Supplementary material for

Selective fluorescence sensing of Cu(II) and Zn(II) using a Schiff base-derived new model compound: Naked eye detection and spectral deciphering of the mechanism of sensory action

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1. Synthesis of 2BIMN1O.

The detailed stepwise synthetic procedure for 2BIMN1O is given below [1,2].

STEP-1: Synthesis of 1-methoxy-naphthalene-2-carboxylic acid methyl ester.

The suspension of 1-hydroxy-naphthalene-2-carboxylic acid (25g, 133 mmol), potassium carbonate (55 g, 399 mmol), and methyl iodide (76g, 532 mmol) in acetone (600 ml) were refluxed for 18 h. After completion of reaction, the reaction mixture was cooled at room temperature. The solid material was filtered off. The filtrate was concentrated; work up with ethyl acetate (500 ml), washed with aqueous $NaHCO_3$ solution, dried, concentrated to afford 1-methoxy-naphthalene-2-carboxylic acid methyl ester (27 g, 95%). ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 3.93 (s, 3H), 3.99 (s, 3H), 7.19 (s, 1H), 7.36 (m, 1H), 7.50 (m, 1H), 7.72 (d, J = 6.2 Hz, 1H), 7.80 (d, J = 6.2 Hz, 1H), 8.29 (s, 1H).

STEP-2: Synthesis of (1-methoxy-naphthalen-2- yl)-methanol.

The solution of ester (20g, 93 mmol) in THF (100 ml) was added to the suspension of $LiAlH_4$ (5.1 g, 139 mmol) at 0 ^{o}C. Then reaction mixture was stirred at room temperature for 1 h and then refluxed for 3 h. After cooling, the reaction mixture was quenched with water (5.1 ml, 15% aqueous NaOH solution (5.1 ml) and water (10.2 ml) respectively at 0^{o}C. After quenching, the reaction mixture was stirred at room temperature 6h and settle. The reaction mixture was filtered through celite powder and the filtrate was concentrated to afford (1-methoxy-naphthalen-2-yl)-methanol (15.5 g, 90%). ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 3.97 (s, 3H), 4.82 (s, 2H), 7.12 (s, 1H), 7.34 (m, 1H), 7.42 (m 1H), 7.73 (m, 3H).

STEP-3: Synthesis of 1-methoxy-2-naphthaldehyde.

PCC (19 g, 88 mmol) with celite powder was added to the (1-methoxy-naphthalen-2-yl)-methanol (15 g, 80 mmol) in DCM (500 ml) at room temperature. The reaction mixture was stirred at room temperature for 1 h. Solid material was filtered off. The filtrate was concentrated, chromatographed (silica gel 100-200 mesh, 15% ethyl acetate-hexane) affording 1-methoxy- 2-naphthaldehyde (11g, 75%). ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 4.02 (s, 3H), 7.18 (s, 1H), 7.37 (m, 1H), 7.53 (m, 1H), 7.73 (d, J = 8.3 Hz, 1H), 7.87 (d, J = 8.3 Hz, 1H), 8.35 (s, 1H), 10.56 (s, 1H).

STEP-4: Synthesis of 1-hydroxy- 2naphthaldehyde (HN12).

A suspension of anhydrous $AlCl_3$ (2 g, powder) in DCM (10 ml) was stirred at room temperature for 2 h. The 1-methoxy- 2-naphthaldehyde (1 g) in DCM (10 ml) was added and stirred for 2 h. The mixture was poured in dilute HCl and extracted with chloroform. The organic layer was concentrated and purified on column chromatography over silica gel in 15% ethyl acetate / hexane to give the 1-hydroxy- 2-naphthaldehyde (0.8 g, 90%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.36 (d, J = 8.1 Hz), 7.47 (d, J = 8.6 Hz, 1H), 7.54 (m, 1H), 7.64 (m, 1H), 7.77 (d, 8.1 Hz, 1H), 8.42 (m, 1H), 9.95 (s, 1H), 12.66 (s, 1H)].

STEP-5: Synthesis of 2-((benzylimino)-methyl)-naphthalen-1-ol (2BIMN1O).

1-hydroxy- 2-naphthaldehyde (1 eqv.) and benzylamine (1 eqv.) in ethanol was refluxed for 2 h in presence of catalytic amount of acetic acid. Then the reaction mixture was cooled down for getting crystal of 2BIMN1O and then filtered and washed with cold ethanol solvent. The compound was repeatedly crystallized before use. The purity of the final product was also established on TLC plate.

The ^{1}H-NMR, ^{13}C-NMR, DEPT and TOF-MS spectra of 2BIMN1O are displayed below (Figure S1 and S2) along with the assignments of the bands.

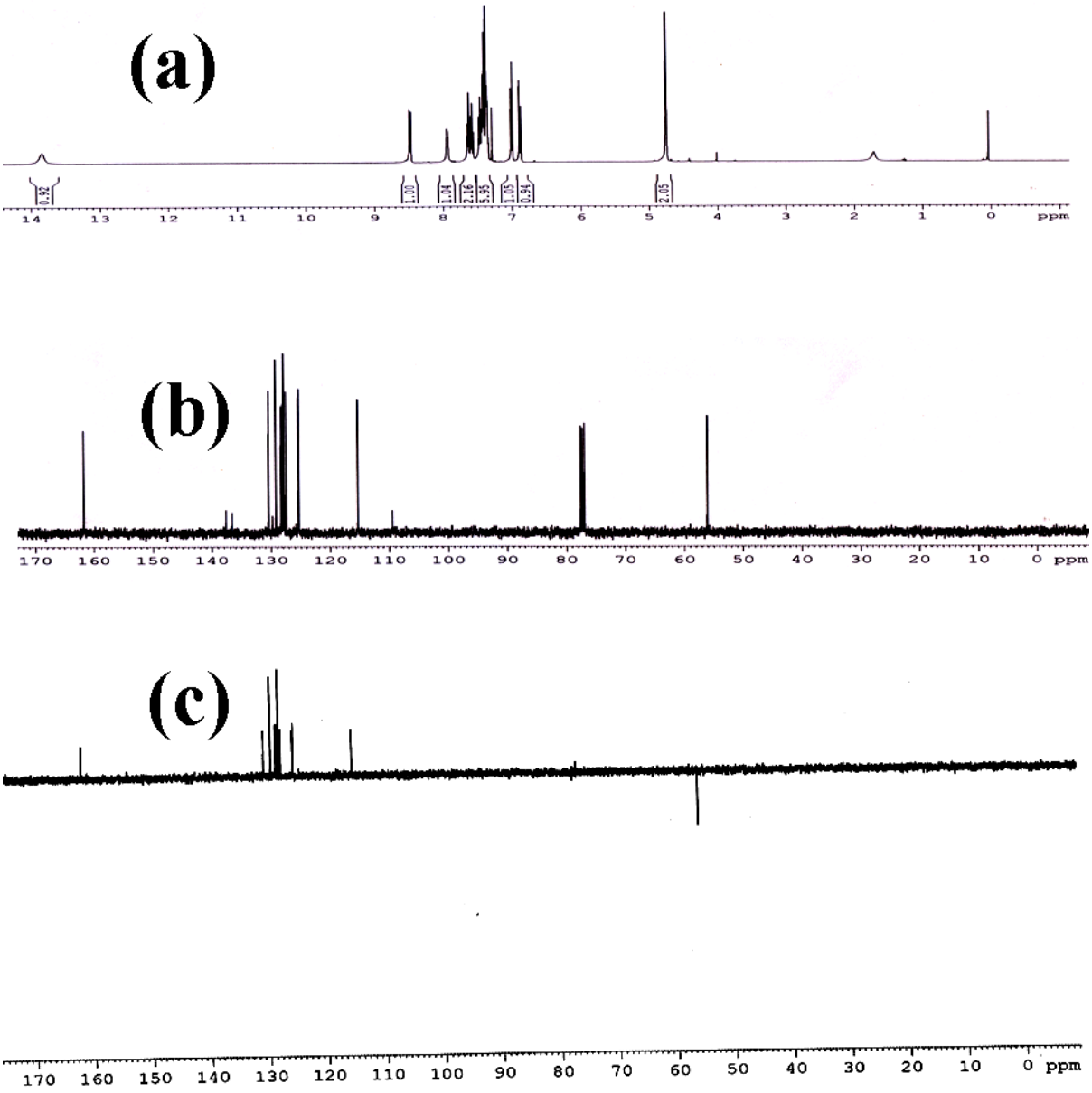


Figure S1: (a) ^{1}H-NMR, (b) ^{13}C-NMR and (c) DEPT spectra of 2BIMN1O

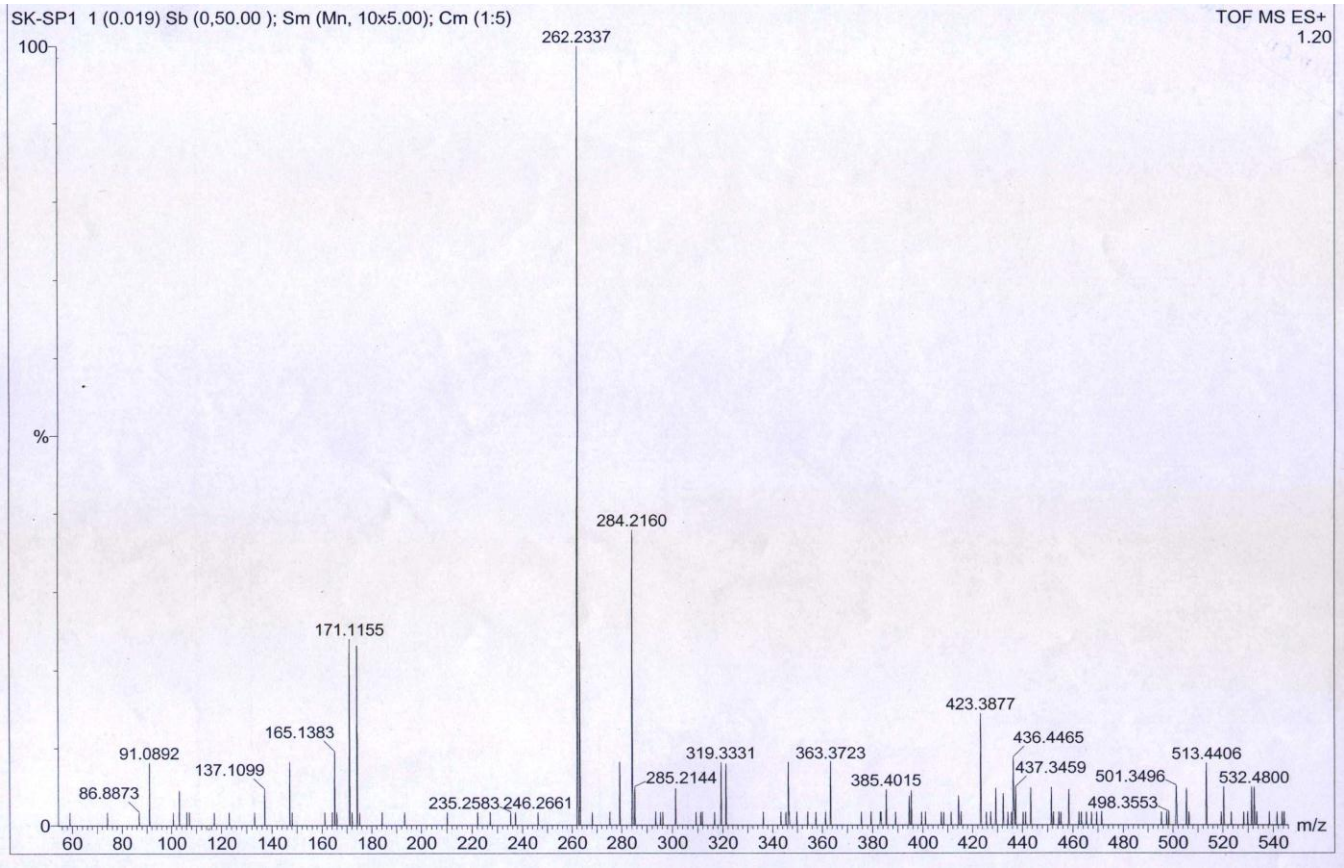
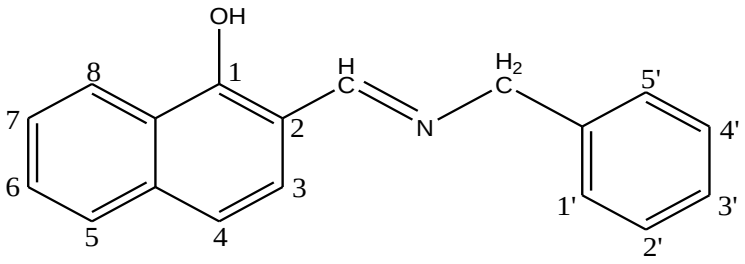


Figure S2: Time of Flight-mass spectra (ESI) of 2BIMN1O



2BIMN1O

^{1}H-NMR (300 MHz, $CDCl_3$) δ: 13.83 (1H, OH), 8.35 (1H, d, J = 8.4 Hz, C_8-H), 7.93 (1H, s, C<u>H</u>=N), 7.55 – 7.64 (2H, m, Ar-H), 7.00 – 7.47 (6H, m, Ar-H), 6.86-7.00 [2H, dd, J = 8.8 Hz, 6.8 Hz, (C_6-H, C_7-H)], 4.67 (2H, s, Ar-C<u>H</u>$_2$-).

^{13}C-NMR (300 MHz, $CDCl_3$) δ: 56.10, 115.32, 125.33, 125.45, 127.49, 127.86, 128.03, 128.32, 129.22, 129.8, 130.42, 161.75.

FT-IR (KBr) $\bar{V}$ (cm^{-1}): 793, 1004, 1030, 1140, 1197, 1251, 1290, 1366, 1449, 1542, 1604, 1641, 1929, 3047.

TOF-MS (m/z): 262.233 (Molecular ion peak, $M+H^+$, calculated molecular weight: 261.12 *vide* Scheme 1 in the main text).

2. Fl. excitation spectra of 2BIMN1O in various solvents

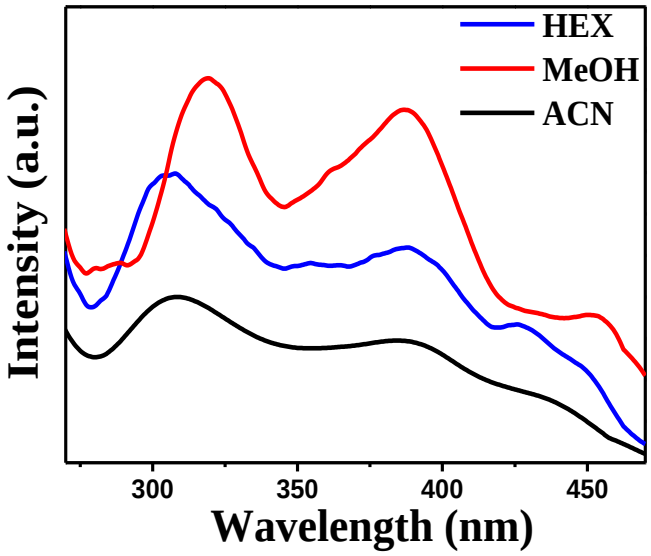


Figure S3: Excitation ($\lambda_{monitored} = \lambda_{em}^{max}$) spectral profile of 2BIMN1O in various solvents as specified in the figure legend.

3. Effect of base on absorption and emission spectra of 2BIMN1O

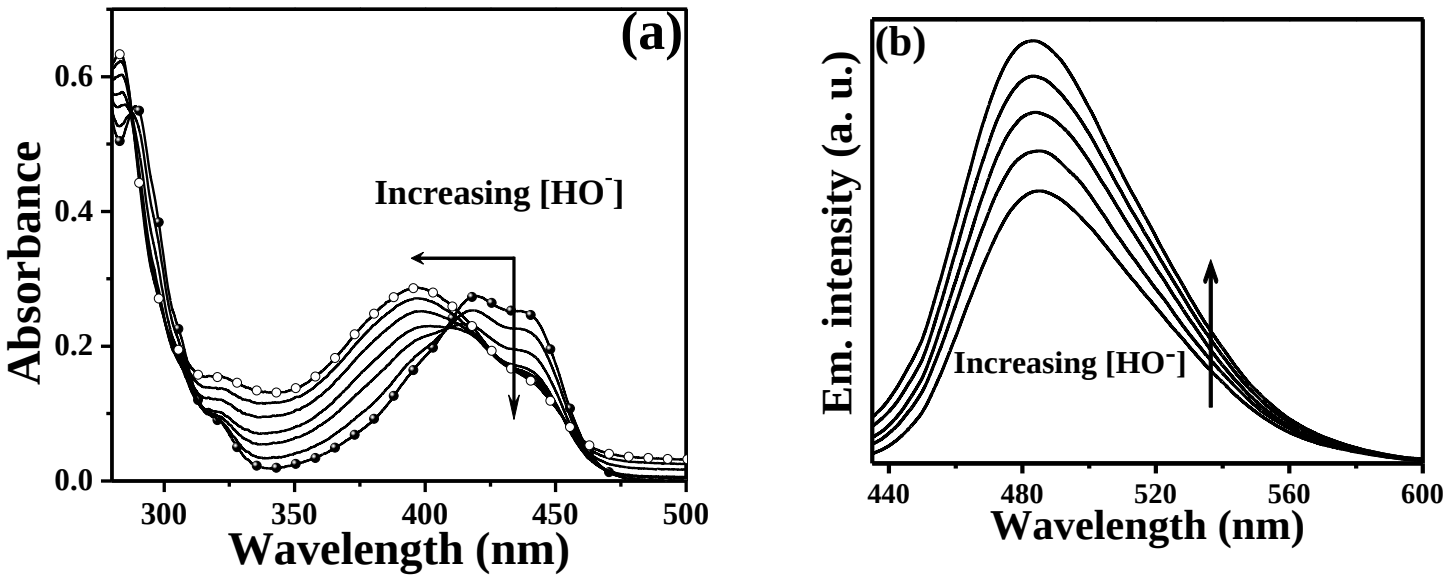


Figure S4: Effect of increasing concentration of base (NaOH) on the (a) absorption profile and (b) emission profile of 2BIMN1O in ACN solvent.

4. Effect of various metal ions on absorption spectra of 2BIMN1O

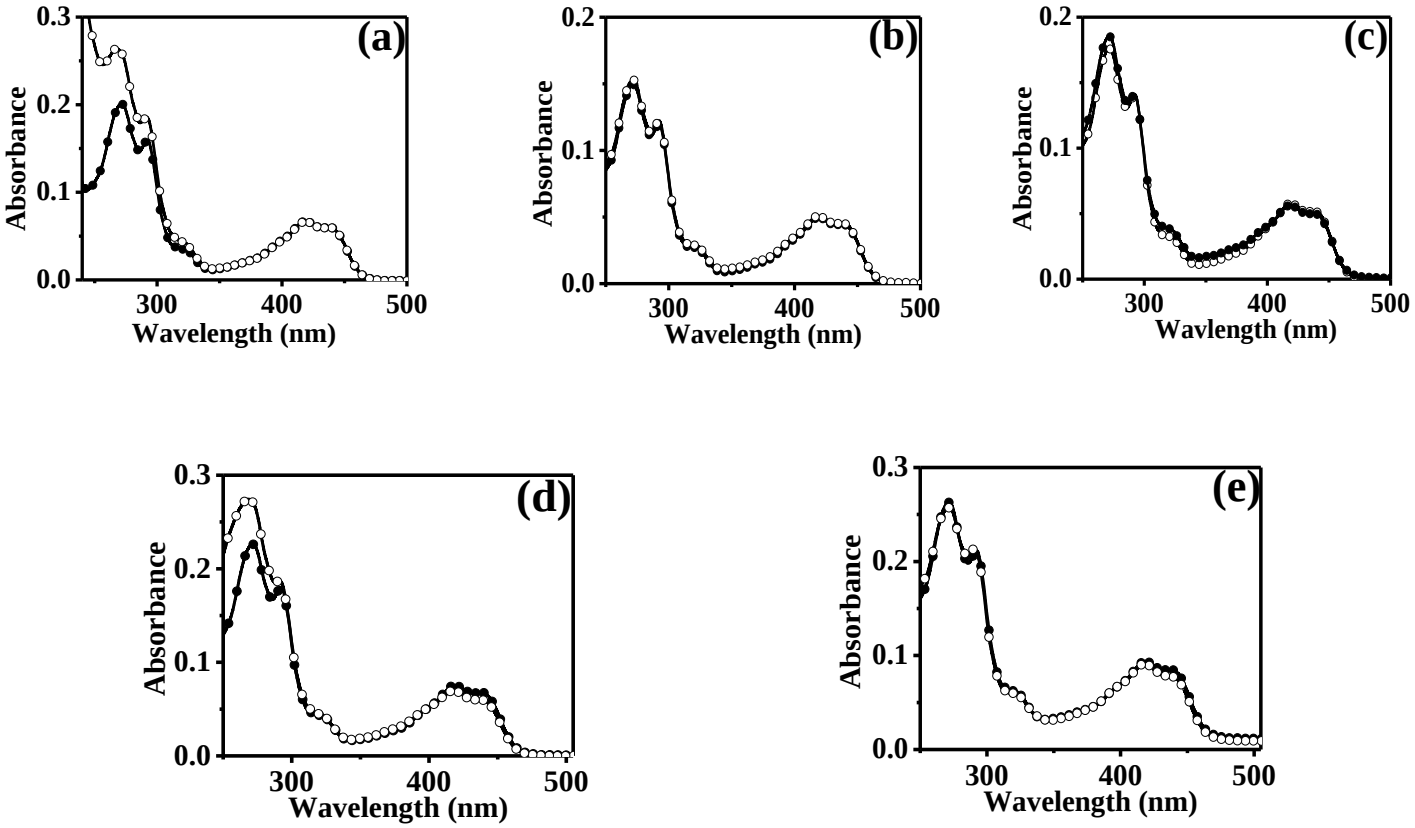


Figure S5: Absorption spectra of 2BIMN1O in ACN solvent (-●-) and in the presence of 30.0 μM of different transition metal ion (-○-) e.g., (a) Cr^{3+}, (b) Mn^{2+}, (c) Fe^{2+}, (d) Co^{2+}, and (e) Ni^{2+}.

5. Effect of various metal ions on emission spectra of 2BIMN1O

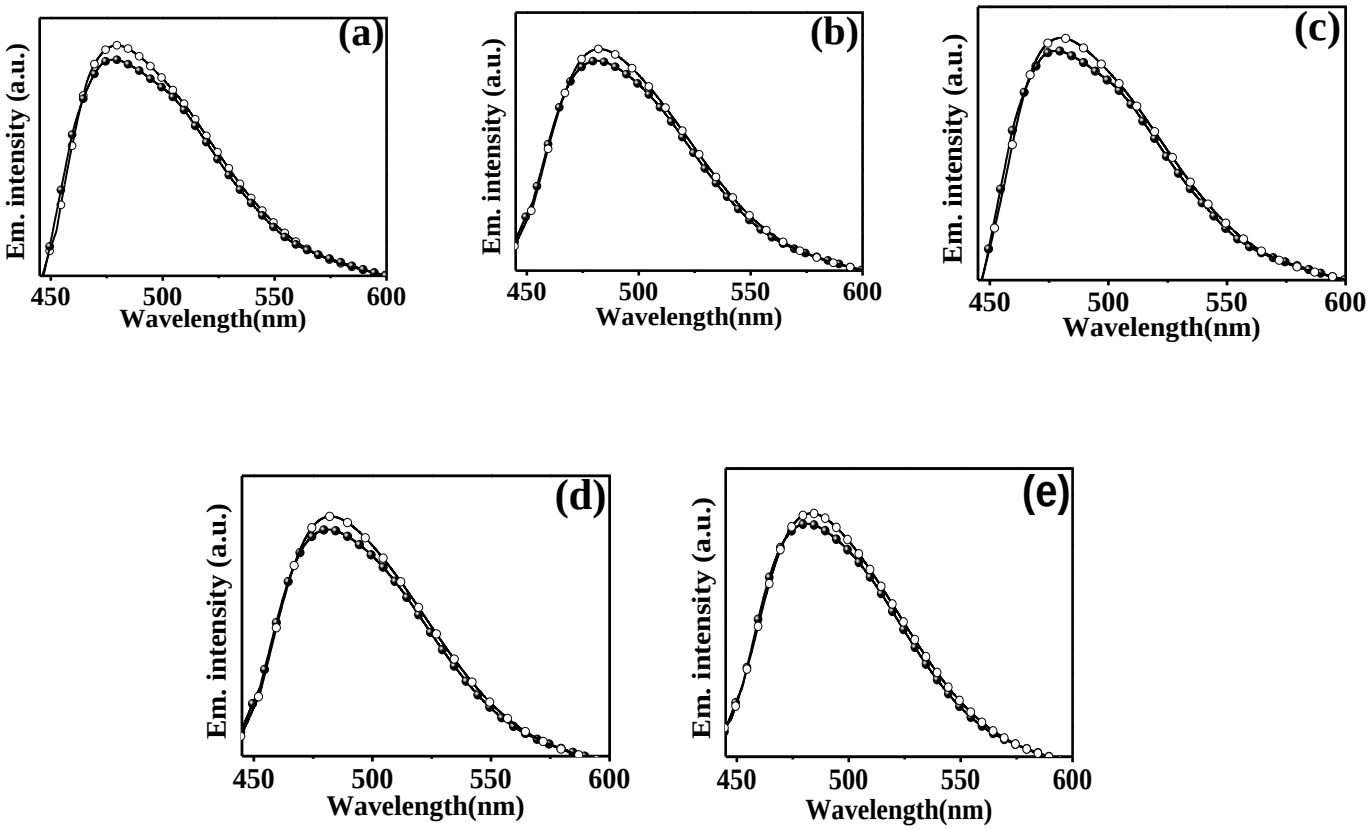


Figure S6: Emission spectra of 2BIMN1O in ACN solvent (-●-) and in the presence of 30.0 μM of different transition metal ion (-○-) e.g., (a) Cr^{3+}, (b) Mn^{2+}, (c) Fe^{2+}, (d) Co^{2+}, and (e) Ni^{2+}.

6. Reference

[1] N. S. Narasimhan, R. S. Mali, **Tetrahedron**, 31 (1975) 1005 – 1009.

[2] R. B. Singh, S. Mahanta, S. Kar, N. Guchhait, **Chem. Phys.**, 331 (2007) 373-384.