Development of Chiral Single Molecule Magnets

Project Completion Report
of SERB Funded Research Project

File Number: EMR/2016/002178

Submitted by

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Closure Report

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Project Title: Development of Chiral Single Molecule Magnets

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Total Sanctioned Amount: 24,93,700 (INR)

Total Released Amount: 23,40,500 (INR)

Start Date of the Project: 16 Nov, 2016

Date of completion: 15 Nov, 2019 (36 months)

Approved Objectives:

- Synthesis of chiral pentagonal bipyramidal Mn(II) and Co(II) complexes having labile axial ligands by using reported chiral macrocylic pentadentate ligands.
- Synthesis and characterization of a new family of pentagonal bipyramidal Mn(II), Fe(II), Co(II) and Ni(II) by chiral modification of a planer pentadentate acyclic ligand.
- Synthesis and characterization of heterometallic {3d-4d/5d} aggregates by interlinking chiral pentagonal bipyramidal complexes prepared above with 4d/5d cyanometallate linkers.
- Investigation of static and dynamic magnetization behavior of the heterometallic {3d-4d/5d} aggregates to confirm their single molecule magnet nature and evaluate key magnetic parameters e.g. blocking temperature, energy barrier for magnetization reversal, magnetization relaxation time etc.
- Magneto-structural correlation of the SMMs prepared during the course of the project to identify key parameters which must be addressed to prepare chiral SMMs with improved characteristics.

Deviation made from original objectives (If Any): None

Ph.D. Produced/Likely to be Produced: 1

Technical Personnel Trained: 0

Total Expenditure: 23,46,075 (INR)

Concise Research Accomplishment:

Several chiral pentagonal bipyramidal Mn(II), Co(II) and Ni(II) complexes were prepared and structurally characterized. The magnetic anisotropy in these compounds were estimated by using ab initio wavefunction based theoretical calculations. Cyanido bridged chiral Co(II)-Fe(III), Mn(II)-Fe(III) and Co(II)-W(V) heterometallic aggregates were prepared by interlinking chiral pentagonal bipyramidal Co(II) and Mn(II) complexes with both hexacyanidoferrate(III) and octacyanidotungstate(V). Heterometallic Co(II)-Fe(III) 1D complex prepared is a multifunctional material that possesses long range ferromagnetic ordering at low temperature and electrical polarization simultaneously. Detailed magnetostructural correlation of the cyanido bridged Co(II)-Fe(III) 1D network was carried out. The chiral cyanide bridged M(II)-Fe(III) [M = Co, Mn] heterobimetallic 1-D networks developed here constitute hitherto unknown examples of water processable cyanido bridged material. Upon dissolution in water, formation of stable colloidal suspension takes place containing particles of average size 125 nm (in case of Co(II)-Fe(III)). Further, the cyanido bridged heterometallic 1D aggregates can be isolated back from the aqueous colloid, without any loss of structural integrity by evaporating the solvent. The water processable cyanido bridged chiral heterometallic M(II)-Fe(III) [M = Co, Mn] polymeric architectures developed during the course of this project pave way for solution processable magnetic materials.

Closure Details

Experimental/ Theoretical Investigation carried out

General synthetic procedure for synthesis of chiral hydrazides: Equimolar amounts of chiral ester and hydrazine monohydrate were mixed and the mixture was allowed to reflux for 6 hours. Methanol and water produced in the reaction were removed under reduced pressure. The final colourless oil was used for further synthesis.

Synthesis of (l)-2-hydroxypropanehydrazide (l-lah): Methyl-*l*(-)-lactate = 5 g, 48.025 mmol and hydrazine monohydrate = 1.5 mL, 48.025 mmol.
Yield: 4.4 g (88%). IR (KBr): $\upsilon/\mathrm{cm}^{-1}$ = 3437 (br), 1649 (m), 1452(w), 1373 (w), 1123 (w), 1045 (m), 992 (w), 930 (w), 874 (w). ^{1}H NMR (δ, ppm, DMSO-d_6): 8.8 (br, 1H, NH), 3.9 (q, J = 7.0 Hz, 1H, CHOH), 1.1 (d, J = 7.0, 3H, CH_3). ^{13}C NMR (δ, ppm, DMSO-d_6): 174.1 (C=O), 67.1 (CHOH) and 21.3 (CH_3).

Synthesis of (d)-2-hydroxypropanehydrazide (d-lah): Methyl-*d*(-)-lactate = 5 g, 48.025 mmol and hydrazine monohydrate = 1.5 mL, 48.025 mmol.
Yield: 4.3 g (86%). IR (KBr): $\upsilon/\mathrm{cm}^{-1}$ = 3437 (br), 1645 (m), 1453 (w), 1373 (w), 1122 (w), 1045 (m), 994 (w), 930 (w), 874 (w). ^{1}H NMR (δ, ppm, DMSO-d_6): 8.8 (br, 1H, NH), 3.9 (q, J = 7.0 Hz, 1H, CHOH), 1.1 (d, J = 7.0, 3H, CH_3). ^{13}C NMR (δ, ppm, DMSO-d_6): 174.0 (C=O), 67.1 (CHOH) and 21.3 (CH_3).

Synthesis of methyl-(R)-3-hydroxyisobutyric acid hydrazide (R-hibh): Methyl (*R*)-3-hydroxyisobutyrate = 5.0 g, 42.326 mmol and hydrazine monohydrate = 2.06 mL, 42.326 mmol.
Yield: 4.6 g (92%). IR (KBr): $\upsilon/\mathrm{cm}^{-1}$ = 3302 (br), 2967 (w), 1653 (m), 1607 (m), 1544 (m), 1452 (w), 1373 (w), 1129 (w), 1078 (m), 993 (m), 892 (m), 787 (m), 669 (s), 480 (m), 453 (m). ^{1}H NMR (δ, ppm, DMSO-d_6): 8.8 (s, 1H, NH), 4.2 (br, 3H, OH and NH_2), 3.4 (dd, *J* = 10.2, 7.6 Hz, 1H, CH_2), 3.2 (dd, *J* = 10.2, 6.3 Hz, 1H, CH_2), 2.3 – 2.1 (sextet, 1H, CH), 0.8 (d, *J* = 6.9 Hz, 3H, CH_3). ^{13}C NMR (δ, ppm, DMSO-d_6): 174.3 (C=O), 64.1 (CH_2OH), 41.5 (CH), 14.6 (CH_3).

Synthesis of methyl-(S)-3-hydroxyisobutyric acid hydrazide (S-hibh): Methyl (*S*)-3-hydroxyisobutyrate = 5.0 g, 42.326 mmol and hydrazine monohydrate = 2.06 mL, 42.326 mmol.
Yield: 4.5 g (90%). IR (KBr): $\upsilon/\mathrm{cm}^{-1}$ = 3303 (br), 2967 (w), 1654 (m), 1543 (m), 1451 (w), 1377 (w), 1129 (w), 1078 (m), 993 (m), 891 (m), 787 (m), 667 (s), 480 (m), 453 (m). ^{1}H NMR (δ, ppm, DMSO-d_6): 8.8 (s, 1H, NH), 4.5 (s, br, 1H, OH), 4.1 (s, br, 2H, NH_2), 3.4 – 3.4 (dd, 1H, CH_2), 3.2 (dd, *J* = 10.1, 6.3 Hz, 1H, CH_2), 2.3 – 2.2 (m, 1H, CH), 0.8 (d, *J* = 6.9 Hz, 3H, CH_3). ^{13}C NMR (δ, ppm, DMSO-d_6): 174.4 (C=O), 64.4 (CH_2OH), 42.1 (CH), 14.5 (CH_3).

Synthesis of chiral bis-hydrazone ligands

General synthetic procedure for synthesis of chiral bis-hydrazone ligands: 2,6-diacetylpyridine (1 equivalent) and chiral hydrazide (2 equivalents) were dissolved in 40 mL ethanol and one drop of hydrochloric acid was added. The resulting solution was heated to reflux and stirred. After about ten minutes a yellow solid began forming. Reflux was continued for another one hour. The mixture was cooled to room temperature and the solid formed was filtered, washed with ethanol and dried.

Synthesis of 2,6-diacetylpyridinebis(l-lactic acid hydrazide) (l-daplh): 2,6-diacetylpyridine = 1.632 g, 10.0 mmol and (*l*)-2-hydroxypropanehydrazide = 2.082 g, 20.0 mmol.
Yield: 3.052 g (91%); M. p.: 187-190°C. IR (KBr): υ/cm^{-1} = 3338 (br), 2998 (w), 2981 (w), 2927 (w), 1668 (s), 1571 (w), 1523 (m), 1453 (m), 1365 (w), 1126 (s), 988 (w), 814 (m), 631 (m), 527 (w). Elemental analysis: Found (calculated for $C_{15}H_{21}N_5O_4$): C, 53.21(53.72); H,6.17(6.31); N,20.34(20.88).

Synthesis of (d)-2, 6-diacetylpyridinebis (lactic acid hydrazone) (d-daplh): 2,6-diacetylpyridine = 1.632 g, 10.0 mmol and (*l*)-2-hydroxypropanehydrazide = 2.082 g, 20.0 mmol.
Yield: 2.984 g (89%); M. p.: 187-190°C. IR (KBr): υ/cm^{-1} = 3338 (br), 2998 (w), 2981 (w), 2927 (w), 1666 (s), 1570 (w), 1524 (m), 1454 (m), 1363 (w), 1128 (s), 989 (w), 815 (m), 636 (m), 528 (w). Elemental analysis: Found (calculated for $C_{15}H_{21}N_5O_4$): C, 53.36(53.72); H,6.09(6.31); N,20.63(20.88).

Synthesis of (R)-2, 6-diacetylpyridinebis(3-hydroxyisobutyric acid hydrazone) (R-daphibh): 2, 6-diacetylpyridine = 1.631 g, 10.0 mmol and methyl-(*R*)-3-hydroxyisobutyric acid hydrazide = 2.363 g, 20.0 mmol.
Yield: 3.12 g (86%); m. p.: 191-195 °C. IR (KBr): υ/cm^{-1} = 3393 (br), 3264 (br), 2966 (w), 2921 (w), 1680 (s), 1531 (m), 1451 (m), 1363 (m), 1192 (m), 1072 (m), 1031 (m), 815 (m), 637 (m), 533 (w).

Synthesis of (S)-2, 6-diacetylpyridinebis(3-hydroxyisobutyric acid hydrazone) (S-daphibh): 2, 6-diacetylpyridine = 1.631 g, 10.0 mmol and methyl-(*R*)-3-hydroxyisobutyric acid hydrazide = 2.363 g, 20.0 mmol.
Yield: 3.15 g (87%). m. p.: 190-195 °C. IR (KBr): υ/cm^{-1} = 3401 (br), 3266 (br), 2967 (w), 2921 (w), 1679 (s), 1531 (m), 1451 (m), 1363 (m), 1193 (m), 1078 (m), 1031 (m), 815 (m), 637 (m), 535 (w).

Synthesis of chiral pentagonal bipyramidal (PBP) 3d building blocks

General synthetic procedure for synthesis of chiral 3d building blocks where the axial sites of pentagonal bipyramid are occupied by H_2O molecules: Chiral bis-hydrazone ligand (1 equivalent) was suspended in 20 mL ethanol and heated to 55 °C. Hydrated metal salt,

$MX_2{\cdot}nH_2O$ [M = Co, Ni, Mn; X = NO_3, ClO_4, Cl] (1 equivalent) was dissolved in 20 mL of ethanol and was added to the ligand suspension. Immediate dissolution of the chiral ligand was observed. The mixture was continued to reflux for one hour. The clear solution resulted was cooled to room temperature and filtered. Slow evaporation of the filtrate at room temperature gave desired crystals (orange-red in case of Cobalt and green in case of Nickel) of chiral PBP 3*d* building block within two to three weeks. The mother liquor was decanted and crystals were washed with minimum amount of ethanol and then dried with diethyl ether.

Synthesis of $[Co(l\text{-}daplh)(H_2O)_2](NO_3)_2{\cdot}2H_2O$ ***(1)****:* *l*-daplh = 1.19 mmol, 0.400 g and $Co(NO_3)_2{\cdot}6H_2O$ = 1.19 mmol, 0.346 g.
Yield: 0.584 g (83%, based on Co). m. p.: >250 °C. IR (KBr): υ/cm^{-1}= 3411 (br), 1641 (s), 1533 (m), 1384 (s), 1273 (w), 1225 (w), 1208 (w), 1176 (w), 1055 (w), 1017 (w), 892 (w), 816 (w), 763 (w), 619 (w). Elemental analysis: Found (calculated for $CoC_{15}H_{29}N_7O_{14}$): C,30.36(30.52); H,4.61(4.95); N,16.53(16.61).

Synthesis of $[Co(d\text{-}daplh)(H_2O)_2](ClO_4)_2{\cdot}2H_2O$ ***(2)****:* *d*-daplh = 1.19 mmol, 0.400 g and $Co(ClO_4){\cdot}6H_2O$ = 1.19 mmol, 0.435 g.
Yield: 0.617 g (81%, based on Co). IR (KBr): υ/cm^{-1}= 3392 (br), 1641 (s), 1532 (m), 1441 (w), 1384 (m), 1227 (w), 1111 (s), 1088 (s), 815 (w), 636 (s), 626 (s). Elemental analysis: Found (calculated for $CoC_{15}H_{31}N_5O_{17}Cl_2$): C,25.82(26.37); H,4.17(4.57); N,10.04(10.25).

Synthesis of $[Co(R\text{-}daphibh)(H_2O)_2](NO_3)_2{\cdot}2H_2O$ ***(3)****:* *R*-daphibh = 3.49 mmol, 1.268 g and $Co(NO_3)_2{\cdot}6H_2O$ = 3.49 mmol, 1.015 g.
Yield: 1.706 g (84%, based on Co). IR (KBr): υ/cm^{-1} = 3411 (br), 1641 (s), 1533 (m), 1384 (s), 1273 (w), 1225 (w), 1208 (w), 1176 (w), 1055 (w), 1017 (w), 892 (w), 816 (w), 763 (w), 619 (w).

Synthesis of $[Co(S\text{-}daphibh)(H_2O)_2](NO_3)_2{\cdot}2H_2O$ ***(4)****:* *S*-daphibh = 3.49 mmol, 1.268 g and $Co(NO_3)_2{\cdot}6H_2O$ = 3.49 mmol, 1.015 g.
Yield: 1.645 g (81%, based on Co). IR (KBr): υ/cm^{-1} = 3409 (br), 1641 (s), 1532 (m), 1384 (s), 1271 (w), 1223 (w), 1209 (w), 1176 (w), 1054 (w), 1018 (w), 893 (w), 815 (w), 764 (w), 621 (w).

Synthesis of $[Ni(l\text{-}daplh)(H_2O)_2](ClO_4)_2.2H_2O$ ***(5)****:* *l*-daplh = 1.19 mmol, 0.400 g and $Ni(ClO_4)_2{\cdot}6H_2O$ = 1.19 mmol, 0.346 g.
Yield: 0.592 g, 79% (Based on Ni). IR (KBr): υ/cm^{-1} = 3436 (br), 2924 (s), 1649 (m), 1539 (m), 1378 (m), 1279 (w), 1088 (s), 887 (w), 816 (w), 626 (s).

Synthesis of $[Ni(d\text{-}daplh)(H_2O)_2](ClO_4)_2.2H_2O$ ***(6)****:* *d*-daplh = 1.19 mmol, 0.400 g and $Ni(ClO_4)_2{\cdot}6H_2O$ = 1.19 mmol, 0.346 g.

Yield = 0.599 g, 80% (Based on Ni). IR (KBr): υ/cm^{-1} = 3378 (br), 1648 (s), 1525 (m), 1377 (m), 1110 (s), 1090 (s), 888 (w), 814 (w), 627 (s).

*Synthesis of [Ni(R-daphibh)(H_2O)$_2$](NO_3)$_2$.2H_2O (**7**):* *R*-daphibh = 1.19 mmol, 0.400 g and $Ni(NO_3)_2{\cdot}6H_2O$ = 1.19 mmol, 0.346 g.
Yield: 0.592 g, 79% (Based on Ni). IR (KBr): υ/cm^{-1} = 3436 (br), 2924 (s), 1649 (m), 1539 (m), 1378 (m), 1279 (w), 1088 (s), 887 (w), 816 (w), 626 (s).

*Synthesis of [Ni(S-daphibh)(H_2O)$_2$](NO_3)$_2$.2H_2O (**8**):* *S*-daphibh = 1.19 mmol, 0.400 g and $Ni(NO_3)_2{\cdot}6H_2O$ = 1.19 mmol, 0.346 g.
Yield = 0.599 g, 80% (Based on Ni). IR (KBr): υ/cm^{-1} = 3378 (br), 1648 (s), 1525 (m), 1377 (m), 1110 (s), 1090 (s), 888 (w), 814 (w), 627 (s).

*Synthesis of [Mn(l-daplh)(H_2O)Cl]Cl·H_2O (**9**):* *l*-daplh (1.49 mmol, 0.500 g) was suspended in 30 mL ethanol and heated to 55°C. $MnCl_2{\cdot}4H_2O$ (1.49 mmol, 0.296 g) was added to the ligand suspension. The mixture was refluxed for three hours. Intense yellow precipitate resulted was cooled to room temperature and filtered, washed with ethanol and then dried with diethyl ether. Yield: 0.574 g (86%, based on Mn). IR (KBr): υ/cm^{-1}= 3378 (m), 3243 (m), 1655 (s), 1539 (s), 1381 (m), 1265 (m), 1223 (m), 1212 (m), 1177 (m), 1050 (m), 1012 (w), 889 (w), 813 (m), 786 (w), 634 (w).

*Synthesis of [Mn(R-daphibh)(H_2O)Cl]Cl·H_2O (**10**):* A reaction similar to that for **9** but with replacement of *l-daplh* with *R*-daphibh yielded fine yellow powder of **10**. *R*-daphibh = 1.38 mmol, 0.5 g and $MnCl_2{\cdot}4H_2O$ = 1.38 mmol, 0.273 g.
Yield: 0.558 g (85%, based on Mn). IR (KBr): υ/cm^{-1}= 3400 (br), 2925 (w), 1654 (s), 1586 (w), 1529 (w), 1457 (m), 1372 (m), 1266 (m), 1200 (s), 1166 (m), 1141 (m), 1129 (m), 1030 (m), 954 (w), 817 (m), 738 (w), 638 (w).

*Synthesis of [Mn(S-daphibh)(H_2O)Cl]Cl·H_2O (**11**):* A reaction similar to that for **10** but with replacement of *R*-daphibh with *S*-daphibh yielded fine yellow powder of **11**. *S*-daphibh = 2.76 mmol, 1 g and $MnCl_2{\cdot}4H_2O$ = 2.76 mmol, 0.546 g.
Yield: 0.892 g (81%, based on Mn). IR (KBr): υ/cm^{-1}= 3413 (br), 1655 (s), 1587 (w), 1532 (w), 1458 (m), 1373 (m), 1266 (m), 1201 (s), 1166 (m), 1141 (m), 1129 (m), 1030 (m), 954 (w), 817 (m), 738 (w), 638 (w).

General synthetic procedure for synthesis of chiral 3d building blocks where the axial sites of pentagonal bipyramid are occupied by -NCS groups:
To a solution of [M(L)(H_2O)$_2$]$X_2{\cdot}nH_2O$ {M = Co, Ni; L = l/d-daplh, R/S-daphibh and X = -NO_3, ClO_4} or [Mn(L)(H_2O)Cl]Cl·H_2O {L = l/d-daplh, R/S-daphibh} (1 equivalent) in 10 mL methanol, a methanolic solution (10 mL) of KSCN (2 equivalents) was added. The reaction mixture was stirred at room temperature for an hour. The reaction mixture was filtered. Slow evaporation of the filtrate at room temperature gave desired crystals of chiral PBP 3*d*

building block within one week. The mother liquor was decanted and crystals were washed with minimum amount of ethanol and then dried with diethyl ether.

Synthesis of [Co(l-daplh)(NCS)$_2$]·3H$_2$O ***(12):*** [Co(*l*-daplh)(H$_2$O)$_2$](NO$_3$)$_2$·2H$_2$O (**1**) = 0.018 mmol, 0.010 g and KSCN = 0.09 mmol, 0.008 g.
Yield: 0.007 g (74 % based on Co). IR (KBr): υ/cm^{-1} = 3436 (br), 2925 (m), 2066 (s), 1639 (s), 1455 (w), 1384 (s), 1205 (w), 1173 (w), 1119 (w), 884 (w), 810 (w), 633 (w).

Synthesis of [Co(R-daphibh)(NCS)$_2$]·3H$_2$O ***(13):*** [Co(*R*-daphibh)(H$_2$O)$_2$](NO$_3$)$_2$·2H$_2$O (**3**) = 0.017 mmol, 0.010 g and KSCN = 0.085 mmol, 0.0083 g.
Yield: 0.008 g (87 % based on Co). IR (KBr): υ/cm^{-1} = 3435 (br), 2932 (w), 2098 (s), 1664 (s), 1635 (s), 1507 (s), 1459 (m), 1429 (m), 1384 (s), 1269 (w), 1178 (s), 1024 (m), 943 (m), 811 (m), 740 (w), 634 (w).

Synthesis of [Ni(l-daplh)(NCS)$_2$]·3H$_2$O ***(14):*** [Ni(*l*-daplh)(H$_2$O)$_2$](ClO$_4$)$_2$·2H$_2$O (**5**) = 0.018 mmol, 0.010 g and KSCN = 0.09 mmol, 0.008 g.
Yield: 0.007 g (74 % based on Ni). IR (KBr): υ/cm^{-1} = 3436 (br), 2925 (m), 2066 (s), 1639 (s), 1455 (w), 1384 (s), 1205 (w), 1173 (w), 1119 (w), 884 (w), 810 (w), 633 (w).

Synthesis of [Ni(R-daphibh)(NCS)$_2$]·3H$_2$O ***(15):*** [Ni(*R*-daphibh)(H$_2$O)$_2$](NO$_3$)$_2$·2H$_2$O (**7**) = 0.018 mmol, 0.010 g and KSCN 0.09 mmol, 0.008 g.
Yield: 0.007 g (74 % based on Ni). IR (KBr): υ/cm^{-1} = 3436 (br), 2925 (m), 2066 (s), 1639 (s), 1455 (w), 1384 (s), 1205 (w), 1173 (w), 1119 (w), 884 (w), 810 (w), 633 (w).

Synthesis of [Mn(l-daplh)(NCS)$_2$]·3H$_2$O ***(16):*** [Mn(*l*-daplh)(H$_2$O)Cl]Cl·H$_2$O (**9**) = 0.021 mmol, 0.010 g and KSCN = 0.105 mmol, 0.010 g.
Yield: 0.007 g (74 % based on Mn). IR (KBr): υ/cm^{-1} = 3436 (br), 2925 (m), 2066 (s), 1639 (s), 1455 (w), 1384 (s), 1205 (w), 1173 (w), 1119 (w), 884 (w), 810 (w), 633 (w).

Synthesis of [Mn(R-daphibh)(NCS)$_2$]·3H$_2$O ***(17):*** [Mn(*R*-daphibh)(H$_2$O)Cl]Cl·H$_2$O (**10**) = 0.018 mmol, 0.010 g and KSCN = 0.09 mmol, 0.008 g.
Yield: 0.007 g (74 % based on Mn). IR (KBr): υ/cm^{-1} = 3436 (br), 2925 (m), 2066 (s), 1639 (s), 1455 (w), 1384 (s), 1205 (w), 1173 (w), 1119 (w), 884 (w), 810 (w), 633 (w).

Synthesis of cyanido bridged chiral M(II)-Fe(III)/W(V) heterometallic aggregates

General synthetic procedure for synthesis of cyanido bridged chiral M(II)-Fe(III) [M = Co, Mn] heterometallic aggregates: To a solution of chiral 3*d* building block (1 equivalent) in 5 mL methanol, KSCN (5 equivalents) was added. The reaction mixture was stirred at room temperature for 1 hour. The solution was then filtered and filtrate was layered with a solution of K$_3$[Fe(CN)$_6$] (1 equivalent) in 1 mL distilled water using water : methanol (5 mL : 5 mL) as buffer. The layered solution was kept undisturbed in dark. Needle-shaped crystals (dark brown in case of Cobalt and golden in case of Mn) were obtained after one week. The mother liquor was discarded and crystals were washed with methanol followed by diethyl ether and then dried.

Synthesis of $[\{K(H_2O)\}\{K(H_2O)_2\}\{Co(l\text{-}daplh)\}_2\{Fe(CN)_6\}_2]_n$ ***(18):*** $[Co(l\text{-}daplh)(H_2O)_2](NO_3)_2\cdot 2H_2O$ (**1**) = 0.036 mmol, 0.020 g, KSCN = 0.18 mmol, 0.018 g and $K_3[Fe(CN)_6]$ = 0.036 mmol, 0.0112 g.

Yield: 0.033 g (72%, based on Co) M. p.: >250 ˚C. IR (KBr): υ/cm^{-1}= 3413 (br), 2926 (w), 2143 (s), 2118 (s), 1659 (s), 1550 (s), 1461 (w), 1434 (w), 1378 (m), 1269 (m), 1131 (m), 1051 (m), 893 (w), 811 (m), 741 (m), 540 (w). Elemental analysis: Found (calculated for $Co_2Fe_2K_2C_{42}H_{48}N_{22}O_{11}$): C, 37.88 (37.51); H, 3.60 (3.60); N, 22.92 (22.68). AAS Found (calculated for $Co_2Fe_2K_2C_{42}H_{48}N_{22}O_{11}$): Co,8.52(8.77); Fe,8.09(8.31); K,5.61(5.82).

Synthesis of $[\{K(H_2O)\}\{K(H_2O)_2\}\{Co(d\text{-}daplh)\}_2\{Fe(CN)_6\}_2]_n$ ***(19):*** $[Co(d\text{-}daplh)(H_2O)_2](ClO_4)_2\cdot 2H_2O$ (**2**) = 0.036 mmol, 0.020 g, KSCN = 0.18 mmol, 0.018 g and $K_3[Fe(CN)_6]$ = 0.036 mmol, 0.0112 g.

Yield: 0.031 g (67%, based on Co). IR (KBr): υ/cm^{-1} = 3401 (br), 2927 (w), 2144 (s), 2120 (s), 1660 (s), 1549 (s), 1461 (w), 1434 (w), 1378 (m), 1270 (m), 1131 (m), 1050 (m), 893 (w), 811 (m), 741 (m), 540 (w). Elemental analysis: Found (calculated for $Co_2Fe_2K_2C_{42}H_{48}N_{22}O_{11}$): C, 37.21 (37.51); H, 3.48 (3.60); N, 22.57 (22.68). AAS Found (calculated for $Co_2Fe_2K_2C_{42}H_{48}N_{22}O_{11}$): Co,8.59(8.77); Fe,8.23(8.31); K,5.68(5.82).

Synthesis of $[K_2\{Co(R\text{-}daphibh)\}_2\{Fe(CN)_6\}_2]_n$ ***(20):*** $[Co(R\text{-}daphibh)(H_2O)_2](NO_3)_2\cdot 2H_2O$ (**3**) = 0.034 mmol, 0.020 g, KSCN = 0.17 mmol, 0.017 g and $K_3[Fe(CN)_6]$ = 0.036 mmol, 0.0112 g. Yield: 0.0308 g (67%, based on Co). IR (KBr): υ/cm^{-1} = 3368 (br), 2925 (w), 2134 (s), 2123 (s), 1639 (s), 1541 (s), 1462 (m), 1437 (m), 1380 (m), 1272 (m), 1209 (m), 1177 (m), 1024 (m), 986 (w), 812 (m), 741 (m), 542 (w), 415 (m).

Synthesis of $[K_2\{Co(S\text{-}daphibh)\}_2\{Fe(CN)_6\}_2]_n$ ***(21):*** $[Co(S\text{-}daphibh)(H_2O)_2](NO_3)_2\cdot 2H_2O$ (**4**) = 0.034 mmol, 0.020 g, KSCN = 0.17 mmol, 0.017 g and $K_3[Fe(CN)_6]$ = 0.036 mmol, 0.0112 g.

Yield: 0.0303 g (66%, based on Co). IR (KBr): υ/cm^{-1} = 3436 (br), 3100 (w), 2924 (w), 2132 (s), 2123 (s), 1639 (s), 1541 (s), 1462 (m), 1437 (m), 1381 (m), 1272 (m), 1209 (m), 1176 (m), 1024 (m), 985 (w), 811 (m), 740 (m), 543 (w), 416 (m).

Synthesis of $[\{K(H_2O)_2\}\{K(H_2O)(CH_3OH)\}\{Mn(l\text{-}daplh)\}_2\{Fe(CN)_6\}_2]_n$ ***(22):*** $[Mn(l\text{-}daplh)(H_2O)Cl]Cl\cdot H_2O$ (**9**) = 0.042 mmol, 0.020 g, KSCN = 0.21 mmol, 0.020 g and $K_3[Fe(CN)_6]$ = 0.042 mmol, 0.0118 g. Yield: 0.032 g (69%, based on Mn). IR (KBr): υ/cm^{-1}= 3413 (br), 2926 (w), 2143 (s), 2118 (s), 1659 (s), 1550 (s), 1461 (w), 1434 (w), 1378 (m), 1269 (m), 1131 (m), 1051 (m), 893 (w), 811 (m), 741 (m), 540 (w).

Synthesis of $[\{K_2\{Mn(R\text{-}daphibh)\}_2\{Fe(CN)_6\}_2]_n$ ***(23):*** $[Mn(R\text{-}daphibh)(H_2O)Cl]Cl\cdot H_2O$ (**10**) = 0.036 mmol, 0.03 g, KSCN = 0.18 mmol, 0.018 g and $K_3[Fe(CN)_6]$ = 0.036 mmol, 0.0112 g.

Yield: 0.032 g (69%, based on Mn). IR (KBr): υ/cm^{-1}= 3401 (br), 2924 (w), 2127 (m), 2066 (s), 1679 (s), 1537 (m), 1451 (m), 1451 (m), 1363 (m), 1266 (m), 1100 (m), 1030 (m), 815 (m), 734 (m), 597 (m), 537 (w).

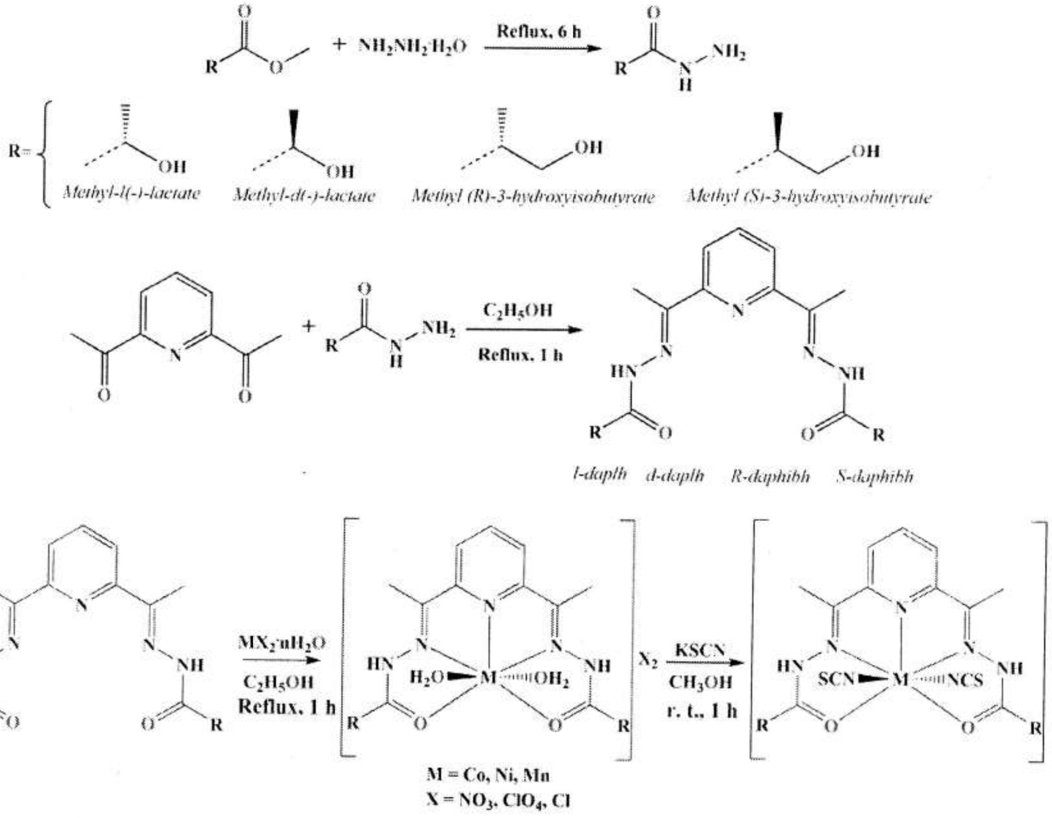
Synthesis of cyanido bridged chiral Co(II)-W(V) heterometallic aggregates derived from $[Co(l\text{-daplh})(H_2O)_2](NO_3)_2\cdot2H_2O$ *and* $Cs_3[W(CN)_8\cdot2H_2O$ ***(24):*** To a solution of $[Co(l\text{-daplh})(H_2O)_2](NO_3)_2\cdot2H_2O$ (**1**) (0.072 mmol, 0.040 g) in 10 mL methanol, KSCN (0.36 mmol, 0.036 g) was added. The reaction mixture was stirred at room temperature for 1 hour. The solution was filtered and the filtrate was layered with an 4 mL aqueous solution of $Cs_3[W(CN)_8\cdot2H_2O$ (0.072 mmol, 0.056 g) using water : methanol (4 mL : 4 mL) as buffer. The layered solution was kept undisturbed in dark. Dark purple coloured block shaped crystals of **24** were obtained after one week at the buffer layer. The mother liquor was discarded and crystals were washed with methanol followed by diethyl ether and then dried. Yield: 0.024 g (71% based on Co). IR (KBr): υ/cm^{-1} = 3435 (br), 2928 (w), 2142 (m), 2115 (m), 2092 (m), 1655 (s), 1536 (s), 1459 (w), 1433 (w), 1373 (m), 1269 (m), 1133 (m), 1056 (m), 888 (w), 810 (m), 667 (m), 540 (w), 439 (w).

Synthesis of cyanido bridged chiral Co(II)-W(V) heterometallic aggregates derived from $[Co(l\text{-daplh})(H_2O)_2](NO_3)_2\cdot2H_2O$ *and* $(TBA)_3[W(CN)_8\cdot2H_2O$ ***(25):*** To an 4 mL aqueous solution of $[Co(l\text{-daplh})(H_2O)_2](NO_3)_2\cdot2H_2O$ (**1**) (0.036 mmol, 0.020 g) a methanolic solution of $(TBA)_3[W(CN)_8\cdot2H_2O$ (0.036 mmol, 0.034 g) is added slowly without agitation. Immediately a dark purple colour clear solution resulted. Slow evaporation of the solution in dark yielded dark red block shaped crystals of **25** within two weeks. The crystals were washed with methanol and diethylether and dried. Yield: 0.021 g (68% based on Co). IR (KBr): υ/cm^{-1} = 3412 (br), 2928 (w), 2119 (s), 2097 (sh), 1640 (s), 1547 (s), 1460 (w), 1437 (w), 1377 (m), 1271 (m), 1130 (m), 1054 (m), 890 (w), 814 (m), 741 (w), 486 (w).

Synthesis of cyanido bridged chiral Mn(II)-W(V) heterometallic aggregates derived from $[Mn(l\text{-daplh})(H_2O)Cl]Cl\cdot H_2O$ *and* $(TBA)_3[W(CN)_8\cdot2H_2O$ ***(26):*** To an 10 mL acetonitrile solution of $[Mn(l\text{-daplh})(H_2O)Cl]Cl\cdot H_2O$ (**9**) (0.042 mmol, 0.020 g) an acetonitrile solution (10 mL) of $(TBA)_3[W(CN)_8\cdot2H_2O$ (0.042 mmol, 0.040 g) was added slowly without agitation. Immediately a clear dark yellow solution was obtained. Slow evaporation of the solution in dark afforded dark orange needle shaped crystals of **26**. The crystals were washed with acetonitrile and diethylether and dried. Yield: 0.021 g (65% based on Mn). IR (KBr): υ/cm^{-1} = 3421 (br), 2926 (w), 2114 (s), 2097 (sh), 1650 (s), 1544 (s), 1458 (w), 1375 (m), 1267 (m), 1169 (m), 1133 (m), 1054 (m), 891 (w), 815 (m), 659 (w).

Detailed Analysis of result

Synthesis and characterization of chiral hydrazides: Chiral hydrazides (l)/(d)-2-hydroxypropanehydrazide and methyl-(R)/(S)-3-hydroxyisobutyric acid hydrazide were prepared by the reaction between equimolar amounts of respective enantiopure ester and hydrazine monohydrate under reflux (Scheme 1). The colourless oil (in case of (l)/(d)-2-hydroxypropanehydrazide) and white crystalline needles (in case of methyl-(R)/(S)-3-hydroxyisobutyric acid hydrazide) obtained as the final product were fully characterized by analytical and spectroscopic techniques.



Scheme 1. Synthetic scheme of chiral hydrazide (*above*), chiral bis-hydrazone (*middle*) and chiral pentagonal bipyramidal (PBP) 3*d* building blocks (*below*).

FT-IR spectroscopy of chiral hydrazides: FT-IR spectra of (*l*)-2-hydroxypropanehydrazide and methyl-(R)-3-hydroxyisobutyric acid hydrazide are shown in Figure 1. The other enantiomers (*d*)-2-hydroxypropanehydrazide and methyl-(*S*)-3-hydroxyisobutyric acid hydrazide also show similar absorption. FT-IR spectra of (*l*)-2-hydroxypropanehydrazide and methyl-(*R*)-3-hydroxyisobutyric acid hydrazide show a broad peak at 3437 cm^{-1} and 3302 cm^{-1} which can be attributed to –NH stretching vibrations. Intense peak observed at 1649 cm^{-1} (*l-lah*) and 1653 cm^{-1} (*R-hibh*) can be assigned to the C=O stretching vibrations. The medium intensity peak at 1123 cm^{-1} and 1129 cm^{-1} correspond to the C-N stretching frequency of *l-lah* and *R-hibh* respectively.

NMR spectroscopy of chiral hydrazides: The ^{1}H and ^{13}C NMR spectra of (*l*)-2-hydroxypropanehydrazide and methyl-(*R*)-3-hydroxyisobutyric acid hydrazide are shown in Figure 1. Their respective enantiomers (*d*)-2-hydroxypropanehydrazide and methyl-(*S*)-3-hydroxyisobutyric acid hydrazide also show similar signals in ^{1}H and ^{13}C NMR spectra. ^{1}H NMR spectrum of (*l*)-2-hydroxypropanehydrazide shows a quartet peak at 3.9 ppm which is assigned to the -CH proton adjacent to the hydroxyl group. A doublet peak at 1.15 ppm corresponds to the methyl protons. A broad singlet at 8.8 ppm can be attributed to the -NH proton. The solvent residual peak for deuterated dimethyl sulfoxide arises at 2.4 ppm. The singlet peak at 3.1 ppm and 3.5 ppm are ascribed to the methyl protons of trace amount of methanol and water present, respectively, which are produced during the condensation reaction. ^{13}C-NMR spectrum of (*l*)-2-hydroxypropanehydrazide displays a peak at 174.1 ppm which corresponds to the carbonyl carbon atom (Figure 1). The peak at 67.1 ppm can be ascribed to the CHOH carbon atom. The methyl carbon atom corresponds to the peak at 21.3 ppm. The peak at 49.1 ppm is assigned to the methyl carbon atom of methanol present in trace amount.

^{1}H NMR spectrum of methyl-(*R*)-3-hydroxyisobutyric acid hydrazide shows a sextet peak at 2.3-2.2 ppm which is assigned to the proton attached to the chiral centre (Figure 1). Two doublets of doublet peaks at 3.4 ppm and 3.2 ppm correspond to the $-CH_2$ protons. A broad singlet at 8.8 ppm can be attributed to the –NH proton. The broad peak at 4.2 ppm is assigned to the –OH and $-NH_2$ protons. For S-isomer, the singlet peaks at 4.5 ppm and 4.1 ppm are assigned to the –OH and $-NH_2$ protons respectively. Solvent residual peak for deuterated dimethyl sulfoxide arises at 2.4 ppm. ^{13}C-NMR spectrum of methyl-(R)-3-hydroxyisobutyric acid hydrazide displays a peak at 174.3 ppm which corresponds to the carbonyl carbon atom (Figure 1). The peak at 64.1 ppm can be ascribed to the CHOH carbon atom. Peak at 41.5 ppm is assigned to the $-CH_2$ carbon atom. The methyl carbon atom corresponds to the peak at 14.6 ppm.

Synthesis and characterization chiral bis-hydrazones: Chiral bis-hydrazone ligands were synthesized by reaction between 2,6-diacetylpyridine and chiral hydrazide in a 1:2 molar ratio under reflux condition (Scheme 1). The fine yellow powder of bis-hydrazone ligands obtained were characterized by using analytical and spectroscopic techniques.

FT-IR spectroscopy of chiral bis-hydrazones: Formations of the chiral bis-hydrazone ligands, *l*/*d*-daplh and *R*/*S*-daphibh are confirmed by FT-IR spectroscopic technique (Figure 1). A characteristic broad peak at 3338 cm^{-1} and 3393 cm^{-1} respectively for *l*-daplh and *R*-daphibh correspond to the –NH stretching vibrations. Intense strong peak at 1668 cm^{-1} and 1680 cm^{-1} for *l*-daplh and *R*-daphibh respectively are attributed to the C=N stretching vibration of the imine group. Their other enantiomers *d*-daplh and *S*-daphibh also show similar absorption peaks as that of their respective counterpart.

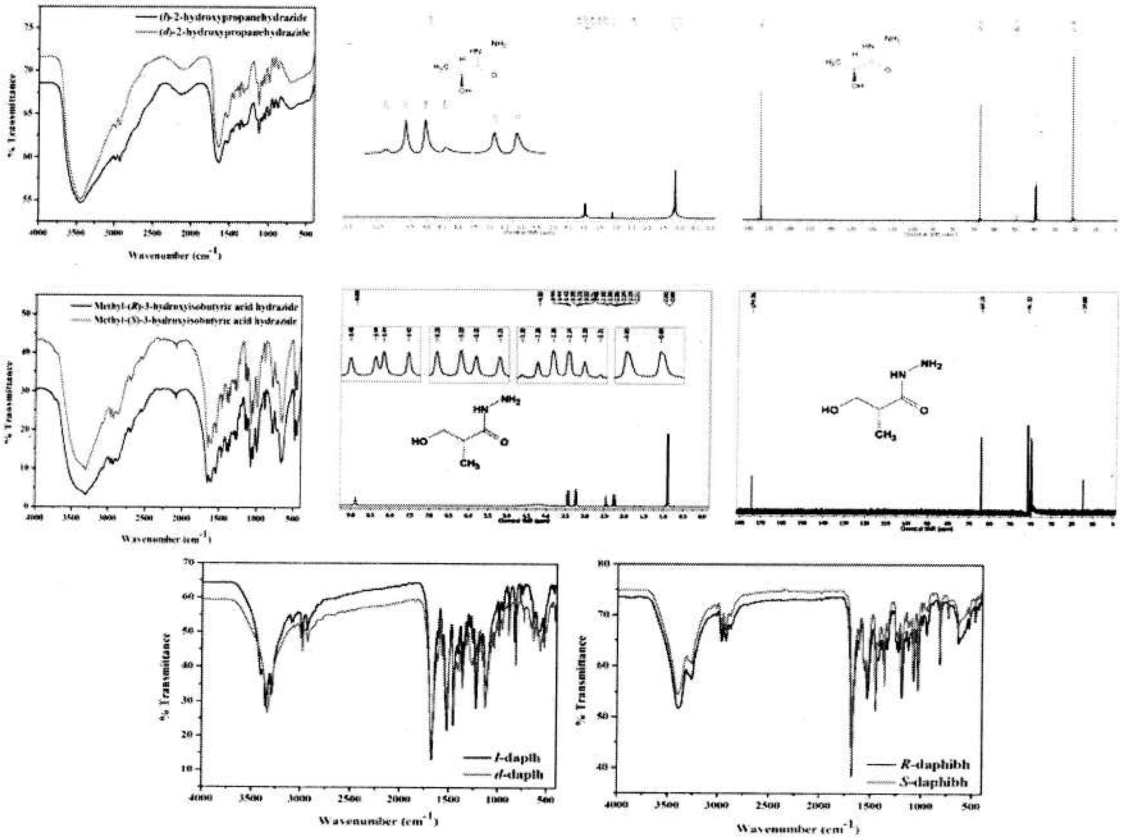


Figure 1. Characterization of chiral ligands. *Above:* FT-IR spectra of chiral hydrazides *(l)*-2-hydroxypropanehydrazide/*(d)*-2-hydroxypropane-hydrazide as KBr diluted discs and ^{1}H and ^{13}C NMR spectra of *(l)-2*-hydroxypropanehydrazide. *Middle:* FT-IR spectra of chiral hydrazides methyl-(R)-3-hydroxyisobutyric acid hydrazide/methyl-(S)-3-hydroxyisobutyric acid hydrazide and ^{1}H and ^{13}C NMR spectra of methyl-(R)-3-hydroxyisobutyric acid hydrazide. *Below:* FT-IR spectra of chiral bis-hydrazone ligands l-daplh/d-daplh (*left*) and R-daphibh/S-daphibh (*right*) as KBr diluted discs.

Synthesis and characterization chiral 3d building blocks: Equimolar reaction between chiral bis-hydrazone ligand and hydrated metal salt, $MX_2 \cdot nH_2O$ [M = Co, Ni, Mn; X = NO_3, ClO_4, Cl] under reflux yielded a clear solution in case of Co and Ni whereas an intense yellow precipitate in case of Mn. Slow evaporation of the filtrate for Co and Ni at room temperature resulted in the formation of desired crystals of chiral PBP 3*d* building blocks in good yield (Scheme 1). All compounds are characterized by FT-IR, elemental analysis, powder X-ray diffraction and single crystal X-ray diffraction analysis. Results obtained from the elemental analysis are in good agreement with the proposed formulation of chiral 3*d* building blocks. Single crystal X-ray analysis of the complexes unambiguously established formation of pentagonal bipyramidal complexes where the equatorial sites are occupied by the planar pentadentate chiral ligand while the axial sites are occupied by labile aquo ligands. Further, the labile axial aquo ligands are replaced by thiocyanate groups using KSCN (Scheme 1).

FT-IR spectroscopy of chiral 3d building blocks: FTIR spectra of chiral 3*d* building blocks recorded as KBr diluted discs are depicted in Figure 2 for compounds **1**, **3**, **5**, **7**, **12, 14, 15** and **16** respectively. In compound **1**, characteristic absorption peaks at 3411 cm^{-1}, 1641 cm^{-1}and 1384 cm^{-1} can be attributed to the *v*(OH), *v*(C=N) and *v*(C=C, phenyl rings) respectively. Similar absorption peaks are also observed for the other chiral 3*d* building blocks where the axial sites are occupied by aquo ligands. For compounds in which perchlorate salts are used as the metal source, a characteristic peak at about 1088 cm^{-1} is observed which confirms the presence of perchlorate as the counter ion. In –SCN based precursors, a characteristic peak at 2066 cm^{-1} is observed which corresponds to the C≡N stretching vibration of the axial thiocyanate group (Figure 2). The purity of the polycrystalline samples of chiral PBP complexes were measured by powder X-ray diffraction technique (Figure 2).

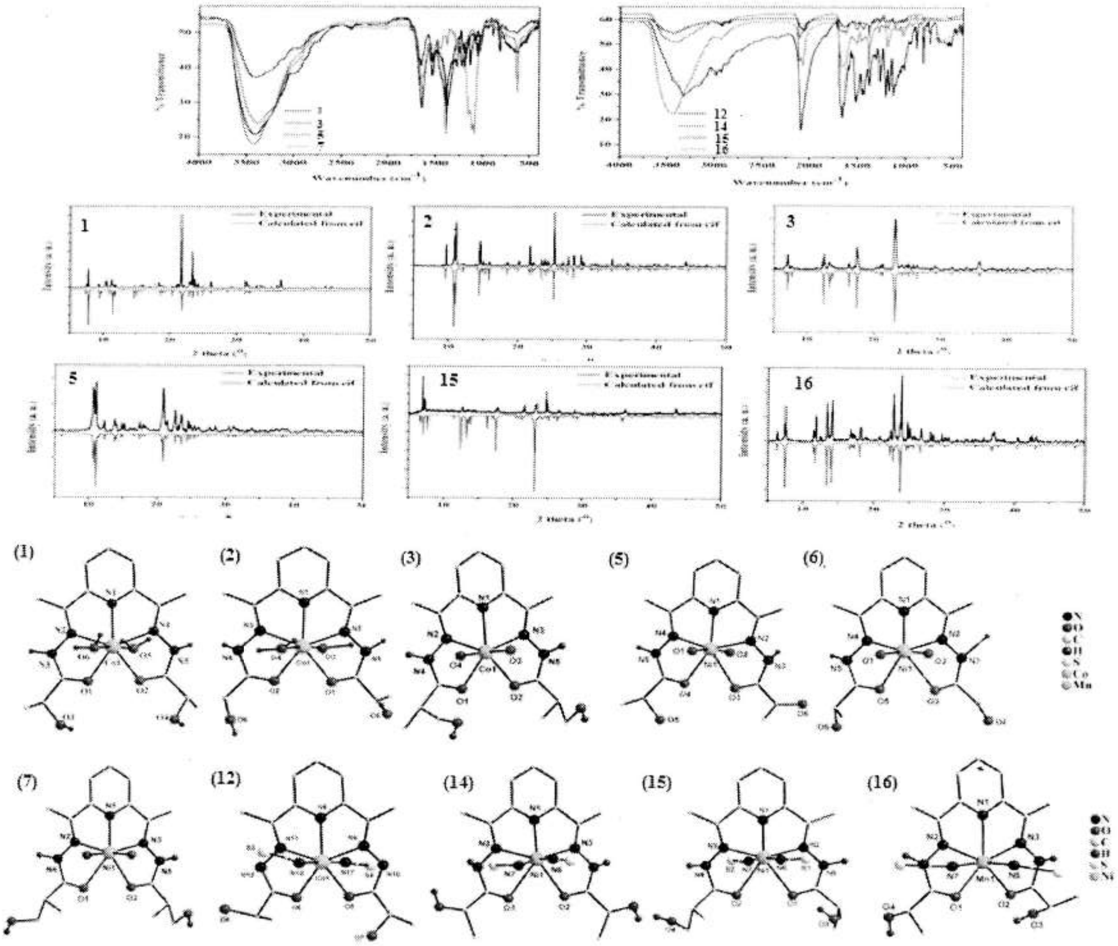


Figure 2. Characterizations of chiral 3*d* building blocks. *Above:* FT-IR spectra of a few selected chiral 3*d* building blocks where the axial positions of pentagonal bipyramid are occupied by H_2O molecules and -NCS groups. *Middle:* Powder X-ray diffraction pattern of a

few selected chiral *3d* building blocks. Black line represents the experimental values and red line represents the calculated pattern. *Below:* Molecular structures of a few selected chiral 3*d* building blocks *viz.* **1**, **2**, **3**, **5**, **6**, **7**, **12**, **14**, **15** and **16**. Counter ions, lattice solvent molecules and hydrogen atoms are omitted for clarity. Only NH and OH hydrogen atoms are shown wherever present.

Molecular structures of chiral 3d building blocks: Molecular structures of chiral 3d building blocks were determined by single crystal X-ray diffraction technique. Representative view of the molecular structures of compounds **1**, **2**, **3**, **5**, **6**, **7**, **12**, **14**, **15** and **16** are depicted in Figure 2. In all compounds, the pentagonal bipyramidal (PBP) geometry has been retained. The equatorial sites of all the compounds have been occupied by the chiral pentadentate bis-hydrazone ligand. The M(II) [M = Co, Ni, Mn] centre is ligated to the pyridine nitrogen atom, two imine nitrogen atoms and two oxygen atoms of the bis-hydrazone ligand in the equatorial environment. The axial sites are occupied by two labile aquo ligands in compounds **1**, **2**, **3**, **5**, **6** and **7**. The electroneutrality of compounds **1**, **3** and **7** are maintained by the presence of two nitrate groups, and two perchlorate groups in case of compounds **2**, **5** and **6** in crystal lattice. In compounds **12**, **14**, **15** and **16**; the axial sites are occupied by two N-atoms of two thiocyanate groups, thereby imparting eletroneutrality to the compound and thereby lending a N_5O_2 coordination environment. The axial M-O(H_2O) [M = Co, Ni] bond distances are found to be 2.144 Å and 2.164 Å respectively. These bond distances are comparable with that of the reported achiral M-O(H_2O) bond distances of the precursor M(II) complex. The axial M-N(thiocyanato) [M = Co, Ni, Mn] bond distances are 2.164 Å and 2.074 Å respectively which are in good agreement with the M-N bond distances observed for identical achiral mononuclear M(II) complexes.

Determination of nature and extent of uniaxial magnetic anisotropy (D) chiral 3d building blocks: The extent of uniaxial magnetic anisotropy (D values) of the synthesized chiral *3d* building blocks were extracted by using the Effective Hamiltonian method from NEVPT2 calculations. D values for a few chiral *3d* building blocks are as follows: +37.28 (**1**), +37.93 (**2**), +40.42 (**3**), -11.78 (**5**), -16.80 (**6**), -19.05 (**7**), +39.48 (**12**) and -18.07 (**15**). These values are found to be comparable with reported D values for achiral PBP 3d building blocks.

Synthesis and characterizations of cyanido bridged chiral M(II)-Fe(III) [M = Co, Mn] heterometallic aggregates: Reaction of chiral PBP M(II) [M = Co, Mn] building blocks with $K_3[Fe(CN)_6]$ in presence of excess KSCN results in the isolation of needle shaped crystals cyanido bridged M(II)-Fe(III) heterometallic aggregates **18-23** (dark brown for Co and golden for Mn). Even though these compounds can be isolated in the absence of KSCN, quality of crystals formed are considerably poor. We anticipate that thiocyanate competes with ferricyanide to occupy the axial coordination sites of M(II). This decelerate the self-assembly of M(II) precursor with $[Fe(CN)_6]^{3-}$ and thereby allow formation of better quality crystals when KSCN is used. Results of elemental analysis, AAS and EDS are in good agreement with the proposed formulation of cyanido bridged M(II)-Fe(III) heterometallic aggregates **18-23.** The purity of the polycrystalline sample of **18-23** was measured by powder X-ray diffraction technique (Figure 3).

FT-IR spectroscopy of cyanido bridged chiral M(II)-Fe(III) [M = Co, Mn] heterometallic aggregates: Intense peak observed in FT-IR spectra of **18-23** at 1659 cm^{-1}, 1660 cm^{-1}, 1639 cm^{-1}, 1639 cm^{-1}, 1659 cm^{-1} and 1679 cm^{-1} respectively can be ascribed to C=N stretching vibration of the imine group from the chiral bis-hydrazone ligands (Figure 3). Apart from the characteristic bands of the chiral ligand, FT-IR spectra of **18-23** also show strong absorption peaks at 2143 cm^{-1}, 2118 cm^{-1}; 2144 cm^{-1}, 2120 cm^{-1}; 2134 cm^{-1}, 2123 cm^{-1}; 2132 cm^{-1}, 2123 cm^{-1}; 2143 cm^{-1}, 2118 cm^{-1} and 2127 cm^{-1}, 2066 cm^{-1} respectively. These bands can be easily assigned to C≡N stretching vibrations of the ferricyanide moiety. The doublet nature of C≡N stretching vibrations is mainly due to presence of two different cyanide groups in **18-23**, *viz.* bridging cyanide (the lower frequency) and free-terminal cyanide (the higher frequency).

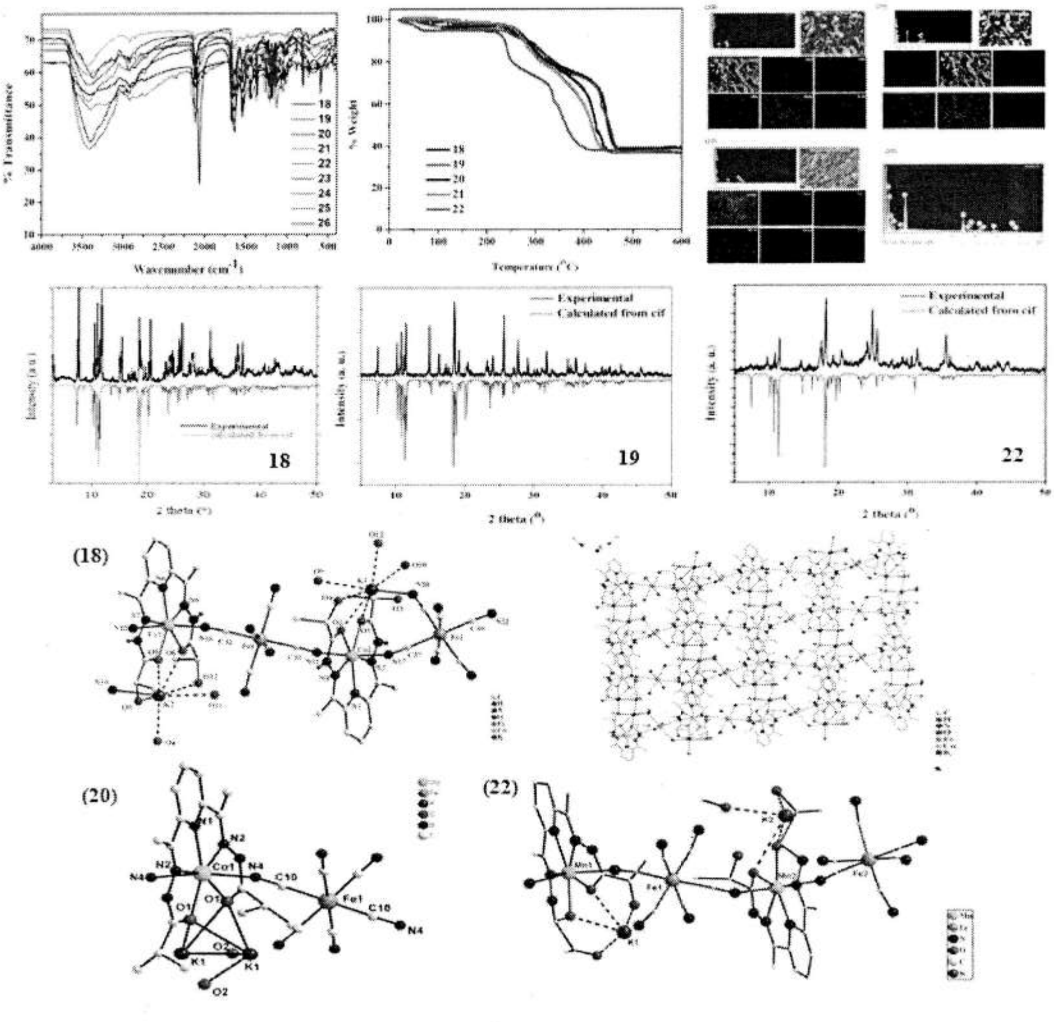


Figure 3. Characterizations of cyanido bridged chiral M(II)-Fe(III)/W(V) heterometallic aggregates. *Above:* FT-IR spectra of cyanido bridged aggregates showing the presence of

bridging and terminal cyanide stretching vibration and inclusion of chiral bis-hydrazone ligand (left), TGA patterns of cyanido bridged aggregates (middle) and EDX spectra and mapping showing the presence and distribution of elements for cyanido bridged aggregates (right). *Middle:* Powder X-ray diffraction pattern of chiral cyanido bridged heterometallic aggregates. Black line represents the experimental values and red line represents the calculated pattern. *Below:* Molecular structures of selected cyanido bridged chiral M(II)-Fe(III) heterometallic aggregates.

Molecular structures of cyanido bridged chiral M(II)-Fe(III) [M = Co, Mn] heterometallic aggregates: Single crystal X-ray diffraction analysis of cyanido bridged aggregates establishes the formation of a cyanido bridged hetero-metallic M(II)-Fe(III) [M = Co, Mn] extended structure. Asymmetric unit of M(II)-Fe(III) aggregate derived from *l-daplh* and *R*-daphibh chiral bis-hydrazone ligand consists of $[M(l\text{-daplh})]^{2+}$ and $[M(R\text{-daphibh})]^{2+}$ units linked by cyanido groups of $[Fe(CN)_6]^{3-}$ units (Figure 3). The pentagonal bipyramidal geometry around the M(II) center in the precursor complex is retained in case of the M(II) centers present in asymmetric unit. As observed in case of the *3d* building blocks, donor atoms from the planar pentadentate chiral ligand, *l*-daplh/*R*-daphibh occupy the five equatorial sites of the M(II) centers. The axial coordination sites of the M(II) centers are occupied by cyanido groups from two neighboring $[Fe(CN)_6]^{3-}$ units. This leads to the formation of cyanido bridged one dimensional polymeric structure. In order to maintain electroneutrality, two K^+ ions are also present within the asymmetric unit of **18** and **22** and one K^+ ion within the asymmetric unit of **20**. It is pertinent to note here that charge assisted self-assembly of pentagonal bipyramidal M(II) complexes (M = Mn(II), Fe(II), Co(II), and Ni(II)etc.) with cyanometallates generally yield charge neutral molecular assemblages. For example, reaction of a pentagonal bipyramidal Co(II) precursor with ferricyanide have earlier yielded a cyanido bridged pentanuclear $\{Co_3Fe_2\}$ aggregate. Thus, the ability of α-hydroxy groups in *l*-daplh and *R*-daphibh ligand to coordinate with potassium ions alters the typical charge assisted aggregation pattern and thereby facilitates formation of two dimensional extended structures (Figure 3).

Synthesis and characterizations of cyanido bridged chiral M(II)-W(V) [M = Co, Mn] heterometallic aggregates: Reaction of chiral PBP complex $[Co(l\text{-daplh})(H_2O)_2](NO_3)_2{\cdot}2H_2O$ with $Cs_3[W(CN)_8]$ in presence of excess KSCN results in the isolation of purple block shaped crystals cyanido bridged Co(II)-W(V) heterometallic aggregates **24** and reaction of chiral PBP complexes $[Co(l\text{-daplh})(H_2O)_2](NO_3)_2{\cdot}2H_2O$ and $[Mn(l\text{-daplh})(H_2O)Cl]Cl{\cdot}H_2O$ with $(TBA)_3[W(CN)_8]$ result isolation of dark red block and orange crystals of cyanido bridged Co(II)-W(V) heterometallic aggregates **25** and **26** respectively. Results of elemental analysis, AAS and EDS are in good agreement with the anticipated formulation of cyanido bridged M(II)-W(V) heterometallic aggregates **24-26.**

FT-IR spectroscopy of cyanido bridged chiral M(II)-W(V) [M = Co, Mn] heterometallic aggregates: FT-IT spectra of **24-26** show intense peaks at 1655 cm^{-1}, 1640 cm^{-1} and 1650

cm^{-1} respectively can be assigned to C=N stretching vibration of the imine group from the chiral bis-hydrazone ligands. FT-IR spectra of **24**-**26** also show strong absorption peaks at 2142 cm^{-1}, 2115 cm^{-1}, 2092 cm^{-1}; 2119 cm^{-1}, 2097 cm^{-1} and 2114 cm^{-1}, 2097 cm^{-1} respectively. These bands can be easily assigned to C≡N stretching vibrations of the octacyanide moiety.

*Magnetic properties of $[\{K(H_2O)\}\{K(H_2O)_2\}\{Co(l\text{-}daplh)\}_2\{Fe(CN)_6\}_2]_n$ **(18)**:*

Magnetic properties of **18** reveal a spin-chain behaviour. The $\chi_M T$ value at 300 K is 3.05 $cm^3\ mol^{-1}\ K$ and in fair agreement with what could be expected for magnetically isolated high spin Co(II) with pentagonal bipyramid coordination sphere and low spin Fe(III) (Figure 4). On lowering the temperature, $\chi_M T$ value slowly increases while below 30 K it rapidly rises to reach 7.5 $cm^3\ mol^{-1}$ K at 2 K. Such behaviour is characteristic for a spin array with ferromagnetic interactions. Analysis of the $\chi_M T$ versus T behaviour by the isotropic Heisenberg exchange model for a chain of alternating spins permitted to estimate a ferromagnetic Co-Fe interaction of $J = 2.92 \pm 0.03$ cm-1 with $g_{Co} = 2.39$, $g_{Fe} = 2$ (fixed), and $zj' = -0.162 \pm 0.03\ cm^{-1}$ (Hamiltonian formalism $H = \Sigma_{(i,j)} - J_{i,j}\boldsymbol{S}_i \cdot \boldsymbol{S}_j$). This ferromagnetic interaction is consistent with the Curie-Weiss analysis (Figure 4) and with reported examples. The field dependence of magnetization recorded at 2 K shows that magnetization reaches 3.1 μ_B at 5 T. This value is lower than the saturation magnetization value expected for such a spin system and reflects the strong magnetic anisotropy of the Co(II) and Fe(III) centers (Figure 4). AC susceptibility studies performed in zero-field and with applied static field did not show any evidence for slow relaxation of the magnetization in **18** (Figure 4).

*Electrical properties of $[\{K(H_2O)\}\{K(H_2O)_2\}\{Co(l\text{-}daplh)\}_2\{Fe(CN)_6\}_2]_n$ **(18)**:*

Electric behaviour of cyanido bridged Co(II)-Fe(III) aggregate **18** was investigated as the structure crystallizes in polar point group. $[\{K(H_2O)_2\}\{K(H_2O)\}\{Co(l\text{-}daplh)\}_2\{Fe(CN)_6\}_2]_n$ **(18)** (C_1 point group) displays a field dependent hysteresis loop (Figure 4). Under 20 kV applied field, the remnant polarization (P_r) is 0.12 $\mu C\ cm^{-2}$ and coercive field (E_c) is 8.5 $kV\ cm^{-1}$. Both the remnant polarization and coercive field observed are comparable to those reported in case of a chiral cyanido bridged Fe(III)-Ni(II) chain. Further electrical characterizations such as polarization hysteresis loop studies under variable temperatures and temperature dependence of dielectric constant measurements are currently ongoing to establish true electric nature of **18**.

Water processibility studies of cyanido bridged chiral M(II)-Fe(III) [M = Co, Mn] heterometallic aggregates:

Cyanido bridged chiral heterometallic Co(II)/Mn((II)-Fe(III)/W(V) aggregates are found to be well soluble in water. The aqueous solubility of cyanido bridged chiral heterometallic aggregates can be primarily attributed to the presence of dangling aliphatic hydroxo groups attached to the chiral ligand. For instance, addition of 10 mL distilled water to 7 mg of **18** immediately results in a transparent yellow colour solution (Figure 4). Mass spectrometric analysis of an aliquot showed m/z values supporting persistence of oligomeric heterobimetallic fragments of **18** in solution (Figure 4). Moreover, UV-visible spectrum of

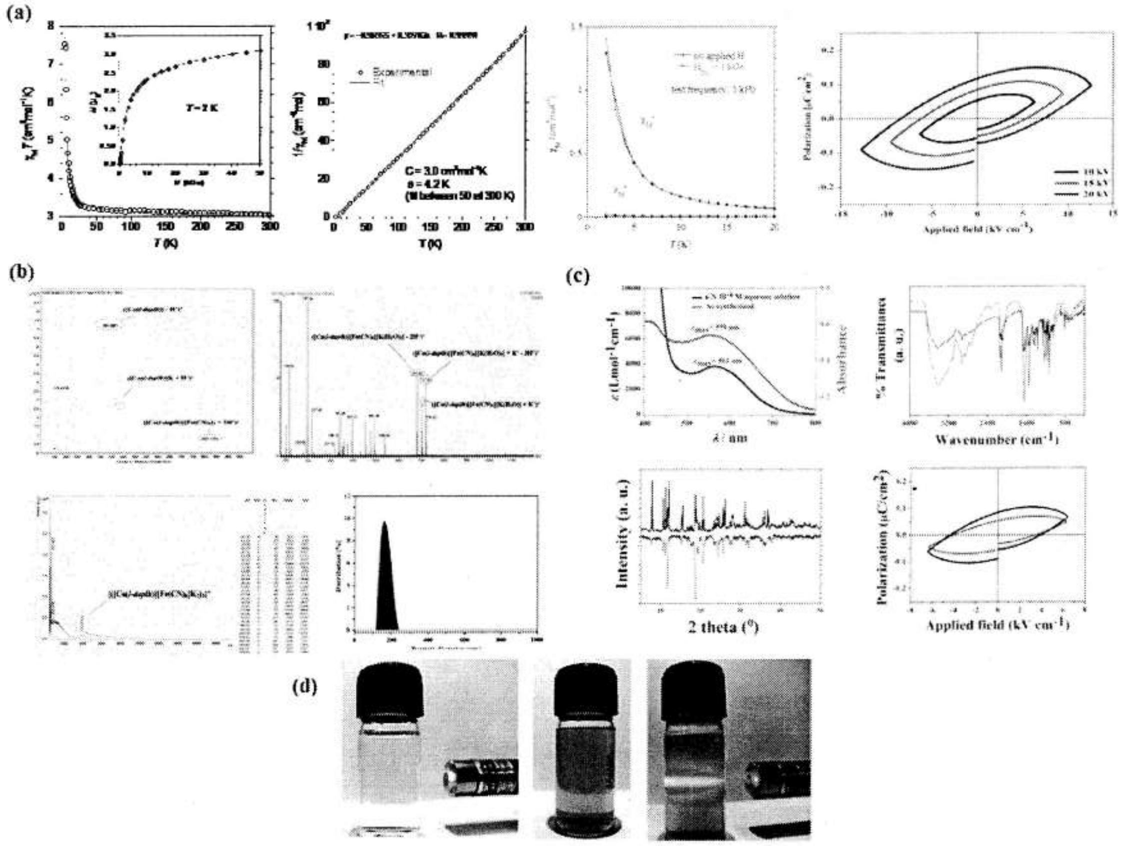


Figure 4: (a): Magnetic and electrical measurements of compound **18**; (b) Solution state studies (ESI- mass, LC-mass, MALDI-TOF and DLS spectrum) of **18**; (c) Comparison between solid and solution state studies of **18** and (d) Photograph of Tyndall effect of **18** in presence of LASER beam.

aqueous solution features a broad peak at λ_{max} = 561 nm which is absent in the spectra of the individual building blocks (Figure 4). This peak can be assigned to metal-to-metal electron transfer from Co(II) to Fe(III) and observed at 559 nm in the diffuse reflectance spectra of **18**. Thus, ESI-MS and UV-visible studies confirmed integrity of the Fe-CN-Co linkages in aqueous medium. The aqueous solution of **18** shows Tyndall effect indicative of formation of a colloidal suspension (Figure 4). Dynamic light scattering measurement of this solution confirms its colloidal nature by showing presence of particles of size ~125 nm (Figure 4). Interestingly, compound **18** can be recovered from its aqueous solution without alteration of its pristine properties. Both the FT-IR spectra as well as powder X-ray diffraction pattern of as synthesized **18** and the sample isolated by evaporating water from an aqueous solution of **18** (i.e. **18'**) are identical (Figure 4). Furthermore, no significant differences in the electrical hysteresis loops are observed between **18** and **18'** (Figure 4).

The aqueous solubility for other cyanido bridged chiral heterometallic aggregates are as follows: 0.68 mg/mL for **19**, 0.65 mg/mL for **20**, 0.62 mg/mL for **21**, 1.34 mg/mL for **22** and 0.83 mg/mL for **24**. Similar to that of compound **18**, these chiral cyanido bridged heterometallic aggregates form a microscopic colloidal suspension in water. Structural integrity of the heterometallic cyanido bridged aggregates is retained in the colloidal suspension and it can be easily recovered from aqueous medium by evaporation without loss of its structural integrity.

Conclusions

Several new chiral planar pentadentate acyclic bis-hydrazone ligands based on 2,6-diacetylpyridine were prepared and their seven coordinated Co(II), Ni(II) and Mn(II) complexes were prepared. Six novel chiral 1D Co(II)-Fe(III) and Mn(II)-Fe(III) heterometallic aggregates were prepared by interlinking chiral pentagonal bipyramidal Co(II) and Mn(II) complexes and hexacyanoferrate. Apart from that three Co(II)-W(V) and Mn(II)-W(V) heterometallic aggregates are also prepared. All new compounds have been characterized with the aid of analytical and spectroscopic studies. Low temperature magnetization measurements have shown strong ferromagnetic ordering at low temperature for the chiral heterometallic Co(II)-Fe(III) 1D complex. Polarization measurements on chiral heterometallic Co(II)-Fe(III) 1D complex have shown ferroelectric hysteresis loop with considerable remnant polarization and coercive field. Chiral heterometallic M(II)-Fe(III) (M = Co, Mn) 1D complexes are well-soluble in water. Results obtained so far indicate that the chiral pentadentate bis-hydrazone ligands formed by 2,6-diacetylpyridine can enforce PBP coordination environment around a large variety of transition metal ions. The pentagonal bipyramidal coordination geometry is an efficient environment to induce strong magnetic anisotropy in transition metal ions which are otherwise considered to be magnetically isotropic in Oh environment. The prepared chiral heterometallic Co(II)-Fe(III) 1D complex is a multiferroic material that possesses ferromagnetism and ferroelectricity simultaneously. Moreover, the solubility of chiral heterometallic M(II)-Fe(III) (M = Co, Mn) 1D complexes in water makes them potentially fruitful for practical applications and exploration of properties in solution phase.

Scope of future work

Based upon the result obtained and experience gained from this project we expect to develop multiferroic magnetic materials for application in information storage, sensor etc. Highly anisotropic transition metal ions in pentagonal bipyramidal geometry using chiral Schiff base ligands are identified during the course of this project. We anticipate that assembling these anisotropic building blocks with 4d/5d cyanometallates shall result in nano-magnets with better characteristics. Due the enhanced 3d-4d/5d exchange interaction and large anisotropy from the 3d building blocks, we anticipate to increase the energy barrier of magnetization reversal U = -DS2 in the proposed hetero-nuclear assemblies.

List of Publications (only from SCI indexed journals) :

Title of the Paper	List of Authors	Journal Details	Month & Year	Volume	Status	DOI No	Impact Factor
Rapid SuzukiMiyaura cross coupling reaction catalyzed by zirconium carboxyphosphonate supported mixed valent Pd(0) /Pd(II) catalyst	Bagmita Bhattacharyya, Jyoti Prasad Biswas, Shashank Mishra, Nayanmoni Gogoi	APPLIED ORGANOMETALLIC CHEMISTRY (International)	May-2019	33 (e5017)	Published	DOI: 10.1002/aoc.5017	3.259
Deciphering the influence of structural distortions on the uniaxial magnetic anisotropy of pentagonal bipyramidal Ni (II) complexes	Mamon Dey, Prashurya Pritam Mudoi, Anup Choudhury, Bipul Sarma and Nayanmoni Gogoi	CHEMICAL COMMUNICATIONS (International)	Oct-2019	55 (11547)	Published	10.1039/c9cc05032a	6.164
Accessing water processable cyanido bridged chiral heterobimetallic Co(II)–Fe(III) one dimensional network	Anup Choudhury, Celine Pichon, Jean-Pascal Sutter, Dobbidi Pamu, Bipul Sarma, Prashurya Pritam Mudoia and Nayanmoni Gogoi	CHEMICAL COMMUNICATIONS (International)	Jan-2021	57 (207)	Published	10.1039/d0cc05356b	5.996
Enhanced catalytic activity and near room temperature gas sensing properties of SnO2 nanoclusters@mesoporous Sn (IV) organophosphonate composite	Suchibrata Borah, Bagmita Bhattacharyya, Jumi Deka, Aditya Borah, Anuchaya Devi, Dhanapati Deka, Shashank Mishra, Kalyan Raidongia and Nayanmoni Gogoi	Dalton Transactions (International)	Jul-2017	(8664-8672)	Published		4.099
Evidence of protonation induced intra-molecular metal-to-metal charge transfer in a highly symmetric cyanido bridged {Fe2Ni2} molecular square	Prashurya Pritam Mudoi, Bipul Sarma, Anup Choudhury and Nayanmoni Gogoi	DALTON TRANSACTIONS (International)	Feb-2021	50 (2057)	Published	10.1039/d0dt02826f	4.174
Pd nanoparticles dispersed on ZrIV organophosphonate: A robust and reusable catalyst for Suzuki-Miyaura cross coupling reactions.	Suchibrata Borah, Shashank Mishra, Luis Cardenas and Nayanmoni Gogoi	European Journal of Inorganic Chemistry (International)	Feb-2018	(751-758)	Published		2.507
Cyano bridged heterometallic Mn (II)-Fe (III) aggregates: synthesis, structure and magnetic properties.	Mamon Dey, Bipul Sarma, Nayanmoni Gogoi	Inorganica Chimica Acta (International)	Jan-2018	469 (20-24)	Published		2.264
Influence of aromatic nitro-substituents on auto-reusability of oxime based fluoride receptors	Suchibrata Borah, Avinash Hazarika, Gorishmita Borah, Nayanmoni Gogoi	JOURNAL OF CHEMICAL SCIENCES (International)	Sep-2018	130 (118)	Published		1.254

List of Papers Published in Conference Proceedings, Popular Journals :

Title of the Paper	List of Authors	Journal Details	Month & Year	Volume	Status	DOI No	Impact Factor
Not Available							

List of Patents filed/ to be filed :

Patent Title	Authors	Patent Type	Country/Agency Name	Patent Status	Application/Grant No.
Not Available					

Equipment Details :

Equipment Name	Cost (INR)	Procured	Make & Model	Utilization %	Amount Spent (INR)	Date of Procurement
Analytical Balance	1,48,125	Yes	METLAR ME204	100	1,00,000	13 Feb, 2017
Vacuum Pump	59,940	Yes	HHV FD-6	100	59,941	20 Mar, 2017
High Perfomance Computer	3,00,000	Yes	Hewlett Peckerd HPZ440	100	3,87,918	22 Mar, 2017
Refrigerator	30,000	Yes	Godrej RT-EON 240	100	26,400	13 Feb, 2017

Plans for utilizing the equipment facilities in future:

Equipment's procured under the present project are planned to be used in the PI's laboratory for related investigations on development of nano-magnetic materials in the near future.

UP-TO-DATE STATEMENT OF EXPENDITURE

1. SERB Sanction Order No and date : EMR/2016/002178 dated 04/11/2016
2. Name of the PI : Dr. NAYANMONI GOGOI
3. Total Project Cost : 24,93,700.00
4. Revised Project Cost : NA
5. Date of Commencement : 16 NOVEMBER 2016
6. Statement of Expenditure
   (Month wise expenditure incurred during current financial year)

Month & year	**Expenditure incurred/committed**
April 2019	NIL
May 2019	42,566.00
June 2019	NIL
July 2019	NIL
August 2019	NIL
September 2019	1,13,648.00
October 2019	4,200.00
November 2019	1,25,483.00
Total Expenditure during F. Y. 2019-2020	**2,85,890.00**

7. Grant received in each year
   a. 1st Year : ₹ 11,90,500.00
   b. 2nd Year : ₹ 4,00,000.00
   c. 3rd Year : ₹ 7,50,000.00
   d. Interest, if any: : ₹ 14,496.00
   e. Total (a+b+c+d) : ₹ 23,54,996.00

Annexure-II

Statement of Expenditure

For the period 16th November 2016 to 15th November 2019

Title: Development of Chiral Single Molecule Magnets. Sanction No. SERB/EMR/2016/002178

Sr No (I)	Sanctioned Heads (II)	Total Fund Allocated (Sanctioned) (III) In₹	Expenditure Incurred				Total Expenditure till 15 November 2019 (VIII = IV + V+ VI+ VII) In₹	Balance as on 15th November 2019 (IX = III – VIII) In ₹	Remarks (If any)
			1st Year (IV) In₹	2nd Year (V) In₹	3rd Year (VI) In₹	4th Year (VII)			
1.	**Manpower**	**4,70,000**	**28,903**	**1,82,000**	**1,54,000**	**98,000**	**4,62,903**	**7,097**	**NIL**
2.	**Consumables**	**9,25,925**	**3,04,362**	**1,79,099**	**3,16,603**	**1,25,553**	**9,25,617**	**308**	**NIL**
3.	**Travel**	**65,000**	**15,650**	**30,199**	**18,730**	**NIL**	**64,579**	**421**	**NIL**
4.	**Contingencies**	**1,35,000**	**16,297**	**22,691**	**32,580**	**62,337**	**1,33,905**	**1095**	**NIL**
5.	**Others, if any**	**NIL**	**NIL**	**NIL**	**NIL**	**NIL**	**NIL**	**NIL**	**NIL**
6.	**Equipment**	**5,39,000**	**5,39,000**	**NIL**	**NIL**	**NIL**	**5,39,000**	**NIL**	**NIL**
7.	**Overhead**	**2,20,071**	**1,08,076**	**47,250**	**64,745**	**NIL**	**2,20,071**	**NIL**	**NIL**
8.	**Total**	**23,54,996**	**10,12,288**	**4,61,239**	**5,86,658**	**2,85,890**	**23,46,075**	**8,921**	**NIL**

Name of the Principal Investigator: **Dr. NAYANMONI GOGOI**

Signature of **PI:**

Date: 10/09/2024

Signature of competent financial authority: 17/9/2024

(with seal)

Finance Officer
Tezpur University

Date:

GFR 12-A
[(See Rule 238(1))]
UTILIZATION CERTIFICATE (UC) FOR THE YEAR 2019-2020
In respect of *RECURRING*
As on 15th November 2019 to be submitted to SERB
Audited UC

Certified that I have satisfied that the conditions on which grants were sanctioned have been duly fulfilled/are being fulfilled and that I have exercised following checks to see that the money has been actually utilized for the purpose for which it was sanctioned:

(i) The main accounts and other subsidiary accounts and registers (including assets registers) are maintained as prescribed in the relevant Act/Rules/Standing instructions (mention the Act/Rules) and have been duly audited by designated auditors. The figures depicted above tally with the audited figures mentioned in financial statements/accounts.

(ii) There exist internal controls for safeguarding public funds/assets, watching outcomes and achievements of physical targets against the financial inputs, ensuring quality in asset creation etc. & the periodic evaluation of internal controls is exercised to ensure their effectiveness.

(iii) To the best of our knowledge and belief, no transactions have been entered that are in violation of relevant Act/Rules/standing instructions and scheme guidelines.

(iv) The responsibilities among the key functionaries for execution of the scheme have been assigned in clear terms and are not general in nature.

(v) The benefits were extended to the intended beneficiaries and only such areas/districts were covered where the scheme was intended to operate.

(vi) The expenditure on various components of the scheme was in the proportions authorized as per the scheme guidelines and terms and conditions of the grants-in-aid.

(vii) It has been ensured that the physical and financial performance under core research grant (CRG) has been according to the requirements, as prescribed in the guidelines issued by Govt. of India and the performance/targets achieved statement for the year to which the utilization of the fund resulted in outcomes given at Annexure – I duly enclosed.

(viii) The utilization of the fund resulted in outcomes given at Annexure – II duly enclosed (to be formulated by the Ministry/Department concerned as per their requirements/specifications.)

(ix) Details of various schemes executed by the agency through grants-in-aid received from the same Ministry or from other Ministries is enclosed at Annexure –II (to be formulated by the Ministry/Department concerned as per their requirements/specifications).

Date: 10/09/2021
Place: TEZPUR UNIVERSITY

10/09/21 **Signature of PI: ....** **Name: Dr. Nayanmoni Gogoi**	13/9/2021 **Signature with Seal: ....** **Name: Dr. B. B. Mishra** **Finance Officer** **Tezpur University**	15/9/21 **Signature with Seal....................** **Name: Dr. Biren Das** **Registrar** **Tezpur University**

Finance Officer
Tezpur University

Registrar
Tezpur University

GFR 12-A
[(See Rule 238(1))]
UTILIZATION CERTIFICATE (UC) FOR THE YEAR 2019-2020
In respect of *RECURRING*
As on 15th November 2019 to be submitted to SERB
Audited UC

1. Name of the grant receiving Organization: **TEZPUR UNIVERSITY**
2. Name of Principal Investigator (PI): **DR. NAYANMONI GOGOI**
3. SERB Sanction order no. & date: **SERB/EMR/2016/002178 dated 04/11/2016**
4. Title of the Project: **Development of Chiral Single Molecule Magnets**
5. Name of the SERB Scheme: **CORE RESEARCH GRANT**
6. Whether recurring or non-recurring grants: **RECURRING**
7. Grants position at the beginning of the Financial year
   - (i) Carry forward from previous financial year : **2,94,551**
   - (ii) Others, If any : **NIL**
   - **(iii) Total** : **2,94,551**
8. Details of grants received, expenditure incurred and closing balances: (Actuals)

Unspent Balance of Grants received previous years [figure as at Sl. No. 7(iii)]	Interest Earned thereon	Interest deposited back to the SERB	Grants received during the year			Total Available funds (1+2-3+4)	Expenditure incurred	Closing Balances (5-6)
1	2	3	4			5	6	7
			Sanction No. (i)	Date (ii)	Amount (iii)			
2,94,551	**260**	**NIL**	**NA**	**NA**	**NIL**	**2,94,811**	**2,85,890**	**8,921**

Component wise utilization of grants:

Grants-in-aid- General	Grant-in-aid-creation for capital assets	Total
2,85,890	**NIL**	**2,85,890**

Details of grants position at the end of the year

- (i) Balance available at end of financial year: **8,921**
- (ii) Unspent balance refunded to SERB (If any): **8,921**
- (iii) Balance (Carried forward to next financial year) if applicable: **NIL**

GFR 12-A
[(See Rule 238(1))]
UTILIZATION CERTIFICATE (UC) FOR THE YEAR 2019-2020
In respect of *NON-RECURRING*
As on 15th November 2019 to be submitted to SERB
Audited UC

1. Name of the grant receiving Organization: **TEZPUR UNIVERSITY**
2. Name of Principal Investigator (PI) : **DR. NAYANMONI GOGOI**
3. SERB Sanction order no. & date: **SERB/EMR/2016/002178 dated 04/11/2016**
4. Title of the Project: **Development of Chiral Single Molecule Magnets**
5. Name of the SERB Scheme: **CORE RESEARCH GRANT**
6. Whether recurring or non-recurring grants : **NON-RECURRING**
7. Grants position at the beginning of the Financial year
    - (i) Carry forward from previous financial year : **NIL**
    - (ii) Others, If any : **NIL**
    - **(iii) Total : NIL**
8. Details of grants received, expenditure incurred and closing balances: (Actuals)

Unspent Balance of Grants received previous years [figure as at Sl. No. 7(iii)]	Interest Earned thereon	Interest deposited back to the SERB	Grants received during the year			Total Available funds (1+2-3+4)	Expenditure incurred	Closing Balances (5-6)
1	2	3	4			5	6	7
			Sanction No. (i)	Date (ii)	Amount (iii)			
NIL	**NIL**	**NIL**	**NA**	**NA**	**NIL**	**NIL**	**NIL**	**NIL**

Component wise utilization of grants:

Grants-in-aid- General	Grant-in-aid-creation for capital assets	Total
NA	**NIL**	**NIL**

Details of grants position at the end of the year

(i) Balance available at end of financial year : **NIL**
(ii) Unspent balance refunded to SERB (If any) : **NIL**
(iii) Balance (Carried forward to next financial year) if applicable : **NIL**

GFR 12-A
[(See Rule 238(1))]
UTILIZATION CERTIFICATE (UC) FOR THE YEAR 2019-2020
In respect of *NON-RECURRING*
As on 15th November 2019 to be submitted to SERB
Audited UC

Certified that I have satisfied that the conditions on which grants were sanctioned have been duly fulfilled/are being fulfilled and that I have exercised following checks to see that the money has been actually utilized for the purpose for which it was sanctioned:

(i) The main accounts and other subsidiary accounts and registers (including assets registers) are maintained as prescribed in the relevant Act/Rules/Standing instructions (mention the Act/Rules) and have been duly audited by designated auditors. The figures depicted above tally with the audited figures mentioned in financial statements/accounts.

(ii) There exist internal controls for safeguarding public funds/assets, watching outcomes and achievements of physical targets against the financial inputs, ensuring quality in asset creation etc. & the periodic evaluation of internal controls is exercised to ensure their effectiveness.

(iii) To the best of our knowledge and belief, no transactions have been entered that are in violation of relevant Act/Rules/standing instructions and scheme guidelines.

(iv) The responsibilities among the key functionaries for execution of the scheme have been assigned in clear terms and are not general in nature.

(v) The benefits were extended to the intended beneficiaries and only such areas/districts were covered where the scheme was intended to operate.

(vi) The expenditure on various components of the scheme was in the proportions authorized as per the scheme guidelines and terms and conditions of the grants-in-aid.

(vii) It has been ensured that the physical and financial performance under core research grant (CRG) has been according to the requirements, as prescribed in the guidelines issued by Govt. of India and the performance/targets achieved statement for the year to which the utilization of the fund resulted in outcomes given at Annexure – I duly enclosed.

(viii) The utilization of the fund resulted in outcomes given at Annexure – II duly enclosed (to be formulated by the Ministry/Department concerned as per their requirements/specifications.)

(ix) Details of various schemes executed by the agency through grants-in-aid received from the same Ministry or from other Ministries is enclosed at Annexure –II (to be formulated by the Ministry/Department concerned as per their requirements/specifications).

Date: 24/09/2021
Place: TEZPUR UNIVERSITY

24/9/21 Signature of PI : .... Name: Dr. Nayanmoni Gogoi	Signature ~~with Seal~~ : 21/9/21.......... Name: Dr. B. B. Mishra Finance Officer Tezpur University	20/9/21 Signature with Seal.................... Name: Dr. Biren Das Registrar Tezpur University

Finance Officer
Tezpur University

Registrar
Tezpur University

File Name : **EMR/2016/002178**

Investigator Name : **Nayanmoni Gogoi**

Project Title : **Development of Chiral Single Molecule Magnets**

Statement of Expenditure

Tezpur University Napaam, Tezpur, Assam TEZPUR - 784028 (ASSAM)

S.No.	**Budget Head**	**Sanctioned Amount (INR)**		**Released Amount (INR)**	**Expenditure incurred from 16/11/2016 to 31/03/2017 (INR)**	**Expenditure incurred from 01/04/2017 to 31/03/ 2018 (INR)**	**Expenditure incurred from 01/04/2018 to 31/03/ 2019 (INR)**	**Expenditure incurred from 01/04/2019 to 15/11/2019 (INR)**	**Total Expenditure incurred (INR)**		**Balance (INR)**	**Commited Expenditure (INR)**
1	**Non-Recurring**	5,39,000		5,39,000	5,39,000	0	0	0	***5,39,000***		0	0
2	**Manpower**	5,28,000	19,54,700	18,01,500	28,903	1,82,000	1,54,000	98,000	***4,62,903***	***18,07,075***	-5,575	0
3	**Consumables**	9,00,000			3,04,362	1,79,099	3,16,603	1,25,553	***9,25,617***			0
4	**Contingency**	1,50,000			16,297	22,691	32,580	62,337	***1,33,905***			0
5	**Travel**	1,50,000			15,650	30,199	18,730	0	***64,579***			0
6	**Others**	0			0	0	0	0	***0***			0
7	**Overheads**	2,26,700			1,08,076	47,250	64,745	0	***2,20,071***			0
8	**SSR**	0			0	0	0	0	***0***			0
9	**Interest accrued (if any)**	0		14,496	2,085	3,572	8,579	260	***0***		14,496	-
Total		***24,93,700***		***23,40,500***	***10,12,288*** [4,73,288 + 5,39,000]	***4,61,239*** [4,61,239 + 0]	***5,86,658*** [5,86,658 + 0]	***2,85,890*** [2,85,890 + 0]	***23,46,075*** [18,07,075 + 5,39,000]		*8,921*	*0*
					View SE/UC (16/11/2016 to 31/03/2017)	View SE/UC (01/04/2017 to 31/03/2018)	View SE/UC (01/04/2018 to 31/03/2019)	View SE/UC (01/04/2019 to12 15/11/2019)				