This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard **Terms & Conditions** and the **Ethical guidelines** still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ARTICLE TYPE

A perception of ferro- and antiferromagnetic interaction in a two dimensional Ni(II) heterochiral coordination polymer showing unusual CO₂ uptake behavior[#]

Himanshu Sekhar Jena, Soumyabrata Goswami, Suresh Sanda, Srinivasulu Parshamoni, Soumava Biswas and Sanjit Konar*†[a]

Abstract: We present a robust two dimensional coordination polymer, [Ni₂(L)₂(N(CN)₂)₂]ₙ (1) (LH = 2-((1-(pyridin-2-yl)ethylimino)methyl)phenol; N(CN)₂⁻ = dicyanamide ion) using a chiral Schiff base (LH), which shows diastereoselectivity in structure via chiral self-discrimination process, ferro- and antiferromagnetic interactions among the metal centers and unusual CO₂ uptake behavior as a porous framework

In recent years, fabrication of porous magnets or Magnetic Metal Organic Frameworks (MMOFs) have attracted much attention since magnetism and porosity could be simultaneously achieved by proper choice or design of the primary and bridging ligands.[1] Most of the molecular magnets studied so far consist of extended coordination networks or discrete polynuclear aggregates, in which paramagnetic metal ions are linked together by short bridging ligands that induce ferromagnetic (FM) or antiferromagnetic (AFM) super-exchange interactions between the local spins.[2,3] Moreover, the exploitation of FM interactions is a straightforward approach towards the new generation of molecular magnets, like single-molecule magnets (SMMs), single-chain magnets (SCMs), ferromagnets, and metamagnets with few exceptions.[4] Apart from carboxylate, cyano and azide ions, dicyanamide (dca) ions are also known to engender ferromagnetic interaction[3,5] because of their diverse bridging modes (Scheme S1).

From the last few years, several phenoxo bridged transition metal complexes encompasing Schiff base and dca ligands showing diverse magnetic properties are reported.[5a] However most of them show antiferromagnetic behavior. In particular, reported dinickel(II) complexes involving a (NiO)₂ core are antiferromagnetically coupled and a very few ferromagnetic phenoxo bridged polynuclear Ni(II) complexes are reported.[6] In comparison to other Schiff base ligands, racemic Schiff bases are not explored in this context. It has been anticipated that the use of racemic Schiff base along with suitable bridging linkers might form homochiral [(···R···B···R···) and (···S···B···S···), where B = bridging linker] *via* spontaneous resolution or racemic [(···R···B···S···)] MOFs or coordination polymers (CPs).[7] Besides structural self-assembly, it might engender significant magnetic interactions between the paramagnetic metal centres and show

selective sorption behavior towards various gases and solvent vapours.

In this paper, we describe the diastereoselective self-assembly of a heterochiral dimer in chiral self-discrimination process using a chiral tridentate Schiff base ligand (L; where LH = 2-((1-(pyridin-2-yl)ethylimino)methyl)phenol) and Ni(II) ion which further extended to form a 2D CP by bridging dca ion and retain the racemic nature as a whole. Magnetic investigation of complex **1** demonstrate an exceptional synergism of weak ferromagnetic, inter-dimer antiferromagnetic interactions and ZFS at low temperature and a hysteresis loop at 1.8 K with a coercive field of 373 Oe. Sorption analysis of **1** shows a very rare phenomenon of low CO₂ uptake at low temperature than at high temperature.
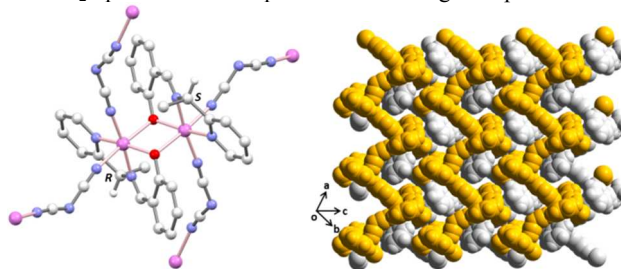

Fig. 1. Illustration of phenoxo bridged heterochiral (*RS*) dinuclear moiety (left) and (b) 2D coordination polymer showing enantiomeric segregation to form a zig-zag arrangement found in complex **1** (right). Colour codes: Ni (magenta), C (gray), N (blue), O (red), H (white). Orange represents *R*-enantiomer of ligand L whereas gray represents *S*-enantiomer of ligand L.

Complex **1** crystallized in space group *P*-1 and its asymmetric unit [Ni(L)(dca)]₂ contains two Ni(II) centers bridged by two ligands **L** and two *μ*-1,5-dca bridging ligands (Fig. S1). The distance between two Ni(II) centers bridged by nitrogen atoms of dca ligands is 8.315(6) Å and the two Ni(II) centers have stereochemistry of *cis,cis,cis*-(O$_P$)₂(N$_D$)₂(N$_Y$N$_I$) (where O$_P$ = phenoxo-O, N$_Y$ = Pyridine-N, N$_I$ = Imine-N and N$_D$ = dicyanamide-N). However, its molecular structure reveals two dinuclear Ni(II) centers bridged by dca ligands. As illustrated in Fig. 1a, each dinuclear unit contains two ligands **L** bridged to each Ni(II) center in meridional manner resulting in a phenoxo bridged (NiO$_P$)₂ core. The coordination geometry around each Ni(II) center is distorted octahedral which is satisfied by N₂O donor set of **L** and two N$_D$ of dca bridging ligands and one O$_P$

bridging of another ligand **L**. It was found that ligand **L** and one dca ligands are sited in square plane whereas the other dca and O_P of another ligand **L** are in axial sites. The overall shape of dinuclear units resembles a butterfly shape. Deep insight into each dinuclear unit reveals that both the $(NiO_P)_2$ cores are similar and have a center of symmetry which leads to the formation of heterochiral dimers (*RS*) by chiral self-discrimination process.[8] However, earlier with same ligands we observed a homochiral dinuclear self-assembly (*RS* or *SS*) in presence of dca and acetate ion by chiral self-recognition process.[8e]

In each dinuclear unit, the ligand **L** is bound to the Ni(II) centers by a five-membered and a six-membered ring and both the chelate rings are puckered. The O_P atom of **L** is slightly asymmetrically bridged to Ni(II) centers having $Ni-O_P$ distances of 2.037(4); 2.147(3) Å around Ni1 center and 2.029(4); 2.140(3) Å around Ni2 center. The angle between adjacent planes containing the cores $(Ni2O2)_2$ and $(Ni1O1)_2$ is 55.8°. The bond parameters around each Ni(II) center are listed in Table 2.

The packing diagram shows that each dinuclear unit is bridged to four nearby dinuclear units by four bridging dca ligands (Fig. S2) and further extended to form 2D CPs (Fig. S3). Hence each heterochiral dimer can be termed as four connected node. The Ni(II)-Ni(II) separations across the dca ion bridged 2D CPs are 8.315(1) and 8.281(1) Å and are lying within the range (7.56 – 8.37 Å) of reported end-to-end dca bridged 2D CPs.[5a] Careful investigation of 2D CP confirms that each nearby heterochiral dinuclear units discriminate each other, i. e. a dimer having (*RS*) combination preferred to link with dimer of (*RS*) combination to form (···*RS*···*RS*···*RS*···) chain which reflects that there is also a center of symmetry lying between two nearby dimers. Also it has been investigated that each enantiomer (*R* or *S*) of ligand **L** is segregated in zig-zag fashion (Fig. 1b). PLATON analysis reveals negligible pore accessible void volume of 68.6 Å^3 (4.4%) per unit cell volume of 1563.3 Å^3. The above perceived arrangement of heterochiral dimers in a CPs or MOFs is never known before and it adds a new example to the Yan's concept of chiral induction and transfer in coordination complexes.[9]

Thermo gravimetric (TG) analysis of complex **1** shows its robustness up to 280 °C followed by a weight loss of ∼ 17.5% (calculated ∼19%) in the temperature range of 280 – 500 °C, which is due to the loss of two dca ligands from complex **1** (Fig. S4). The bulk phase powder X-ray diffraction patterns of **1** is in good agreement with the simulated one based on the single crystal structure data (Fig. 3b), indicating the purity of the as-synthesized product.

Variable temperature DC magnetic studies has been performed on polycrystalline sample of complex **1** and the χ_M values (χ_M = molar magnetic susceptibility) have been corrected for diamagnetism.[10a] Measurement showed that upon cooling from room temperature, $\chi_M T$ increases from a value of 2.05 cm^3 K mol^{-1} at 300 K, to a maximum of 7.33 cm^3 K mol^{-1} at 14 K and then falls sharply to reach a value of 3.3 K at 1.8 K (Fig. 2a). The $\chi_M T$ value at 300 K is consistent with the expected value (1.92 cm^3 K mol^{-1}) for two uncoupled Ni(II) ions with g = 2.02. The overall behaviour of $\chi_M T$ with temperature reveals the presence of FM exchange interactions between two Ni(II) ions. The abrupt decrease in $\chi_M T$ below 14 K is due to zero field splitting (ZFS) and inter-dimer antiferromagnetic (AFM) interactions within the

2D network.[5d,e]

The field dependence of reduced magnetization ($M/N\mu_B$) (Fig. S5) showed a value of 3.45 $N\mu_B$ at 2 K and 7 T per Ni2 unit, which is a bit lower than the saturation value of 3.92 $N\mu_B$ for two uncoupled Ni(II) ions with g = 2.02. The unsaturated nature of the plot and slightly lower value of the reduced magnetization arises probably due to the simultaneous presence of inter-dimer AFM interactions and ZFS at lower temperature region. Magnetization plot also showed a nice hysteresis loop at 1.8 K with a coercive field of 373 Oe which clearly gave hint of the existence of weak FM interaction in the complex even at lower temperature regime (Fig. 2b). The effect of ZFS of the ground state and the exchange interaction at lower temperatures are dependent on each other[10b] and cannot be well determined from magnetic susceptibility data of polycrystalline material in the low-temperature range.[10c] Hence the data in the temperature range 30 - 300 K were included in the fitting procedure (shown as red line in Fig. 2a) to obtain the isotropic exchange parameter J using equation **1** by means of the Hamiltonian $\hat{H} = - J.S_1.S_2$ where $S_1 = S_2 = 1$.

$$\chi_M = \frac{2Ng^2\beta^2}{kT}\left[\frac{A}{B}\right] \quad (1)$$

where, $A = \exp(J/kT) + 5\exp(3J/kT)$ and $B = 1 + 3\exp(J/kT) + 5\exp(3J/kT)$.

The best fit led to $J/k = 20$ cm^{-1} and g = 2.02. The positive sign of the J factor verifies the ferromagnetic nature of the exchange. The observed intra-metallic ferromagnetic exchange interactions pathways can also be justified on the basis of the Ni−O−Ni bond angle (Ni1-O1-Ni1A = 99.0(1)° and Ni2-O2-Ni2A = 98.0(1)°). Literature scrutiny reveals Ni−O−Ni angle of ≤99°, favors ferromagnetic, whereas larger values correspond to antiferromagnetic interactions.[3f, 10a]
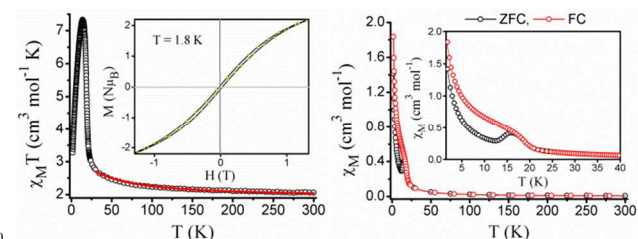

Fig. 2. Temperature dependence of the DC susceptibility for complex **1** (left) (inset shows hysteresis loop at 1.8 K with a coercive field of 373 Oe). The red line represents the best fit obtained. (b) Illustration of zero-field cooled (ZFC) and field cooled (FC) curves for complex **1** (right) (inset shows the zoomed-in low tempertaure zone).

The zero-field cooled (ZFC) and field cooled (FC) curves for complex **1** are also shown in Fig. 2b which exhibited a bifurcation at ~15 K. At this temperature (Néel temperature) the χ_M value in the ZFC plot suddenly decreased which indicated the presence of weak inter-dimer antiferromagnetic interaction in **1**. But below ~13 K, χ_M again increased sharply because of ferromagnetic interaction operative in the complex. This feature in the ZFC and FC plots in the title complex is indicative of the complications arising perhaps due to the concurrent presence of ZFS, weak FM and inter-dimer AFM interactions at low temperature.

Adsorption analysis of complex **1** with N$_2$ at 77 K shows 4.8 cm^3 g^{-1} implies surface adsorption (Fig. S6).[11] Adsorption study of **1**

with CO_2 shows 11 cm^3 g^{-1} of uptake at 298 K. This might be due to dipole–induced-dipole interaction between polar cyano groups as well as π-electron clouds of dicyanamide ion and π-electron clouds of CO_2 molecules, where the quadrupole moment of CO_2 (-1.4 × 10^{-39} Cm^2) interacts with the electric field gradient as suggested by Kitagawa et al.[12] Surprisingly the adsorption amount was decreased in the low temperature region and attained a value of 4 cm^3 g^{-1} at 195 K (Fig. 3a). In order to verify the veracity, the experiments were repeated two times at same condition. The observed behaviour of complex **1** towards CO_2 uptake at the mentioned two temperatures is very rare and unprecedented.[13] Generally, the gas adsorption amount decreases with increasing temperature due to the weak adsorbate–adsorbent interactions and high kinetic energy of adsorbates at elevated temperatures. We anticipate that, the observed unusual adsorption behaviour of CO_2 might be due to the flexibility of crystalline framework (expansion-shrinkage) owing to the flexible dca ion bridges. In addition we expect that, at low temperatures, the dipole-induced-dipole interaction are quite strong which blocks other molecules from passing into the adsorption sites and in turn results lesser adsorption amount.[12] To get more insight, we recorded the variable PXRD in the range of 298 K-195 K (Fig. 3b). At 195 K, the peak at 2Θ = 8.8° in the as-synthesized compound which corresponds to [110] plane slightly shifted to high angles (2Θ = 9.3°) which confirms the shrinkage of framework in the low temperature region.[14] The structural analysis reveals that [110] plane just passes in between the dca linkage which further supports our assumption (Fig. S7). Interactions between the framework and CO_2 was further confirmed by the isosteric heat of adsorption value (Qst = -10 kJ mol^{-1} at zero coverage) as calculated from the adsorption data collected at 298 and 273 K (Fig. S8). Sorption profile with CH_4 did not reveal significant uptake (Fig. S9). The observed selective adsorption of CO_2 over CH_4 at around room temperature might be due to its less kinetic diameter (3.3 Å) (Fig. S10).
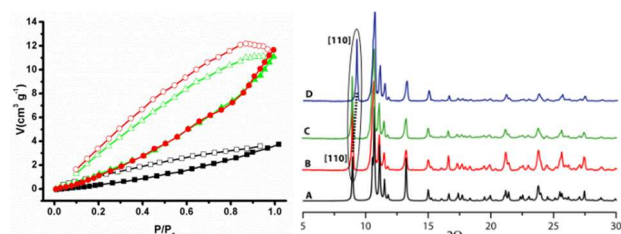

Fig. 3. CO_2 adsorption isotherms at 298 K (red), 273 K (green) and 195 K (black), (left) and (b) variable temperature PXRD patterns of complex **1** (right); (A) simulated, (B) as-synthesized, (C) at 273 K and (D) at 195 K.

In order to correlate the effect of CO_2 adsorption on the magnetic properties[15] of complex **1**, variable temperature DC magnetic study of CO_2 loaded complex **1** (complex **1@CO$_2$**) has been performed. The magnetic susceptibility plot of complex **1@CO$_2$** looks similar to the as-synthesized one (Fig. S11), which confirms that upon CO_2 adsorption, the magnetic properties of **1** do not alter. To further rationalize it, PXRD analysis of complex **1@CO$_2$** has been performed and result demonstrates that the patterns are matching well with the as-synthesized one, signifying no structural transformation or phase transition upon CO_2 adsorption (Fig. S12). As we have already noticed a surface adsorption of CO_2 molecule in complex **1**, we anticipate that, it is

not altering the coordination environment around the Ni(II) centres which results in no change in magnetic properties. In conclusion, the present example is a new demonstration of the versatility of dicyanamide ion for building molecular-based materials using racemic Schiff base ligands. The magnetic investigation shows exceptional concomitant presence of ZFS, weak ferromagnetic and inter-dimer antiferromagnetic interactions at low temperature and a hysteresis loop at 1.8 K with a coercive field of 373 Oe. Sorption analysis reveals a very rare phenomenon of low CO_2 uptake at low temperature than at high temperature.

Acknowledgement

Notes and references

^{a} Department of chemistry, IISER Bhopal, MP, India. Email: skonar@iiserb.ac.in, Fax: +91-755-6692392; Tel: +91-755-6692339.

† X-ray crystallographic data in CIF format, synthetic details, materials and method, structural Figures, TGA plots, magnetic plots, sorption plots and crystallographic table and tables containing bond distances and angles. This material is available free of charge via the Internet at http://pubs.rsc.org.

1 (a) H. O. Stumpf, L. Ouahab, Y. Pei, D. Grandjean and O. Kahn, *Science,* 1993, **261**, 447; (b) M. Kurmoo, *Chem. Soc. Rev.,* 2009, **38**, 1353; (c) E. Coronado and G. M. Espallargas, *Chem. Soc. Rev.,* 2013, **42**, 1525; (d) S. Horike, S. Shimomura and S. Kitagawa, *Nat. Chem.,* 2009, **1**, 695; (e) E. Pardo, R. Ruiz-Garcıa, J. Cano, X. Ottenwaelder, R. Lescouezec, Y. Journaux, F. Lloret and M. Julve, *Dalton Trans.,* 2008, 2780; (f) P. Dechambenoit and J. R. Long, *Chem. Soc. Rev.,* 2011, **40**, 3249; (g) J. S. Miller, *Chem. Soc. Rev.,* 2011, **40**, 3266; (h) K. E. Funck, M. G. Hilfiger, C. P. Berlinguette, M. Shatruk, W. Wernsdorfer and K. R. Dunbar, *Inorg. Chem.,* 2009, **48**, 3438.

2 (a) D-F. Weng, Z-M. Wang and S. Gao, *Chem. Soc. Rev.,* 2011, **40**, 3157; (b) L. M. C. Beltran and J. R. Long, *Acc. Chem. Res.,* 2005, **38**, 325.

3 (a) I-R. Jeona and R. Clérac, *Dalton Trans.,* 2012, **41**, 9569; (b) M. P. Shores, L. G. Beauvais, and J. R. Long, *J. Am. Chem. Soc.,* 1999, **121**, 775; (c) S. S. Kaye and J. R. Long, *J. Am. Chem. Soc.,* 2005, **127**, 6506; (d) S.S. Kaye, H. J. Choi and J. R. Long, *J. Am. Chem. Soc.,* 2008, **130**, 16921; (e) J. A. Sheikh, H. S. Jena, A. Adhikary and S. Khatua and S. Konar, *Inorg. Chem.,* 2013, **52**, 9717; (f) J. A. Sheikh, A. Adhikary, H. S. Jena, S. Biswas, and Konar, S. *Inorg. Chem.* 2014, **53**, 1606; (g) S. Goswami, A. Adhikary, H. S. Jena, S. Biswas, and S. Konar, *Inorg. Chem.,* 2013, **52**, 12064; (h) S. Biswas, H. S. Jena, A. Adhikary, and S. Konar, *Inorg. Chem.,* 2014, **53**, 3926; (i) A. Adhikary, H. S. Jena, S. Khatua, S. Konar, *Chem. Asian. J.,* 2014, **9**, 1083.

4 (a) X-B. Li, J-Y. Zhang, Y-Q. Wang, Y. Song and E-Q. Gao, *Chem. Eur. J.,* 2011, **17**, 13883 and references are therein; (b) E. Coronado and P. Day, *Chem. Rev.,* 2004, **104**, 5419; (c) D. R. Talham, *Chem. Rev.,* 2004, **104**, 5479.

5 (a) S. R. Batten, and K. S. Murray, *Coord. Chem. Rev.,* 2003, **246**, 103; (b) S. R. Batten, P. Jensen, B. Moubaraki, K. S. Murray and R. Robson, *Chem. Commun.,* 1998, 439; (c) S. Mukherjee and P. S. Mukherjee, *Acc. Chem. Res.,* 2013, **46**, 2556; (d) M. Monfort, I. Resino, J. Ribas and H. Stoeckli-Evans, *Angew. Chem. Int. Ed.,* 2000, **39**, 191; (e) S. Konar, P. S. Mukherjee, E. Zangrando, F. Lloret and N. R. Chaudhuri, *Angew. Chem. Int. Ed.,* 2002, **41**, 1561; (f) B. Manna,. A. K. Chaudhari, B. Joarder, A. Karmakar and S. K. Ghosh, *Angew. Chem. Int. Ed.,* 2013, **52**, 998.

6   (*a*) P. Mukherjee, M. G. B. Drew, M. Estrader and A. Ghosh, *Inorg. Chem.,* 2008, **47**, 7784; (*b*) P. Mukherjee, M. G. B. Drew, C. J. Gómez-García and A. Ghosh, *Inorg. Chem.,* 2009, **48**, 4817; (*c*) P. Mukherjee, M. G. B. Drew, C. J. Gómez-García and A. Ghosh, *Inorg. Chem.,* 2009, **48**, 5848; (*d*) L. K. Das, A. Biswas, J. S. Kinyon, N. S. Dalal, H. Zhou and A. Ghosh, *Inorg. Chem.,* 2013, **52**, 11744; (*e*) P. Seth, A. Figuerola, J. Jover, E. Ruiz, and A. Ghosh, *Inorg. Chem.,* 2014, **53**, 9296.

7   (*a*) S. G. Telfer and R. Kuroda, *Coord. Chem. Rev.,* 2003, **242**, 33; (*b*) S. G. Telfer, R. Kuroda and T. Sato, *Chem. Commun.,* 2003, 1064; (*c*) S. G. Telfer, T. Sato, T. Harada, R. Kuroda, J. Lefebvre, and D. B. Leznoff, *Inorg. Chem.,* 2004, **43**, 6168 and reference are therein; (*f*) T. J. Burchell and R. J. Puddephatt, *Inorg. Chem.,* 2005, **44**, 3718; (g) J. M. Rowland, M. M. Olmstead, and P. K. Mascharak, *Inorg. Chem.,* 2002, **41**, 1545.

8   (*a*) H. S. Jena, *RSC Adv.,* 2014, **4**, 3028; (*b*) H. S. Jena, *New J. Chem.,* 2014, **38**, 2486; (*c*) H. S. Jena, *Inorg. Chim. Acta,* 2014, **410**, 156; (*d*) H. S. Jena, *Inorg. Chim. Acta,* 2014, **421**, 52; (e) H. S. Jena, J. Subramanian and V. Manivannan, *Inorg. Chim. Acta,* 2011, **365**, 177; (*f*) H. S. Jena and V. Manivannan, *Inorg. Chim. Acta,* 2012, **390**, 154; (g) H. S. Jena and V. Manivannan, *Inorg. Chim. Acta,* 2012, **394**, 210.

9   (*a*) E-Q. Gao, S-Q. Bai, Z-M. Wang, and C-H. Yan, *J. Am. Chem. Soc.,* 2003, 125, 4984; (*b*) E-Q. Gao, Y-F. Yue, S-Q. Bai, Z. He and C-H. Yan, *J. Am. Chem. Soc.,* 2004, **126**, 1419.

10 (*a*) O. Kahn, Molecular Magnetism; VCH Publishers Inc.: New York, 1991; (*b*) A. P. Ginsberg, R. L. Martin, R. W. Brookes and R. C. Sherwood, *Inorg. Chem.,* 1972, **11**, 2884; (*c*) A. Escuer, R. Vicente and J. Ribas, *J. Magn. Magn. Mater.,* 1992, **110**, 181.

11 (*a*) J. R. Li, J. Sculley and H. C. Zhou, *Chem. Rev.,* 2012, **112**, 869. (*b*) C. M. Doherty, D. Buso, A. J. Hill, S. Furukawa, S. Kitagawa and P. Falcaro, *Acc. Chem. Res.,* 2014, **47**, 396; (*d*) S. K. Ghosh, R. Azhakar and S. Kitagawa, *Chem.–Asian J.,* 2009, **4**, 870; (*e*) S. Parshamoni, S. Sanda, H. S. Jena, K. Tomar and S. Konar, *Cryst. Growth Des.* 2014, **14**, 2022; (*f*) S. Sanda.; S. Goswami.; H. S. Jena.; S. Parshamoni and S. Konar. *CrystEngComm.,* 2014, **16**, 4742; (*g*) S. Parshamoni, S. Sanda, H. S. Jena, and S. Konar, *Dalton Trans.,* 2014, **43**, 7191; (*h*) S. Biswas, H. S. Jena, S. Goswami,.; S. Sanda and S. Konar, *Cryst. Growth Des.,* 2014, **14**, 1287; (*i*) S. Parshamoni, H. S. Jena, S. Sanda, and S. Konar, *Inorg. Chem. Front.,* 2014, **1**, 611.

12 T. K. Maji, R. Matsuda and S. Kitagawa, *Nat. Mater.,* 2007, **6**, 142.

13 (*a*) P. Kanoo, S. K. Reddy, G. Kumari, R. Haldar, C. Narayana, S. Balasubramanian and T. K Maji, *Chem. Commun.,* 2012, **48**, 8487; (*b*) L. Pan, K. M. Adams, H. E. Hernandez, X. Wang, C. Zheng, Y. Hattori and K. Kaneko, *J. Am. Chem. Soc.,* 2003, **125**, 3062.

14 (*a*) S. Sanda, S. Parshamoni, S. Konar, *Inorg. Chem.,* 2013, **52**, 12866; (*b*) J. Seo, R. Matsuda, H. Sakamoto, C. Bonneau and S. Kitagawa, *J. Am. Chem. Soc.,* 2009, **131**, 12792; (c) R. Matsuda, R. Kitaura and S. Kitagawa, Y. Kubota, T. C. Kobayashi, S. Horike, M. Takata, *J. Am. Chem. Soc.,* 2004, **126**, 14063.

15 (*a*) J. A. R. Navarro, E. Barea, A. Rodrıguez-Dieguez, J. M. Salas, C. O. Ania, J. B. Parra, N. Masciocchi, S. Galli, and A. Sironi, *J. Am. Chem. Soc.,* 2008, **130**, 3978; (*b*) J. Ferrando-Soria, P. Serra-Crespo, M. de Lange, J. Gascon, F. Kapteijn, M. Julve, J. Cano, F. Lloret, J. Pasán, C. Ruiz-Pérez, Y. Journaux, and E. Pardo, *J. Am. Chem. Soc.,* 2012, **134**, 15301; (*c*) D. Maspoch, D. Ruiz-Molina, K. Wurst, N. Domingo, M. Cavallini, F. Biscarini, J. Tejada, C. Rovira, J. Veciana, *Nat. Mater.* 2003, **2**, 190.
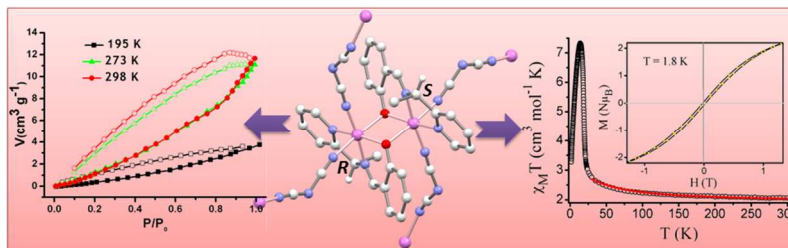
Journal Name

ARTICLE TYPE

For Table of Contents Only

A robust 2D heterochiral Ni(II) coordination polymer has been reported which shows exceptional synergism of weak ferromagnetic, inter-dimer antiferromagnetic interactions, ZFS at low temperature, a hysteresis loop at 1.8 K with a coercive field of 373 Oe and unusual

5 CO_2 uptake behaviour.