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Nickel(II) complexes with mixed ligands: Synthesis, WORM memory applications, and potential biological applications as anticancer and antifungal agents

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Six novel nickel(II) complexes have been synthesized using Nickel(II) nitrate hexahydrate, *ortho*-phenanthroline (*o*-phen), or 2,2′-bipyridine (bipy) and 1-cyano-1-carboethoxyethylene-2,2-dithiolate (CED^{2-}) ligands in various stoichiometric ratios, showing good solubility across organic solvents. Weight loss experiments suggest water of crystallization, and molar conductance studies indicated electrolytic behavior for some complexes. UV-visible absorption spectra has confirmed octahedral coordination around Ni(II), and fluorescence studies show excitation-dependent emissions. IR has confirmed structural details, and current-voltage (I-V) measurements have demonstrated resistive switching behavior in memory devices, with compounds exhibiting write-once-read-many (WORM) characteristics. Cytotoxicity studies show noteworthy activity against the A-549 lung cancer cell line, especially for compounds **1**, **4**, and **6**. Antifungal assays have revealed notable activity against certain fungi, enhanced by the metal-ligand interaction increasing lipophilicity. These findings highlight the potential of the complexes in memory devices, anticancer treatments, and antifungal applications.

Keywords: Nickel(II) mixed ligand complexes, Dithiolates, *ortho*-Phenanthroline, Cytotoxic activity, Antifungal activity

The study of complex compounds of both non-transition and transition metal dithiolates has captivated researchers for decades[1-3]. This interest extends to the synthesis of novel complexes and the realm of biological inorganic chemistry. Dithiolates have observed successful applications as fungicides, herbicides, pesticides, and bactericides. They are also used as insulators, UV stabilizers for polyethylene and nylon, semiconductors, and vulcanization accelerators, demonstrating their versatility as well as industrial importance[4-11]. These complexes have further applications in optical recording materials[12] and have been explored for their radio-protective properties, with several sulfur-containing compounds showing significant potential in this regard[13]. Notably, the anti-tumor activities of gallium dithiolate complexes have been examined, revealing their effectiveness as anti-tumor agents *in vitro* at concentrations of 1 to 50 mg/kg in the mice[14]. The wide-range of relevance of 1,1-dithiolate derivatives in industrial and biological processes have spurred extensive research, leading to numerous patents[6,12,14,15]. This ongoing research highlights the significant role these compounds play in advancing both scientific understanding and practical applications.

The coordination chemistry of 1-cyano-carboethoxyethylene-2,2-dithiolate (CED^{2-}) compounds has garnered significant attention because of their distinctive structural and electrical properties, which have implications in various fields, including catalysis and materials science. Early research by Coucouvanis *et al.* highlighted the preparation and structural depiction of nickel(II) complexes with dithiolate ligands, setting a observedational understanding of their chemical behavior[16]. Subsequent studies by Jensen and Henriksen expanded on this by exploring the coordination chemistry of CED complexes with various metal centers, revealing their potential for forming stable and diverse coordination compounds[17]. In the late 20th century, significant advancements were made in understanding the electronic properties of these complexes. Geary provided a comprehensive review of metal dithiolate complexes, emphasizing their coordination chemistry and potential applications[18]. This work was further expanded by McCleverty *et al.*, who investigated the specific coordination behavior of CED complexes, contributing to a deeper understanding of their structural dynamics[19]. Recent studies have focused on the synthesis of mixed ligand complexes involving CED and various nitrogen donors. Singh, Das, and Paul synthesized and characterized nickel(II) complexes with CED^{2-} and various nitrogen donor ligands, demonstrating the potential for creating complexes with diverse stereochemistry and electronic properties[20]. This work was followed by Singh, Sutradhar, and Das[21], who explored the preparation and structural depiction of nickel(II) complexes with CED^{2-} and 1,8-diaminonaphthalene, showcasing the versatility of CED^{2-} in forming stable coordination compounds. The continued interest in CED complexes is driven by their unique ability to act as bidentate chelating agents, forming stable and electronically rich coordination environments. This has major consequences for the development of new materials and catalytic processes, as evidenced by the extensive body of research spanning several decades[6,22,23]. The ongoing exploration of these complexes promises to yield further insights into their potential applications and fundamental chemical properties.

The coordination chemistry plays a vital role in understanding the connections between metal ions and organic ligands. Recent studies have expanded this field by exploring various mixed-ligand complexes. For instance, Dağlı *et al.*[24] synthesized Cu(II), Ni(II), Co(II), and Zn(II) metal complexes with coumarilic acid and *ortho*-phenanthroline, highlighting their thermal properties, while Dzhardimalieva and Uflyand[25] focused on a nickel trimesinate complex with *ortho*-phenanthroline for dye adsorption and nanostructured material synthesis. In particular, nickel(II) complexes with mixed ligands such as 2,2′-bipyridine (bipy) and 1,1-dithiolate have garnered significant interest due to their unique structural and reactivity properties. Miller and Sykes[26] explored their synthesis and structural characteristics, emphasizing reactivity, while Khan and Nair[27] highlighted their catalytic potential. Liu, Xu, and Xu[28] investigated their coordination behaviors, and Wang and Zhang[29] examined their synthesis and structural features in detail. These studies collectively underscore the versatility and significance of nickel(II) complexes and mixed-ligand coordination chemistry.

Considering the literature reviews mentioned above, we are fascinated to make mixed-ligand complexes of *ortho*-phenanthroline, 2,2′-bipyridine, and CED^{2-} ligands with nickel which could display potential biological activity such as antifungal activity, cytotoxic activity and electrical behaviour, memory device applications, *etc*. Hence, here we report the preparation, optical properties, current-voltage characteristics, cytotoxic and antifungal studies of six nickel complexes with *ortho*-phenanthroline or 2,2′-bipyridine, and CED^{2-} ligand.

Experimental Section

Materials and methods

ortho-Phenanthroline (*o*-phen), 2,2′-bipyridine (bipy), Nickel(II) nitrate hexahydrate were collected from Sigma-Aldrich by procure procedure and then used devoid of additional purification. $K_2CED.H_2O$ was synthesized by a well-known literature method[30]. For elemental analysis (CHN) Perkin-Elmer 2400 Series II instrument was employed. In order to investigate the UV-Vis absorption data of the prepared Ni-complexes, a commercially available absorption spectrophotometer (Shimadzu, UV 1800) has been utilized. The fluorescence data of the synthesized Ni-complexes were recorded utilizing a commercially available Fluorescence spectrometer (Parkin Elmer, LS-55). The Infrared absorptions for the ligands and Ni-complexes were measured in the 400–4000 cm^{-1} region by Bruker Alpha II spectrophotometer. Electrical properties were carried out with Source meter Keithley-2614 B with Everbeing C2 Probe Station.

Synthesis of complexes

Preparation of Ni(*o*-phen)(CED).4H₂O (1)

An ethanolic solution (20 mL) of *ortho*-phenanthroline (0.9011 g, 5.000 mM) was mixed to a 50 mL aq. solution of $Ni(NO_3)_2.6H_2O$ (1.455 g, 5.000 mM) which gave bluish violet coloured solution. In this reaction mixture, 30 mL aq. solution of $K_2CED.H_2O$ (1.417 g, 5.000 mM) was introduced with continuous stirring which produced light brown ppt. The ppt was filtered off, thoroughly washed by water, ethanol then with diethyl ether and dehydrated *in vacuo* over dried $CaCl_2$.

Yield 3.5 g. 76%. Anal. Calcd for $C_{36}H_{34}N_6O_8S_4Ni_2$: C, 46.78; H, 3.71; N, 9.09. Obsd: C, 45.68; H, 3.24; N, 9.12%. UV-Vis (DMSO) λmax (in nm): 272, 347, 442 nm. IR: K_2i-MNT.H_2O (Ligand): 2190s (C≡N str.), 1642s (C=O), 1320 *vs*., 1375 *vs*. (C=C), 1020s (=CS_2), 930m (=CS_2), 886m (C–S str.). Complex **1**: 3065w, 2980w (Aromatic/Aliphatic C-H str.), 2200s (C≡N str.), 1627s (C=O), 1371 *vs*. (C=C), 1028 *vs*. (=CS_2), 926m (=CS_2), 845m (C–S str.), 644w cm^{-1} (In-plane ring deformation).

Preparation of Ni(*o*-phen)$_2$(CED) (2)

An ethanolic solution (20 mL) of *ortho*-phenanthroline (1.982 g, 10.00 mM) was mixed with 50 mL aq. solution of $Ni(NO_3)_2.6H_2O$ (1.455 g, 5.000 mM) with continuous shaking which gave pinkish violet colour solution. In this reaction mixture, 30 mL aq. solution of $K_2CED.H_2O$ (1.417 g, 5.000 mM) introduced with continuous stirring which produced brown ppt. The ppt was thoroughly washed by water, ethanol then with diethyl ether and dehydrated *in vacuo* over dried $CaCl_2$. Yield 2.6 g. 78%. Anal. Calcd for $C_{30}H_{21}N_5O_2S_2Ni$: C, 59.43; H, 3.49; N, 11.55. Obsd: C, 59.68; H, 3.34; N, 11.06%. UV-Vis (DMSO) λmax (in nm): 272, 292, 330, 348, 442 nm. IR: 3061w, 2980w (Aromatic/Aliphatic C-H str.), 2200s (C≡N str.), 1627s (C=O), 1370 *vs*. (C=C), 1029s (=CS_2), 961m (=CS_2), 847m (C–S str.), 643w cm^{-1} (In-plane ring deformation).

Preparation of Ni(*o*-phen)$_3$(CED) (3)

An ethanolic solution (20 mL) of *ortho*-phenanthroline hydrate (2.973 g, 15.00 mM) was mixed to a 50 mL aq. solution of $Ni(NO_3)_2.6H_2O$ (1.455 g, 5.000 mM) with shaking which gave wine-red colour solution. In this reaction mixture, 30 mL aq. solution of $K_2CED.H_2O$ (1.417 g, 5.000 mM) introduced with continuous stirring which produced yellow coloured ppt and change to yellowish brown colour after stirring for one hour. The ppt was filtered off, thoroughly washed by water, ethanol then with diethyl ether and dehydrated *in vacuo* over dried $CaCl_2$. Yield 3.7 g. 86%. Anal. Calcd for $C_{42}H_{29}N_7O_2S_2Ni$: C, 64.13; H, 3.72; N, 12.47. Obsd: C, 64.45; H, 3.43; N, 12.12%. UV-Vis (DMSO) λmax (in nm): 272, 294, 327, 345 nm. IR: 3071w, 2977w (Aromatic/Aliphatic C-H str.), 2194 *vs*. (C≡N str.), 1643s (C=O), 1370 *vs*. (C=C), 1029s (=CS_2), 946m (=CS_2), 844m (C–S str.), 643w cm^{-1} (In-plane ring deformation).

Preparation of Ni(bipy)(CED).4H_2O (4)

An ethanolic solution (20 mL) of 2,2′-bipyridine (0.7810 g, 5.000 mM) was added to a 50 mL aq. solution of $Ni(NO_3)_2.6H_2O$ (1.455 g, 5.000 mM) which gave pinkish violet coloured solution. In this reaction mixture, 30 mL aq. solution of $K_2CED.H_2O$ (1.417 g, 5.000 mM) introduced with continuous stirring which produced brown coloured ppt. The ppt was suction filtered, thoroughly washed by water, ethanol then with diethyl ether and dehydrated *in vacuo* over dried $CaCl_2$. Yield 3.6 g. 82%. Anal. Calcd for $C_{32}H_{34}N_6O_8S_4Ni_2$: C, 43.86; H, 3.91; N, 9.59. Obsd: C, 45.68; H, 3.24; N, 20.12%. UV-Vis (DMSO) λmax (in nm): 298, 309, 348, 441 nm. IR: 3079w, 2978w (Aromatic/Aliphatic C-H str.), 2201s (C≡N str.), 1605s (C=O), 1370 *vs*. (C=C), 1025s (=CS_2), 924m (=CS_2), 846m (C–S str.), 633w cm^{-1} (In-plane ring deformation).

Preparation of Ni(bipy)$_2$(CED) (5)

An ethanolic solution (20 mL) of 2,2′-bipyridine (1.562 g, 10.00 mM) was added to a 50 mL aq. solution of $Ni(NO_3)_2.6H_2O$ (1.455 g, 5.000 mM) with stirring which gave first brick red solution and finally changed to pinkish violet. In this reaction mixture, 30 mL aq. solution of $K_2CED.H_2O$ (1.417 g, 5.000 mM) introduced with continuous stirring which produced reddish-brown ppt. The ppt was suction filtered, thoroughly washed by water, ethanol then with diethyl ether and dehydrated *in vacuo* over dried $CaCl_2$. Yield 2.2 g. 79%. Anal. Calcd for $C_{26}H_{21}N_5O_2S_2Ni$: C, 55.93; H, 3.79; N, 12.54. Obsd: C, 55.68; H, 3.23; N, 12.16%. UV-Vis (DMSO) λmax (in nm): 298, 308, 346, 444 nm. IR: 3091w, 2978w (Aromatic/Aliphatic C-H str.), 2200s (C≡N str.), 1606s (C=O), 1369s (C=C), 1028 *vs*. (=CS_2), 924m (=CS_2), 842m (C–S str.), 652w cm^{-1} (In-plane ring deformation).

Preparation of Ni(bipy)$_3$(CED) (6)

An ethanolic solution (20 mL) of 2,2′-bipyridine (2.343 g,15.00 mM) was added to a 50 mL aq. solution of $Ni(NO_3)_2.6H_2O$ (1.455 g, 5.000 mM) with stirring which resulted orange-red solution. In this reaction mixture, 30 mL aq. solution of $K_2CED.H_2O$ (1.417 g, 5.000 mM) introduced with continuous stirring which produced brown colour ppt. It was suctioned filtered and thoroughly washed by water, ethanol then with diethyl ether and dehydrated *in vacuo* over dried $CaCl_2$.

Yield 2.9 g. 81%. Anal. Calcd for $C_{36}H_{29}N_7O_2S_2Ni$: C, 60.52; H, 4.09; N, 13.72. Obsd: C, 60.45; H, 3.24; N, 13.84%. UV-Vis (DMSO) λmax (in nm): 287, 296, 308, 348, 441 nm. IR: 3075w, 2974w (Aromatic/Aliphatic C-H str.), 2181s (C≡N str.), 1652s (C=O), 1370 *vs*. (C=C), 1021 *vs*. (=CS_2), 958m (=CS_2), 836m (C–S str.), 634w cm^{-1} (In-plane ring deformation).

Cytotoxicity assay

The cytotoxicity evaluation has been done using the MTT assay. The assessment is based on the conversion of the MTT assay to blue formazan with the succinate dehydrogenase mitochondrial enzyme in living cells. The A-549 lung cancer cell line has been developed at 37 °C and 5% CO_2 in DMEM medium by means of 10% FBS. Cells were extracted at 80% confluency and begun at a concentration of 10^4 cells for each well in 96-well dishes for an overnight culture. Following a 4-hours incubation period, new serum-free media were added to the cell medium. Subsequently, 100 µL of medium for each well were treated by compounds **1**, **2**, **3**, **4**, **5**, **6**, and **L-CED** at varying doses (10, 500 ng/mL, 1, and 50 µg/mL), with *cis*-platin serving as a positive control. The plate was cultivated in a 5% CO_2 environment at 37°C for 24 hrs. The old media is changed out for 100 µL of freshly prepared serum-free media after 24 hrs, and 10 µL of 12 mM MTT assay is mixed to every well before the plate is incubated for a further 4 hrs. Next, 75µL of medium carefully discarded from each well without disturbing the formazan crystals. Add 50µL of DMSO and stirred thoroughly to dissolve the formazan crystals. After 10 minutes of incubation, the plate was read at 540 nm using a blank in the Synergy H1 plate reader[31].

Antifungal activity study

The anti-fungal behavior of $K_2(CED).H_2O$ and the corresponding complexes were assessed by the disc diffusion method against various plant and animal-based fungi, with a positive control as Griseofulvin as standard (10 µg/disc). Cultures of fungi were grown in Sabouraud dextrose agar media. For the disc diffusion assay, a 20% (w/v) every dry extract's stock solution (both for complexes and the ligand) was set in pure DMSO solvent. To prepare suspended spore for moulds, developed spores were softly washed from the solidus media using a 0.05% (v/v) Tween-80 solution, and the suspended solution was in sync with 10^6 spores/mL. The inoculated agar plates were covered with Whatman No. 4 filter paper of 6 mm in diameter discs, which had been saturated in 15 µL of the standard solutions. DMSO (15 µL) was utilized as the negative run, and discs containing Griseofulvin of 10 µg/disc were utilized as the positive controls. The plates were kept in incubation at 25°C for 96 hours for observation of antifungal activity. Every experiment was done in quintuplicate.

Results and Discussion

Synthesis of complexes

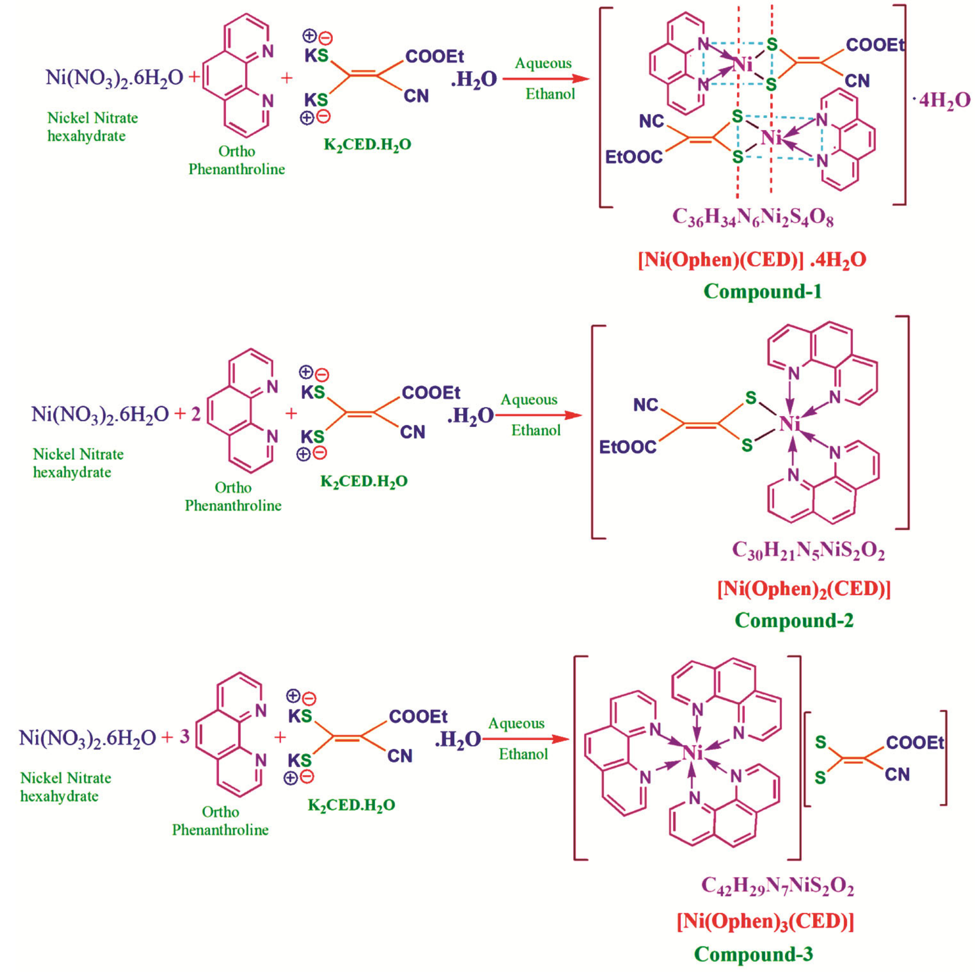
Six nickel-complexes, labeled as **1**, **2**, **3**, **4**, **5**, and **6**, were successfully prepared through the combination of Nickel(II) nitrate hexahydrate, with *ortho*-phenanthroline (*o*-phen) or 2,2′-bipyridine (bipy) and CED^{2-} ligands. This was achieved by using different stoichiometric ratio such as 1:1:1, 1:2:1 and 1:3:1 (Ni : *o*-phen or bipy : CED) in a solvent combination of ethanol-water. Amazingly, these synthesized compounds display noteworthy solubility over a broad array of organic solvents. The representative schemes of reactions for the preparation of all the six complexes are given in Scheme 1 and Scheme 2.

Weight loss experiment

A little amount of the material (0.500 g) was heated in a fusion tube for four hours in an electric stove-top to perform the weight loss experiment for six compounds maintained at 100°C, 120°C, 150°C, and 180°C. The complexes **1** and **4** exhibited weight loss (0.039 g and 0.041 g for complexes **1** and **4**, respectively) equivalent to four water molecules below 140°C, indicating that the molecules of water are water of crystallization and not connected to the metal center in these compounds[32].

Molar conductance study

The value of molar conductance for the complexes **3** and **6** was observed to be 73.0 and 68.0 ohm^{-1} cm^2 $mole^{-1}$, respectively, while the remaining complexes show values in the range of 22.0-38.0 ohm^{-1} cm^2 $mole^{-1}$ in DMF solvent (10^{-3} M). A comparison of the data of molar conductance in DMF for the complexes suggests a (1:1) electrolytic character for **3** and **6** and a non-electrolytic nature for the remaining complexes[33].



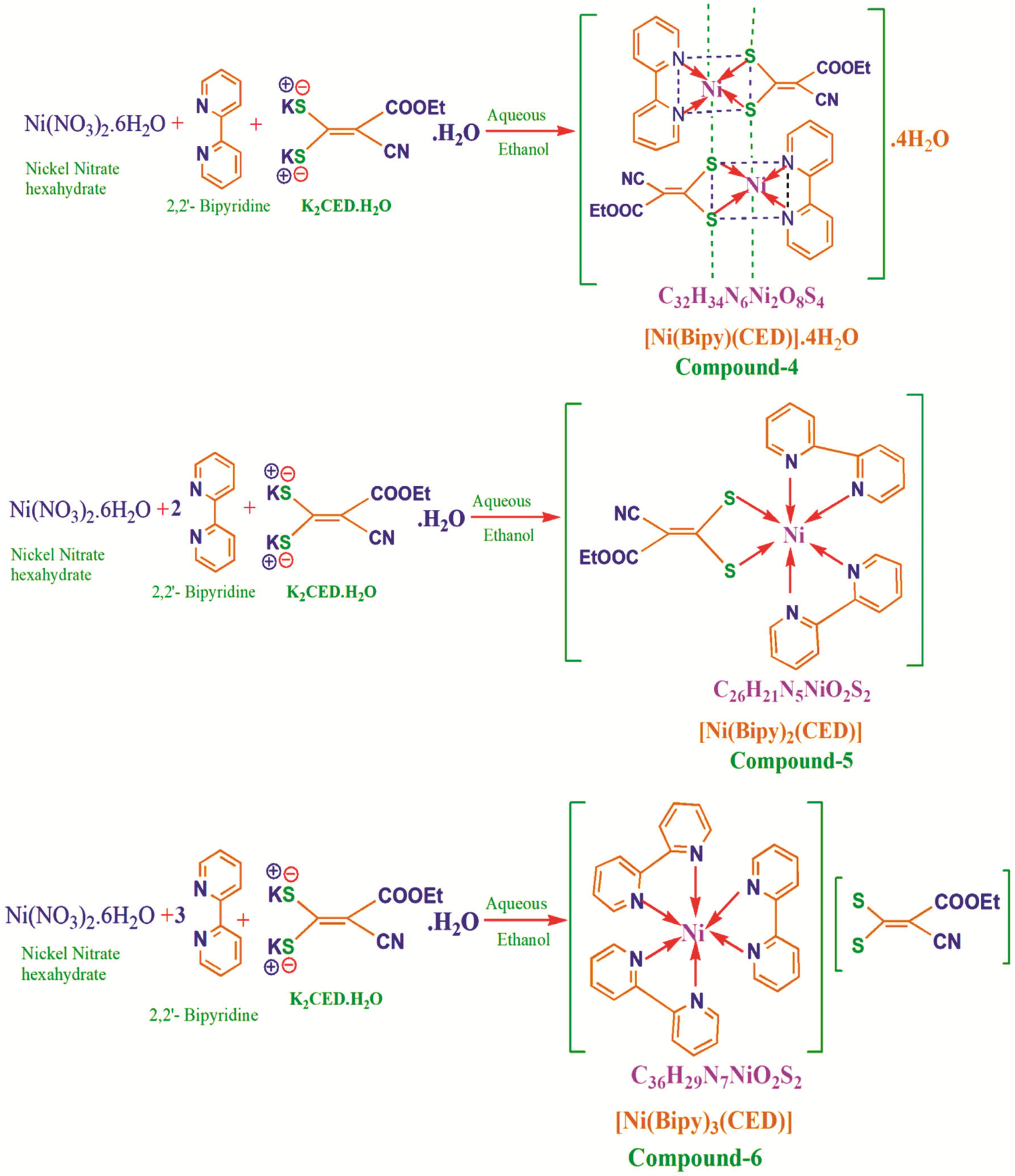
Scheme 1 — Reaction Scheme for the synthesis of complexes **1**, **2**, and **3**

UV-Vis absorption spectra

The UV-Vis absorption spectra of all the compounds are recorded in DMSO solutions. The corresponding spectra of the compounds are shown in Fig. 1a-g. While obtaining the spectra, the concentration of all the solutions were kept very low in order to avoid aggregation. As observed from Fig. 1a, the compound L-CED exhibits to characteristic absorption bands at 274 nm and 356 nm. Compound **1** exhibits three distinct absorption bands (Fig. 1b) at 272 nm, 347 nm and 442 nm. Moreover, the absorption spectra of compound **2** (Fig. 1c) also show three major bands at 272 nm, 348 nm and 442 nm, respectively, along with two shoulders at 272 nm and 330 nm. In case of compound **3** also, a prominent peak was viewed at 272 nm to diethyl ether with a shoulder at 298 nm in the UV range (Fig. 1d). Apart from that, the absorption spectra of compound **3** also showed two bands in the observable range at 327 nm and 345 nm, respectively (Fig. 1d). The UV-Vis-absorption spectra of compound **4** and compound **5** exhibit similar characteristics (Fig. 1e and 1f) with two major bands at 298 nm and 441 nm. Apart from these bands, compound **5** and **6** exhibit significant absorption at 348 nm and 346 nm, respectively. Moreover, a shoulder is observed for both compounds at 309 nm and 308 nm, respectively. Three characteristic bands are there in the spectra of compound **6** at 287 nm, 348 nm and 441 nm. Moreover, two shoulders are also observed at 296 nm and 308 nm, respectively. The characteristic absorption bands near 440 nm in the complexes is characteristics of $^{3}A_{2g}\rightarrow{}^{3}T_{1g}(P)$ transition suggesting octahedral coordination around Ni(II)[33].

Fluorescence study

The fluorescence study reveals that all the compounds (**L-CED** and **1-6**) exhibit fluorescence in various regions. The subsequent spectra are shown in



Scheme 2 — Reaction Scheme for the synthesis of complexes **4**, **5**, and **6**

Fig. 2. The fluorescence spectra of all the compounds depend on the excitation energy. As observed from Fig. 2a, the compound L-CED exhibits well-built fluorescence at 344 nm while excited at 272 nm wave length, whereas it exhibited two distinct emission bands at 417 nm and 436 nm while excited at 356 nm. Compound **1** showed fluorescence at 335 nm, 387 nm and 507 nm when excited at 272 nm, 347 nm and 442 nm, respectively (Fig. 2b). Compound **2** showed strong fluorescence at 334 nm when excited at 272 nm while, when it was excited at 348 nm, it exhibited fluorescence at 388 nm and 417 nm (Fig. 2c). Moreover, compound **2** also exhibited weak emission peak at 507 nm while excited at wavelength 442 nm. Compound **3** also showed emission bands at 345 nm, 337 nm and 360 nm while excited at 272 nm, 347 nm and 442 nm, respectively (Fig. 2d). When excited at 298 nm, compound **4** exhibited a prominent peak at

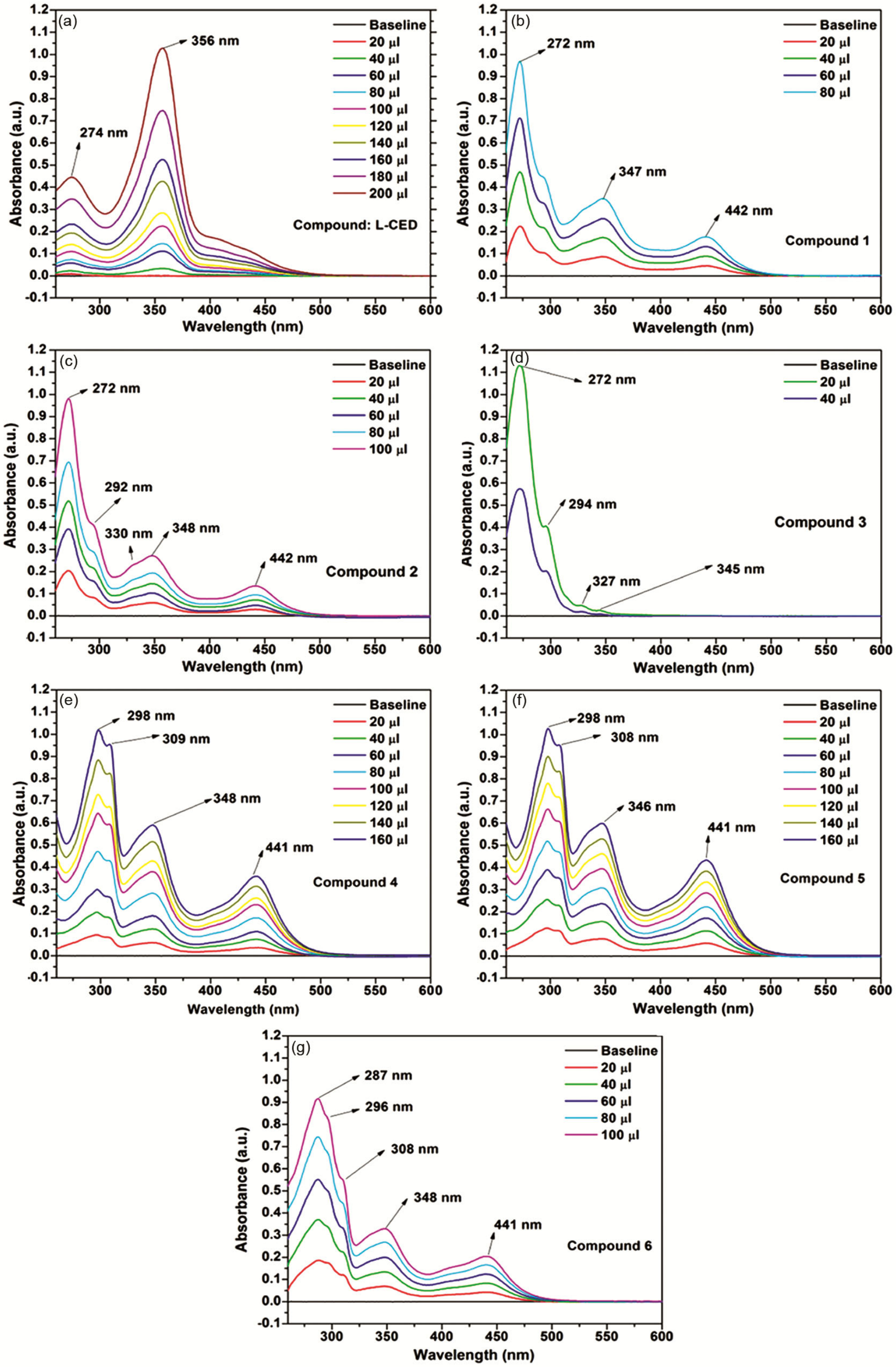


Fig. 1a-g — The UV-Vis absorption spectra of ligand (L-CED) and compounds 1-6, respectively

345 nm (Fig. 2e). Moreover, two strong emission bands at 417 nm and 436 nm are also observed when compound **4** is excited at 348 nm and a weak emission peak is observed at 505 nm when the compound is excited at 441nm. In case of compound **5**, strong emission bands are observed at 346 nm, and 342 nm while excited at 298 nm and 308 nm (Fig. 2f). Apart from these bands, the compound exhibits weak emissions while excited at 346 nm (emission at 385 nm & 417 nm) and 441 nm (emission at

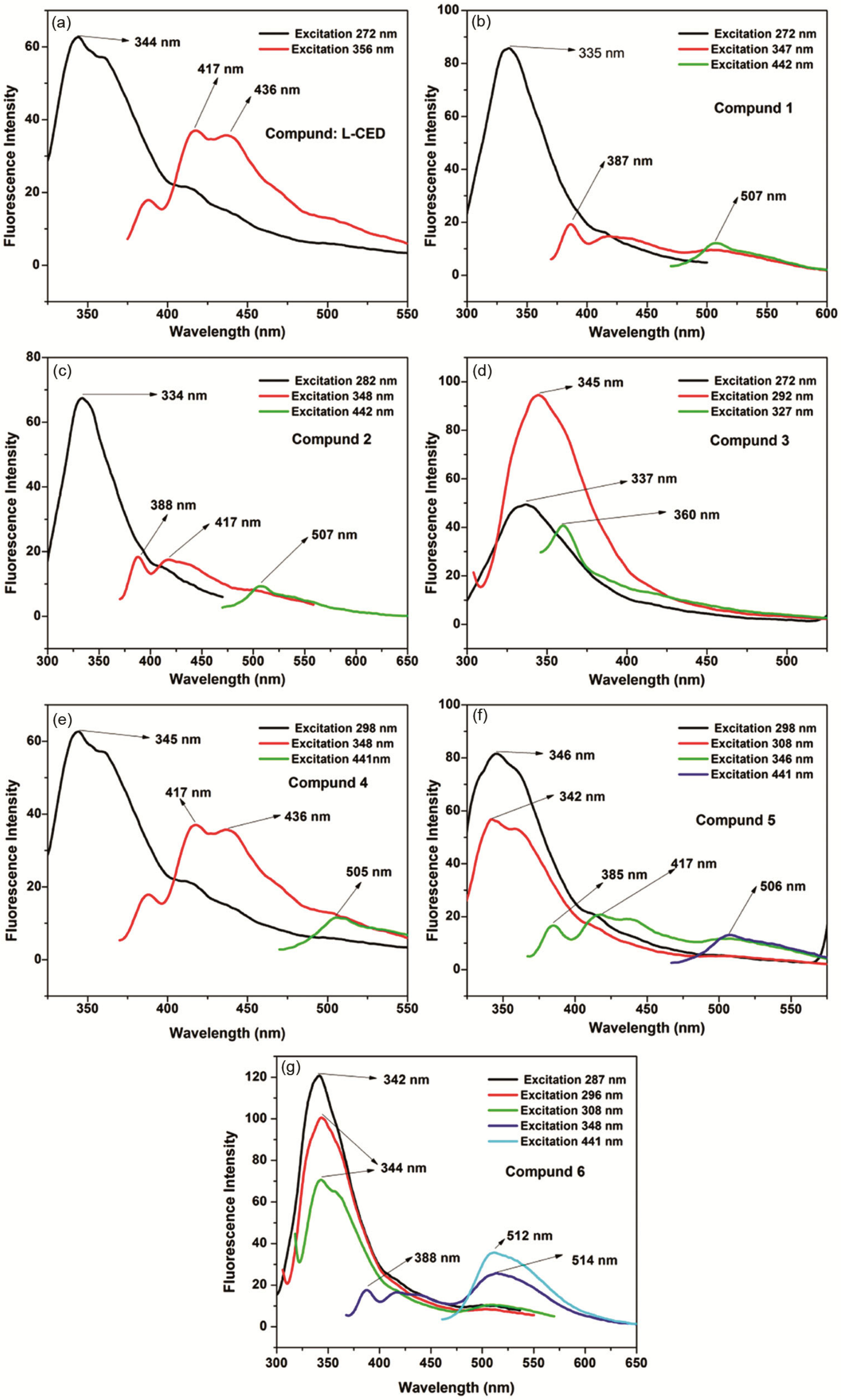


Fig. 2a-g — The Fluorescence spectra of compound L-CED and Compound **1**-**6**, respectively

506 nm). Fig. 2g depicts the emission spectra of compound **6**. Here, the strong emission peak at 342 nm is observed when the compound was excited at 287 nm. Similar emissions were observed (at 342 nm) while excited at 396 nm and 308 nm. The compound also showed weak emission at 388 nm and 514 nm while excited at the wavelength of 348 nm. Moreover, compound **6** also exhibited fluorescence at 514 nm while excited at 514 nm.

IR spectroscopy

Previous research on metal 1,1-dithiolates[34-40] has significantly contributed to our understanding of the IR spectra of mixed ligand complexes. Each component within these complexes exhibits distinct vibrational modes that result in specific bands in the Infrared spectra. The electron shifting within the chelated CED^{2-} ring causes the coupling of various vibrational modes, making it difficult to identify pure vibrations in the spectra. The IR spectra of the mixed ligand N,S-donor complexes reveal typical stretching vibrations linked to >C=O, >C=CS_2, –C≡N, C–S, and M–S from CED^{2-} moiety, along with aryl heterocyclic vibrations and M-N vibrations from *ortho*-phenanthroline (*o*-phen) and 2,2'-bipyridine (bipy). The υ(C≡N) band at 2190 cm^{-1} in CED^{2-} while in its mixed ligand N,S-donor complexes is found in the region of 2181-2201 cm^{-1}, indicating that the ligand's nitrile group is not directly bonded. Again, the complexes containing an non-conjugated and a conjugated acetyl group demonstrate υ(C=O) bands in the ranges 1720-1750 cm^{-1} and 1620-1630 cm^{-1}, respectively. The stretching mode υ(C=O) of the acetyl group in these complexes manifests as a prominent band within the 1605-1652 cm^{-1} range, indicating a shift to lower frequencies compared to typical α,β-unsaturated compounds. This suggests conjugation of the C=O bond with the adjacent C=C bond. The presence of the υ(C=O) wave number in these the complexes **1**-**6**, similar to that observed for CED^{2-}, implies that the carbonyl-O does not bonded. Additionally, all the complexes display significant bands at 1369-1371 cm^{-1}, 1021-1029 cm^{-1}, and 924-961 cm^{-1}, which correspond to υ_1[υ(C=C)], υ_4[υas(=CS_2)], and υ_2[υs(=CS_2)] stretching vibrations of the >C=CS_2 structural unit, with similar frequencies noted in CED^{2-} at 1320, 1020, and 930 cm^{-1}, respectively[30]. In certain compounds, the υ(C=C) vibration appears as a triplet or doublet, representing a reduction in symmetry. The detection of a band in 836-847 cm^{-1} range for υ(C–S) suggests symmetrical coordination of both sulfur atoms from the CED^{2-} ligand. All N,S-donor mixed ligand complexes featuring N-donors (heterocyclic) exhibit in-plane deformation bands between 633-652 cm^{-1}, representing bonding through the N-atoms, with these absorption bands showing up shifts relative to their positions in the free ligand form[41]. The Ni(II) complexes **1-6** also present weak-medium strength bands in the 1092-1105 cm^{-1} range, credited to the ring breathing vibration of the nitrogen donors (heterocyclic) in these complexes[42]. These bands confirm the coordination of the nitrogen donors to the metal center. The υ(C–H) vibrations from aromatic ligands are detected as very weak bands in 3055-3082 cm^{-1} range, while the aliphatic υ(C–H) bands appear as weak absorption in the 2974-2980 cm^{-1} region, indicating the presence of CED^{2-} in the N,S-donor mixed ligand complexes. The asymmetric and symmetric stretching modes of υ(O–H) from lattice water in the complexes are observed as broad band between 3000-3500 cm^{-1} with H-O-H bending vibration appearing in the 1630-1610 cm^{-1} range, which may overlap with the υ(C=O) of the CED^{2-} ion.

Current-Voltage (I-V) characteristics

As a way to evaluate the I-V features of the synthesized compounds, seven devices with device structures Au/X/ITO (X = corresponding compounds) have been fabricated. The I-V report of these devices have been recorded by applying linear voltage scans using a source meter (Keithley, 2614B) with an operating voltage range of 0V to ±3 V. The consequent I-V data of the compounds are given in Fig. 3 in semi-logarithmic level; the insets show the subsequent I-V response in linear level. The voltage sweeps up direction, range and sequence have been shown in the figures. As observed from Fig. 3, all the compounds, except compound **3**, are observed to be in high resistance state (HRS) at low applied bias (scan 1). However, with the increase in the applied voltage (scan 1), all the compounds, except compound **3**, undergo a transition with a sudden increase in current, from the HRS to LRS. This transition is analogous to an electronic switching device's SET process. The voltage at which the devices undergo such HRS to LRS transition is known as SET voltage (V_{SET})[43]. Moreover, during the subsequent voltage sweeps (3V→0V→-3V→0V), the compounds remain in the LRS. Clearly, all the compounds, except compound 3, show typical write-once-read-many (WORM) form resistive switching (RS) ways with acceptable memory windows[44]. Fig. 3d represents the I-V curve of the compound **3** in semi-logarithmic scale while the inset shows the same in linear scale. As observed from the figure, compound **3** exhibits linear I-V connection signifying the conductive (Ohmic) nature of the thin film. Clearly, the synthesized compounds, except compound **3**, may be used as active layer materials in resistive switching WORM memory devices which have diversified applications such as data security, archival storage, compliance and regulatory requirements, medical and legal records,

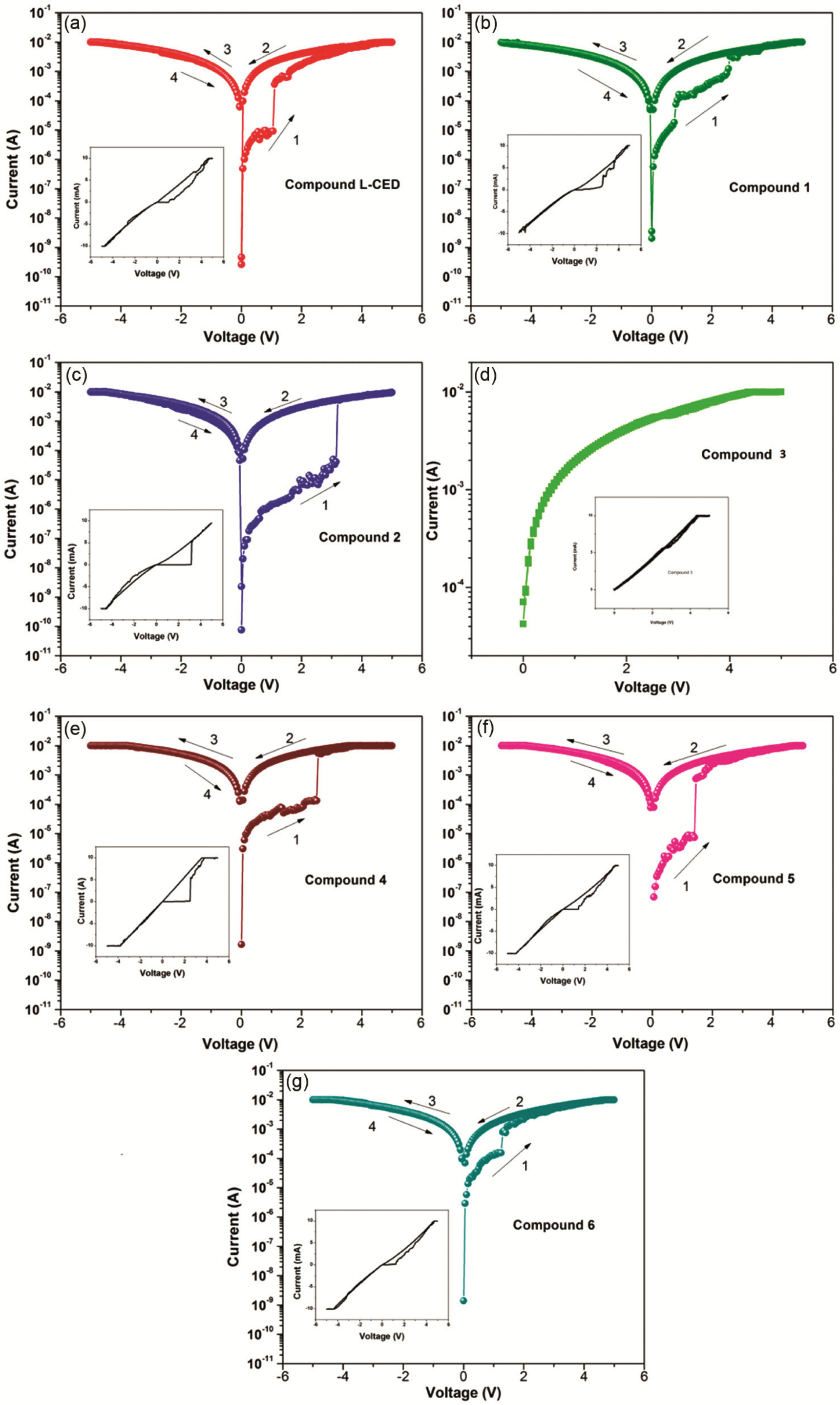


Fig. 3a-g — I-V response of **L-CED** ligand, Compounds **1**, **2**, **3**, **4**, **5**, and **6**, respectively, in semi logarithmic scale

content distribution embedded systems, historical data logging block chain technology, *etc*.[45]

In case of a memory tool, it is important to assess the time for which device can retain the stored data[46]. In order to assess the data ration time of the devices, the HRS and LRS resistance values have been determined at the read voltage (0.2 V) for all compounds showing the WORM RS behaviour. The subsequent values are shown in Fig. 4. As can be seen from the figures, all the compounds with WORM RS

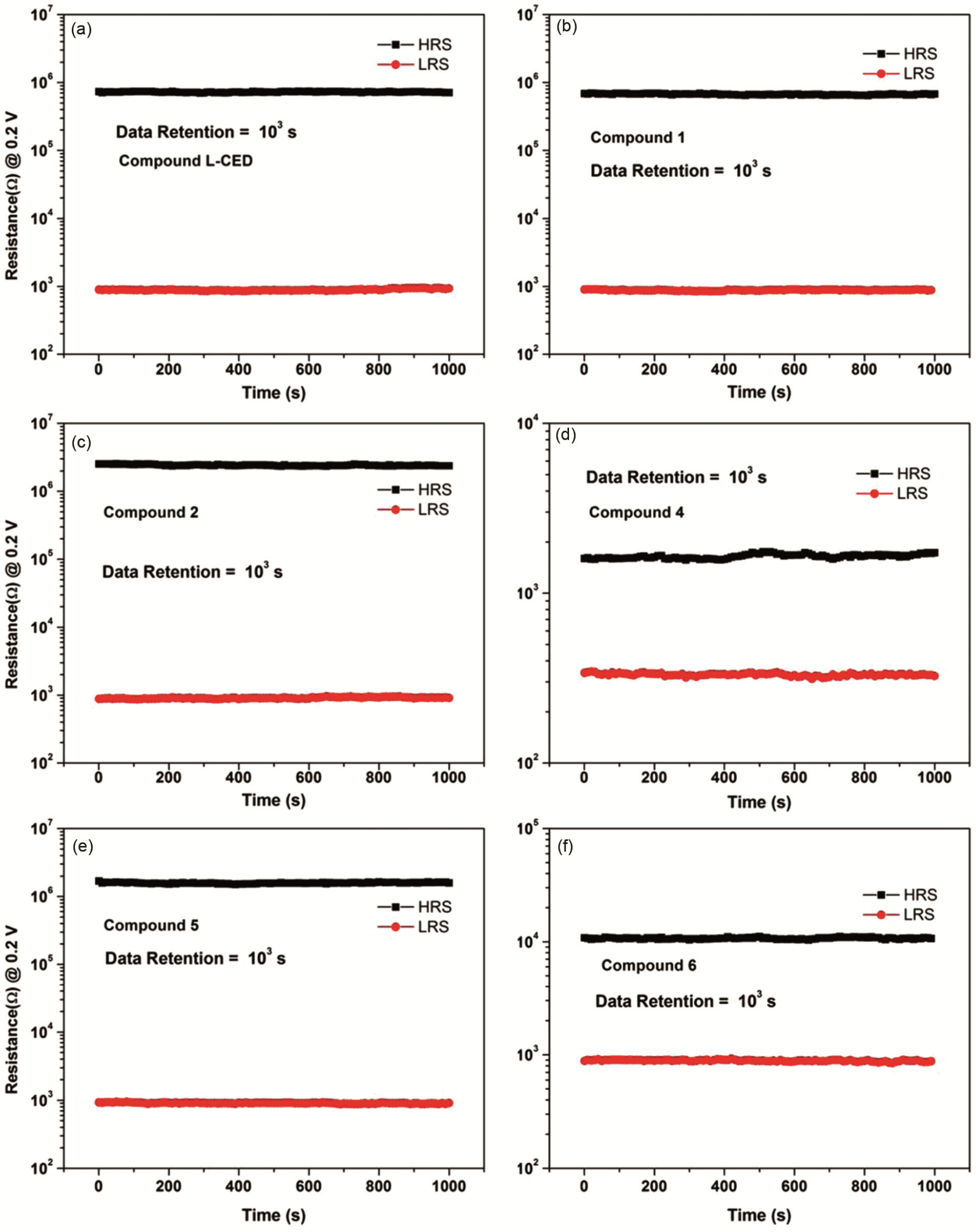


Fig. 4a-f — Data retention characteristics of **L-CED, 1**, **2**, **4**, **5**, and **6**, respectively

behaviour can retain both HRS and LRS for at least 10^3 s with a reliable memory window. Table 1 shows the various RS memory parameters devices. A thorough examination of Table 1 clearly indicates that compound **2** and **5** show superior RS memory characteristics in terms of memory window (~ 10^3). A larger memory window is desirable in RS devices as it minimizes the data read out error[46]. Moreover, a lower SET voltage is desirable for RS devices to minimize operational power consumption[47]. In the present, as observed from Table 1, the set voltage of the devices varies from 1.14 V to 3.15 V. The device with compound L-CED as an active layer has been observed to have the minimum SET voltage (1.14V) making it a suitable RS material in terms of power consumption.

Cytotoxic activities

The Fig. 5 indicates that no compound had a noteworthy effect on the A-549 lung cancer cell line at concentrations of 10 ng/mL. The cytotoxicity is significant at 500 ng/mL of each compound, although it reaches its maximum at a 0.05 level of significance. However, in contrast, when the cells were exposed to

Table 1 — Resistive switching parameters of the synthesized compounds

Compd	I-V Response	V_{SET}	Memory Window(@ 0.2V)	Retention time
L-CED	WORM	1.14 V	7.9×10^1	10^3
1	WORM	2.54 V	8×10^1	10^3
2	WORM	3.15 V	2×10^3	10^3
3	Ohmic	NA	NA	NA
4	WORM	2.5 V	4.8×10^1	10^3
5	WORM	1.4 V	1.1×10^3	10^3
6	WORM	1.25	1.4×10^1	10^3

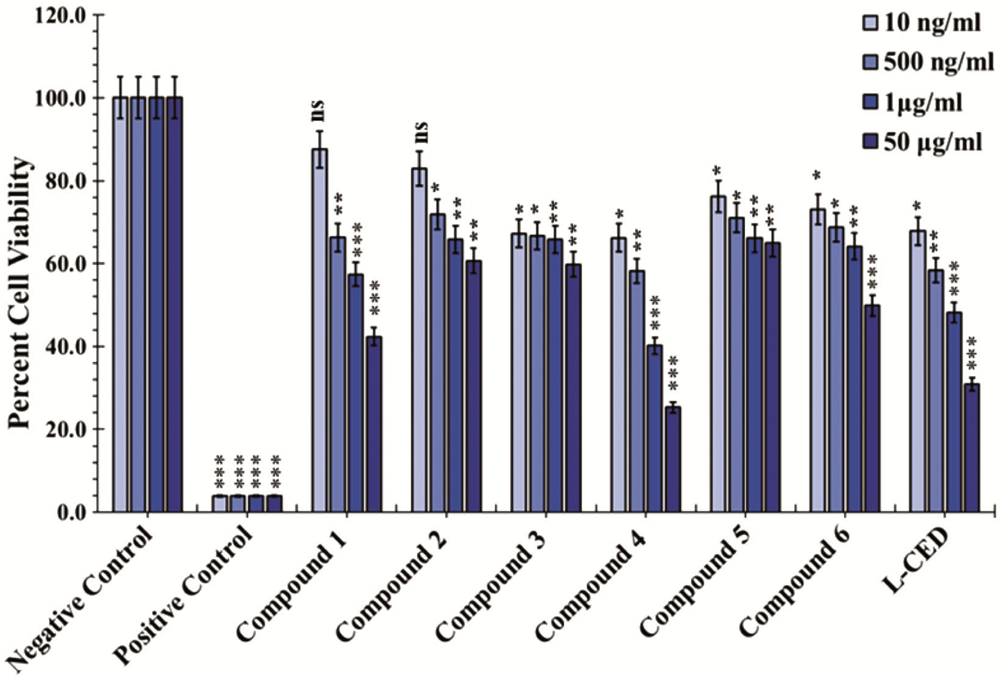


Fig. 5 — Percent cell viability of the compounds at different concentrations. Statistical significance was recognized by One way ANOVA followed by Tukey's Post. Hoc. Analysis where control has been compared to all other concentrations and detected significant values as *$p<0.05$, ** $p<0.01$, *** $p<0.001$ and ns (no significance)

a 1 µg/mL concentration, the cytotoxicity against compounds **1**, **4**, and **L-CED** was drastically altered, reaching a 0.001 level. The highest cytotoxicity has been observed for the concentration of 50 µg/mL against compound **1**, **4**, **6**, and **L-CED** at a very significant level. Compounds **1**, **4**, **6**, and **L-CED** were observed to have viable cell percentages of 44%, 26% and 52%, respectively.

Both U.S. FDA-approved medications and many biomolecules have core structures made of heterocycles based on oxygen and sulphur. Additionally, they have a broad spectrum of biological properties, for instance, anti-inflammatory and anti-cancer properties. Therefore, in the quest to find novel anticancer drugs, O- and S-containing heterocycles have drawn more interest recently. Dried oxygen and sulphur-based heterocyclic compounds have been created in several trials because combining two heterocyclic moieties may enhance a molecule's biological profile[48]. In this study, as the compounds holds sulphur as a primary ligand in their chemical assembly it might be picked up to design agents with anti-cancer activity. According to *Tanzimjahan A. Saiyed* et. al Ni(II) or Zn(II) N-methyl-phenyl dithiocarbamate substituted bipyridine adducts have been prepared by reacting the dithiocarbamate compounds through 4,4′-bipyridine, 4,4′-dimethyl-2,2-bipyridine, 4,4′-dimethoxy-2,2′-bipyridine, and 4,4′-ditertbutyl-2,2′-bipyridine, despite the compounds that showed structural analogies, no discernible trends were discovered, despite the fact that all of the biological studies that were done generally displayed a profile dependant on concentration. When compared to the standard

Table 2 — Anti-Fungal activity of the complexes **1**, **2**, **3**, **4**, **5**, **6**, $K_2(CED).H_2O$, and Griseofulvin

Material (1 mg/mL)	Minimum Inhibitory Concentration (MIC) (mg/mL)				
	Magnaporthe grisea	*Cochliobolus miyabeanus*	*Synchitrium endobioticum*	*Candida albicans*	*Trichophyton mentagrophytes*
$Ni(ophen)(CED).4H_2O$ (**1**)	12(FS)	08(FS)	11(FS)	–	04
$Ni(ophen)_2(CED)$ (**2**)	15(FC)	13(FC)	12(FS)	02	–
$Ni(ophen)_3(CED)$ (**3**)	08(FS)	09(FS)	15(FC)	05	05
$Ni(bipy)(CED).4H_2O$ (**4**)	14(FC)	14(FS)	14(FC)		–
$Ni(bipy)_2(CED)$ (**5**)	09(FS)	09(FS)	11(FS)	04	03
$Ni(bipy)_3(CED)$ (**6**)	08(FS)	14(FC)	09(FS)	–	–
$K_2(CED).H_2O$	–	–	–	–	–
Control (DMSO Solvent)	–	–	–	–	–
Standard Compound Griseofulvin (10μg/disc)	0.1	0.1	0.3	0.2	0.4

All the readings based on 5 replicates ± SEM, (–) = No anti-fungal effect. FC = Fungicidal, FS = Fungistatic

compound 5-Fluorouracil (5 FU) employed in the cytotoxic analysis, the compounds demonstrated greater action, with an IC_{50} from 0.0003-17.38 µg/mL range[49]. In a study, *Balachandran et al.* synthesized and characterized novel poly(bipyridine) ligands (bpy: 2,2′-bipyridyl) with 1-3 bipyridine ligand moieties that shown anticancer activity against the U937, Jurkat, HeLa S3, MOLT-4, and A549 cell lines. The MTT assay findings showed that the tris(bpy) and bis(bpy) ligands have strong anticancer effects on cancer cell killing[50]. As the compound contains a bipyridine molecule it could be assumed from the above studies that the formulated compound could be our chemical of interest for designing novel therapeutics against various cancer cell lines. Therefore, it may be said that the compound **4** serves maximum cytotoxic effect against A549 lung cancer cell line but the exact mechanism of action through which this compound imparts cytotoxicity is excluded as a part of present study.

Candida albicans. Notably, the CED^{2-} ligand alone showed no antifungal effect. The enhanced antifungal activity of the metal-ligand complexes is attributed to increased lipophilicity, which improves their ability to penetrate microbial membranes and inhibit growth. Metal ions bind to cell walls of microbes, troublemaking respiration and protein production, which hinders further microbial proliferation. The effectiveness of these complexes can vary depending on microbial cell impermeability or changes in ribosomal function.

Conclusions

In conclusion, the six newly synthesized nickel complexes, prepared with ligands such as *ortho*-phenanthroline, 2,2'-bipyridine, and CED^{2-} ligand, exhibited unique structural, electrochemical, and biological properties. The complexes are characterized by spectroscopic techniques such as UV-Visible and IR spectroscopy. The current-voltage (I-V) analyses of these complexes demonstrated distinct electrical behaviors, with most showing resistive switching (WORM) behavior, suggesting their potential in memory device applications. Additionally, the cytotoxicity studies revealed significant anticancer activity, particularly in compound **4**, against the A549 lung cancer cell line, although advance analysis are necessary to disclose the accurate mechanistic action. The antifungal activity of the complexes, especially against *M. grisea* and *C. miyabeanus*, highlights their potential as antifungal agents, underscoring the contribution of metal ions in enhancing the lipophilicity and biological effectiveness of these compounds. Overall, these results suggest that the synthesized nickel complexes hold promising applications in the fields of electronic memory devices, anticancer therapeutics, and antifungal treatments.

Supplementary Information

Supplementary information is available in the website http://nopr.niscpr.res.in/handle/123456789/58776.

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Conflicts of interest

The authors have reported no potential conflicts of interest.

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