Accepted Manuscript

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PII:	S1010-6030(19)30974-8	
DOI:	https://doi.org/10.1016/j.jphotochem.2019.111987	
Article Number:	111987	
Reference:	JPC 111987	
To appear in:	Journal of Photochemistry and Photobiology A: Chemistr	
Received date:	7 June 2019	
Revised date:	17 July 2019	
Accepted date:	22 July 2019	

Please cite this article as: Majumder S, Pramanik A, Mandal S, Mohanta S, Experimental and theoretical exploration of sensing and magnetic properties of a triply bridged dicopper(II) complex: The first discrete metal complex to sense picric acid in pure water, *Journal of Photochemistry and amp; Photobiology, A: Chemistry* (2019), https://doi.org/10.1016/j.jphotochem.2019.111987

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Experimental and theoretical exploration of sensing and magnetic properties of a triply bridged dicopper(II) complex: The first discrete metal complex to sense picric acid in pure water

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Graphical abstract

Syntheses, crystal structures, magnetic and fluorescence properties and turn-off fluorescent sensing behaviour in pure water, for PA, of a triply bridged μ -phenoxo-bis(μ -chloro) dinuclear copper(II) complex, derived from a dinucleating acyclic Schiff-base ligand, for selective detection of PA in aqueous medium are performed in this investigation. DFT modelling of the sensing and magnetic properties are also discussed.



Highlights of the Work:

This article reports the syntheses, crystal structures, fluorescence spectra, picric acid (PA) sensing and magnetic property of a μ -phenoxo-bis(μ -chloro) dicopper(II) compound of composition [Cu₂L(μ -Cl)₂]Cl·4.5H₂O (**1**), where HL is the [1+2] condensation product of 2,6-diformyl-4-ethylphenol and 2-(2-aminoethyl)pyridine. Compound **1** is water soluble and exhibits fluorescence behaviour in water.

The major outcomes of the present investigation may be summarized as follows:

- The title compound (1) is the first example of a discrete metallo-organic system to sense picric acid in pure water.
- The title compound is the first example of a structurally characterized copper(II) compound to sense picric acid;
- The values of quenching constant and association constant of the title compound is the highest among the known PA sensors in pure water;
- Experimental and theoretical magnetic properties of **1** have been studied and this is the first time that *J* value (experimental or theoretical) of a copper(II) system having μ -O-bis(μ -chloro) bridging moiety (O = any of phenoxo, hydroxo, alkoxo, oxo) has been determined.

Abstract

This article reports the syntheses, crystal structures, fluorescence spectra, picric acid (PA)

sensing and magnetic properties of a µ-phenoxo-bis(µ-chloro) dicopper(II) compound of

composition $[Cu_2L(\mu-Cl)_2]Cl\cdot 4.5H_2O(1)$, where HL is the [1+2] condensation product of 2,6-

diformyl-4-ethylphenol and 2-(2-aminoethyl)pyridine. Compound 1 is water soluble and exhibits fluorescence behaviour in pure water. Interestingly among the various aromatic, non aromatic nitro compounds as well as non nitro aromatic compounds screened, PA specifically quenches the fluorescence intencity of **1** significantly in water, revealing that **1** is a turn-off fluorosensor for PA. The sensing pathways have been investigated by spectral titration, time resolved fluorescence decay and DFT studies. Spectral and theoretical (DFT) studies suggest that the observed fluorescence quenching is associated with ground state (GS) charge transfer as well as electrostatic interactions between 1 and picrate ion. Unaltered fluorescence life time of 1 in the absence and presence of PA strongly suggests that quenching follows a static mechanism. Nature of binding modes or interactions between the complex 1 and PA was disclosed by the single crystal structure analysis of the corresponding association complex of composition $[Cu^{II}_{2}L(\mu -$ Cl) $(H_2O)_2$]2Picrate·DMF (2). The quenching constant (K_{sv}), association constant (K_a) and detection limit (LOD) of the complex 1 for picric acid was found to be 1.1×10^5 M⁻¹, 4.64×10^{10} M⁻² and 4.8 µM respectively. Variable-temperature (2.5–300 K) magnetic susceptibility measurement of the complex 1 reveals antiferromagnetic exchange interaction with J = -132.40cm⁻¹. The magnetic property has been nicely rationalized in terms of spin density and magnetic orbitals within broken-symmetry (BS) framework. Compound 1 is the first example of a discrete metal compound to sense picric acid in pure water. Some other interesting aspects have been discussed.

Keywords: Triple bridged dicopper(II); Picric acid sensing in water; Magnetic property; Crystal structure; DFT

1. Introduction

Development of cheap and efficient fluorescent chemosensors having high selectivity and sensitivity for detection of hazardous or explosives molecules/ions has attracted much attention in recent times for wide applications in both national security and environmental protection [1–4]. Trinitrophenol or picric acid (PA), being a powerful explosive among different nitroexplosives and a highly water-soluble hazardous pollutant, has received considerable attention recently in the field of chemosensors. In this regard, a wide variety of fluorosensors based on small organic molecules [5,6], organic polymers including conjugated polymers [7], discrete metallo-organic compounds [8], including macrocycles/cages [8i,8j], coordination polymers including MOFs [9-11], nanoaggregates [12], carbon or quantum dots [13], have been reported for detection of PA. The detection mechanism for PA is mostly composed of proton transfer from the hydroxy group of PA to the chemosensor, leading to a hydrogen bonding network followed by electron transfer from the donor to the acceptor. However, most of them show one or more of the following drawbacks: (i) Real applicability is limited as most sensors function in non-aqueous media; (ii) There is synthetic difficulty because of the requirements of time consuming multi-step synthesis procedure (which usually ends in low yield of the final product), high temperature and expensive materials in the synthesis of most of the chemosensors. Moreover, structural evidence of the association complex formed between PA and fluorescent chemosensors, which is very important to gain deep insight into the exact interaction, is scarce. In this regards, Schiff base sensors deserve special attention due to their simplicity, sensitivity and low cost features. Their structures and solubility can be chemically tuned to increase the sensing selectivity. Therefore, it is highly desirable to explore new Schiff bases or their metal

complexes as inexpensive and efficient fluorescent chemosensors for the detection of PA in aqueous medium.

Copper is the third most abundant transition metal found in living system, and it plays an essential role in biological systems. Over the past few decades extensive studies have been made on the chemistry of copper(II) complexes derived from N,O donor type ligands to explore the areas such as magnetism [14,15], optical properties [16], gas adsorption [17], homogeneous and heterogeneous catalysis [18], DNA and antibacterial activities [14i–14k,19], etc. In contrast, sensing properties of such Cu^{II} compounds have been seldom reported [20]. It is worth mentioning also that there is no structurally characterised copper(II) system that senses PA. Clearly, exploration of copper(II) complexes as PA sensor, particularly in pure water, deserve attention.

Although magnetic properties of copper(II) compounds have been well investigated [14,15], there are definitely types of systems for which magnetic studies have not been yet well explored. The copper(II) compounds having μ -O-bis(μ -chloro) bridging moiety belong to such unexplored area [15f]. Therefore, magnetic studies of such systems deserve attention.

DFT method has been established as a powerful tool to model observed properties. There are several reports in which magnetic properties and sensing behaviours have been understood in-depth by DFT calculations [5a–5c,5f,6b,6c,6g,6f,8a,8b,9b,10c,14e–14k,21].

Over the last few years, we have been working on the structural, biomimetic, spectroscopic, magnetic and sensing aspects of metal compounds derived from iminophenol/aminophenol types of N,O-donor ligand having 2,6-diformyl-4-ethylphenol as a fragment in the synthesis of the final ligands [15a–15d,22]. Some interesting structures/ properties have been observed in the complexes derived from some acyclic or macrocyclic

ligands having 2,6-diformyl-4-ethylphenol as a fragment. In continuation of our efforts, we present herein the syntheses, crystal structures, magnetic and fluorescence properties and turn-off fluorescent sensing behaviour in pure water, for PA, of a triply bridged μ -phenoxo-bis(μ -chloro) dinuclear copper(II) complex [Cu₂L(μ -Cl)₂]Cl·4.5H₂O (1), derived from a dinucleating acyclic Schiff-base ligand (HL; Chart 1), for selective detection of PA in aqueous medium. DFT modelling of the sensing and magnetic properties are also discussed.

2. Experimental

2.1. Materials and Physical Methods

All reagents and solvents were purchased from commercial sources and used as received. 2,6-diformyl-4-ethylphenol was synthesized by a known procedure [23]. (**Caution:** PA and 2,4-dinitrophenol (DNP) are highly explosives and should be handled carefully and in small amounts). HL was synthesized by the previous reported method [15a]. Elemental (C, H, and N) analyses were performed on a Perkin-Elmer 2400 II analyzer. IR spectra were recorded in the region 400–4000 cm⁻¹ on a Bruker-Optics Alpha–T spectrophotometer with samples as KBr disks. Absorbance spectra were recorded using a Shimadzu UV-3600 spectrophotometer, and a Perkin-Elmer LS-50B spectrofluorometer was utilized to study emission spectra. In all measurements, the sample concentration 50 μ M was maintained. Only freshly prepared solutions were used for spectroscopic study, and all experiments have been carried out at room temperature (298 K). Time resolved fluorescence decay was recorded using a TCSPC lifetime system of Horiba Jobin Yvon IBH Ltd. having a picoseconds diode laser (Model: Fluorocube-01-NL). Fluorescence quantum yield (ϕ) of the compound **1** was estimated at room temperature for its water solution by a relative method using quinine sulphate ($\phi = 0.546$ in 0.5 (M) H₂SO₄) [24]

as the secondary standard using the following equation Where I is the area under the emission spectral curve, OD

$$\frac{\varphi_s}{\varphi_R} = \frac{I_s}{I_R} \times \frac{(OD)_R}{(OD)_s} \times \frac{\eta_s^2}{\eta_R^2}$$

denote absorbance at the wavelength of exciting light, η is the refractive index of the medium and φ is the fluorescence quantum yield and subscripts S and R stand in the recognition of the respective parameters of studied sample and reference, respectively. Fluorescence lifetimes were determined from time-resolved intensity decay by the method of time correlated single-photon counting using a diode laser at 512 nm and 375 nm as light source. The excellence of the fits was judged by the χ^2 criterion. Average fluorescence life time ($\langle \tau_f \rangle$) for the multiexponential decay curve was obtained from the decay time constants (τ) and pre-exponential factors (α) using the following equation in which α_i is the pre-exponential factor corresponding to the ith decay time

$$\langle \tau_{f} \rangle = \frac{\sum_{i} \alpha_{i} \tau_{i}^{2}}{\sum_{i} \alpha_{i} \tau_{i}}$$

constant τ_i . Magnetic susceptibility measurements at 0.1 T magnetic field were performed with a SQUID-VSM (Quantum Design) instrument. Diamagnetic correction was done using Pascal constants.

2.2.1. Synthesis of the Ligand (HL)

The ligand, HL, 2,6-bis[N-(2-pyridylethyl)formidoyl]-4-ethylphenol, was prepared [15a] by condensation of 2,6-diformyl-4-ethylphenol (0.890 g, 5 mmol) with 2-(2-aminoethyl)pyridine (1.22 g, 10 mmol) in methanol. The mixture was refluxed for 2 h. After cooling and filtration to remove any suspended particles, the volume of the solution was adjusted to 50 mL. This

"solution of HL" was considered to contain 5 mmol of the ligand HL and was used for subsequent reaction without further purification.

2.2.2. Synthesis of $[Cu^{II}_{2}L(\mu-Cl)_{2}]Cl\cdot 4.5H_{2}O(1)$

To a mixture of a 10 mL "solution of HL", containing 1 mmol HL, a methanol (10 mL) solution of copper(II) chloride (0.268 g, 2 mmol) was added under reflux. Immediately a brown compound started to deposit. Reflux was continued for 3 h, and then the resulting deep brown solid was collected by filtration and washed with methanol. Recrystallization from water produced crystalline compound containing diffraction quality single crystals. Yield: ~0.59 g (~85%). Anal. Calc. for $C_{24}H_{34}N_4O_{5.5}Cl_3Cu_2$: C, 41.19; H, 4.89; N, 8.00%. Found: C, 41.46; H, 4.81; N, 8.15. IR (KBr pellet, cm⁻¹): v(H₂O), 3443 (b); v (C=N), 1645 (s).

2.2.3. $[Cu^{II}_{2}L(\mu-Cl)(H_{2}O)_{2}]$ 2Picrate·DMF (2)

An aqueous (5 mL) solution of **1** (0.345 g, 0.5 mmol) was added to an aqueous solution (5 mL) of picric acid (0.229 g, 1 mmol) at room temperature. The solution was stirred for 10 min and a green precipitate appeared. This was dissolved by adding the requisite amount of dimethylformamide (DMF). After one hour stirring, the solution was filtered and the filtrate was kept for slow evaporation. The green crystalline compound, containing diffraction quality green crystals, that deposited over a period of a few days was collected by filtration and washed with water. Yield: 0.39 g (70%). Anal. Calc. for $C_{39}H_{40}N_{11}O_{18}ClCu_2$: C, 42.07; H, 3.62; N, 13.84%. Found: C, 42.32; H, 3.70; N, 13.68%. IR (KBr pellet, cm⁻¹): v(H₂O), 3417 (b); v (C=N), 1641 (s); v_{as} (NO₂), 1561,; v_s (NO₂), 1362 (m), 1333 (m).

2.3. Crystal structure determination of 1 and 2. The crystallographic data of the compounds **1** and **2** are summarized in Table S1 (Supplementary material). Intensity data of **1** and **2** were collected at 296 K and 292 K respectively, on a Bruker-APEX II SMART CCD diffractometer using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The packages SAINT [25a] and SADABS [25b] were used for data processing and absorption correction. All data were corrected for Lorentz-polarization effects. The structures were solved by direct and Fourier methods and refined by full-matrix least-squares based on F^2 using SHELXL-97 [25c] and SHELXL-2014/7 [25d] packages.

During the development of the structure of 1, the counter chloride anion (Cl3) was found as disordered over two sites. The disorder was modelled by refining these two positions freely for each case and setting sum of their occupancies to be equal to one and the final occupancy parameters were set as 0.60/0.40 for Cl3A/Cl3B. It was not possible to assign properly the solvent water molecules in the structure of 1 and therefore these solvent molecules were eliminated by using the SQUEEZE facility of PLATON to improve the refinement [26]. The number of solvent of crystallization in formula has been taken as $4.5 \text{ H}_2\text{O}$, as the electron count per unit cell for the eliminated solvent molecules is 88 and the Z value for all of 1 is 2. All other hydrogen atoms in 1 were inserted at geometrically calculated positions with isotropic thermal parameters and refined. In 2, four hydrogen atoms of two coordinated water molecules were located from a difference Fourier map and refined with constraints. All other hydrogen atoms in 2 were inserted at geometrically calculated positions with isotropic thermal parameters and refined. All the hydrogen atoms were refined isotropically, while all the non hydrogen atoms were refined anisotropically. The final least-squares refinements (R_1) based on $I > 2\sigma$ (I) converged to 0.0586 and 0.0618 for **1** and **2**, respectively.

2.4. Calculation of Stern-Volmer constant (K_{SV}), association constant (K_a) and limit of **detection** (LOD): The K_{SV}, K_a and LOD values were calculated by comparing the fluorescence intensity obtained for **1** in the presence and absence of PA as reported earlier in literature.^{5b,5c,6e,8c,9e,24,27} The fluorescence quenching titrations were carried out in pure water placing 3 mL (50 μ M solution) of **1** in a quartz cuvette of 1cm path length. Then, an aqueous solution of PA (0–1.5 equiv.) was added in an incremental fashion. The sensitivity of 1 towards PA was determined by calculating the Stern-Volmer constant (K_{SV}).^{5c,6e,9e,24} The relative fluorescence intensity was plotted against the PA concentration to estimate K_{sy} using the well known Stern-Volmer equation $(I_0/I) = K_{SV} [A] + 1$. Binding stoichiometry and association constant (K_a) of 1 with PA in water solution have been determined by using Benesi-Hildebrand (B-H) plot of fluorescence intensity as a function of PA concentration.²⁷ The limit of detection (LOD) was also calculated on the basis of the fluorescence titration. The detection limit was calculated using the following equation; Detection limit = $3\sigma/k$ where σ is the standard deviation of blank measurement, and k is the slope of the calibration curve obtained from linear dynamic plot of fluorescence intensity vs PA concentration.^{5b,8c}

2.5. Theoretical Calculations. All DFT calculations (exchange coupling constant and full geometry optimization) were done using ORCA program package (version 4.0.1.2) [28]. At the DFT level, the magnetic exchange coupling constant was predicted within the broken symmetry (BS) framework [29] by considering the experimental X-ray structure without further geometrical optimization. Geometry optimizations were performed for the singlet state of picric acid and picrate anion and the molecular fragments based on the experimental X-ray structures of **1**. The hybrid B3LYP functional [30] and polarized triple- ζ quality basis set def2-TZVP [31] have been used in all calculations as implemented in the ORCA program package (version

4.0.1.2). All the calculations utilized the chain-of-spheres (RIJCOSX) [32] approximation. Increased integration grids (Grid4 in ORCA convention) and tight SCF convergence criteria were used in all calculations. In the theoretical calculation of magnetic coupling, relativistic effects have been incorporated by zeroth-order regular approximation (ZORA) within the BS [33]. AutoAux procedure is incorporated using the keyword "AutoAux" for BS calculation as described in the program manual [34a]. Auxiliary Def2/J coulomb fitting basis set was used in geometry optimizations [34b]. The spin densities, magnetic orbitals and highest occupied molecular orbitals (HOMO) as well as lowest unoccupied molecular orbitals (LUMO) were visualized with the programs VESTA 3 and Avogadro (version 1.2.0) [35].

3. Results and discussion

3.1. Syntheses and characterisation.

The compound of composition $[Cu^{II}_{2}L(\mu-Cl)_{2}]Cl\cdot4.5H_{2}O(1)$ was readily obtained in high yield on reacting copper(II) chloride and HL in 1:2 ratio; methanol was used as the medium of reaction and water as the solvent of recrystallization. On the other hand, treatment of **1** with picric acid in water-dmf mixture results in the formation of compound of composition $[Cu^{II}_{2}L(\mu-Cl)(H_{2}O)_{2}]$ 2Picrate·DMF (**2**).

The characteristic C=N stretching in **1** and **2** appears as a strong band in almost the same position $(1641-1645 \text{ cm}^{-1})$. The presence of water molecules in both complexes is evidenced by the appearance of a broad band centred at 3443 cm⁻¹ for **1** and 3417cm⁻¹ for **2**. Absence of the O–H stretching band at 3106 cm⁻¹, as observed in case of free picric acid [36], clearly indicates the presence of picrate ion instead of picric acid in **2**. The stretching frequencies due to asymmetric

and symmetric vibrational modes of $-NO_2$ group of the picrate moiety in **2** arises at 1561 cm⁻¹ and 1333–1362 cm⁻¹, respectively.

3.2. Description of crystal structures of 1 and 2. The crystal structure of $[Cu^{II}_{2}L(\mu-Cl)_{2}]Cl\cdot4.5H_{2}O(1)$ is shown in Fig. 1, while the selected bond lengths and angles are listed in Table S2 (Supplementary material). The structure reveals that **1** is a dicopper(II) system. The dicopper(II) moiety is monocationic and the charge is balanced by one chloride anion. Each of the two N(pyridine)N(imine)O(phenoxide) compartments of L⁻ is occupied by a copper(II) ion. The metal centers are also coordinated to two bridging chloride ligands. This way, the two metal centres are triply bridged by the phenoxide oxygen atom and two chloride atoms. Clearly, both metal centres are pentacoordinated by two nitrogen, one oxygen and two chlorine atoms. The values of distortion parameter (τ) for the pentacoordinated CuN₂OCl₂ environment of Cu1 and Cu2 are 0.276 and 0.352, respectively, which indicate significantly distorted square pyramidal geometry; Cl1 occupies the apical position for Cu1 and Cl2 occupies the apical position for Cu2. Obviously, each of the two bridging chloride ligands is equatorial to one copper(II) centre and axial to the second copper(II) centre, i. e., both chlorides bridge the metal ions in equatorial-axial (eq-ax) fashion.

The deviation of the donor centres and the displacement of the metal ion from the respective least-squares basal plane are 0.350 and 0.194 Å for Cu1 and 0.359 and 0.226 Å for Cu2. In the basal plane, the Cu–N/O bond distances are close and lie in the ranges 1.959–1.996 Å for Cu1 and 1.963–1.997 Å for Cu2. Both Cu–Cl bond distances are significantly longer than the Cu–N/O bond distances. However, Cu–Cl(ax) bond distances (Cu1–Cl1 = 2.811 Å, Cu2–Cl2 = 2.761 Å) are much longer than the Cu–Cl(eq) bond distances (Cu1–Cl2 = 2.339 Å, Cu2–

Cl1 = 2.342 Å), which is caused by Jahn-Teller distortion of the copper(II) ion. The two transoid angles in the basal plane are 151.21 and 167.78° for Cu1 and 169.46 and 148.34° for Cu2. The ranges of cisoid angles for Cu1 and Cu2 are 72.97–116.01° and 74.03–116.88°, respectively. In brief, the bond angles are deviated much from the ideal values and the overall ranges of bond distances (1.959–2.811 Å and 1.963–2.761 Å) indicate appreciable distortion of coordination geometry. The Cu–O(phenoxide)–Cu and Cu–Cl–Cu bridge angles are, respectively, 99.94, 70.63 and 71.60°, and the two metal ions in the dinuclear core are separated by a distance of 3.003 Å.

The crystal structure of $[Cu^{II}_{2}L(\mu-Cl)(H_{2}O)_{2}]$ 2Picrate-DMF (**2**) is shown in Fig. 2 and the selected bond lengths and angles are listed in Table S3 (Supplementary material). The structure reveals that it is a heterobridged μ -phenoxo- μ -chloro dicopper(II) compound in which the metal centers are boubly bridged by the phenoxo oxygen atom of L⁻ and one chloride ligand. The heterobridged μ -phenoxo- μ -chloro dicopper(II) moiety is dipositive cationic in **2**, where the charge is balanced by two picrate anions. There is one dimethylformamide as solvent of crystallization. The basic difference of the dicopper(II) core in **2** from that in **1** is that one of the two chloride bridges in the latter are replaced by two monodentate water ligands, each of which is coordinated to one copper(II) centre. Here also, both metal centers are pentacoordinated and square pyramidal. However, the CuN₂O₂Cl environment for Cu1 and Cu2 in **2** are less distorted than the CuN₂OCl₂ environment in **1**, as evidenced by much smaller values of discrimination parameter ($\tau = 0.156$ for Cu1 and 0.005 for Cu2 in **2**). Notably, the bridging chloride ligand in **2** occupies an equatorial position for both copper(II) centers, i. e., here it is eq-eq.

The deviation of the donor centres and the displacement of the metal ion from respective least-squares basal plane are 0.135 and 0.213Å for Cu1 and 0.039 and 0.142 Å for Cu2. Interestingly, the Cu–Cl bond distances (Cu1–Cl1 = 1.907 Å, Cu2–Cl1 = 1.919 Å) in 2 are clearly shorter than the Cu–N/O bond distances (1.957–1.995 Å for Cu1, 1.963–2.001 Å for Cu2) in the basal plane. As usual, the apical bond distances (Cu–O(water) = 2.366 Å for Cu1 and 2.360 Å for Cu2) are appreciably longer than the bond lengths in the basal plane. The two transoid angles in the basal plane are 159.79 and 169.15° for Cu1 and 167.77 and 168.06° for Cu2. The ranges of cisoid angles for Cu1 and Cu2 are 78.14–107.15° and 78.17–95.33°, respectively. All these values indicate that the geometry of both Cu1 and Cu2 is distorted square pyramidal, where the amount of distortion is much smaller than that in 1. As shown in Fig. 2, one hydrogen atom of the coordinated water molecule (O3) in Cu2 forms strong hydrogen bond with phenoxide (O4) oxygen atom of picrate anion, where the donor...acceptor distance is 2.839 Å. Another interesting structural feature of compound 2 is the presence of a π - π interaction. The aromatic ring, C(1)C(2)C(3)C(4)C(5)C(6), of the ligand interacts with the aromatic ring, C(31)C(32)C(33)C(34)C(35)C(36), of a picrate anion; the distance between the two centroids is 3.668 Å and the dihedral angle between the two least-squares planes is 2.95°. The combined effect of hydrogen bonding and $\pi - \pi$ interactions is likely to favour and stabilize the dicopper(II) molety...picrate adduct $[Cu^{II}_{2}L(\mu$ -Cl) $(H_2O)_2$]2Picrate·DMF (2).

3.3. Magnetic Properties of 1. Variable-temperature magnetic susceptibility data in the temperature range 2.5–300 K of complex **1** is shown in Fig. 3 in the form of a $\chi_{M}T$ vs. T plot. The $\chi_{M}T$ value at 300 K for **1** is 0.64 cm³ K mol⁻¹, which is smaller than the expected value of

0.75 cm³ K mol⁻¹ for two isolated copper(II) ions with g = 2.0 and $S_1 = S_2 = \frac{1}{2}$. On lowering of temperature, $\chi_M T$ decreases gradually to reach 0.012 cm³ K mol⁻¹ at 2.5 K. The profile clearly indicates that the metal centers in 1 are coupled by antiferromagnetic interaction. Taking $\hat{H} =$ $-2JS_1 \cdot S_2$ as the model Hamiltonian, the simulation (Fig. 3) was performed using PHI software [37] and the converging parameters are J = -132.40 cm⁻¹, g = 2.20, temperature independent paramagnetism (TIP) = 259×10^{-6} cm³ mol⁻¹ and impurity (ρ) = 1.3%. To the best of our knowledge, this is the first example of a triply bridged μ -phenoxo-bis(μ -chloro) dicopper(II) complex for which the magnetic property is explored. As already discussed, while the bridging phenoxide oxygen atom occupies basal positions (eq-eq), each of the two bridging chloride atoms are eq-ax. So, the magnetic interactions mediated by chloride bridges should be insignificant in comparison to that propagated through the phenoxide bridge. Crystal structure analysis reveals that both Cu^{II} centers in **1** have square-pyramidal geometry. Thus, the unpaired electron in each Cu^{II} center will be in $d_{x^2-v^2}$ magnetic orbital. Consequently, there exists an appreciable overlap between the magnetic-orbitals through the bridging phenoxide oxygen atom. The Cu–O(phenoxide)–Cu bridge angle is 99.94(14)°, greater than the cross-over angle (ca. 97.5). As a result, moderate antiferromagnetic interaction takes place.

3.4. Theoretical rationalization of magnetic-exchange in 1. In order to get better insight into magnetic exchange phenomena in the dinuclear complex 1, "broken-symmetry" density functional theory (DFT) calculations have been carried out using hybrid B3LYP functional in the ORCA program. The calculations were performed on molecular cation $[Cu_2L(\mu-Cl)_2]^+$ of 1. The *J*-values were evaluated from the energy difference (Δ), between the high spin (HS) and broken-symmetry (BS) states ($\Delta = E_{BS} - E_{HS}$) by Ginsberg's approach [38]

$$J = (E_{\rm BS} - E_{\rm HS})/S^2_{\rm max}$$

where the following spin Hamiltonian for the dinuclear system was used

$$\hat{\mathbf{H}} = -2J(\mathbf{S}_1 \cdot \mathbf{S}_2)$$

The BS-state ($M_s = 0$) is found to be more stable compared to the high-spin state (HS-state) ($M_s = 1$) and thus antiferromagnetic interaction is normal. Following the above equation, the *J* value is calculated to be -59.77 cm^{-1} which is correct in sign but somewhat smaller than the experimental value of -132.40 cm^{-1} .

To understand the exchange-pathway, we have investigated the Mülliken spin-density of HS state and the BS state. The spin density values on the Cu centers and the donor atoms of the ligands are listed in Table 1 and corresponding plots of HS and BS states of compound 1 is presented in Fig.4. For the high-spin state (HS), the Mülliken spin density data show that significant spin (0.78 e) is delocalized through the ligands, and the rest (1.22 e) is present in Cu ions. The spin density in the high-spin state is slightly higher in the phenoxide O atom (0.135 e) compared to the two μ -chloride atoms (0.108 e and 0.116 e for Cl1 and Cl2, respectively), which indicates that the largest overlap was observed through bridging phenoxide O atom. In Table 1 it is shown that the spin densities on the two Cu(II) ions in 1 have similar values but opposite in sign in the broken symmetry state which clearly indicates the existence of antiferromagnetic exchange interaction [14e]. Importantly, the bridging phenoxide oxygen atom has a spin-density of 0.135 in the HS-state, which is found to be reduced to a value of -0.002 in the BS-state. This indicates that phenoxide bridge is involved in the overlapping of two Cu^{II} centers. It is evident from the values in the Table 1 that the sign of spin density in broken-symmetry state on one of the two bridging chloride atom (Cl2) is positive and is the same to the sign of the Cu1 center. For the other bridging chloride (Cl1) atom, the sign of the spin density of broken-symmetry state is

the same (negative) as that of Cu2. This shows that the bridging chloride atom (Cl2) which is equatorial to Cu1, is mainly affected by the delocalization from Cu1, while for the other bridging chloride atom (Cl1) which is equatorial to Cu2, the delocalization from Cu2 is predominant. The spin population computed at the imine (N1 and N4) and pyridine (N2 and N3) nitrogen atoms in the BS-state have the same signs as that of the Cu centers to which they are bonded.

Obviously, in this dinuclear structure, the effect of spin delocalization (~39% of the spin is delocalized to the ligand framework) results in the occurrence of a strong antiferromagnetic interaction. Analysis of magnetic orbitals (Fig. 5) shows that each of the two HOMOS, 147 α (alpha-HOMO) and 147 β (beta-HOMO),contains one unpaired electron where one HOMO is located on one copper(II) while the second is located on the second copper(II) centre. A close scrutiny reveals that magnetic orbital on each copper(II) interacts with p orbitals of the phenoxide oxygen atom and one chloride chlorine atom in antibonding sense. Notably, one chloride is involved in bonding with one copper(II) while the second chloride is involved with the second copper(II) and therefore exchange interactions between the two Cu^{II} ions are efficiently blocked through the chloride bridges. As a result, the magnetic orbitals of the broken symmetry state are significantly coupled (S_{aβ} = 0.107) through the phenoxide bridge resulting in an antiferromagnetic exchange.

3.5. Electronic absorption spectra, Luminescent Properties and Detection of PA. The

electronic spectra of complex **1** was recorded in pure water in the range of 200–800 nm. The electronic spectrum of the complex **1**, as shown in Fig. S1 (Supplementary material), exhibits one highly intense band at 253 nm ($\varepsilon = 57400 \text{ M}^{-1} \text{ cm}^{-1}$) due to $\pi \rightarrow \pi^*$ transition and one ligand-

to-metal charge–transfer band at 368 nm ($\varepsilon = 8580 \text{ M}^{-1} \text{ cm}^{-1}$). The d–d transition for the Cu^{II} centre(s) for **1** appears at 625 nm ($\varepsilon = 119 \text{ M}^{-1} \text{ cm}^{-1}$) which is shown in the inset of Fig. S1 (Supplementary material). Fluorescence spectra of the complex **1** has been investigated in pure water at room temperature. As evident from Fig. S2 (Supplementary material), the fluorescence spectrum (excited at 375 nm) of **1** in aqueous medium exhibits a fluorescence maximum at 525 nm with a quantum yield of 3.1×10^{-3} in reference to quinine sulphate as the secondary standard ($\varphi = 0.546$ in 0.5 (M) H₂SO₄). This emission band for the complex **1** can be tentatively attributed to the intra-ligand $\pi \rightarrow \pi^*$ fluorescence.

The fluorescence of **1** in aqueous medium prompted us to investigate its potential application in the selective sensing of explosive aromatic/non-aromatic nitro analytes (NACs). To check the nitro explosive sensing ability of 1 in water, fluorescence intensities of 1 in water were monitored upon addition of aqueous or methanol solutions (50 mM; 3µL each) of various analytes such as picric acid (PA), p-nitrophenol (PNP), 2,4-dinitrophenol (DNP), mdinitrobenzene (DNB), p-nitrotoluene (NT), 4-nitrobenzaldehyde (NBZ), nitrobenzene (NB), nitromethane (NM), p-nitrobenzoic acid (NBC), phenol (PH) and p-cresol (PC). To our delight, as evident from Fig. 6, an efficient fluorescence quenching of ~77% of 1 occurs after adding just one equivalent of PA, which indicates its effectiveness to detect PA over other analytes. In case of nitrophenols, the order of quenching proficiency follows the order, PA > 2,4-DNP > NP, which is in agreement with the order of the acidity of these nitrophenols. The fluorescence intensity of compound 1 decreases like an on-off sensing response. To understand whether acidic property of PA is responsible for fluorescence change, fluorescence spectrum of 1 was recorded in presence of an protic acid, HCl. It can also be seen from Fig. 6 that addition of HCl leads to no noteworthy effect on fluorescence quenching which clearly suggests that there is no significant

structural change of the fluorophore moieties present in the complex **1** due to the acidic nature of PA and clearly acidic property of PA is not the reason of the observed fluorescence quenching. This way, the capability of complex **1** towards sensing of picric acid in water is established.

We have performed fluorescence titration of complex **1** in water by incremental addition of PA to revive more information about the interaction between complex **1** and PA. Fig. 7 shows the changes in the fluorescence behaviour upon titrating complex **1** with PA in water. As can be seen in Fig. 7, addition of PA is accompanied by band broading, which is indicative of charge transfer characteristics. The fluorescence quenching data were analysed using Stern-Volmer (S-V) equation: $(I_0/I) = K_{SV} [A] + 1$, where I₀ is the initial fluorescence intensity of **1** before the addition of analyte (A), *I* is the fluorescence intensity of **1** in the presence of analyte, [A] is the molar concentration of analyte, and K_{SV} is the quenching constant (unit: M⁻¹). It is evident from Fig. 8 that at low concentration range of PA a linear increase in the S-V plot was observed, whereas at higher concentration range the curve deviates from linearity and shows an upward curvature. From this it is clear that quenching efficiency increases with increasing concentration of PA and may be termed as super amplified quenching effect [5b,12c].

The nonlinear nature of the S-V plot may be attributed to many reasons such as existence of both static and dynamic quenching processes or an energy transfer (fluorescence resonance energy transfer) or self-absorption processes [8d,10a,11j]. At lower concentration of PA, a linear Stern-Volmer plot was obtained (inset of Fig. 8) and it furnishes a quenching constant (K_{SV}) of 1.1×10^5 M⁻¹.

Next, we constructed the Benesi-Hildebrand (B-H) plot to investigate the binding stoichiometry and association constant. The association constant and binding stoichiometry were determined by the fluorescence spectral change using B-H plot analysis, as reported in literature [27]. As

shown in Fig. 9, the B-H plot of $1/(F_0-F)$ vs $1/[PA]^2$ from the fluorescence titration of **1** with PA provides a straight line through out the entire range of PA concentration indicating 1:2 complex formation with association constant (K_a) $4.64 \times 10^{10} \text{ M}^{-2}$. To confirm our assumption, we also constructed the B-H plot for 1:1 complexation as shown in inset of Fig. 9. The nonlinear plot in this case again supports that complexation occurs only through 1:2 stoichiometry. The high value of association constant indicates that strong complex formation takes place between PA and 1. The limit of detection (LOD) of PA is 4.8 µM (Fig. S3, Supplementary material). Time-resolved fluorescence quenching experiments were carried out in order to explore the quenching mechanism (static versus dynamic). In these experiments, the fluorescence decays of 1 were monitored with and without the addition of PA. It is evident from Fig. 10 and Table S4 (Supplementary material) that the average life time ($\langle \tau_{av} \rangle$) of **1** (4.62 ns) does not display any significant change after adding PA (4.48 ns and 4.47 ns on addition of 0.2 and 1.0 equivalent respectively). Since the life time remains almost constant in presence of PA, this confirms that quenching occured primarily via a static mechanism and ruled out the possibility of fluorescence resonance energy transfer (FRET) in the quenching process [7c]. The static quenching can be attributed due to the ground-state charge-transfer complex formation, which is confirmed by Uvvis and single-crystal X-ray diffraction experiments. We recorded the Uv-vis spectrum of 1 in the presence of PA in water. The UV-visible titration of **1** with the incremental addition of PA is shown in Fig. 11. Remarkable increase of absorbance with a shift in peak of 1, as shown in Fig. 11, suggests the formation of ground state complexation between electron deficient picric acid and **1**. All the absorption curves in this spectrophotometric titration pass through an isobestic point at about 272 nm which indicates that ground state complex formation takes place more or less smoothly. The electronic spectra of the compound 2 (50 µM) in methanol, as shown in fig.

11, is found to be identical with the spectra of 1:2 mixture of **1** and PA. Little difference in the electronic spectra definitely may be due to the solvent effect. In order to understand the interactions in the solid state, we isolated and determined the single crystal X-ray structure of the association complex, $[Cu^{II}_{2}L(\mu-Cl)(H_{2}O)_{2}]$ 2Picrate·DMF (**2**), formed between PA and complex **1**. As discussed earlier, the association complex **2** contains a weak interaction directed aggregate of a dicopper(II) moiety, $[Cu^{II}_{2}L(\mu-Cl)(H_{2}O)_{2}]^{2+}$, and two picrate anions; in the course of the formation of the aggregate **2**, one of the two bridging chlorides is replaced by two monodentate water ligands. Obviously, the formation of the aggregate **2** not only confirms that static quenching but also depicts the reason of picric acid sensing behaviour of complex **1**.

DFT based theoretical calculations were performed to support the static mechanism and ground state charge transfer between 1 and PA or picrate. The HOMO-LUMO energy calculation of the sensor 1 along with PA and picrate by gas-phase DFT calculations reveal (as shown in the Fig. 12) that the LUMO (-5.66 eV) of 1 resides above the HOMO (-8.37 eV) of PA and the HOMO (-8.71 eV) of 1 resides below the LUMO (-4.04 eV) of PA. Therefore, ground-state charge transfer from sensor to PA as well as from PA to sensor are unfavourable processes. On the other hand, the energy of the LUMO of 1 is less than the energy of the HOMO (-3.17 eV) of picrate and so the ground state electron charge transfer from the HOMO of picrate to the LUMO of 1 can take place and it is the reason of the efficient fluorescence quenching.

3.6. Comparison of 1 with the reported related systems. Several fluorescent materials have been reported previously as sensors of picric acid. Most of these are fluorescent turn-off sensors and only a few are fluorescent turn-on sensors [5g,5h,6d,6g]. It is worth mentioning that most of the PA sensors exhibit the sensing property in non-aqueous media

[5c-5e,5g-5i,6a-6d,6f,7c,7f,8c-8k,9a-9c,10,12a-12c]. Although some picric acid sensors in aqueous medium are known, majority of them exhibit the properties in buffer solutions of various pH values [8a,8b,8k,13]. There are only a few examples of picric acid sensors in pure water but those are coordination polymers including MOFs (Table S5; Supplementary material) [7a-7c,9d,9e,11]. Interestingly, the title compound **1** is the only example of a discrete metal complex that senses PA in pure water. Notably, sensing of PA in aqueous medium is vital for practical utility. Moreover, it is more desirable for practical application that the sensing takes place in pure water as the electrolytes used in the buffer solutions may bring secondary pollution. From that perspective, being the first discrete metal complex to sense PA in pure water, the title compound is an important addition.

The previously reported metallo-organic PA sensors (aqueous or non-aqueous) contain various metal ions such as Zr^{IV}, Sn^{IV}, Eu^{III}, Tb^{III}, Ir^{III}, Al^{III}, Pt^{II}, Pd^{II}, Hg^{II}, Cd^{II}, Zn^{II} [8c–8j,9,10,11]. There are rare examples of Cu^{II} complexes as PA sensors but those examples were not structurally characterized [8a,8b]. Hence, the title compound is the first example of a structurally characterized copper(II) complex to show PA sensing behaviour.

The isolation and structural characterization of the sensor…analyte aggregate is crucial to understand the origin of sensing behaviour. Notably, as already discussed, its has been possible to characterize the sensor…analyte aggregate by determination of single crystal X-ray structure. At this context, it is worth mentioning that the number of structurally characterized sensor…analyte aggregates in the family of PA sensors is much less than the number of reported sensors [5d,5e,6a,6b,6d,8c,8g,11i,11k].

The Stern-Volmer quenching contant (K_{SV}), association constant (K_a) and limit of detection (LOD) of **1** and the most of the known metallo-organic PA sensors in pure water, are

listed in Table S5 (Supplementary material). Although there are sensors having better LOD values (12.9 nM, 0.06 μ M, 0.11 μ M, 0.12 μ M and 0.27 μ M), this value of **1** is comparable to those of the most of the reported sensors. However, K_{SV} value of **1** is the best among the known PA sensors in pure water. The K_a values of the metallo-organic PA sensors in pure water were not reported. However, it may be mentioned that the K_a value ($4.64 \times 10^{10} \text{ M}^{-2}$) of **1** is better than the K_a values ($1.67 \times 10^9 \text{ M}^{-1}$) the best organic PA sensors in pure water [5f]. All in all, the title compound **1** is a good sensor for PA.

As per CSD search (CSD version 5.38) [39], there is only four copper(II) system in which the there are μ -O-bis(μ -chloro) bridging moiety (O is any type of oxygen atom such as phenoxide, hydroxide, alkoxide, oxide, N-oxide) [15f,18e,19]. Out of these, two are dinuclear and other two are trinuclear. One dinuclear and two trinuclear compounds have μ -O(phenoxo)-bis(μ -chloro) bridging moiety while the second dinuclear compound is μ -O(N-oxide)-bis(μ -chloro) bridging moiety. Among these four, magnetic properties have been studied only for the μ -O(N-oxide)-bis(μ -chloro) dicopper(II) compound [15f]. However, magnetic data were collected only at two temperatures (305 K and 89 K), from which it was only concluded that the nature of magnetic exchange interaction is not significant. On the other hand, variable-temperature (2.5-300 K) magnetic behaviour have been done for compound 1 in this investigation. Clearly, the present investigation may be taken as the first report of magnetic properties of a copper(II) compound having μ -O-bis(μ -chloro) bridging moiety.

4. Conclusions

In this study, $[Cu_2L(\mu-Cl)_2]Cl\cdot4.5H_2O$ (1) has been established as a turn-off fluorescent sensor for picric acid (PA). The sensing property has been explored by spectral titration, crystal structure determination of the sensor…analyte aggregate and DFT calculations. Magnetic property of **1** has been studied and the moderate antiferromagnetic interaction has been well modelled by DFT calculations ($J_{exp} = -132.40 \text{ cm}^{-1}$; $J_{DFT} = -59.77 \text{ cm}^{-1}$). The major outcomes of the present investigation may be summarized as follows: (i) The title compound is the first example of a discrete metallo-organic system to sense picric acid in pure water; (ii) The title compound is the first example of a structurally characterized copper(II) compound to sense picric acid; (iii) The values of quenching constant and association constant of the title compound is the highest among the known PA sensors in pure water; (iv) Experimental and theoretical magnetic properties of **1** have been studied and this is the first time that *J* value (experimental or theoretical) of a copper(II) system having μ -O-bis(μ -chloro) bridging moiety (O = any of phenoxo, hydroxo, alkoxo, oxo) has been determined.

Appendix A. Supplementary data

CCDC 1915604 and 1892390 contains the supplementary crystallographic data for **1** and **2** respectively. Supplementary material related to this article can be found online.

Acknowledgements

Financial support for this work has been received from Government of India through Department of Science and Technology (INSPIRE Fellowship to S. Mandal), Council for Scientific and Industrial Research (Fellowship to A. Pramanik) and University Grants Commission (contingency from CAS-V project to S. Mohanta). S. Majumder thanks

Department of Chemistry, Bhairab Ganguly College for providing chemical facilities. Crystallography was performed at the DST-FIST-funded Single Crystal Diffractometer Facility at the Department of Chemistry, University of Calcutta. Centre for Research in Nanoscience and Nanotechnology (CRNN), University of Calcutta, is acknowledged for magnetic studies.

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Figure Captions

- Fig. 1. Crystal structure of complex $[Cu_2L(\mu-Cl)_2]Cl\cdot4.5H_2O$ (1). Counter chloride anion and all the hydrogen atoms are omitted for clarity.
- Fig. 2. Crystal structure of complex $[Cu^{II}_{2}L(\mu-Cl)(H_2O)_2]$ 2Picrate·DMF (2). DMF molecule and all the hydrogen atoms except the hydrogen atoms of co-ordinated water molecules are omitted for clarity.
- Fig. 3. $\chi_M T$ vs T plot of $[Cu^{II}_2L(\mu-Cl)_2]Cl\cdot 4.5H_2O(1)$. The solid line is the best fitting to the experimental data.
- Fig. 4. Graphical representation of the spin densities of 1 corresponding to (a) the high spin state and (b) the broken symmetry state . The isodensity surfaces are plotted with the cut-off values of $0.0045ea_0^{-3}$ for high spin state and broken symmetry state. Positive and negative spin densities are represented by magenta and canary yellow surfaces, respectively. Hydrogen atoms were omitted for clarity.
- Fig. 5. The non-orthogonal magnetic orbitals of the broken-symmetry spin state of 1. The isodensity surfaces are plotted with the cut-off values of 0.04 ea_0^{-3} . Hydrogen atoms were omitted for clarity.
- Fig. 6. Fluorescence responses of complex 1 (50 μ M, λ_{ex} = 375 nm) in water upon the addition of various analytes (1.0 equiv).
- Fig. 7. The change in fluorescence intensity of 1 (50 μ M, λ_{ex} = 375 nm) with the incremental addition of PA in water.
- Fig. 8 Stern-Volmer plot of corresponding fluorescence quenching of 1 in presence of different amount of PA in water. Inset shows the linear part of the plot of I_0/I versus [PA].

- **Fig. 9.** Benesi-Hildebrand (B-H) plot for 1:2 complexation between **1** and PA. Inset shows B-H plot for 1:1 complexation.
- Fig. 10. Time resolved fluorescence decays of 1 (50 μ M) before and after addition of PA in water. The fluorescence was monitored at 512 nm.
- Fig. 11. UV-visible spectra of $1 (50 \mu M)$ with increasing concentration of PA in water.

Fig 12. Pictorial representation of calculated energy level diagram of 1, PA and Picrate.



Chart 1. Chemical Structure of HL



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Fig.4. Graphical representation of the spin densities of **1** corresponding to (a) the high spin state and (b) the broken symmetry state . The isodensity surfaces are plotted with the cut-off values of $0.0045ea_0^{-3}$ for high spin state and broken symmetry state. Positive and negative spin densities are represented by magenta and canary yellow surfaces, respectively. Hydrogen atoms were omitted for clarity.



Fig. 5. The non-orthogonal magnetic orbitals of the broken-symmetry spin state of 1. The isodensity surfaces are plotted with the cut-off values of 0.04 ea_0^{-3} . Hydrogen atoms were omitted for clarity.



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Fig 12. Pictorial representation of calculated energy level diagram of 1, PA and Picrate.

Table 1. DFT-calculated net Mülliken spin densities on the selected atoms of 1 for HS and BS state.

Atom label	HS	BS	
Cu1	0.610	0.607	
Cu2	0.612	-0.609	
01	0.135	-0.002	
Cl1	0.107	-0.102	
Cl2	0.115	0.109	
N1	0.097	0.093	
N2	0.107	0.106	
N3	0.099	-0.098	
N4	0.105	-0.103	

50