



Research article

Explosive and pollutant nitroaromatic sensing through a Cd(II) based ladder shaped 1D coordination polymer

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A B S T R A C T

In the existing leanings of environmental and national security issues, establishment of appropriate sensors for explosive as well as pollutant nitroaromatic compounds may be considered as one of the most prodigious job for material researchers. In the current study a new Cd(II) based 1D ladder coordination polymer (CP), [Cd(4-bpd)(3-cbn)₂]_n, has been synthesized and well characterized through single crystal X-ray diffraction analysis. Interestingly, the supramolecular assembly of this compound has efficiently identified 2,4,6-trinitrophenol through fluorescence quenching method. The Stern–Volmer coefficient (K_{SV}) has been calculated as $6.047 \times 10^3 \text{ M}^{-1}$, which can be attributed to the quenching of the emission intensity. The limit of detection (LOD) has been determined as $0.260 \mu\text{M}$ following the 3σ method along with almost 95% fluorescence intensity reduction. FESEM study revealed that the crystalline nature of the compound has been altered upon interaction with the above mentioned nitroaromatic analyte. Theoretical studies were performed to get the insight idea of fluorescence quenching mechanism which also substantiated the experimental observation. The present study can pave the way for the fabrication of future generation technology in sensor field.

1. Introduction

These days, development of new coordination polymers and their application in various fields are considered as one of the most increasingly appealing research areas due to the diversities in their structure and their prospective applications in numerous fields of scientific and industrial research such as storage of gas [1–7], catalysis [8–16], fabrication of electronic devices [17–23], sensing [24–29], magnetism [30,31], biomedical research [32–36] etc. Coordination polymers exhibiting varying geometries can be synthesized by varying both the nature and the stoichiometry of the metal ions and the organic ligands associated with metal centers under appropriate reaction conditions. Generally, coordination polymers containing luminescent organic ligands were found to exhibit different kind of sensing properties. Over last few decades researchers focused on the implementation of such kind of coordination polymers in sensing purposes though emission quenching mechanism. It has been observed that nitroaromatic compounds exhibit a general tendency to reduce the intensity of emission of the coordination polymers. This observation can be utilized in the detection of explosive as well as pollutant nitro aromatic (epNAC) compounds [37,38]. These days, terrorist activities across all over the globe become a threat to human civilization [38]. News related to terrorist activities in various parts of the planet appears in the headlines nearly every week. So, for the purpose of the security of the homeland and to restrict the terrorist activity it is of extreme importance to build up appropriate system which can easily identify explosives.

There is a general perception among the common people about the explosive nature of TNT and through the print as well as electronic media we are more familiar with the term TNT [39–43], but 2,4,6 trinitrophenol by no means exhibits lesser potential as an

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explosive compared to TNT [44,45]. Therefore, designing a suitable chemosensor that can effectively detect TNP has extreme importance in the field of forensic science. In addition to this, TNP is extensively used in pharmaceutical industries, in preparation of dyes, analytical chemicals, fireworks, staining materials [46,47], etc. Upon releasing in the surroundings it has the potential to contaminate ground water as well as soil [48–52]. TNP can change the pH level of river water if discharged in river as industrial waste [53]. Pollution originated by this nitroaromatic compound can potentially cause numerous health hazards like infertility, anemia, disease in respiratory track, carcinogenesis in human cells as well as in other living beings [54–57], etc. Therefore, detection of 2,4,6-trinitrophenol has a significant importance because of its pollutant as well as explosive nature.

Coordination polymers synthesized by metal ions of d^{10} electronic configuration along with π -conjugated aromatic moieties are considered to be capable materials to exhibit the photoactive properties [58–64]. Luminescent properties of this kind of coordination polymers can be effectively utilized to sense different materials through the process of fluorescence quenching. Several coordination polymers based on d^{10} metal systems were reported to effectively sense various nitroaromatic compounds through fluorescence quenching mechanism [65–74].

In this background, we report herein the synthesis, characterization and TNP sensing property of a Cd(II)-based coordination polymer, $[\text{Cd}(4\text{-bpd})(3\text{-cbn})_2]_n$ (**1**) (where 4-bpd is 1,4-Bis(4-pyridyl)-2,3-diaza-1,3-butadiene and 3-cba is 3-chlorobenzoate). Coordination polymer **1** was synthesized in suitable reaction conditions and thereafter it was characterized by usual spectroscopic methods. 4-Bpd was opted for its elongated π -conjugation. Coordination polymers containing this kind of ligands as its building block are familiar to exhibit noticeable fluorescence emission. This persuaded us to utilize **1** towards detection of the nitroaromatic compounds through emission quenching mechanism.

2. Experimental

2.1. Materials and physical methods

The chemicals utilized during this work were bought from commercial sources. They were used as received. No further purification was performed. Synthesis of 1,4-Bis(4-pyridyl)-2,3-diaza-1,3-butadiene was done with the help of an earlier reported process [75]. An elemental analyzer (Perkin-Elmer 2400C) was utilized for the purpose of Elemental analyses. Emission spectra were recorded by using a Perkin-Elmer LS-45 fluorometer. The fluorescence lifetime measurements were performed by utilizing a HORIBA Jobin-Yvon time-correlated single-photon counting instrument. SEM imaging was performed with JEOL scanning electron microscope. PXRD-analyses of the materials were performed by using Bruker D8 Discover instrument with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$).

2.2. Synthesis of $[\text{Cd}(4\text{-bpd})(3\text{-cbn})_2]_n$

2.0 mmol of sodium salt of 3-chlorobenzoic acid dissolved in 4.0 mL of water was mixed well with 1.0 mmol of 4-bpd dissolved in 4.0 mL of methanol. The resulting solution containing the mixed ligands was gradually layered above an aqueous solution containing 1.0 mmol of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ using 1:1 (v/v) water/methanol mixture (5.0 mL) functioning like buffer. Block shaped yellow-colored crystals, which can be used for X-ray diffraction study, appeared after a week. After collection, these crystals were rinsed with water-methanol mixture; thereafter the crystals were dried out under vacuum. (Yield = 0.482 g; 76%.) Anal. Calc. For $\text{C}_{26}\text{H}_{18}\text{N}_4\text{O}_4\text{Cl}_2\text{Cd}$: C, 49.22; H, 2.84; N, 8.84; Cd, 17.74. Found: C, 49.28; H, 2.79; N, 8.81; Cd, 17.76%.

2.3. Detection limit calculation

The limit of detection (LOD) was determined by utilizing the empirical equation as follows:

$$\text{Limit of detection (LOD)} = 3\sigma/k.$$

(where, σ = the standard deviation and k = the slope).

For coordination polymer **1** the standard deviation has been evaluated by the data obtained from fluorescence spectroscopic analyses. The fluorescence intensity of **1** as suspension in acetonitrile medium at 428 nm during emission quenching titration with 2,4,6-trinitrophenol has been plotted against the concentration of 2,4,6-trinitrophenol. The slope (k) can be obtained from the graphical plot.

2.4. Crystallographic data collection and refinement

The block shaped single crystal of **1** obtained by slow diffusion process mounted on a glass-fiber tip using super glue purchased from commercial source. At 298 K data collection of the single crystal X-ray diffraction analysis was accomplished by the use of a X-ray diffractometer (Bruker APEX II) which was endowed with a fine-focus and sealed tube of the source of X-ray with graphite monochromated Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$). The collected data were integrated by utilizing a SAINT program [76] and SADABS was used in absorption correction. The structure solution was done by SHELXT [77] by utilizing direct methods and refinement was done by full matrix least-squares on F^2 utilizing SHELXL-2016/6 [78]. Data collection parameters as well as the parameters of structure refinement are provided in Table S1. CCDC 2181620 has the supplementary crystallographic data for **1**.

2.5. Theoretical calculations

The GAUSSIAN-09 [79] program package was utilized for optimization of the geometries as well as for attaining the molecular

functions of the material. The DFT-B3LYP hybrid [80] theoretical functional was employed all the way through the process. The LanL2DZ basis set was used for both the coordination polymer and the nitroaromatic compound. The coordinates found from X-ray diffraction analyses of the single crystal were considered during the process. The time-dependent density functional theory (TDDFT) [81–83] formalism of the material was build up for the assignment of the low-lying electronic transitions in the spectra. Gauss sum [84] was utilized to evaluate the fractional involvement of the molecular orbitals of the metal as well as those of the ligands.

3. Results and discussion

3.1. Description of crystal structure of 1

X-ray diffraction analysis of the single crystal shows that Coordination polymer **1** crystallized in triclinic P-1 space group. Fig. 1 displays the asymmetric unit of **1**. Selected bond lengths and bond angles of this coordination polymer are provided in Table S2 and Table S3 respectively. The asymmetric unit of the coordination polymer contains one cadmium(II) ion, two chlorobenzoate ions along with one 4-bpd ligand. The cadmium atom, remaining at the centre, exhibits distorted pentagonal bipyramidal coordination geometry. The equatorial pentagonal plane is generated by the oxygen atoms of 3-chlorobenzoate ions whereas nitrogen atoms of the 4-bpd moieties occupy the axial positions. Two such Cd(II) centers are connected to each other by the bridging oxygen atoms of 3-chlorobenzoate moiety. The other end of the axially attached 4-bpd ligand is connected to another Cd(II) centre generating an one dimensional ladder like chain structure. The π - π stacking interactions present within this coordination polymer help in building the supramolecular architecture. Fig. 2 represents a perspective view of the polymeric network of **1**.

In the structural architecture of the molecular system, there exist a number of potential secondary interactions to generate supramolecular assembly. Hydrogen bonding interactions ($C-H \cdots Cl = 2.956 \text{ \AA}$) are there between H-atoms of pyridyl ring and Cl-atoms of 3-chloro benzoic acid (Fig. 3); some Cl-atoms are oriented such a way towards aromatic pyridyl ring and originated $Cl \cdots \pi$ (3.487 \AA) short contacts (Fig. 4). In addition to these, there exists $C-H \cdots \pi$ (3.584 \AA) interactions in between the aromatic rings of the nitrogen donor ligand and hydrogen atoms of chloro-benzoic acid (Fig. 5). However, these supramolecular interactions have played pivotal role in the documentation of structure-property relationship as well as functionality; sometimes, in the process of molecular recognition such non-covalent contacts created favorable electronic atmosphere towards analytes.

3.2. Nitroaromatic explosives detection

The dispersion of **1** in acetonitrile was employed for the luminescence studies. **1** exhibits a peak of high intensity in its emission

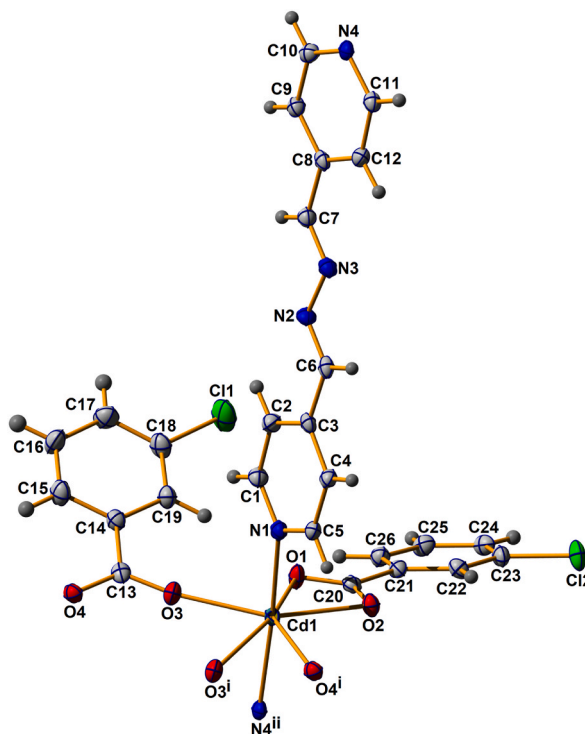


Fig. 1. ORTEP diagram of the asymmetric unit of **1** drawn with 50% ellipsoidal probability. Symmetry codes: (i) $-x, 2 - y, 1 - z$; (ii) $-1 + x, y, 1 + z$.

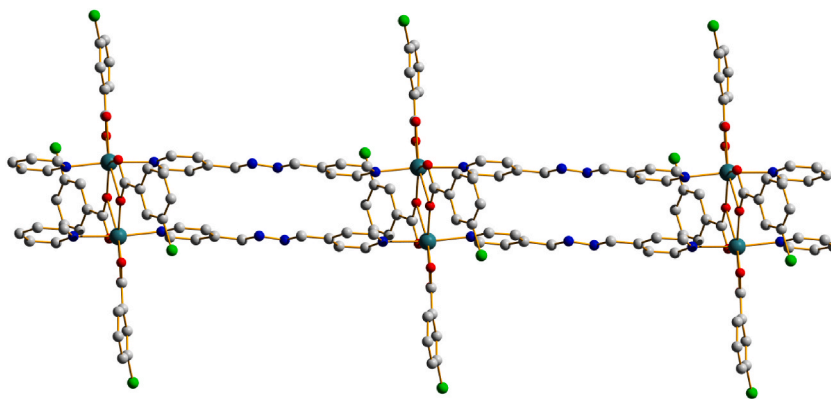


Fig. 2. A perspective view of the polymeric network of 1. H-atoms are excluded for clarity.

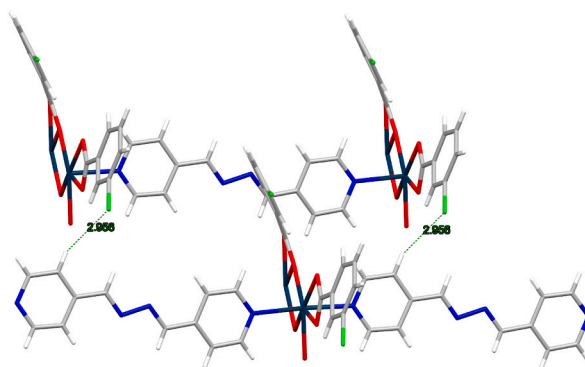


Fig. 3. Hydrogen bonding interactions between H-atoms pyridyl ring and Cl-atoms of 3-chloro benzoic acid.

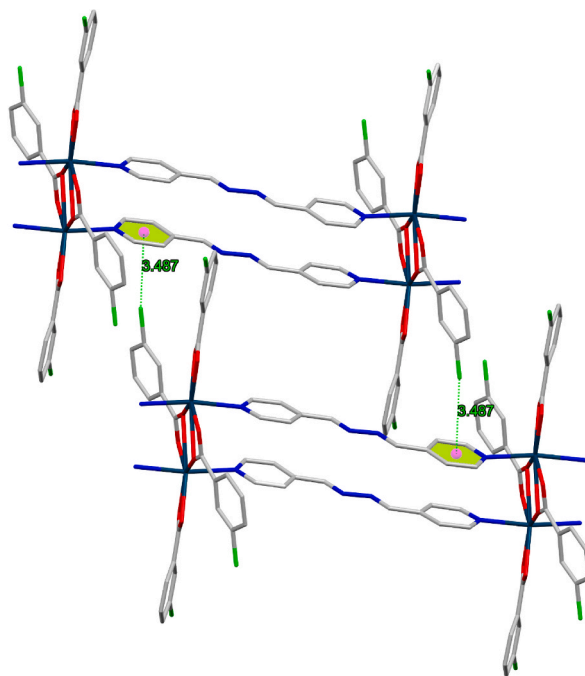


Fig. 4. Cl... π interaction between Cl-atoms of 3-chloro benzoic acid and pyridyl aromatic ring.

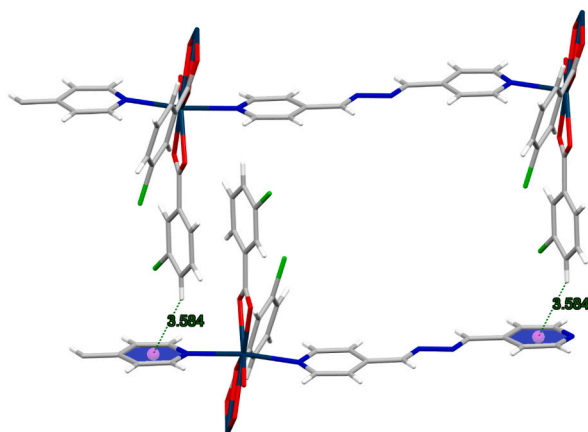


Fig. 5. C–H \cdots π interactions in between the aromatic rings of the nitrogen donor ligand and hydrogen atoms of chloro-benzoic acid.

spectra at 428 nm on excitation at 350 nm. Generally both oxidation and reduction of Cd^{2+} systems are difficult due to d^{10} electronic configuration [85,86]. Therefore, the emission maximum exhibited by this coordination polymer cannot be inferred as an LMCT or an MLCT [60]. Intra-ligand ($\pi^*-\pi$ or π^*-n) emission may be reason behind this kind of strong emission exhibited by this coordination polymer [87,88]. Other than this, enhancement of the rigidity due to the complexation between the ligand and the metal centre may reduce the non-radiative decay [89–91]. The emissive properties exhibited by this coordination polymer, encouraged us to investigate about some useful applications of it. Consequently, we have investigated its application in sensing of various nitroaromatic compounds. For ensuring the purity of the material to be used for the sensing purpose, the PXRD-patterns of the coordination polymer were recorded and compared with the single crystal X-ray diffraction analysis generated simulated patterns (Fig. S1). The similarity between these two patterns ensures the purity of the bulk material to be used for the sensing purpose. The detection ability of this coordination polymer for 1,3-DNB (1,3-dinitro benzene), 4-NA (4-nitro aniline), 3-NBA (3-nitrobenzoic acid), 4-NT (4-nitro toluene), 3-NT (3-nitro toluene), 2-NT (2-nitro toluene), 2-NP (2-nitro phenol), 2,4-DNP (2,4-dinitro phenol) and TNP (2,4,6-trinitro phenol) has been studied (with 10^{-3} M concentration of each nitroaromatic compounds). To ensure the ability of detection of this coordination polymer, the aqueous solution of the nitroaromatic compounds have been slowly added with steady increase in concentration to the dispersion of the coordination polymer in acetonitrile medium. It has been observed that TNP has quenched the emission property of this coordination polymer; whereas, other nitroaromatic compounds like 1,3-DNB, 4-NA, 3-NBA, 4-NT, 3-NT, 2-NT, 2-NP, 2,4-DNP do not have considerable influence on the emission intensity of **1** dispersed in acetonitrile (Fig. 6). In this context, it is necessary to reveal that the initial emission intensity of **1** dispersed in acetonitrile medium remains unperturbed in the presence of water.

Since the emission quenching of this coordination polymer takes place in the presence of 2,4,6-trinitro phenol, a titration has been performed. The titration has been carried out by gradual addition of aqueous solution of 2,4,6-trinitro phenol (10^{-3} M) to the dispersion of **1** in acetonitrile medium (3 μL). Fig. 7 displays that the fluorescence intensity at 428 nm is extremely quenched on addition of TNP. The intensity of emission of **1** dispersed in acetonitrile is reduced by 95.0% in the presence of 57 μL of 2,4,6-trinitro phenol.

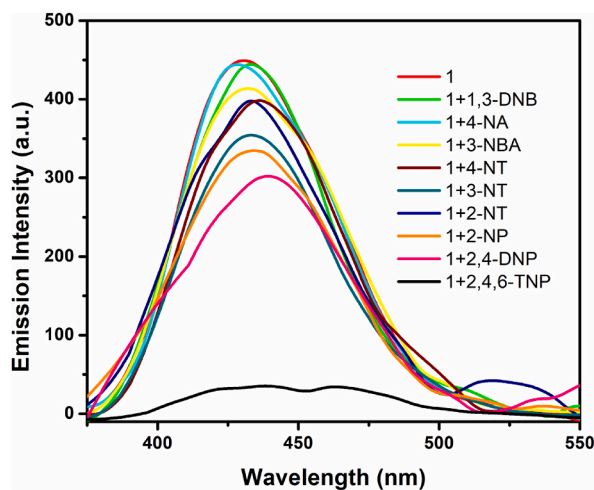


Fig. 6. Selectivity of **1** for TNP compare to other epNACs.

The ratio of emission intensity (I_0/I) has been plotted against TNP-concentration to obtain Stern–Volmer plot (Fig. S2). The Stern–Volmer coefficient (K_{sv}) has been calculated as $6.047 \times 10^3 \text{ M}^{-1}$, which suggests the quenching in the emission intensity. For quantification of the efficiency of sensing, the calculation of the limit of detection (LOD) is extremely important. The limit of detection has been determined as $0.260 \times 10^{-6} \text{ M}$ (Fig. S3). Shenthilkumar et al. reported a Cd(II) complex and its TNP sensing properties. The detection limit was reported as $16.9 \times 10^{-6} \text{ M}$ [92]. Another Cd(II) based complex reported by Venkateswarulu et al. was reported to sense TNP with limit of detection reported as $1.7 \times 10^{-9} \text{ M}$ [93]. Hu et al. reported a Cd(II) based MOF which was reported to exhibit TNP sensing properties with LOD value of $1 \times 10^{-6} \text{ M}$ [94]. Dutta et al. reported TNP-detection properties of a Cd(II) based CP and the LOD was reported as $0.91 \times 10^{-6} \text{ M}$ [20]. Halder et al. reported a Cd(II) based MOF and utilized it in TNP sensing. The LOD of this MOF for TNP sensing was reported to be $6 \times 10^{-5} \text{ M}$ [70]. Another Cd(II) based coordination polymer reported by Dutta et al. reported to exhibit TNP sensing properties with LOD reported as $1.65 \times 10^{-6} \text{ M}$ [95]. The values of the detection limit of these earlier reported Cd-based metal complexes for the detection of TNP are tabulated in Table S4. Comparing with some of these recently reported values, the value of limit of detection for the coordination polymer $[\text{Cd}(4\text{-bpd})(3\text{-cbn})_2]_n$ for TNP sensing, seems to be good enough for selective sensing of 2,4,6-trinitrophenol.

To check whether the emissive nature of the coordination polymer is the intrinsic property of the material or not, the emission spectra of a mixture of $\text{Cd}(\text{NO}_3)_2$, 1,4-Bis(4-pyridyl)-2,3-diaza-1,3-butadiene and 3-chlorobenzoic acid in acetonitrile medium was recorded. The emission intensity of this mixture was very low when compared with that of the suspension of **1** in acetonitrile medium (Fig. S4). The emission spectra of each of the ligands also do not exhibit as strong emission intensity as **1** dispersed in acetonitrile. This observation suggests that the emission intensity exhibited by **1** may be due to the rigidity imparted to the system on formation of the polymeric architecture.

To ensure the recyclability of the coordination polymer as a sensor of TNP, a paper strip made of filter paper was dipped into the acetonitrile medium containing the suspension of **1**. When placed under UV light chamber this paper strip displayed emission. Thereafter aqueous solution containing TNP was added to this paper strip. The emission of this paper strip sharply quenched on addition of TNP solution. When the paper strip was washed with distilled water several times to remove TNP from it, the emission reappeared under illumination of UV light. This observation repeated for several cycles which confirmed the recyclability of **1** for the detection of TNP.

To ensure the stability of coordination polymer **1** after interaction with TNP, the coordination polymer was washed thoroughly with distilled water after its interaction with TNP to make it completely free from TNP and thereafter it was dried. The PXRD pattern of this material matched well with the simulated pattern which ensured its stability even after interaction with TNP (Fig. S1).

Nitroaromatic compounds are generally considered to be oxidizers due to the occurrence of low-lying vacant π^* molecular orbitals, where readily acceptance of electron can take place from fluorophores in their excited state and thereby these types of compounds effectively quench the emission intensity of the fluorophore materials. For an effective emission quenching of a fluorophore to occur in the presence of a nitroaromatic explosive compound, it is extremely necessary for the nitroaromatic molecule to come nearer to the fluorophore sensor molecule and ultimately interact with the fluorophore. These types of interactions between fluorophore molecule and nitroaromatic molecules are mainly π -interactions, like $\pi \dots \pi$ stacking interactions, C–H $\dots \pi$ interactions etc. Here, due to the presence of poly aromatic rings in **1**, it becomes electron rich and the structure of this coordination polymer reveals the possibility of $\pi \dots \pi$ stacking interaction. The density functional theory computation adopting the B3LYP/LanL2DZ method was utilized on **1** and energy levels for lowest unoccupied molecular orbital (LUMO_1) and highest occupied molecular orbital (HOMO_1) were calculated as -3.07 eV and -6.25 eV , respectively. The energy level of the LUMO of TNP (LUMO_{TNP}) was found to be -4.85 eV , which was lower in energy compare to LUMO_1 , but higher in energy than HOMO_1 (Fig. 8). The electrons, those have jumped on excitation from the HOMO_1 to the LUMO_1 , cannot revert back to HOMO_1 because of the presence of LUMO_{TNP} . As a result, the electrons have to proceed from the LUMO_1 to the LUMO_{TNP} and thereafter they can return to the ground state. As a result, emission quenching of **1** has occurred in the presence of 2,4,6-tri nitro phenol.

It is evident from Fig. 9 that the emission decay profiles of both **1** and **1** in the presence of 2,4,6-trinitro phenol display bi-exponential nature. The fluorescence lifetime of this coordination polymer was found out to be 0.497 ns , which was observed to be increased to 2.384 ns in the presence of 2,4,6-trinitro phenol. From the fluorescence decay study it can be stated that the quenching has been taken place through dynamic mechanistic way.

The interaction between **1** and 2,4,6-trinitro phenol is also substantiated by SEM-EDS study. The change in morphology of **1** on interaction with TNP can be clearly understood by comparing Fig. 10(a) and Fig. 10(b). EDS analysis of **1** after interaction with TNP, displays lowering in the weight percentage of cadmium and carbon as well as enhancement in the weight percentage of nitrogen and oxygen compare to the weight percentage of these elements found from single crystal X-ray diffraction analysis (Fig. S5).

4. Conclusion

In summary, a new Cd(II) based 1D ladder shaped coordination polymer $[\text{Cd}(4\text{-bpd})(3\text{-cbn})_2]_n$ have been synthesized and characterized. The outstanding emission properties of **1**, encouraged us to implement this coordination polymer as a sensor for the detection of explosive as well as pollutant 2,4,6-trinitro phenol. The quenching in emissive properties of this coordination polymer in the presence of 2,4,6-trinitro phenol has been analyzed extensively. Fascinatingly, **1** can selectively detect 2,4,6-trinitro phenol among other nitroaromatic compounds. Thus, **1** can be utilized as an excellent material for the detection of 2,4,6-trinitro phenol during security checking. These observations ultimately ascertained this one dimensional Cd(II) based coordination polymer as a general sensor for the detection of 2,4,6-trinitro phenol. It is also expected that in near future these classes of coordination polymer may be paved the way towards fabrication of explosive detection device.

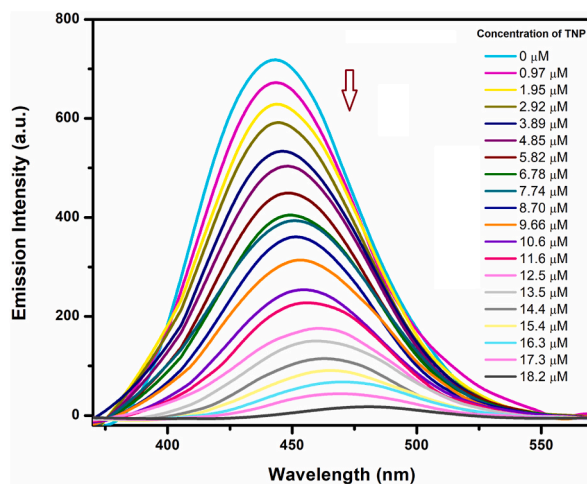


Fig. 7. Emission quenching of 1 on addition (0–57 μL) of 10^{-3} M aqueous solution of 2,4,6-trinitro phenol.

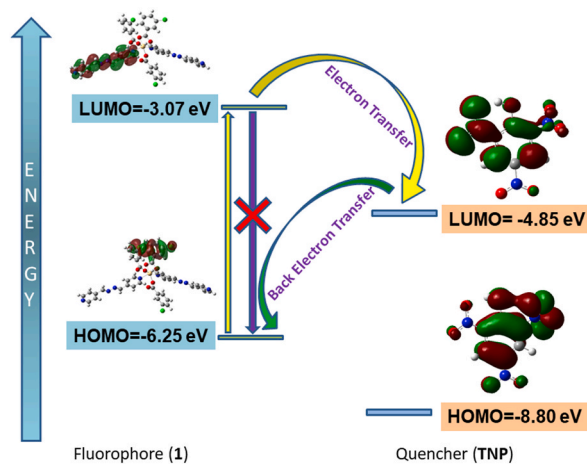


Fig. 8. Frontier orbitals energy relationship illustration through electron transfer fluorescence quenching mechanism.

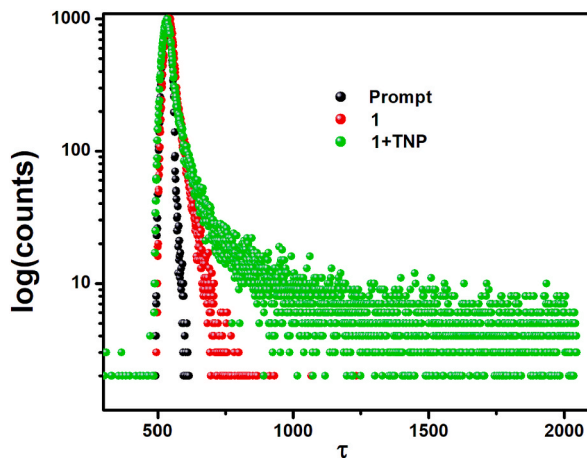


Fig. 9. Fluorescence decay profile of 1 and 1 with TNP.

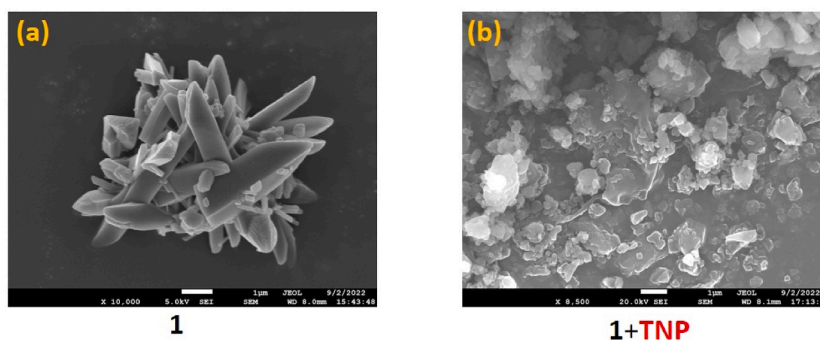


Fig. 10. SEM images of (a) 1 and (b) 1 after interaction with TNP.

Author contribution statement

Basudeb Dutta: Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Sukanya Paul: Performed the experiments; Analyzed and interpreted the data.

Shibashis Halder: Conceived and designed the experiments; Wrote the paper.

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Data availability statement

Data included in article/supp. material/referenced in article.

Declaration of interest's statement.

The authors declare no conflict of interest.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.heliyon.2023.e13504>.

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