7236-7245.
39. L. Liu, X. Chen, J. Qiu, C. Hao
Dalton Trans., 44 (2015) p. 2897–2906.
40. J. Wang, J. Wu, L. Lu, H. Xu, M. Trivedi, A. Kumar, J. Liu, M, Zheng
Front. Chem. 7 (2019) p. 244.