Cu(II) MOFs Based on Bipyridyls: Topology, Magnetism, and Exploring Sensing Ability toward Multiple Nitroaromatic Explosives

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Supporting Information

ABSTRACT: In this work, a series of three copper(II) metal-organic frameworks (MOFs), [Cu(4,4′-DP)Cl]n (1), [Cu(4,4′-DP)0.5Cl]n (2), and [Cu(4,4′-TMDP)Cl]n (3) (4,4′-DP = 4,4′-dipyridyl, 4,4′-TMDP = 4,4′-trimethylene-dipyridyl), is designed and synthesized under solvothermal conditions. Crystallographic investigations reveal that 1 and 2 have tetrahedral and 3 has octahedral environment around the Cu(II) ion. By varying the solvent conditions and ligand derivatives, the topology can be interestingly tuned. TOPOS Pro provides topological conclusions that 1 is stabilized by unusual 2D + 2D → 3D polycatenation of layers lying in (110) and (110) planes with dihedral angle of 90° showing altogether fes, hcb, and sql topologies. On the other hand, 2 exhibits a bey (3,4-c net) topology and 3 shows 4-fold interpenetration with the diu topology. The dc measurements for 1–3 performed on polycrystalline samples in a 0.1 T field confirm strong ferromagnetic behaviors for 1 and 2 and moderate antiferromagnetic behavior for 3. To examine the sensing properties of the three MOFs, various hazardous nitroaromatic compounds (NACs) were used as analytes. While 1 is a potent fluorescence sensor for highly sensitive detection of multiple NACs, 2 selectively detects meta-dinitrobenzene (m-DNB) with KSV = 5.73 × 103 M⁻¹ and a remarkably lower limit of detection (LOD) value of 1.23 × 10⁻⁷ M. 3 does not show sensing ability toward any NAC probably due to the coordination environment being different from those in 1 and 2. The work demonstrates fine-tuning of the topology and in turn magnetic and sensing properties by changing the reaction conditions.

INTRODUCTION

In the past decade, the design and synthesis of highly connected metal-organic frameworks (MOFs) have been of great interest for their fascinating topologies and their potential properties as functional materials. These framework structures among well-ordered pores are exclusive materials for various applications in gas storage, gas separation, sensing, and catalysis. Although various MOFs could be designed by using multideterminate ligating systems, their ultimate topologies are finely tuned by several factors, including metal–ligand ratio, pH, solvent, temperature, as well as the oxidation state of the metal ion. Most of such MOFs have recently been employed in optoelectronics, magnetism, and material science. The most important strategy to design such frameworks classically used in this area is the building-block approach. It is reported that (CuX)n units can be used as incredible inorganic functional materials owing to their rich network as well as their rich photophysical properties. At this point, copper halide metal-organic frameworks (MOFs) have shown interesting structural characteristics ranging from low-dimensional coordination complexes to three-dimensional (3D) nets with various structural motifs such as cubane Cu₄X₄ tetramers, rhomboid Cu₂X₂ dimers, double-stranded [Cu₂X₂]₅ ladders, zigzag [CuX]₅ chains, and hexagonal [CuₓX₆]₄ grid chains. However, such MOFs have not yet been exploited for sensing applications. Chemosensors, which work through fluorescence quenching, have gained much emphasis in recent times. Detection based on fluorescence has gained significant attention due to its high sensitivity, short response time, simplicity, and its ability to work in both solid and solution phases. Several pi-electron-rich fluorescent conjugated polymers have been formed and are used in the detection of nitroaromatic explosives in trace amounts. Especially, MOFs provide several advantages over usual fluorophores when used as luminescent sensors. Their structural design allows enhanced host–guest interactions and for them to be used as preconcentrators for target analytes. The detection of highly explosive and explosive-like substances selectively and sensitively is now a serious problem regarding security as well as environment issues. Nitrobenzene, a highly volatile and explosive organic solvent, is the basic constituent of nitroaromatic compounds. There are many nitro compounds that are used in landmines and were used during World War II as explosive materials; some of them are 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (2,4-DNT), 2,4,6-trinitropholen (TPN), nitrobenzene (NB), etc. The electron-rich con-
jugated polymers are excellent sources for the detection of nitroaromatic explosives. The delocalized π electrons of such conjugated polymers enhance the electrostatic interaction between the polymer and electron-deficient species.\textsuperscript{19} In recent times, apart from the organic conjugated systems, some examples of fluorescent MOFs acting as explosive vapor sensors have been reported.\textsuperscript{20} Such MOFs, due to the high surface area, allow more analyte moieties to be contacted, thus facilitating high sensitivity.\textsuperscript{21} Especially, the detection of nitrobenzene sensors based on MOFs is a challenging task with regard to safety and environmental protection.\textsuperscript{16b}

Herein, we report 2D and 3D MOFs with organic conjugated ligands, 4,4′-dipyridyl and 4,4′-trimethylenedipyridyl, and copper chloride as starting materials. We demonstrate a facile approach based on varying solvents to control the topology of MOFs, and we further studied their magnetism and luminescent properties. In this respect, two bidentate dipyridyl derivatives were selected, and a 2D + 2D (interpenetrated or polycatenated) MOF, namely, [[Cu(4,4′-DP)Cl]₃ (1)], a two-dimensional (2D) MOF, namely, [Cu(4,4′-DP)₃Cl]₃ (2), and one three-dimensional (3D) MOF, namely, [Cu(4,4′-TMDP)]₃ (3), with different topologies were designed (Scheme 1). Further, these three MOFs were examined for their possible application as sensors against various hazardous nitroaromatic compounds (NACs).

**RESULTS AND DISCUSSION**

Structural Description and Topologies of 1–3. The color and shape of the crystals of all the three MOFs are the same (Figure 1). Crystal data with refinement parameters are summarized in Table 1. Single-crystal X-ray diffraction analysis reveals that 1 crystallizes in the tetragonal space group I₄/₁acd as shown in Figure 2. The asymmetric unit of 1 contains one Cu ion, one chloride ion, and one 4,4′-dipyridyl ligand. All Cu(II) ions show distorted tetrahedral geometries, where the CuI ion is surrounded by two μ₁-bridged chloride atoms (Cl1) and two nitrogen atoms (N1 and N2) of the 4,4′-dipyridyl ligand. The bond lengths of CuI–N1 (1.971 Å) and CuI–N2 (1.986 Å) are shorter than the bond lengths of CuI–Cl1 (2.436 Å) and CuI–Cl1 (2.420 Å), respectively. Due to the difference in bond lengths, the bond angles are also different, which are shown in Table 1S, SI. The difference in bond angles between Cl1–CuI–Cl1 (104.31°) and N1–CuI–N2 (128.49°) is much more as compared to the difference between those of N2–CuI–Cl1 (99.75°) and N1–CuI–Cl1 (107.80°). In the 2D sheet of 1, there are two types of bridging between two CuI ions; the first type of bridging involves two chlorine atoms between the two CuI ions and the second type of bridging involves a 4,4′-dipyridyl ligand between the two CuI ions.

The extended structure comprises layers consisting of the Cu₄Cl₂ clusters connected by means of the DP (4,4′-dipyridyl) ligands (Figure 3). The 2D + 2D → 3D polycatenation of layers lying in (110) and (110) planes with dihedral angle of 90° is observed (Figure 3b). The layers cross along the c-axis direction. The topological description of a coordination polymer includes the simplification procedure, that is, representation of a network in terms of the graph-theory approach. In the standard simplification procedure, metal atoms remain intact during simplification, but ligands are represented by their center of mass, keeping the connectivity of the ligands with their neighbors. The subsequent secondary simplification of the net obtained at the previous step includes removing the 0- and 1-coordinated nodes (extra framework and terminal structural groups) and replacing the 2-coordinated nodes (bridge structural groups) by net edges. Thus, this description characterizes the way ligands and metal centers are connected. The standard representation of the structure resulted in the underlying net of the fes topological type (Figure 4). The cluster simplification procedure implemented in Topos Pro allows one to identify more complex building blocks of a structure and characterize their connection mode. In the structure under examination, the connectivity of the Cu₄Cl₂ clusters by means of the 4,4′-DP ligands is described by the 3-coordinated underlying net of the hub topological type (Figure 5). The connection mode of more complex (Cu₄Cl₂·4,4′-DP)₂ building units identified by ToposPro is described by the 4-coordinated underlying net of the sq1 topological type (Figure 6).

Crystal structure of 2 crystallizes in the monoclinic space group P2₁/c as shown in Figure 2. The asymmetric unit of 2 contains one Cu ion, one chloride ion, and half of the 4,4′-dipyridyl ligand. Each Cu²⁺ ion shows distorted tetrahedral geometry where the CuI ion is surrounded by three chlorine atoms (Cl1) and one nitrogen atom (N1) of the 4,4′-dipyridyl...
and forms a square net of $\text{Cu}_2\text{Cl}_2$. These square nets are the tetrahedral $\text{Cu}_1$ center with a triply bridged chlorine atom that each tetrahedral $\text{Cu}_1$ center is attached to the next unit of $\text{Cu}_2\text{Cl}_2$, are present in this structure (Figure 7b). The rods of Figure 7a. It should be noted that the rods, whose composition and one type of ligand form a square net. Further, these fragments are connected in infinite layers (Figure 8) in the direction (110). The topology of the resulting underlying 3,4-c net is bey (Figure 9) in standard representation of the valence-bonded MOFs.

Crystal structure of 3 crystallizes in the tetragonal space group $I4_1/a$ as shown in Figure 1. The asymmetric unit of 3 consists of two free metal centers $\text{Cu}_1$ and $\text{Cu}_2$, and each metal center contains one chlorine atom and one 4,4′-trimethylenediprydyl ($4,4′$-TMDP) ligand (Figure 10a,b). Both metal centers $\text{Cu}_1$ and $\text{Cu}_2$ are hexa-coordinated by two chlorides at the axial position and four nitrogen atoms of the resulting underlying 3,4-c net is bey (Figure 9) in standard representation of the valence-bonded MOFs.

| Table 1. Crystal Data and Refinement Parameters for 1–3 |
|---------------------------------------------------------|
| 1            | 2            | 3            |
| CCDC no.     | 1902912      | 1902913      | 1902914      |
| empirical formula | $\text{C}_{10}\text{H}_8\text{Cl}\text{Cu}_2\text{N}_2$ | $\text{C}_7\text{H}_9\text{Cl}\text{Cu}_2\text{N}_2$ | $\text{C}_{21}\text{H}_{20}\text{Cl}_2\text{Cu}_2\text{N}_4$ |
| formula weight | 255.17       | 177.09       | 530.99       |
| temperature/K | 296(2)       | 100(2)       | 100(2)       |
| space group   | $I4_1/a$     | $P2_1/c$     | $I4_1/a$     |
| a/Å           | 13.9629(10)  | 3.7495(8)    | 17.2920(5)   |
| b/Å           | 13.9629(10)  | 12.724(2)    | 17.2920(5)   |
| c/Å           | 38.8651(9)   | 11.3220(18)  | 40.805(3)    |
| α/deg         | 90           | 90           | 90           |
| β/deg         | 90           | 90           | 90           |
| γ/deg         | 90           | 90           | 90           |
| volume/Å³     | 7577.2(2)    | 539.05(17)   | 12201.3(9)   |
| Z             | 32           | 4            | 16           |
| $\rho_{calc}$/g/cm³ | 1.789      | 2.1819       | 1.1562       |
| $\mu$/mm⁻¹   | 2.541        | 4.406        | 0.909        |
| $\ell$(000)  | 4096.0       | 350.0        | 4411.3       |
| crystal size/mm³ | 0.300 × 0.210 × 0.150 | 0.35 × 0.25 × 0.16 | 0.37 × 0.26 × 0.16 |
| radiation     | Mo Kα ($\lambda = 0.71073$) | Mo Kα ($\lambda = 0.71073$) | Mo Kα ($\lambda = 0.71073$) |
| 2θ range for data collection/deg | 4.62–49.992 | 6.4–52.06 | 4.72–50 |
| reflections collected | 42 134 | 2759 | 64 325 |
| independent reflections | 1669 [Refl = 0.0289, Rsig = 0.0082] | 1059 [Refl = 0.0830, Rsig = 0.1285] | 5362 [Refl = 0.0944, Rsig = 0.0536] |
| data/restraints/parameters | 1669/0/127 | 1059/0/68 | 5362/0/299 |
| goodness-of-fit on $\ell$ | 1.071 | 1.110 | 1.720 |
| final R indexes [$I > 2\sigma(I)$] | $R_1 = 0.0185$, $wR_2 = 0.0471$ | $R_1 = 0.0580$, $wR_2 = 0.0905$ | $R_1 = 0.1066$, $wR_2 = 0.3792$ |
| final R indexes [all data] | $R_1 = 0.0220$, $wR_2 = 0.0510$ | $R_1 = 0.0957$, $wR_2 = 0.1061$ | $R_1 = 0.1352$, $wR_2 = 0.4181$ |

The crystal structure of the C₅H₄NClCu coordination polymer consists of one type of metal atom, that is, a Cu atom with tetrahedral coordination, which is bound by chlorine atoms, and one type of ligand — C₁₀H₈N₂ (4,4′-DP) — as presented in Figure 7a. It should be noted that the rods, whose composition is Cu₂Cl₂, are present in this structure (Figure 7b). The rods form a square net. Further, these fragments are connected in the crystal structure of the C₅H₄NClCu coordination polymer.
valence angles are in the normal range for coordination bonds (Table 1S, SI).22,23

Figure 2. Structures of the basic building blocks of MOFs (1–3).

Figure 3. (a) Fragment of the layer. Hydrogen atoms are omitted for clarity. (b) Layers (110) (yellow) and (110) (green) interlace in an inclined fashion. (c) The way the two perpendicular layers interweave.

Figure 4. Standard representation of the coordination polymer layers. (Left) The net obtained after primary simplification. Black spheres represent the 4,4'-DP ligands. (Right) The 3-c underlying net of the fes topological type obtained after the secondary simplification procedure.

Figure 5. Underlying net of the structure obtained by the cluster representation procedure at 6-ring. (Left) The net obtained after primary simplification. Purple spheres correspond to Cu2Cl2 clusters; orange spheres represent the 4-pyridyl moiety. (Right) The 3-c underlying net of the hcb topological type obtained after the secondary simplification procedure.
The resulting network has a 3-periodic motif. Due to large spacing of nodes, the pores in the network are filled by three other networks, producing 4-fold interpenetration. The 4,4′-TMDP bridges can be simplified in edges, and the 6-c Cu atoms represent 4-c nodes after removing 1-c Cl atoms. This (standard) representation gives a 4-c underlying net of widespread dia topology. The interpenetration can be described as “normal” for dia nets:24−26 each adamantane-like cage hosts only one node of another net located on the diagonal, and each window of one net is threaded only by one edge of another net. In total, one 6-ring of one net catenates 18 other 6-rings from three other nets.

FTIR Spectra and PXRD Pattern. The solid-state FTIR spectra were recorded in the range 4000−400 cm\(^{-1}\). This gives ample information about the bonding modes in 1−3 (Figure S1, SI). The FTIR spectra of 1, 2, and 3 are approximately similar and give well-resolved peaks in the range of the −2925 cm\(^{-1}\) region, which can be assigned to aromatic C-H stretching frequency. 1, 2, and 3 also show \(\nu(C≡N)\) and \(\nu(C≡C)\) stretching vibration bands in the 1612−1408 cm\(^{-1}\) region. The medium-intensity bands for 1, 2, and 3 in the ranges of 474, 451, and 518 cm\(^{-1}\) are consistent with the formation of the M−N bond. The PXRD patterns of 1, 2, and 3 were recorded in crystalline materials at ambient conditions to check the bulk purity of the synthesized MOFs. The recorded PXRD patterns of 1, 2, and 3 are identical to the simulated data (Figure S2-S4, SI), confirming the phase purity of the MOFs.

Magnetic Studies. The temperature dependence of the magnetic susceptibility was measured under an applied dc field of 0.1 T in the temperature range 2−300 K. Field (H)-dependent magnetization (M) of the complexes was also investigated at three temperatures (2, 3, and 5 K). Plots of \(\chi_M H\) product versus \(T\) (\(\chi_M\) is the molar magnetic susceptibility per two Cu(II) ions) showing strong ferromagnetic behaviors for 1 and 2 and antiferromagnetic behavior for 3 are given in Figure 11a,b. For the MOFs 1 and 2, the experimental \(\chi_M H\) values at room temperature (1.03 (1) and 1.01 (2) \(\text{cm}^3 \text{K mol}^{-1}\)) are much higher than the theoretical one expected for the two uncoupled copper(II) ions \(\chi_M T = 2(Np^2 g^2/3k)S(S + 1) = 0.749 \text{ cm}^3 \text{ K mol}^{-1}\), where \(g = 2.00\) is the spectroscopic splitting factor, \(N\) is Avogadro’s number, \(\beta\) is the Bohr magneton, \(k\) is Boltzman’s constant, and \(S = 1/2\).27 These MOFs (1 and 2) exhibit the typical behavior of ferromagnetically coupled dinuclear molecules with a continuous increase of the \(\chi_M T\) value on lowering the temperature. These attain a maximum value of \(\chi_M T\) [1.15(1) and 1.13(2) \(\text{cm}^3 \text{K mol}^{-1}\)] at 20 K after which they get populated. It is interesting to note that the factors like lesser Cu···Cu separation and Cu−Cl−Cu angle (<97) \([\text{Cu−Cl−Cu} = 69.18\ (1)\ and\ 72.34°\ (2)\ and\ \text{Cu−Cu} = 2.758\ (1)\ and\ 2.881\ \AA\ (2)\)] give rise to strong ferromagnetic exchange between the neighboring Cu(II) centers in the MOFs 1 and 2.

To evaluate the magnetic coupling constant, the experimental susceptibility curves for 1 and 2 have been fitted using the Bleaney−Bowers equation for \(S = 1/2\) dinuclear models (eq 1)\(^{28}\)

\[
\chi_M(T) = \frac{2N\beta^2 g^2}{K_BT} \frac{3}{3 + \exp(-J/K_BT)}
\]

Best-fit parameters were obtained by minimization of the agreement factor \(R\) (eq 2)

\[
R = \frac{\sum (\chi_M^{\text{calc}} T - \chi_M^{\exp} T)^2}{\sum \chi_M^{\exp} T^2}
\]

An additional temperature-independent paramagnetic (TIP) contribution\(^{29}\) was at first included in the calculation. The fitting procedure gives \(J = 194(2) \text{ cm}^{-1}\) with \(R = 5.98 \times 10^{-4}\) for 1 and \(J = 165(3) \text{ cm}^{-1}\) with \(R = 5.82 \times 10^{-4}\) for 2. A fixed value of \(g = 2.0\) is adopted in both fittings.

In contrast, MOF 3 exhibited moderate antiferromagnetic behavior. Figure 11B displays the magnetic property of 3 as the
plot of $\chi_M T$ vs T ($\chi_M$ = molar magnetic susceptibility). At room temperature, the $\chi_M T$ value is 0.52 cm$^3$ K mol$^{-1}$, which is slightly lesser than the expected spin-only value for an isolated Cu(II) ion ($S = 1/2$, $g = 2.00$). With lowering of the temperature, the $\chi_M T$ value slightly decreases up to 120 K and reaches a plateau value after this temperature up to 2 K. Fitting the magnetic susceptibility data with the Curie–Weiss law gives the Curie constant, $C = 0.45$ cm$^3$ K mol$^{-1}$, and the Weiss constant, $\theta = -0.49$ K. The $C$ value is in the expected range for a mononuclear Cu(II) species in the monomeric unit of the MOF (3), and $\theta$ arises due to the polymeric nature and the presence of weak noncovalent interactions. The magnitude of $\theta$ discloses the presence of moderate antiferromagnetic interactions between neighboring Cu(II) ions. The nature of interactions, that is, weak antiferromagnetic, is due to large Cu(II)···Cu(II) distances across the bridging 4,4′-dipyridyl derivative ligand in 3.30

The reduced magnetizations (per Cu entity), expressed in terms of $\mu_B$, of 1–3 at low temperatures, that is, at 2, 3, and 5 K, were examined by varying the field from 0 to 7 T (Figure 12). The reduced magnetization ($M/N\beta$) vs the applied field (H) curves of the complex increased rapidly at low fields but
more slowly at higher fields. The magnetization increases linearly at low applied fields up to \( \sim 2.0\ T \) in all the MOFs and then progressively tends toward saturation. The magnetization values at the highest measured field (7 T) and the lowest temperature (2 K) are 2.30 (1), 1.71 (2), and 0.62 (3) \( \mu B \).

**Sensing Properties. Preparation of Stock Solution for Sensing Studies.** The stock solutions of 1 and 2 were prepared using a concentration of 0.0001 M, and various other nitroaromatic compounds, namely, nitrobenzene, picric acid, \( o \)-nitroaniline, \( o \)-nitrophenol, \( m \)-dinitrobenzene, \( m \)-nitroaniline, and 2,4-dinitrophenol, were prepared in dichloromethane (for 1) or ethanol (for 2) with a concentration of 0.001 M. In a 1 cm quartz cuvette, a 3 ml solution of 1 in dichloromethane, a 3 ml solution of 2 in ethanol, and the fluorescence responses at excitation wavelengths of 270 (1) and 240 (2) were measured in situ with incremental addition of freshly prepared nitroanlyte solution in the range 220–700 nm, with 10 nm slit width for both source and detection.

**Luminescent and NAC Sensing Property of 1.** To study the potential luminescence sensing application of 1 for detection of nitroaromatic compounds, the luminescent properties of 1 dispersed in common solvents were investigated. The solvents used are dichloromethane, methanol, ethanol, and water (Figure S5, SI). Here, the fluorescence measurements of 1 will be described in detail. Before the fluorescence study, a finely ground powder sample of 1 (1 mg) was immersed in different organic solvents (3 mL), treated by ultrasonication for 20 min, and then aged for 2 days to form stable suspensions. The fluorescence spectra of 1 dispersed in dichloromethane possess a strong fluorescence band at 321 nm. To determine the sensing ability of 1 for different nitroaromatic analytes, fluorescence titration experiments were carried out by the gradual addition of 1 mM stock solution of various nitro explosives, namely, NB (nitrobenzene), PA (picric acid), \( o \)-NA (\( o \)-nitroaniline), \( o \)-NP (\( o \)-nitrophenol), \( m \)-DNB (\( m \)-dinitrobenzene), \( m \)-NA (\( m \)-nitroaniline), and 2,4-DNP (2,4-dinitrophenol). Incremental addition of 2,4-dinitrophenol has a minor effect on fluorescence intensity of 1 (Figure S6, SI).

It is interesting to note that fast and high fluorescence quenching was observed upon incremental addition of NB, \( o \)-NP, PA, \( m \)-NA, \( o \)-NA, and \( m \)-DNB solution as shown in Figure 13. The stability of 1 after fluorescence titrations with different analytes (Figure S2 SI) was also ascertained by PXRD. Further, the fluorescence quenching efficiency was analyzed using the Stern–Volmer (SV) equation, \( (I_0/I) = K_{SV}[Q] + 1 \), where \( I_0 \) is the initial fluorescence intensity before the addition of analyte, \( I \) is the fluorescence intensity in the presence of analyte, \([Q]\) is the molar concentration of analyte, and \( K_{SV} \) is the quenching constant (M\(^{-1}\)). The SV plot for NB was nearly linear at low concentrations and subsequently deviated from linearity, bending upward at higher concentrations; those for \( m \)-NA and PA were nonlinear at low concentrations but sigmoidal at higher concentrations; and all the remaining nitro compounds, viz. \( o \)-NP, \( o \)-NA, \( m \)-DNB, and 2,4-DNP, showed a linear SV plot (Figure 14). The quenching constants for NB, \( o \)-NP, PA, \( m \)-NA, \( o \)-NA, and \( m \)-DNB were found to be \( 1.99 \times 10^4\), \( 2.11 \times 10^4\), \( 1.66 \times 10^4\), \( 1.72 \times 10^4\), \( 3.1 \times 10^4\), and \( 8.0 \times 10^3\) M\(^{-1}\), respectively. As can be seen from Figures 13 and S7, SI, 1

**Figure 12.** M vs H plots for 1–3 recorded at 2, 3, and 5 K.

**Figure 13.** Changes in fluorescence intensity of 1 upon incremental addition of NAC solution of (a) nitrobenzene, (b) \( o \)-nitrophenol, (c) picric acid, (d) \( m \)-nitroaniline, (e) \( o \)-nitroaniline, and (f) \( m \)-dinitrobenzene.
shows a magnificent quenching ability toward NB, which is quenched to approximately 97% of its initial intensity with the addition of only 100 μL of analyte. Further, o-NP, PA, m-NA, and o-NA also show drastic changes in their initial intensities. The limits of detection (LODs) were calculated for 1 using the formula 3σ/m (where σ is the standard deviation and m is the slope of the graph) [Figure S8, Tables 2S and 3S, SI]. The MOF (1) showed good LOD values, that is, 5.10 × 10⁻⁶ (NB), 6.16 × 10⁻⁶ (o-NP), 4.88 × 10⁻⁶ (PA), 4.91 × 10⁻⁶ (m-NA), 5.57 × 10⁻⁶ (o-NA), and 6.23 × 10⁻⁶ (m-DNB), confirming its good sensing behavior toward multiple NACs. Moreover, the colorimetric analysis of 1 in dichloromethane toward various NACs, NB, o-NP, PA, m-NA, o-NA, m-DNB, and 2,4-DNP was studied.

As shown in Figure 15, the change in color of the solution from colorless to pale yellow under daylight and disappearance of fluorescence under UV light after the addition of 2 equiv of different NACs.

**Figure 15.** Photographs (a) under daylight and (b) under 360 nm UV light of 1 (1.0 × 10⁻³ M in dichloromethane) upon the addition of 2 equiv of different NACs.

**Luminescent and NAC Sensing Property of 2.** To study the potential luminescent sensing application of 2 for detection of nitroaromatic compounds, the luminescent properties of 2 dispersed in common solvents were investigated. The solvents are ethanol, acetonitrile, methanol, and acetone. Here, the fluorescence measurements of compound 2 will be described in detail. Before the fluorescence study, a finely ground powder sample of 2 (1 mg) was immersed in different organic solvents (3 mL), treated by ultrasonication for 20 min, and then aged for 2 days to form stable suspensions. The fluorescence spectrum of 2 dispersed in ethanol possesses a strong fluorescence band at 318 nm. To determine the sensing ability of 2 for different nitroaromatic analytes in ethanol, fluorescence titration experiments were carried out by the gradual addition of 1 mM stock solution of various nitro explosives, namely, nitrobenzene (NB), picric acid (PA), o-nitroaniline (o-NA), o-nitrophenol (o-NP), m-dinitrobenzene (m-DNB), m-nitroaniline (m-NA), and 2,4-dinitrophenol (2,4-DNP). It is interesting to note that fast and high fluorescence quenching was observed upon incremental addition of m-DNB (Figure 16). Incremental addition of NB, o-NP, PA, m-NA, o-NA, and 2,4-DNP solution had a minor effect on fluorescence intensity of 2 (Figures S10–S15, SI). The powder X-ray diffraction (PXRD) patterns of 2 showed that the compound remains stable even after fluorescence titrations with different analytes (Figure S3, SI). Further, the fluorescence quenching efficiency was analyzed using the Stern–Volmer (SV) equation, \(I_0/I = K_{SV}[Q] + 1\), where \(I_0\) is the initial fluorescence intensity before the addition of analyte, \(I\) is the fluorescence intensity in the presence of analyte, \([Q]\) is the molar concentration of analyte, and \(K_{SV}\) is the quenching constant (M⁻¹). The SV plot for m-DNB was nearly linear at low concentrations and subsequently deviated from linearity, bending upward at higher concentrations. All the remaining nitro compounds, viz. o-NP, o-NA, m-NA, NB, PA, and 2,4-DNP, showed linear SV plots, as shown in Figure 17. The quenching constant for m-DNB was found to be 5.73 × 10⁵ M⁻¹. As evidenced by Figures 16 and S16, SI, 2 shows a good quenching ability toward m-DNB, and it is quenched to approximately 77% of its initial intensity with addition of only 17.5 μL of analyte. Further, m-NA, PA, NB, 2,4-DNP, o-NA, and o-NP do not show noticeable changes in their initial intensities, so 2 can be used as a selective sensor to detect small quantities of m-DNB in ethanol. The LOD value for 2 toward m-DNB is calculated to be 1.23 × 10⁻⁷ M, which is the lower than those calculated for 1 toward any NAC (Figure S17, Tables S2 and S3, SI). Furthermore, the colorimetric analysis of 2 in ethanol toward the NACs, NB, o-NP, PA, m-NA, o-NA, m-DNB, and 2,4-DNP was also studied. As shown in Figure 18, the change in color of the solution from colorless to pale

**Figure 16.** Change in fluorescence intensity of 2 upon incremental addition of m-DNB solution in ethanol.

**Figure 17.** Stern–Volmer (SV) plots of 2 for various NACs.

**Figure 18.** Change in color of the solution from colorless to pale...
yellow under daylight and disappearance of fluorescence under UV light after the addition of \( m \)-DNB to 2 confirmed the visual and fluorimetric detection of \( m \)-DNB using 2. The present sensing results toward various NACs, in view of the sensitivity, \( K_{SV} \), or LOD, are comparable with those of the MOFs reported in the literature.17

Interestingly, 3 does not show sensing ability toward any NAC probably due to the saturated octahedral environment around the Cu(II) center or due to the lack of molecular recognition ability of 3 with NACs.

**CONCLUSIONS**

In view of the material importance of the metal-organic systems, three Cu(II)-based metal-organic frameworks (MOFs) containing dipyridyl ligands, namely, [Cu(4,4′-DP)Cl]\(_n\) (1), [Cu(4,4′-DP)\(_3\)Cl]\(_n\) (2), and [Cu(4,4′-TMDP)-Cl]\(_n\) (3), have been synthesized using different solvothermal conditions. Single-crystal X-ray data show different coordination geometries around the Cu(II) ion in the MOFs. In 1 and 2, Cu(II) is tetrahedral, whereas in 3 Cu(II) is octahedral. The topological studies show that 1 has \( fes \), \( hcb \), and \( sq1 \) topologies, 2 has \( bby \) (3,4-c net) topology, and 3 has 4-fold interpenetration and \( dia \) topology. Magnetic studies show that 1 and 2 exhibit strong ferromagnetic and 3 exhibits moderate antiferromagnetic behaviors. Further, the fluorescence sensing properties of the present MOFs toward various nitro explosives (NACs) were examined. The fluorescence data reveal that 1 displayed fluorescence quenching toward all NACs so it can be used as a sensor to detect multiple nitroaromatic compounds. On the other hand, 2 selectively detects \( m \)-DNB in the presence of other analytes with considerably low LOD value of 1.23 \( \times 10^{-7} \) M. The PXRD pattern shows that 1 and 2 are stable in the presence of different analytes and the framework does not break. 3 does not show sensing property toward any NAC probably due to the saturated octahedral environment around the Cu(II) center. Thus, fine-tuning of the reaction conditions could lead to the products differing in structures, topologies, and desirable magnetic and sensing properties.

**EXPERIMENTAL SECTION**

**Materials.** CuCl\(_2\)-2H\(_2\)O, 4,4′-dipyridyl, 4,4′-trimethylene-dipyridyl, DMF, ethanol, and all the nitroaromatic compounds were obtained from Sigma-Aldrich Chemical Co. India and were used without further purification.

**Physical Methods.** The FTIR spectra of the compound were recorded within the range 4000–400 cm\(^{-1}\) utilizing KBr pellets on a Perkin Elmer Model range GX spectrophotometer. Melting points were controlled by the open narrow technique and were uncorrected. The elemental C, H, and N investigations were acquired from Micro-Analytical Laboratory of Central Drug Research Institute (CDRI), Lucknow, India. The electronic range of the 10\(^{-3}\) M arrangement in methanol was recorded utilizing a Perkin Elmer \( \lambda \)-45 UV-visible spectrophotometer with cuvettes of 1 cm path length. Magnetic susceptibility was measured using a Quantum Design MPMS-XL7 SQUID magnetometer. Data were corrected for the diamagnetic contribution as calculated from the Pascal constants.

**X-ray Crystal Structure Determination and Refinements.** Crystallographic data of 1–3 were recorded at 296 K on a Bruker SMART APEX CCD diffractometer. Single-crystal X-ray data were collected using graphite monochromated Mo K\(_\alpha\) radiation (\( l = 0.71073 \) Å). Scattering factors for the atoms, the anomalous dispersion corrections, and the linear absorption coefficients were taken from the International Tables for X-ray Crystallography.31 The data integration and reduction were processed using SAINT Software.32 An empirical absorption correction was applied to the collected reflections using SADABS,33 and the space group was determined using XPREP.34 The structures were solved by direct methods using SIR-9735 and refined on \( F^2 \) by full matrix least squares using the SHELXL-2016/6 program package.36 All non-hydrogen atoms were refined with anisotropic displacement parameters. A summary of the crystallographic data and the structure refinement for the complexes is given in Table 1.

**Synthesis of [Cu(4,4′-DP)Cl]\(_n\) (1).** 1 was synthesized by putting the reaction mixture of CuCl\(_2\)-2H\(_2\)O (0.2 mmol), 4,4′-dipyridyl (0.2 mmol), and DMF (5 mL) in a 10 mL Teflon reactor under autogenous pressure at 180 °C for 2 days and then cooled to room temperature at a rate of 10 °C/h. Blue-black crystals of 1 suitable for X-ray analysis were obtained. The complex decomposes at 280 °C. Yield: 58%, elemental analysis (\%): C = 46.86, H = 3.79, N = 10.73; calc. for C\(_7\)H\(_8\)ClCuN\(_2\): C = 46.70; H = 3.92; N = 10.89. IR (KBr cm\(^{-1}\)): 3044 (s), 2924 (m), 1600 (s), 1527 (m), 1480 (s), 1410 (s), 1215 (m), 1062 (w), 819 (s), 723 (m), 631 (w), and 474 (s).

**Synthesis of [Cu(4,4′-DP)\(_3\)Cl]\(_n\) (2).** 2 was synthesized by putting the reaction mixture of CuCl\(_2\)-2H\(_2\)O (0.2 mmol) and 4,4′-dipyridyl (0.2 mmol) in mix solvents [DMF (2 mL), H\(_2\)O (2 mL), and C\(_2\)H\(_5\)OH (1 mL)] in a 10 mL Teflon reactor under pressure at 180 °C for 2 days. The solution was cooled to room temperature at the rate of 10 °C/h, and the brown crystals of 2 suitable for X-ray analysis were obtained. The complex decomposes at 280 °C. Yield: 55%, elemental analysis (\%): C = 33.94, H = 2.75, N = 7.91; calc. for C\(_5\)H\(_4\)ClCuN\(_2\): C = 33.72; H = 2.83; N = 7.86. IR (KBr cm\(^{-1}\)): 2925 (s), 2854 (w), 1737 (w), 1601 (s), 1532 (w), 1408 (m), 1110 (w), 1031 (w), 807 (s), 629 (w), and 451 (m).

**Synthesis of [Cu(4,4′-TMDP)Cl]Cl\(_n\) (3).** 3 was synthesized by reacting a mixture of CuCl\(_2\)-2H\(_2\)O (0.2 mmol) and 4,4′-trimethylenedipiyridyl (0.2 mmol) in mix solvents [DMF (2 mL), H\(_2\)O (2 mL), and C\(_2\)H\(_5\)OH (1 mL)] in a 10 mL Teflon reactor under pressure at 180 °C for 2 days. The solution was cooled to room temperature at the rate of 10 °C/h. The blue crystal of 3 suitable for X-ray analysis was obtained. The
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