Naphthoquinone based chemosensors for transition metal ions: experiment and theory†

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The synthesis and characterization of 2-((pyridine-2-yl)methy lamino)naphthalene-1,4-dione (H-1), 2-((thiophen-2-yl)methy lamino)naphthalene-1,4-dione (H-2) and 2-((pyridine/thiophen-2-yl)ethylamino)naphthalene-1,4-dione (H-3 and H-4) have been carried out. Molecular recognition abilities of these ligands toward transition metal ions in methanol, methanol–water, methanol–triethylamine or methanol–water–triethylamine mixtures, stoichiometries and association constants of H-1 and H-3 have been determined. It has been shown that H-1 and H-3 coordinate to metal ions via two nitrogen atoms and oxygen and exhibit remarkable selectivity towards Cu²⁺ ions in methanol or methanol–water mixtures, the complexation being accompanied by a color change from orange to intense blue. LOD (Limit of Detection) of Cu²⁺ with H-1, H-3 are 1.48 × 10⁻⁸ mol L⁻¹ and 1.59 × 10⁻⁸ mol L⁻¹ respectively. The vibrational spectra, ¹H NMR chemical shifts and optical properties of H-1 to H-4 derived from density functional theory are also presented.

Introduction

The α,β-unsaturated carbonyl derivatives of 1,4-naphthoquinones are of growing interest owing to their anti-cancer, antimicrobial, antifungal, antitumor and antiviral activities. Their molecular attributes, namely conjugation and electrophilicity, govern metabolic pathways and the key processes in chemotherapy that require redox cycling drugs. The underlying redox switching of such naphthoquinones, which on the acceptance of one or two electrons yield a radical anion or dianion, are thus interesting. It is further discernible to note that the intra-molecular charge transfer (ICT) transition is shown to be strongly dependent on the amine substituent and in particular, the charge density on the nitrogen center. These ligands, which serve as chemosensors, have shown remarkable molecular recognition and gave easily detectable, sensitive signals. A colorimetric and ratiometric fluorescent chemosensor combined with attributes such as high fluorescence sensitivity and aesthetic appeal of colorimetric assay makes these naphthoquinone sensors very fascinating.

Naphthoquinone based chemosensors viz., 2-((pyridin-2-yl)methy lamino)naphthalene-1,4-dione (H-1), 2-((thiophen-2-yl)methy lamino)naphthalene-1,4-dione (H-2) 2-((pyridine/thiophen-2-yl)ethylamino)naphthalene-1,4-dione (H-3 and H-4) (Fig. 1) are synthesized and characterized using FT-IR, ¹H and ¹³C NMR and single-crystal X-ray diffraction studies. The chemosensing ability of ligands with metal ions; La³⁺, Hg²⁺, Cd²⁺, Zn²⁺, Cu²⁺, Ni²⁺, Co²⁺, Mn²⁺, Cr³⁺ and Ca²⁺ in methanol, methanol–water mixture and in the presence of a mild base such as triethylamine has been evaluated. Moreover, the chemosensors H-1 and H-3 are shown to be useful for detection of different metal ions viz., Cu²⁺, Ni²⁺ and Co²⁺ revealing a color change that can be observed with the naked eye and further can be studied through the UV-visible and fluorescence experiments.

Fig. 1 Molecular structure of H-1, H-2, H-3 and H-4.
On the other hand, H-2 and H-4 do not show any chemosensing ability toward the metal ions studied herein.

**Experimental**

**Materials and methods**

1,4-napthoquinone, 2-methoxy-1,4-napthoquinone, 2-picolyl amine, 2-thiophenemethylamine, 2-(2'-aminoethyl)pyridine, 2-thiopheneethylamine from Sigma-Aldrich; CuCl$_2$·2H$_2$O, CuCl, NiCl$_2$·6H$_2$O, ZnCl$_2$, HgCl$_2$, CoCl$_2$, CaCl$_2$, triethylamine, methanol and dichloromethane from Merck chemicals; FeCl$_3$·6H$_2$O from Qualigens Chemicals, CrCl$_3$·6H$_2$O, CdSO$_4$, MnCl$_2$·4H$_2$O from Fluka; LaCl$_3$·7H$_2$O from Thomas and Baker were obtained. Milli-Q water was used for preparation of aqueous solutions. Anhydrous methanol was prepared by literature reported procedure.$^{25}$ FT-IR spectra (Fig. S1 in ESI†) were recorded between 4000 and

Fig. 2 ORTEP of H-1, H-2, H-3 and H-4. The ellipsoid was drawn with 50% probabilities.
of 2-thiophenemethylamine was added drop wise. The reaction mixture was stirred for 24 hours at room temperature (26 °C) with a constant magnetic stirring and the completion of the reaction was monitored on TLC. After 24 hours the mixture was transferred to a beaker and kept for 24 to 48 hours so that the solvent evaporates. A solid crude product was obtained by evaporation purified by column chromatography with toluene : methanol (9 : 1) as eluent. A red colored product was obtained subsequent to a slow evaporation of eluent.

**Synthesis of 2-((pyridine/thiophen-2-yl)ethylamino)naphthalene-1,4-dione (H-1 and H-4).** 1 g of 1,4-naphthoquinone

### Table 1  Single crystal X-ray data for H-1, H-3 and H-4

| Identification code | H-1 | H-3 | H-4 |
|---------------------|-----|-----|-----|
| Empirical formula   | C_{16}H_{12}N_{2}O_{2} | C_{17}H_{14}N_{2}O_{2} | C_{16}H_{13}NO_{2}S |
| Formula weight      | 264.28 | 278.3 | 283.33 |
| Temperature         | 100(2) K | 100(2) K | 100(2) K |
| Wavelength          | 0.71073 Å | 0.71073 Å | 0.71073 Å |
| Crystal system      | Monoclinic | Monoclinic | Triclinic |
| Space group         | \(P_2_1/n\) | \(P_2_1/n\) | \(P\) |
| Unit cell dimensions| \(a = 5.7063(4) Å\), \(b = 8.4245(6) Å\), \(\beta = 93.229(2)°\) |
|                      | \(c = 25.6881(19) Å\) |
|                      | \(Z = 1232.94(15) Å^3\) |
| Volume              | 4 | 4 | 4 |
| Density (calculated) | 1.424 Mg m\(^{-3}\) | 1.434 Mg m\(^{-3}\) | 1.465 Mg m\(^{-3}\) |
| Absorption coefficient | 0.096 mm\(^{-1}\) | 0.096 mm\(^{-1}\) | 0.252 mm\(^{-1}\) |
| \(f(000)\)          | 552 | 584 | 592 |
| Crystal size        | 0.34 \(\times\) 0.26 \(\times\) 0.24 mm\(^3\) | 13.000 \(\times\) 0.210 \(\times\) 0.070 mm\(^3\) | 0.41 \(\times\) 0.21 \(\times\) 0.04 mm\(^3\) |
| Theta range for data collection | 2.893 to 28.388° | 2.713 to 28.345° | 2.841 to 28.611° |
| Index ranges        | \(-7<\h<7, -11<\k<11, -34<\l<34\) |
| Reflections collected | 48104 | 5719 | 24810 |
| Independent reflections | 3076 [\(R(int) = 0.0306\)] | 3213 [\(R(int) = 0.0643\)] | 6062 [\(R(int) = 0.0553\)] |
| Completeness to theta = 25.242° | 99.90% | 99.90% | 97.60% |
| Refinement method   | Full-matrix least-squares on \(F^2\) | Full-matrix least-squares on \(F^2\) | Full-matrix least-squares on \(F^2\) |
| Data/restraints/parameters | 3076/0/181 | 3213/0/191 | 6062/0/361 |
| Goodness-of-fit on \(F^2\) | 1.032 | 1.054 | 1.155 |
| Final \(R\) indices [\(I > 2\sigma(I)\)] | \(R_1 = 0.0393\), \(wR_2 = 0.1039\) | \(R_1 = 0.0610\), \(wR_2 = 0.1054\) | \(R_1 = 0.0926\), \(wR_2 = 0.2044\) |
| \(R\) indices (all data) | \(R_1 = 0.0445\), \(wR_2 = 0.1079\) | \(R_1 = 0.0784\), \(wR_2 = 0.1114\) |
| Extinction coefficient | n/a | 0.0039(6) | n/a |
| Largest diff. peak and hole | 0.344 and \(-0.273\) e Å\(^{-3}\) | 0.440 and \(-0.361\) e Å\(^{-3}\) | 0.756 and \(-0.593\) e Å\(^{-3}\) |

**Synthesis of 2-((pyridine/thiophen-2-yl)ethylamino)naphthalene-1,4-dione (H-1 and H-4).** 1 g of 1,4-naphthoquinone
(6.32 mmol) was dissolved in 25 ml methanol and mixture stirred for about 20 min. To this solution 0.70 ml of 2-(2’-aminoethyl)-pyridine (7.1 mmol) for H-3 and 0.69 ml of 2-thiopheneethanamine (7.1 mmol) for H-4 were added drop wise. The reaction mixture was stirred for 24 hours at room temperature (26 °C) with constant magnetic stirring till completion of the reaction monitored on TLC. The reaction mixture was evaporated under the reduced pressure. The residue was column chromatographed over silica gel in methanol/toluene (1:9) solvent system. Red coloured solid products were obtained after evaporation of pure fraction from the column.

**Characterization**

2-((Pyridin-2-yl)methylamino)naphthalene-1,4-dione; H-1.

Dark red colour crystal. Yield: 0.174 g (62.14%). mp 156.42 °C.

Anal. data calcd for C16H12O2N2 (%): C, 66.89; H, 4.11; N, 10.64.

Found (%): C, 72.99; H, 4.21; N, 10.64. FT-IR (KBr, cm⁻¹): 3355, 1670, 1599, 1506, 1453, 1429, 1306, 1258, 1158, 1122, 1091, 1049, 976, 827, 778, 767, 551, 498, 460, 443. 1H NMR (DMSO-d₆, 499.81 MHz, δ (ppm)): 3.45 (t, J = 5 Hz, 2H, CH₂), 5.72 (s, 1H, Ar), 6.94 (d, J = 3.5 Hz, 1H, Ar), 7.23 (d, J = 5 Hz, 1H, Ar), 7.73 (t, J = 7.5 Hz, 1H, Ar), 7.93 (d, J = 8 Hz, 1H, Ar), 7.97 (d, J = 7.5 Hz, 1H, Ar). 13C NMR (DMSO-d₆, 125.69 MHz, δ (ppm)): 40.42, 100.67, 125.31, 125.33, 125.86, 126.10, 126.75, 130.32, 132.27, 132.87, 134.82, 140.38, 148.00, 181.48, 181.53. UV-vis, (λmax, methanol (nm)): 448.

X-ray crystal structures

X-ray data for H-1, H-3 and H-4 were collected on D8 Venture PHOTON 100 CMOS diffractometer using graphite monochromated Mo-Kz radiation (λ = 0.7107 Å) with exposure/frame = 10 s. The X-ray generator was operated at 50 kV and 30 mA. An initial set of cell constants and an orientation matrix were calculated from total 24 frames. The optimized strategy used for data collection included different sets of ϕ and ω scans with 0.5° steps in ϕ/ω. Crystal to detector distance was 5.00 cm with 512 × 512 pixels/frame, oscillation/frame = 0.5°, maximum detector swing angle = 30.0°, beam centre = (260.2, 252.5), in plane spot width = 1.24. Data integration was carried out by Bruker SAINT program and empirical absorption correction for intensity data were carried out using the Bruker SADABS. The programs are integrated in APEX II package. The data were corrected for Lorentz and polarization effect. The structure was solved by direct method using the SHELX-97 (ref. 27) with the final refinement of the structure performed by a full-matrix least-squares technique with anisotropic thermal data for non-hydrogen atoms on F². The non-hydrogen atoms were refined anisotropically where the hydrogen atoms were refined at the calculated positions as riding atoms with isotropic displacement parameters. Molecular diagrams were generated using the ORTEP-3 (ref 28) and Mercury programs. Structural calculations were performed using SHELXTL and PLATON.

Metal ion binding studies, job plot, competitive binding studies, pH studies and limit of detection (LOD) experiments

Metal ion binding studies were evaluated by following methods, (i) in methanol, (ii) in 1:1 methanol–water, (iii) in presence of triethylamine in (i) and (ii). In typical experiments 2 ml of H-1 and H-3 was mixed with 2 ml of metal ion solutions at room temperature (26 °C). 1 ml of triethylamine was added in chemosensor solution in case of (i) and (ii) prior to addition of metal ion solutions. UV-visible and fluorescence spectra of all solutions were measured; the concentration of ~2.5 × 10⁻⁴ M was used.

Micromolar concentration (100–100 μM) of H-1, H-3 and metal ions was used for Jobs plot experiment. Solutions were prepared...
by varying concentration of ligands and metal ions. Binding constant of Cu$_2^+$ and Ni$_2^+$ was determined by Stern–Volmer plot. 5 x 10$^{-4}$ M solution of chemosensor and 1 x 10$^{-3}$ M metal ion solutions in methanol were used to obtained the same.

For competitive binding of metal ions (5 x 10$^{-3}$ M) with H-1 and H-3 (5 x 10$^{-3}$ M) equal volumes were mixed and fluorescence spectra of all solutions were measured.

For quantum yield experiment fluorescence is used as standard. Fluorescence (1 x 10$^{-6}$ M), H-1 and H-3 (1 x 10$^{-6}$ M) concentration is used. 0.1 M NaOH was used for the deprotonation of fluorescence.

In pH dependent metal ion binding studies experiments, 2 ml of chemosensor H-1 and H-3 was mixed with 2 ml of metal ion solutions (Cu$^{2+}$, Ni$^{2+}$, Zn$^{2+}$ and Co$^{2+}$) at room temperature (26 °C). 2 ml of buffer solution at pH 4, pH 7 and pH 9 was added respectively prior to addition of metal ion solutions. UV-visible spectra of all solutions were measured.

Micromolar concentrations (10 to 100 µM) of H-1, H-3 and Cu$^{2+}$ metal ions were used for LOD experiments. Solutions were prepared by varying concentrations of H-1, H-3 and Cu$^{2+}$ metal ions.

**Computational methodology**

Optimizations of naphthoquinone derivatives were carried out using the GAUSSIAN-09 program.$^{32}$ Global hybrid meta GGA (M06-2X) functional was used in conjunction with the internally stored 6-311+G(d,p) basis set. Stationary point structures thus obtained were confirmed to be the local minima on the potential energy surfaces through vibrational frequency calculations. Frontier orbitals were derived in the same framework of theory. Electronic spectra were computed using the time dependent density functional theory (TD-DFT).

**Results and discussion**

**Synthesis and characterization of H-1, H-2, H-3 and H-4**

Chemosensor H-1, H-2, H-3 and H-4 were synthesized and obtained in high yields at the room temperature (26 °C) without

**Table 2 Hydrogen bonding geometries of H-1, H-3 and H-4**

| Compound | D···H···A (Å) | D···H (Å) | H···A (Å) | D···A (Å) | D···H···A (°) | Symmetry |
|----------|---------------|---------|----------|---------|-------------|---------|
| H-1  | N(1)···H(1)···O(1) | 0.8797 | 2.3087(8) | 2.672(1) | 104.79 | Intramolecular |
|       | C(15)···H(15)···O(1) | 0.949(1) | 2.5782(8) | 3.363(1) | 140.27(6) | 2 – x, 1 – y, – z |
|       | C(16)···H(16)···N(2) | 0.950(1) | 2.539(1) | 3.391(1) | 146.41(7) | 2 – x, 1 – y, – z |
|       | C(13)···H(13)···O(2) | 0.950(1) | 2.3931(8) | 3.166(1) | 145.14(7) | – x, – y, – z |
|       | C(14)···C(3) | | 3.398(2) | | |
|       | C(4)···O(1) | | 3.216(1) | | |
|       | C(5)···O(2) | | 3.065(1) | | |
| H-3  | N(1)···H(1)···O(1) | 0.88 | 2.252 | 3.099(1) | 161.65 | Intramolecular |
|       | N(1)···H(1)···O(1) | 0.88 | 2.302 | 2.667(2) | 104.91 | Intramolecular |
|       | C(3)···H(3)···O(2) | 0.951 | 2.511 | 3.446(2) | 168.1(3) | 2 – x, – y, 2 – z |
|       | C(14)···H(14)···O(2) | 0.949 | 2.633 | 3.562(2) | 167 | 2 – x, – y, 2 – z |
|       | C(11)···H(11B)···O(2) | 0.989 | 2.717 | 3.346(2) | 121.84 | 2 – x, – y, 2 – z |
|       | C(12)···H(12A)···O(1) | 0.99 | 2.658 | 3.211(2) | 115.5 | – x, – y, 1 – z |
|       | C(12)···H(12B)···O(2) | 0.99 | 2.624 | 3.421(2) | 137.64 | 1 – x, – y, 2 – z |
|       | C(11)···H(11A)···C(8) | 0.99 | 2.807 | 3.476(2) | 125.4 | 1 – x, – y, 2 – z |
|       | C(11)···H(11B)···C(3) | 0.989 | 2.789 | 3.650(2) | 145.7 | 1 – x, – y, 2 – z |
|       | C(4)···O(1) | | 3.167(2) | | |
|       | C(1)···O(2) | | 3.141(7) | | |
|       | C(1)···N(1) | | 3.223(2) | | |
|       | C(13)···C(7) | | 3.384(2) | | |
| H-4  | N(1)···H(1)···O(1) | 0.880(4) | 2.258(3) | 3.104(5) | 161.4(3) | Intramolecular |
|       | N(1A)···H(1A)···O(1A) | 0.880(4) | 2.280(3) | 3.121(5) | 159.7(3) | 2 – x, – y, 1 – z |
|       | N(1)···H(1)···O(1) | 0.88 | 2.307 | 2.670(5) | 104.8 | Intramolecular |
|       | C(3)···H(3)···O(2) | 0.950(5) | 2.649(3) | 3.584(6) | 168.3(3) | 3 – x, 1 – y, 2 – z |
|       | C(13)···H(13A)···O(2A) | 0.951(5) | 2.607(3) | 3.545(6) | 168.9(3) | 3 – x, 1 – y, 2 – z |
|       | C(14)···H(14)···O(2) | 0.950(5) | 2.504(3) | 3.440(6) | 168.2(3) | – x, – y, – z |
|       | C(16)···H(16)···S(1A) | 0.949(5) | 2.951(3) | 3.681(5) | 134.7(3) | 3 – x, – y, 1 – z |
|       | C(14A)···H(14A)···O(2A) | 0.950(5) | 2.508(3) | 3.445(6) | 168.5(3) | 3 – x, – y, 1 – z |
|       | C(7)···C(13) | | 3.387(7) | | |
|       | N(1)···C(1) | | 3.244(7) | | |
|       | N(1A)···C(1A) | | 3.240(7) | | |
using any exhaustive synthetic procedures. H-1, H-2, H-3 and H-4 were characterized by FT-IR (Fig. S1 ESI†), \(^1\)H and \(^{13}\)C NMR (Fig. S2 through Fig. S5 in ESI†), elemental analysis, UV-visible spectroscopy and single crystal X-ray diffraction studies. Melting point of chemosensor ligands were obtained by Differential Scanning Calorimetry (DSC) (Fig. S6 in ESI†). FT-IR spectra of the ligands reveals characteristic N-H stretching observed at the 3355 cm\(^{-1}\) (H-1), 3354 cm\(^{-1}\) (H-2), 3336 cm\(^{-1}\) (H-3) and 3338 cm\(^{-1}\) (H-4). The carbonyl frequency was assigned to the ~1672 cm\(^{-1}\) in H-1 and H-3, 1670 cm\(^{-1}\) in H-2 and ~1669 cm\(^{-1}\) in H-4. The C-S frequency was observed in the range ~1467 cm\(^{-1}\) (in H-3) to 1432 cm\(^{-1}\) (in H-1).

ORTEP of H-1, H-3 and H-4 are shown in Fig. 2 and crystallography data have been summarized in Table 1. H-1 and H-3 shows the monoclinic space group while H-4 shows triclinic space group. The carbonyl bond distances (1.21 Å and 1.23 Å) in these compounds resemble to those observed in the oxidized form of compounds. The bond distances represent quinonoid distortion with two short and four long C-C bonds. The carbonyl C(1)-O(1) and C(4)-O(2) bond distances are found to be 1.220 Å and 1.234 Å, respectively. The C(2)-N(1) bond distances (1.335 Å) match well with those of amino derivatives of 1,4-naphthoquinone.\(^{33-38}\)

As may readily be noticed, H-1 shows naphthoquinone and pyridyl rings to be coplanar (Fig. S7 in ESI†) in and render inter- as well as the intra-molecular N-H···O hydrogen bonding which arise from quinonoid oxygen (Table 2).

Two molecules of H-1 oriented in the opposite directions orientations which facilitate further intermolecular C-H···N (C(16)-H(16)···N(2)) and C-H···O(C(15)-H(15)···O(1)) hydrogen bonding. Subsequently the dimeric units are linked by the C-H···O (C(13)-H(13)···O(2)) interactions along a polymeric chain down a-axis (cf. Fig. 3 and 4) facilitate C-H···π interactions between the alkyl proton C(11)-H(11B) and quinonoid ring; with the corresponding distance being 3.231 Å. Benzenoid carbon C(5) in close contact with neighbouring molecules pyridine ring carbon C(14) (3.398(2) Å, (1 - x, -y, -z) (cf. Fig. 5); the C(4)···O(1) (1 + x, y, z) separation of neighbouring molecules was 3.216 Å.

The mutual orientation of pyridyl ring with naphthoquinone show a marginal deviation (Fig. S8 in ESI†) from the planarity as adjudged from the C(11)-N(1)-C(2)-C(1) dihedral angle parameters. A bidentate coordination of H-3 ligand with the metal ions is favoured; as inferred earlier in ref. 39-41.

As far as H-3 is concerned the opposite orientation was noticed (with respect pyridine ring) with a polymeric chain therein extending from one end by N(1)-H(1)···O(1) and C(12)-H(12A)···O(1), C(3)-H(3)···O(2), C(12)-H(12B)···O(2) and C(14)-H(14)···O(2) hydrogen bonding interactions, which are depicted in Fig. 6 and 7. Furthermore the polymeric chain brings about C-H···π, C···C(C(7)···C(13)), C···N (C(1)-N(1)) and C···O(C(4)···O(4)) stacking interactions as shown in Fig. 8. Besides the C-H···π interactions from ethyl protons and C(11)-(11A) of
Sensing metal ion binding of H-1 and H-3

No significant colour change was observed in metal ions binding studies experiments of H-2 and H-4. The metal ion binding studies thus focuses on H-1 and H-3 ligands. Metal ion binding studies were carried out (i) in methanol (ii) in methanol–water, (iii) in presence of mild base triethylamine (TEA) in (i) and (ii) conditions. TEA was used for deprotonation of ligand for detection of metal ions.

Equal volumes of (2.5 x 10^{-4} M) of different metal ion solutions were mixed with H-1 and H-3 in methanol at room temperature (26 °C). A color change from orange to grey was noticed only for Cu+, Cu2+, Ni2+, Zn2+ and Co2+ ions which is accompanied by an emergence of a new band in ~500–700 nm region (Fig. 13d and Fig. S9d in ESI†).

Interestingly H-3 only shows color change with Cu+ and Cu2+ in methanol as can readily be noticed from Fig. 12a, subsequent addition of triethylamine led to binding with Cu+, Cu2+, Ni2+ and Co2+ ions concomitantly bringing about the color change for H-3 as evident from Fig. 12b (and also Fig. S9 shown in ESI†).

Fig. 11c displays H-1 in the 1 : 1 mixture of methanol–water. Here the color change from yellow to grey was noticed only for the Cu2+. No color change was observed for the rest of the metal ions studied. In other words, H-1 selectively detects Cu2+ ion in methanol–water solvent mixture with the naked eye. Similar inferences are drawn for the H-3 ligand shown in Fig. 12c.

As inferred from Fig. 11d and 12d; H-1 and H-3 do not show any noticeable color change for triethylamine and methanol–water solvent mixtures. On addition of Ni2+ and Zn2+ solution the UV-visible spectra emerge with new bands near λ_{max} 340 nm and 360 nm displayed in Fig. 13d and Fig. S9d in ESI†.

Competitive binding, pH dependent binding studies and detection limit of H-1 and H-3

The stoichiometry of H-1 (Fig. S10 through Fig. S12 in ESI†) and H-3 (Fig. S14 through Fig. S16 in ESI†) for Cu2+, Ni2+ was determined by the Job’s plot method. As illustrated H-1 with Cu2+ showed 1 : 1 stoichiometry in methanol as well as methanol–water mixtures, whereas the 2 : 1 stoichiometry was suggested for the Ni2+ in methanol (Fig. S10 in ESI†). Besides Cu2+ in methanol–water–triethylamine mixture (Fig. S11 in ESI†) revealed 2 : 1 stoichiometry. Likewise the H-3 on combining with
Cu\(^{2+}\) in methanol, methanol–triethylamine and methanol–water solvent mixture the stoichiometry was shown to be in 1:1 proportions. H-1 and H-3 ligands coordinating in tridentate manner with two nitrogen and a quinonoid oxygen bound to metal ions. The tetrahedral 1:1 complex Cu\(^{2+}\) and 1:2 octahedral complex of Ni\(^{2+}\) was proposed for such type of ligands.\(^{30,41}\)

Association constant of Cu\(^{2+}\) ion was determined using the Stern–Volmer plots from fluorescence experiments (Fig. S13 for H-1 and Fig. S17 for H-3) in ESI†. The concentrations of H-1 or H-3 used were 5 × 10\(^{-4}\) M and that for the metal being 1 × 10\(^{-3}\) M. The methanol solutions were used. The association constants (K\(a\)) for H-1 turned out to be 4932 M\(^{-1}\) for Cu\(^{2+}\) whereas that for the Ni\(^{2+}\) was 1542 M\(^{-1}\) (Fig. S13a and b in ESI†). Likewise the association constants (K\(a\)) for H-3 were observed to be 938.9 M\(^{-1}\) and 790.7 M\(^{-1}\) respectively, for Cu\(^{2+}\) and Ni\(^{2+}\).

A competitive binding of metal ions was further studied through experiments in which equal volumes of H-1 and H-3 (1 × 10\(^{-4}\) M) were mixed with those of Cu\(^{2+}\), Ni\(^{2+}\) and Co\(^{2+}\) (1 × 10\(^{-3}\) M). Noticeable colour changes can be noticed in solution mixture of metal ions (Fig. 14 and S18 in ESI†) for H-1 and H-3. UV-visible (Fig. S19 in ESI†) and fluorescence spectra of selected metal ion are displayed in Fig. 15. Ligands H-1 and H-3 are fluorescent and showed low quantum yields of 0.99% and 1.89%, respectively. Noteworthy enough, Cu\(^{2+}\) demonstrate significant fluorescence quenching for H-1 and H-3. The experiments further showed Ni\(^{2+}\) and Co\(^{2+}\) bring about competitive binding to H-1 and H-3 however Cu\(^{2+}\) prevailing over other metal ions which is in accordance with its large binding constant.

pH dependent metal ion binding experiments of H-1 and H-3 were carried out on metal ions Zn\(^{2+}\), Cu\(^{2+}\), Ni\(^{2+}\) and Co\(^{2+}\) in buffer solution of pH 4, 7 and 9. The metal ion binding was observed only in the basic pH (Fig. S20 in ESI†) and not for pH = 4.

The limit of detection (LOD) from the fluorescence experiments\(^{30,41}\) with Cu\(^{2+}\) and H-1 or H-3 ligands are observed to be 1.48 × 10\(^{-8}\) mol L\(^{-1}\) for H-1 (Fig. S21 in ESI†) and 1.59 × 10\(^{-8}\) mol L\(^{-1}\) (Fig. S22 in ESI†) for H-3.
DFT investigations

Optimized structures of aminonaphthoquinone derivatives obtained from the M06-2X based density functional theory are depicted in Fig. 16. Selected bond distances and angles are compared with X-ray crystal data in Table 3. As shown the overall structural parameters agree well with the experiments. A comparison of H-1 and H-2 shows that carbonyl C(1)O(1) bond distances are marginally elongated on substitution of thiophene instead of pyridine.

Structural ramifications in vibration frequencies are analyzed. Calculated vibrational frequencies of H-1, H-2, H-3 and H-4 are compared with the experiment in Table 4. As may be inferred the N–H stretching assigned to 3247 cm⁻¹ of H-1 engenders the frequency up shift of ~42 cm⁻¹ for the ethyl substituted H-3. As oppose to this in case of thiophene on substitution of the ethyl functionality engender the lowering of...
frequency from 3311 cm\(^{-1}\) (H-2) to 3285 cm\(^{-1}\) (H-4). The inferences borne out from DFT are thus in consonance with the experiment.

1H-NMR chemical shifts (\(\delta_\text{H}\)) in H-1, H-2, H-3 and H-4 in DMSO (as solvent) were simulated through the SCRF-PCM theory. A comparison with the experiment is given in Table 5. The H(1) proton participating in N–H/O and N–H/N interactions in H-1 emerge with relatively large deshielding (8.1 ppm) in the spectra. The signals of the corresponding proton in the rest of aminonaphthoquinone derivatives facilitate the N–H/O interactions and appear at 6.5 ppm. The alkyl protons emerge with up-field \(\delta_\text{H}\) signals in the calculated 1H NMR. These inferences on the calculated \(\delta_\text{H}\) values concur with the experiment.

### Table 3

| Bond Distance (Å) | H-1 | H-2 | H-3 | H-4 |
|-------------------|-----|-----|-----|-----|
| C=O1              | 1.209 | 1.219 | 1.210 | 1.220 |
| C=O2              | 1.217 | 1.234 | 1.216 | 1.237 |
| C3–H3             | 1.083 | 0.950 | 1.083 | 0.950 |
| N1–H1             | 1.015 | 0.880 | 1.012 | 0.880 |

### Table 4

| Vibrational Frequency (cm\(^{-1}\)) | H-1 | H-2 | H-3 | H-4 |
|------------------------------------|-----|-----|-----|-----|
| \(\nu(N1–H1)\)                     | 3247 | 3355 | 3311 | 3354 |
| \(\nu(C3–H3)\)                     | 2936 | 3061 | 2926 | 3061 |
| \(\nu(C=O1)\)                      | 1650 | 1672 | 1645 | 1670 |
| \(\nu(C=O2)\)                      | 1610 | 1632 | 1620 | 1617 |
| \(\nu(C=\ C)\)                     | 1541 | 1593 | 1541 | 1599 |

### Table 5

| 1H Chemical Shift (ppm) | H-1 | H-2 | H-3 | H-4 |
|-------------------------|-----|-----|-----|-----|
| H1                      | 8.1 | 8.08 | 6.5 | 8.11 |
| H3                      | 6.2 | 5.59 | 6.1 | 5.74 |
| H5                      | 8.4 | 7.90 | 9.0 | 7.90 |
| H6                      | 9.0 | 7.81 | 8.6 | 7.80 |
| H7                      | 8.6 | 7.77 | 8.5 | 7.71 |
| H9                      | 9.4 | 8.00 | 9.1 | 7.97 |
| H11                     | 4.6 | 4.52 | 4.9 | 4.61 |
| H13                     | 8.3 | 7.37 | 7.7 | 7.10 |
| H14                     | 8.5 | 7.73 | 7.7 | 6.97 |
| H15                     | 8.0 | 7.30 | 8.1 | 7.40 |
| H16                     | 9.7 | 8.55 | 9.6 | 8.51 |
| H17                     | 3.6 | 3.04 | 3.4 | 3.12 |

**Fig. 16** Optimized geometries of (a) H-1, (b) H-2, (c) H-3 and (d) H-4.

**Fig. 17** Frontier molecular orbitals of (a) H-1, (b) H-2, (c) H-3 and (d) H-4.
The molecular Frontier orbital’s HOMO and LUMO (isosurface of ±0.04 au) in aminonaphthoquinone ligands are portrayed in Fig. 17. The complimentarily of charge distributions between HOMO and LUMO is thus transparent. The electronic absorption spectra except H-4 revealed the band near \(\sim 336\) nm assigned to the HOMO to LUMO transition. The HOMO–LUMO energies, global indices of reactivity, namely, chemical potential (\(\mu\)), hardness (\(\eta\)), and electrophilicity index (\(\omega\)), are summarized in Table 6.

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Table 6  HOMO, LUMO gap (in eV) and global indices in H-1, H-2, H-3 and H-4

| Molecular properties | H-1 | H-2 | H-3 | H-4 |
|----------------------|-----|-----|-----|-----|
| \(\Delta E_{\text{HOMO-LUMO}}\) | 5.6 | 5.6 | 5.7 | 5.6 |
| Global hardness (\(\eta\)) | 2.8 | 2.8 | 2.9 | 2.8 |
| Electronic chemical potential (\(\mu\)) | 4.7 | 4.9 | 4.9 | 4.9 |
| Electronegativity (\(\chi\)) | 4.7 | 4.9 | 4.9 | 4.9 |
| Global electrophilicity index (\(\omega\)) | 4.0 | 4.3 | 4.3 | 4.3 |

Conclusions

Naphthoquinone based chemosensors are characterized from the X-ray diffraction and spectroscopy experiments in conjunction with the density functional theory. X-ray diffraction experiments revealed the C-H–π interactions in molecular packing those bring about a variation in their optical properties. The metal ion binding of H-1 and H-3 in methanol, methanol–water mixture and in the presence of mild base triethylamine were examined. The binding of H-1 and H-3 with Cu\(^{2+}\) revealed 1 : 1 stoichiometry in methanol water mixture compared to that of Ni\(^{2+}\) which was 1 : 2 proportions when the methanol or methanol–triethylamine mixture were used. The association constant of Cu\(^{2+}\) with H-1 was observed to be \(\sim 5.2\) times as larger than that for the H-3. Secondly, the ligands H-1 and H-3 display remarkable recognition ability toward the Cu\(^{2+}\), Ni\(^{2+}\), Co\(^{2+}\) ions in methanol. Both ligands showed remarkable selectivity in the detection of Cu\(^{2+}\) in methanol/H\(_2\)O solution. The experimental investigations further were corroborated through the inferences drawn based on the \(^1\)H NMR and infrared spectra derived from the density functional theory.

Conflicts of interest

There are no conflicts to declare.

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