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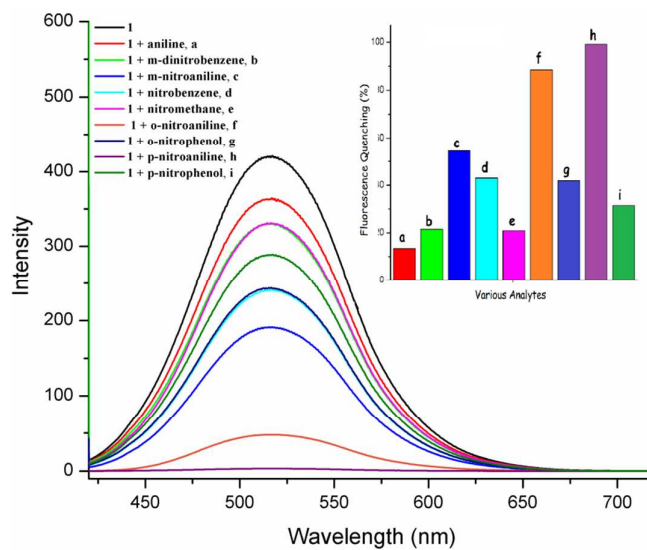
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Art work and Synopsis

Crystal structure of the first homochiral luminescent compound of a dansylated amino acid (tyrosine) of Cu(II), [Cu₂(HTyr-N-Dan)₄(H₂O)₂].2H₂O (**1**) (H₂Tyr-N-Dan = N-dansyltyrosine), and selective sensing of nitroanilines by both the ligand and **1** are reported.



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ARTICLE TYPE

A homochiral luminescent compound with a four-fold symmetry as a potential chemosensor for nitroanilines

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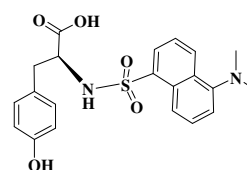
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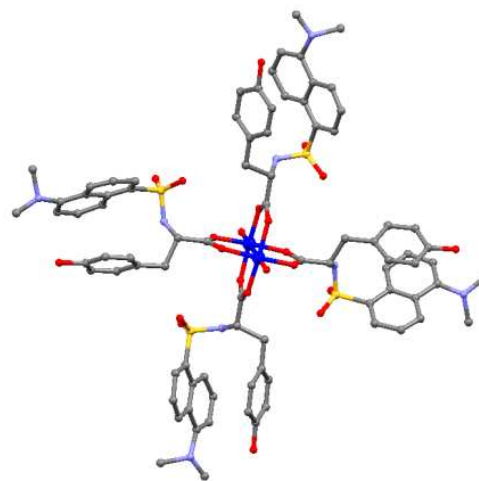
A homochiral compound of a dansylated amino acid ligand, [Cu₂(HTyr-N-Dan)₄(H₂O)₂]·2H₂O (**1**) (H₂Tyr-N-Dan = N-dansyltyrosine), is synthesized and crystallographically characterized. Its supramolecular chain structure is formed via intermolecular hydrogen bonding between the phenolic and the sulfato groups of the ligand while the intra-ligand π-π interactions exist between the aromatic rings of the dansyl and the tyrosine moiety of the ligand. Utilizing the luminescent property, selective sensing of nitroanilines by both the ligand and **1** is demonstrated.

In the past few decades, diverse coordination architectures have been explored in an extensible manner due to their potential application in various fields like gas storage and separation,^{1,2} heterogeneous catalysis,^{1,3} magnetism,^{1,2b,4} luminescence,^{1,5} sensors,^{1,6} nonlinear optics,^{1,7} thin film,^{1,8} drug delivery,^{1,9} chiral separation^{1,10-11} and enantioselective sensing.^{1,10-11} Having a large database of such coordination architectures, various research groups now focus on fine-tuning of components, such as linkers and ancillary ligands, to obtain examples with multiple properties. Among these coordination architectures, the supramolecular assemblies of homochiral luminescent compounds are one of those which are highly enviable but not much investigated in the literature. The chirality in these compounds can be achieved by using cheap and readily available L-amino acids. The use of amino acids can also provide another aspect in the structural aesthetics of these coordination architectures by showing various supramolecular interactions (e.g. hydrogen bonding, π-π, C-H...O interactions, etc.) due to the presence of multiple hydrogen bond acceptor/donor entities in them. The luminescence property in these homochiral compounds can be demonstrated by tagging the amino acids with some fluorophore. Herein, we report a new homochiral luminescent compound, [Cu₂(HTyr-N-Dan)₄(H₂O)₂]·2H₂O (**1**), prepared by stirring a methanolic solution of H₂Tyr-N-Dan (N-dansyltyrosine)¹² and CuSO₄ (see footnotes‡ for further details) under ambient conditions. To the best of our knowledge, this is the first time the crystal structure of a chiral compound of Cu(II) made from a chiral dansylated amino acid (tyrosine) is reported. Prior to this study, the only crystal structure of a metal-dansylated amino acid complex of Cu(II) reported in the literature was the monomeric Cu(II)-dansylated glycine complex, which is

achiral.¹³ In the literature the dansylated amino acids are used as sensors for various metal cations¹⁴ but the use of these for sensing nitro aromatics is not explored yet. We also report the selective sensing of nitroanilines, particularly p-nitroaniline, by the ligand and **1**.

Fig. 1 Structure of H₂Tyr-N-Dan.

Green block-shaped crystals of **1** are obtained from the evaporation of its methanolic solution within couple of weeks. It crystallizes in the tetragonal chiral space group *I4*.¹⁵⁻¹⁹ A 4-fold axis that passes through the two Cu(II) centers of a dinuclear unit and the coordinated water molecules generates the whole molecule in the asymmetric unit. Each Cu(II) center of the dinuclear unit has four oxygens of the carboxylates from four different ligands in equatorial positions with the Cu-O distances in the range of 1.949(4) - 1.968(4) Å, and an oxygen from the water molecule at the axial position, completing the square pyramidal geometry around it. Thus, four carboxylates from four HTyr-N-Dan ligands bridge between the two Cu(II) ions of a

Fig. 2 The paddle-wheel structure of **1**.

dinuclear unit to form a paddle-wheel structure with a Cu...Cu distance of 2.638(1) Å as shown in Fig. 2. All bond distances and bond angles around the Cu(II) center in **1** are comparable to the paddle-wheel structure present in Cu₂(μ-O₂C)₄ cores.²⁰ In all these examples, the Cu-O_{axial} distances lie in the range of 2.130(4)-2.231(4) Å whereas those in **1** are 2.130(10) and 2.161(11) Å. The selected bond distances and angles for **1** are listed in Table S1, ESI†.

The supramolecular array formed in the tetra-μ-acetato-bis(aquo)dicopper(II)^{20a,d} involves the axial water molecules and the oxygen of the bridging acetate group whereas in **1** the axial water molecules do not participate in the formation of the supramolecular network. This is due to the fact that the axial water molecules are hydrogen bonded to the lattice water molecules (O...O distance: 3.112(19) Å), thus preventing these to get involved with the bridging carboxylate oxygens for hydrogen bonding. Very few examples of paddle-wheel complexes are reported in the literature where the axial water is not involved in any kind of hydrogen bonding.^{20a,21} In **1**, the phenolic oxygen (O7) of the ligand of one dinuclear unit is hydrogen bonded to the oxygen atom (O6) of the sulphato group in the ligand of the next dinuclear unit, giving rise to a supramolecular chain (O6...O7 distance: 2.858(11) Å, ∠O7-H...O6: 173°; symmetry 1/2-y, 1/2+x, -1/2+z) as shown in Fig. 3. The four phenolic OH from four ligands

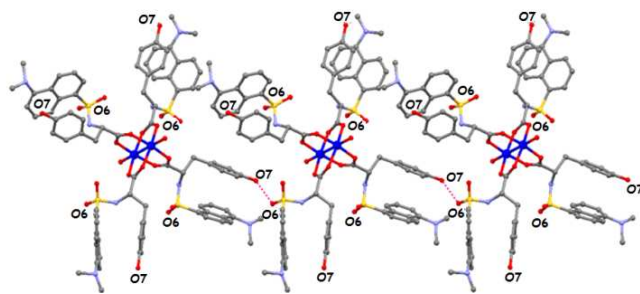


Fig. 3 Supramolecular chain (growth shown in one direction only) in **1**.

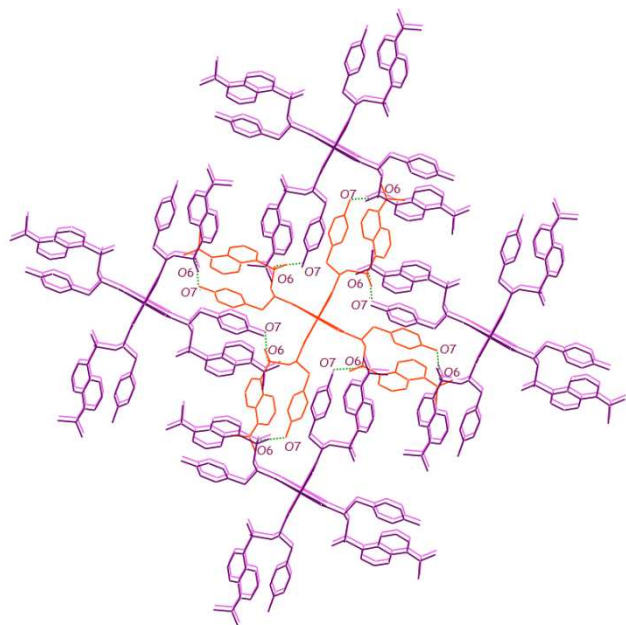


Fig. 4 Hydrogen bonding of each dinuclear subunit with eight other dinuclear subunits.

coordinated to each dinuclear unit are intermolecularly hydrogen bonded to oxygen atom (O6) of the sulphato group of the ligand of four different dinuclear subunits (Fig. S1, ESI†). Similarly, the oxygen atom (O6) of each sulphato group in a dinuclear unit is intermolecularly hydrogen bonded to the phenolic OH (O7) of four other dinuclear subunits. Thus, each dinuclear subunit is hydrogen bonded to eight other dinuclear subunits (Fig. 4) forming an extended 3D supramolecular network.

The presence of a four-fold symmetry gives rise to a square synthon, where the Cu(II) ions of four dinuclear subunits surrounding a single dinuclear subunit form its nodes (see Fig. 5). Further growth of this synthon into a 3D network is due to the symmetry as well as the intermolecular hydrogen bonding (Fig. 6 and Fig. S2, ESI†, respectively). The supramolecular network is further strengthened by the intra-ligand π-π interactions between the aromatic rings of the dansyl and the tyrosine moiety of the ligand (Fig. S3, ESI†).

Further spectroscopic characterization of **1** was performed by FTIR and UV-vis spectroscopy. The FTIR spectrum of **1** (Fig.

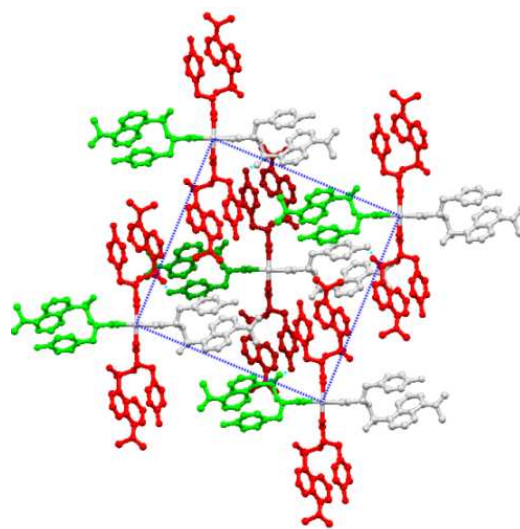


Fig. 5 Square synthon formed due to four fold symmetry (different colors represent the symmetry operations).

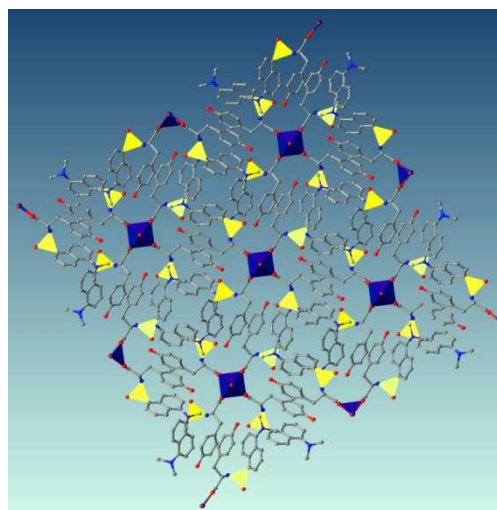


Fig. 6 Perspective view of the growth of the square synthon (blue polyhedral: metal dinuclear unit; yellow polyhedral; sulphato group of the ligand).

S4, ESI[†]) shows broad peaks at 3410 cm⁻¹ and 3271 cm⁻¹ corresponding to the lattice and coordinated water molecules, respectively. The peak at 2941 cm⁻¹ corresponds to the NH of the ligand. The asymmetric and symmetric stretch for the carboxylate of the ligand appears at 1589 cm⁻¹ and 1452 cm⁻¹, respectively. Thus, based on the difference ($\Delta\nu = \nu_{\text{asymm}} - \nu_{\text{symm}}$) of 137 cm⁻¹ a bridging type binding mode of the carboxylate is present in **1** which is confirmed by its single crystal structure described above. The sharp peaks at 1232 and 1140 cm⁻¹ correspond to the C-O and SO₂, respectively. Compared to the ligand, in its UV-Vis spectrum **1** shows an additional absorbance at $\lambda_{\text{max}} = 738$ nm due to the d-d transition (Fig. S5, ESI[†]). In the UV part, the absorbances at 280 nm and 380 nm are due to the n- π^* or π - π^* transitions. In order to provide an evidence for the existence of the solid state structure in solution, a UV-visible titration experiment was carried out varying the M:L ratio from 1:0 to 1:3. As can be seen from Fig. S6 (ESI[†]), the λ_{max} observed with highest intensity for **1** is attained with a 1:2 (M:L) ratio; further addition of L (1:3 ratio) simply decreases the absorbance due to a dilution effect.

The thermal behaviour of **1** was studied as a function of temperature in the range of 25-500 °C (Fig. S7, ESI[†]). It is a three-step weight loss profile. The first weight loss of 5.2% between 50-150 °C corresponds to the loss of six lattice water molecules (ca. 5.6%). The second step showing weight loss of 12.1% between 150-220 °C indicates loss of two coordinated water molecules along with loss of four carbon dioxide molecules, each from one ligand (ca. 11.7%). The third step between 300-500 °C shows a gradual weight loss of the ligand moiety.

The presence of the dansyl moiety in the ligand makes **1** fluorescent. Thus, a comparative study of the photoluminescence behaviour of the ligand and **1** was done. Both solutions of the ligand and **1** were excited at $\lambda_{\text{exc}} = 370$ nm and their photoluminescence spectra were recorded in the range of 385-700 nm. The λ_{emi} for both ligand and **1** were observed at 530 nm with the fluorescence quenching is quite evident in the latter; the fluorescence intensity of **1** is nearly one-third of that of the ligand (Fig. S8, ESI[†]). This quenching can be due to the non-radiative decay of dansyl fluorophore due to the presence of Cu(II) by dexter type energy transfer between the orbitals of Cu(II) and the dansylated tyrosine.²²

The photoluminescence property of the ligand and its Cu(II) complex was further employed into the sensing of various nitro compounds. A systematic analysis of various analytes gives a deeper insight into the role of functional groups present in the analytes on the fluorescence quenching of the ligand (Fig. 7 and Fig. S9, ESI[†]). Comparing the quenching ability of nitromethane (19%), nitro benzene (43%) and aniline (11%), it is well understood that for quenching the presence of an electron withdrawing nitro group is a must and also aromatic moieties are better off for the π - π interaction between the sensor and the analytes. However, the presence of two electron withdrawing nitro groups, meta to each other, does not facilitates the quenching (22%) to a greater extent. On the other hand, the presence of an electron donating NH₂ or OH group along with an electron withdrawing NO₂ group on the aromatic ring makes them better analytes to be sensed by the dansylated tyrosine.

Among them, p-nitroaniline is the best analyte which quenches the fluorescence of the ligand almost completely (99.5%). This is the first time a chiral sensor is used to demonstrate its selective sensing of nitroanilines. In the literature, few sensors have been reported for sensing p-nitroaniline where the sensors are based on either macrocycles (generally calixarene) or cyclodextrin capped nanoparticles.²³ However, the cumbersome and costly synthetic

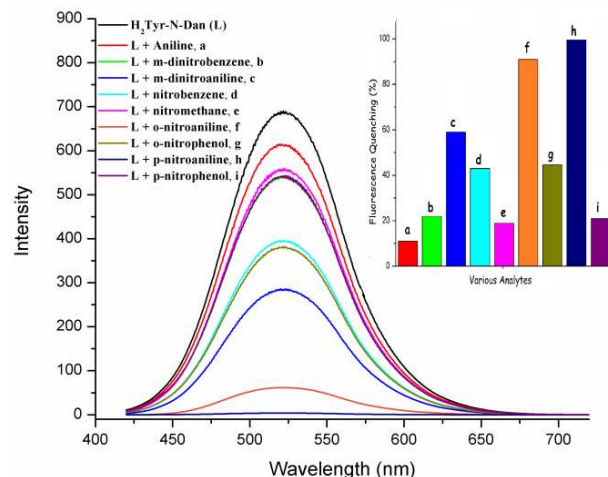


Fig. 7 Change in Fluorescence intensity for H₂Tyr-N-Dan in methanol upon addition of various analytes.

procedures make the reported sensors not so practically viable whereas the ligand reported in this work is made easily and cost-effectively. Since the aromatic moieties (dansyl part) that are involved in the π - π interactions with the analyte are far from the Cu(II) centers in **1**, there is no marked difference observed in the quenching ability of various analytes towards **1** as compared to the ligand itself (Fig. S10, ESI[†]).

In conclusion, a new homochiral luminescent compound with a four-fold symmetry [Cu₂(HTyr-N-Dan)₄(H₂O)₂]₂H₂O (**1**) was synthesized using dansylated tyrosine. In addition to its spectroscopic and thermal properties, the single crystal structure has provided some rare structural features: each dinuclear subunit is hydrogen bonded to eight other dinuclear subunits forming an extended 3D supramolecular network. A systematic study of various analytes has indicated its selective behaviour as a potential chemosensor for the nitroanilines, particularly p-nitroaniline. We believe that this study provides a new path for the application of such materials as new sensors for various analytes. Further development of several new derivatives of **1** is the current activity in our laboratory.

Notes and references

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[†]Electronic Supplementary Information (ESI) available: Crystallographic data of the structure **1** in CIF format (CCDC 1018411). Additional figures related to NMR, FTIR, UV and CD

spectroscopy, X-ray crystallography, and selected bond distances and angles of **1**. See DOI: 10.1039/b000000x/

‡ Synthesis of **1**: In a 10 mL round bottom flask, 38 mg (0.09 mmoles) of H₂Tyr-N-Dan and 5 mg (0.09 mmoles) of KOH was dissolved in 1.5 mL of methanol. To this was added 11.5 mg (0.045 mmoles) of CuSO₄·5H₂O along with 1.5 mL of methanol with stirring. The resultant green solution was further stirred for 6 hours at room temperature. The green filtrate was evaporated to dryness to get a green solid. Isolated yield: 25 mg (63%). Anal. Calc. for C₈₄H₁₀₀N₈O₂₈S₄Cu₂ (MW 1925.04): calc. C, 52.36; H, 5.19; N, 5.81. Found: C, 52.67; H, 4.81; N, 5.75. The formula used for CHN analysis was with six lattice water molecules. Selected FTIR peaks (KBr, cm⁻¹): 3410 (br, OH), 2941 (m, NH), 1589 (s, COO⁻ (asymm)), 1452 (s, COO⁻ (symm)), 1232 (s, C-O), 1140 (s, SO₂). Other prominent peaks: 3271 (br), 1614 (m), 1574 (s), 1515 (s), 1395 (s), 1090 (m), 788 (s), 627 (s), 586 (s). For sensing experiments: 2 mL methanolic solution of H₂Tyr-N-Dan (2.5 mM) or **1** (0.12 mM) was used for 300 μL methanolic solution of each analyte (2 mM).

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