Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supplementary Information

The Effect of Substituted Benzene Dicarboxylic Acid linkers on the Optical Band Gap Energy and Magnetic Coupling in Manganese Trimer Metal Organic Frameworks

K. S. Asha,[a] Arthur C. Reber,[b] N. Ahmed,[c] R. Nath[*c], Shiv N. Khanna*[b], and Sukhendu Mandal*[a]

*[a]School of Chemistry, Indian Institute of Science Education and Research Thiruvananthapuram, Thiruvananthapuram, Kerala-695016, INDIA, E-mail: sukhendu@iisertvm.ac.in

*[b]Department of Physics, Virginia Commonwealth University, Richmond, VA, USA, E-mail: snkhanna@vcu.edu

[*c]School of Physics, Indian Institute of Science Education and Research Thiruvananthapuram, Thiruvananthapuram, Kerala-695016, INDIA, E-mail: rnath@iisertvm.ac.in

Contents

I. Materials and Methods

II. Synthesis

Table S1-S2. The table of crystallographic parameters of compounds **1** – **7**.

Figure S1. The PXRD pattern of all compounds

Figure S2. The IR spectra of all compounds

Figure S3. The TGA analysis of all compounds

Figure S4. Optical absorption spectra of the Mn3-Benzoic acid complex with DMF molecules

Figure S5. Energy landscape for the magnetization direction

I. Materials and Methods

All chemicals were of reagent-grade quality obtained from Sigma-Aldrich and used as received without further purification. The FT-IR spectrum was recorded from KBr pellets in the range of 4000-400 cm^{-1} on a Prestiage-21 SHIMADZU FT-IR spectrometer. The TGA was performed on SDT Q600 (Shimadzu) analyzer in flowing nitrogen with a heating rate of 10^{0}C per minute. The Powder X-ray diffraction data were collected using X'pert PRO (PANalytics) powder diffractometer equipped with Cu Kα radiation (1.540598 Å).

I.A Single Crystal X-ray Diffraction.

Suitable crystal for all the compounds (**1**-**7**) were selected under a polarizing microscope and glued to a thin glass fiber for single crystal studies. The single crystal diffraction data were collected on a Bruker AXS Smart Apex CCD diffractometer at 298 K. The X-ray generator was operated at 50 kV and 35 mA using MoKα (λ = 0.71073 Å) radiation. Data were collected with ω scan width of 0.3°. A total of 606 frames were collected in three different settings of φ (0°, 90°, 180°) keeping the sample to-detector distance fixed at 6.03 cm and the detector position (2θ) fixed at -25°. The data were reduced using SAINTPLUS[1] and an empirical absorption correction was applied using the SADABS program.[2] The crystal structure was determined by direct methods using SHELXS2014 and refined using SHELXL2014 present in the SHELXTL V6.14[3] package. All hydrogen atoms were placed in calculated positions during the final step of the refinement process. For the final refinement, the hydrogen atoms were placed in geometrically ideal positions and refined using the riding mode. The last cycles of the refinement included atomic positions, anisotropic thermal parameters for all the non-hydrogen atoms, and isotropic thermal parameters for all the hydrogen atoms. Full-matrixleast-squares structure refinement against F2 was carried out using the WINGX[4] package of programs.

The crystallographic parameters for compounds **1** to **7** are provided in table S1-S2. CCDC- 1474408-1474414 contain the crystallographic data for **1** to **7**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre (CCDC) via www.ccdc. cam.ac.uk/data_request/cif

I.B Optical Band-Gap Measurements

The optical absorption spectra of **1** to **8** were collected on a Shimadzu UV/Vis/NIR spectrophotometer. The room temperature diffuse reflectance spectra was measured using $BaSO_4$ as a reference material and converted to a Kubelka–Munk function, from which the band gap of the compound was estimated.[5] This two-flux model, which considers only diffuse light, is used to determine the absorption coefficient from a surface that both scatters and absorbs incident radiation. For a crystalline solid with a band gap (Ebg), the frequency dependence (ν) of the absorption coefficient (**κ**) can be approximated as

$$\kappa(v) = \frac{B_T\left(hv - E_{bg}\right)^n}{hv} \text{ ---------------------} \quad (1)$$

where BT is a constant derived from the square of the averaged dipolar momentum matrix element and n is equal to 0.5 and 2 for direct and indirect band gap transitions, respectively.[5] The absorption coefficient (κ) can be measured from the reflectance (R) and expressed as $\kappa = (1 - R)^2/(2R)$. Using the above equation, the band gap of a material can be obtained by extrapolating to zero with the linear fit to a plot of (khν)1/n *vs* hν.

I.C Theoretical Studies of Atomic and Electronic Structure, Band gap, and Magnetic Properties:

To gain insight into the observed electronic and magnetic properties, electronic structure calculations on the periodic solids were carried out using the Vienna Ab initio Simulation Package (VASP) code.[6,7] The atomic structures were derived from the experimental X-ray diffraction data, and then the crystal structure was corrected using the identity of the reactants. Due to symmetry, the crystal structures showed all molecules to be di-substituted, while the reactants are singly substituted. A plane wave basis with an energy cutoff of 400 eV was used.[7] We used only the gamma point due to the large size of the unit cells, and for exchange and correlation functional, we used a generalized gradient approximation (GGA) functional as proposed by Perdew, Burke, and Ernzerhof (PBE).[8] The theoretical studies on the linker molecules were carried out using ADF.[9] The TZ2P basis was used with a small core. Time Dependent Density Functional Theory (TD-DFT) was used for the optical absorption calculation, while VASP was used for the Magnetic Anisotropy calculation.

II. Synthesis

Compound 1: $[Mn_3(BDC)_3(DMA)_4]$

0.137 g (0.5 mmol) of $Mn(NO_3)_2 \cdot 6\, H_2O$ was dissolved in 3 mL Methanol and mixed with 0.089 g (0.5 mmol) of terephthalicacid in 3 mL DMA (N,N’-dimethylacetamide). Then 10 mg pyrazine and 20 mg of benzotriazole were added to the above mother solution and sonicated for five minutes. The whole mixture was taken in a closed glass vial and kept at 100 ^{0}C in oven for three days. The colourless crystals were formed, washed with DMF (N,N’-dimethylformamide) many times and dried under vacuum and used for SXRD measurement.

Compound 2: [$Mn_3(FBDC)_3(DMF)_4$]

0.1375 g (0.54 mmol) of $Mn(NO_3)_2 \cdot 6H_2O$ was weighed and dissolved in 3 mL methanol and mixed with 0.0994 g (0.54 mmol) of 2-fluoroterephthalic acid (FBDC) dissolved in 3 mL N,N'-Dimethylformamide (DMF). The mixture was sonicated for 5 minutes and transferred to a closed glass vial. The mixture then was heated at 100 ºC for 72 hrs. Colourless crystals were formed, washed with DMF many times and dried.

Compound 3 : [$Mn_3(ClBDC)_3(DMF)_4$]

0.1375 g (0.54 mmol) of $Mn(NO_3)_2 \cdot 6H_2O$ was weighed and dissolved in 3 mL methanol and to this 0.108 g (0.54 mmol) of 2-chloroterephthalic acid (ClBDC) dissolved in DMF was added. The mixture was sonicated for 5 minutes and transferred to a closed glass vial. The mixture then was heated at 100 ºC for 72 hrs. Colourless crystals were formed, washed with DMF many times and dried.

Compound 4: [$Mn_3(BrBDC)_3(DMF)_4$]

0.1375 g (0.54 mmol) of $Mn(NO_3)_2 \cdot 6H_2O$ was weighed and dissolved in 3 mL methanol and to this 0.132 g (0.54 mmol) of 2-bromoterephthalic acid (BrBDC) dissolved in DMF was added. The mixture was sonicated for 5 minutes and transferred to a closed glass vial. The mixture then was heated at 100 ºC for 72 hrs. Colourless crystals were formed, washed with DMF many times and dried.

Compound 5: [$Mn_3(NO_2BDC)_3(DMF)_2(H_2O)_2$]

0.1375 g (0.54 mmol) of $Mn(NO_3)_2 \cdot 6H_2O$ was weighed and dissolved in 3 mL methanol and mixed with 0.114 g (0.54 mmol) of 2-nitroterephthalic acid (NO_2BDC) dissolved in DMF. The mixture was sonicated for 5 minutes and transferred to a Teflon lined autoclave. The mixture then was heated at 130 ºC for 60 hrs. Brown coloured crystals were formed, washed with DMF many times and dried.

Compound 6: [$Mn_3(OH\text{-}BDC)_3(DMA)_4$]

0.137 g (0.5 mmol) of $Mn(NO_3)_2 \cdot 6\ H_2O$ was dissolved in 3 mL Methanol and mixed with 0.098 g (0.5 mmol) of 2-hydroxy terephthalicacid in 3 mL DMA and sonicated for five minutes. The whole mixture was taken in a closed glass vial and kept at 100º C in oven for three days. The colourless crystals were formed, washed with DMF many times and dried under vacuum and used for SXRD measurement.

Compound 7: [$Mn_3(NH_2\text{-}BDC)_3(DMF)_4$]

0.137 g (0.5 mmol) of $Mn(NO_3)_2 \cdot 6\ H_2O$ was dissolved in 3 mL Methanol and mixed with 0.097 g (0.5 mmol) of 2-amino terephthalicacid in 3 mL DMF and sonicated for five minutes. The whole mixture was taken in a Teflon lined autoclave and kept at 130º C in oven for 60 h. The colourless crystals were formed, washed with DMF many times and dried under vacuum and used for SXRD measurement.

Compound 8: [$Mn_3(N_3\text{-}BDC)_3(DMF)_4$]

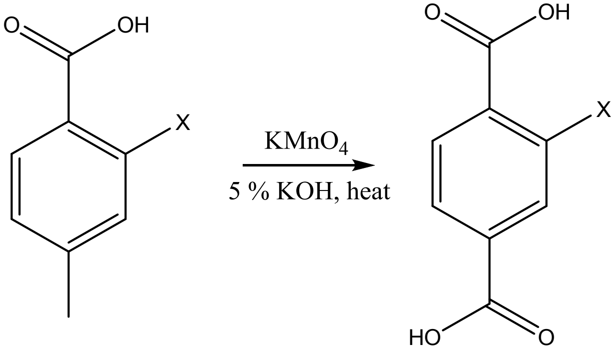
Compound **8** was synthesized by post synthetic modification of compound **7**.[10] For this, 0.078 g (0.27 mmol) of compound **7** was weighed to a 50 mL RB flask under N_2 atmosphere. Then 15 mL dry THF was added to this and cooled to 0 ºC using an ice bath. When it is cooled, 2.18 mL tert-butylnitrite and 5.1 mL Trimethyl silylazide (TMSA) were added and stirred the mixture at room temperature for three days. After three days of reaction, the THF solvent was removed using vacuum rota and the product was washed with THF and DCM three times and then filtered and dried under vacuum. The $-NH_2$ to $-N_3$ conversion was confirmed by using IR spectroscopic analysis and purity was estimated using PXRD technique.

Ligand L2 (2-fluoroterephthalic acid)

3-fluoro-4-methylbenzoic acid (1.0 g, 5.7 mmol) and of $KMnO_4$ (3.42 g, 21.4 mmol) were dissolved in aqueous KOH solution (35 mL, 5%) and the solution was refluxed for 4 hours. The solution was then allowed to cool to room temperature and was stirred overnight and filtered. The filtrated was diluted with water (25 mL) and acidified with conc. HCl to pH 1. The white precipitate was collected by filtration, washed with water, and dried under vacuum to afford 2-fluoroterephthalic acid as a white powder (62% yield).[11]

Ligand L3 (2-chloroterephthalicacid)

3-chloro-4-methylbenzoic acid (1.0 g, 6.5 mmol) and $KMnO_4$ (3.16 g, 19.8 mmol) were dissolved in aqueous KOH solution (30 mL, 5%) and the solution was refluxed for 4 h. The solution was then allowed to cool to room temperature and was stirred overnight and filtered. The filtrate was diluted with water (25 mL) and acidified with conc. HCl to pH 1. The white precipitate was collected by filtration, washed with water, and dried under vacuum to afford 2-chloroterephthalic acid as a white powder (78 % yield). [11]



where x = F or Cl

References:

1. SMART (V 5.628), SAINT (V 6.45a), XPREP, SHELXTL; Bruker AXS Inc.: Madison, WI, **2004**.
2. G. M. Sheldrick, Siemens Area Correction Absorption Correction Program; University of Göttingen: Göttingen, Germany, **1994**.

3. G. M. Sheldrick, SHELXL-97 Program for Crystal Structure Solution and Refinement; University of Göttingen: Göttingen, Germany, **1997**.
4. J. L. Farrugia, *J. App. Crystallography*. **1999**, *32*, 837-838.
5. N. Laidani, R. Bartali, G. Gottardi, M. Anderle, P. Cheyssac, *J. Phys. Condens. Matter* 2008, 20, 015216.
6. G. Kresse and J. Furthmüller, *Phys. Rev. B* **1996**, *54*, 11169.
7. G. Kresse and D. Joubert, *Phys. Rev. B* **1999**, *59*, 1758.
8. J.P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
9. G. te Velde, F.M. Bickelhaupt, E.J. Baerends, C. Fonseca Guerra, S.J.A. van Gisbergen, J.G. Snijders, and T. Ziegler*, J. Comput. Chem.* **2001**, *22*, 931.
10. Z. Wang, J. Liu, H. K. Arslan, S. Grosjean, T. Hagendorn, H. Gliemann, S. Bräse, C. Wöll *Langmuir* **2013**, *29*, 15958.
11. S. T. Meek, J. J. Perry, S. L. Teich-McGoldrick, J. A. Greathouse, M. D. Allendorf *Cryst. Growth Des,* **2011**, *11*, 4309.

Table S1. The table of crystallographic parameters of Compounds **1** – **3**.

Parameters	**Compound 1**	**Compound 2**	**Compound 3**
Empirical formula	$C_{40}H_{45}Mn_3N_4O_{16}$	$C_{36}H_{34}F_6Mn_3N_4O_{16}$	$C_{36}H_{33}Cl_6Mn_3N_4O_{16}$
Formula weight	1002.62	1057.49	1155.18
Crystal System	Triclinic	Triclinic	Triclinic
Space Group	*P*(-1) (no. 2)	*P*(-1) (no. 2)	*P*(-1) (no. 2)
a(Å)	9.8767(5)	9.8540(3)	9.9485(3)
b(Å)	14.7211(8)	12.8734(4)	15.3562(5)
c(Å)	16.9215(9)	16.6711(6)	15.7178(5)
$\alpha(^0)$	69.762(2)	74.880(2)	71.6270(10)
$\beta(^0)$	86.925(2)	88.8270(10)	85.4230(10)
$\gamma(^0)$	84.366(2)	87.055(2)	83.9950(10)
Volume(Å^3)	2146.9(3)	2038.84(12)	2263.53(12)
Z	2	2	2
Calculated density (g/cm^3)	1.450	1.723	1.695
θ range (^{0})	1.28 to 28.38	1.27 to 28.43	2.42 to 28.34
Absorption coefficient (mm^{-1})	0.884	1.020	1.251
Reflections collected	41098	10024	39549
Unique reflections	11439	34869	11151
Goodness-of-fit	0.875	1.074	1.201
Number of parameters	556	589	591
Final R indices [I>2sigma(I)]	R_1 = 0.0480, wR_2 = 0.1450	R_1 = 0.0629, wR_2 = 0.1654	R_1 = 0.0933, wR_2 = 0.2667
R indices (all data)	R_1 = 0.0658, wR_2 = 0.1741	R_1 = 0.0765, wR_2 = 0.1763	R_1 = 0.1160, wR_2 = 0.2958
Largest diff. peak and hole e Å^{-3}	1.297 and -0.769	2.568 and -0.872	1.838 and -2.105

Table S2. The table of crystallographic parameters of Compounds **4** – **7**.

Compound 4	**Compound 5**	**Compound 6**	**Compound 7**
$C_{36}H_6Br_6Mn_3N_4O_{16}$	$C_{15}H_{13}Mn_{1.50}N_3O_{12}$	$C_{18}H_7Mn_{1.5}N_2O_{11}$	$C_{16.50}H_{18.5}Mn_{1.5}N_{2.5}O_7$
1394.73	509.69	509.67	446.25
Triclinic	Orthorhombic	Monoclinic	Monoclinic
P(-1) (no. 2)	*Pbca*	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
9.9807(10)	9.8696(6)	15.5340(3)	13.4214(12)
15.3744(17)	18.0782(12)	9.9019(2)	10.0260(9)
15.5563(17)	27.2802(17)	16.3563(3)	16.6604(14)
71.720(3)	90	90	90
85.721(4)	90	111.1260(10)	106.733(4)
84.763(4)	90	90	90
2254.5(4)	4867.5(5)	2346.77(8)	2146.9(3)
2	8	4	4
2.055	1.391	1.443	1.381
1.38 to 26.37	2.99 to 24.71	1.55 to 28.27	2.40 to 28.70
6.217	0.848	0.876	0.933
33859	18867	21292	34406
8881	4047	5774	5265
1.316	1.585	1.148	1.514
590	289	285	272
R_1 = 0.1386, wR_2 = 0.3350	R_1 = 0.1388, wR_2 = 0.4009	R_1 = 0.0868, wR_2 = 0.2645	R_1 = 0.1269, wR_2 = 0.3459
R_1 = 0.1996, wR_2 = 0.3787	R_1 = 0.1844, wR_2 = 0.4281	R_1 = 0.1249, wR_2 = 0.3037	R_1 = 0.1598, wR_2 = 0.3790
3.311 and -1.936	2.032 and -0.784	2.126 and -1.253	4.494 and -1.060

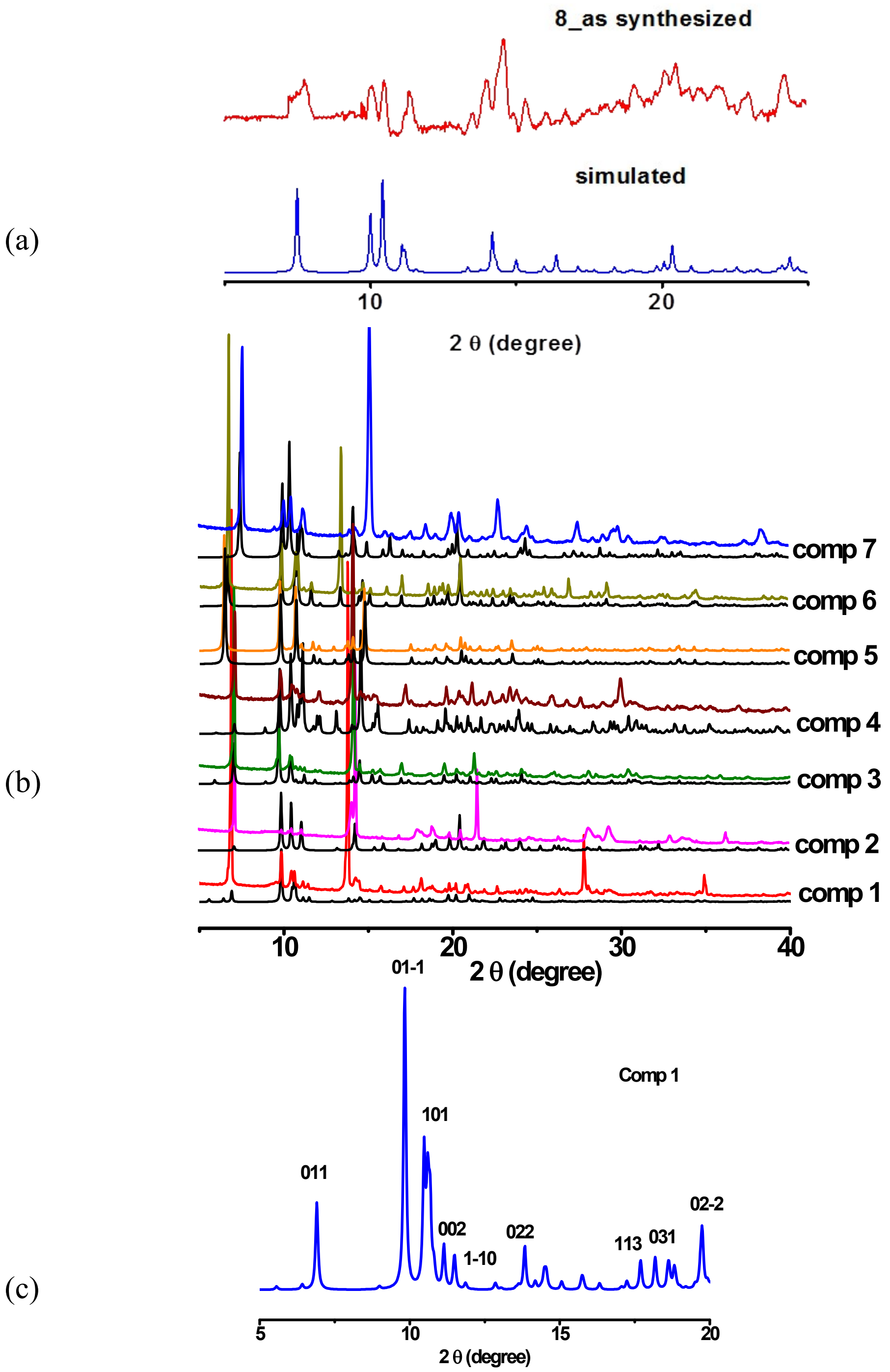


Figure S1. (a) and (b) the comparison of experimental PXRD pattern with that of simulated one for all the compounds, (c) indexed PXRD data of compound **1**.

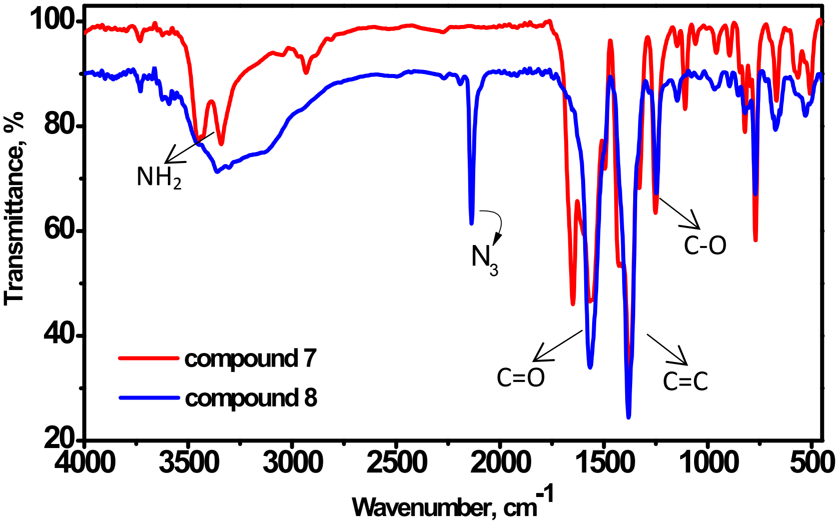


Figure S2: The IR spectra for compound **7** and **8** and it gives clear evidence for the conversion of amino group to azide with the disappearance of NH_2- peaks at 3300 and 3450 cm^{-1} and the new peak formed at 2200 cm^{-1} due to N_3 stretching.

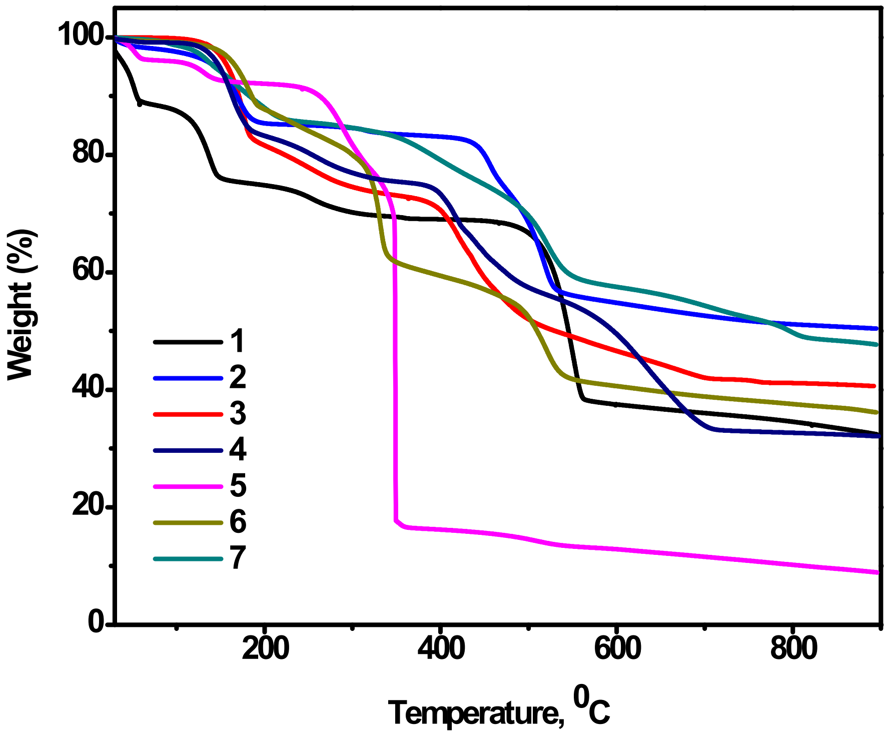


Figure S3. The thermogravimetric analysis of compounds **1** -**7**.

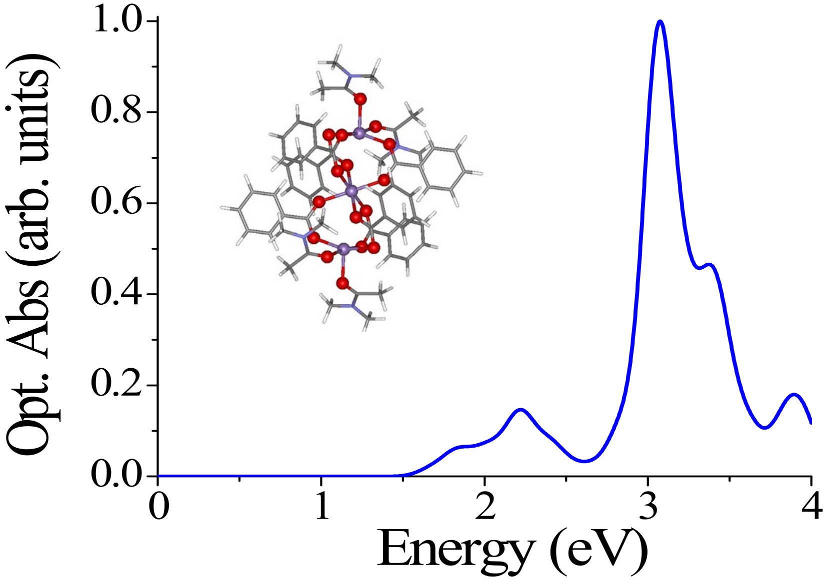
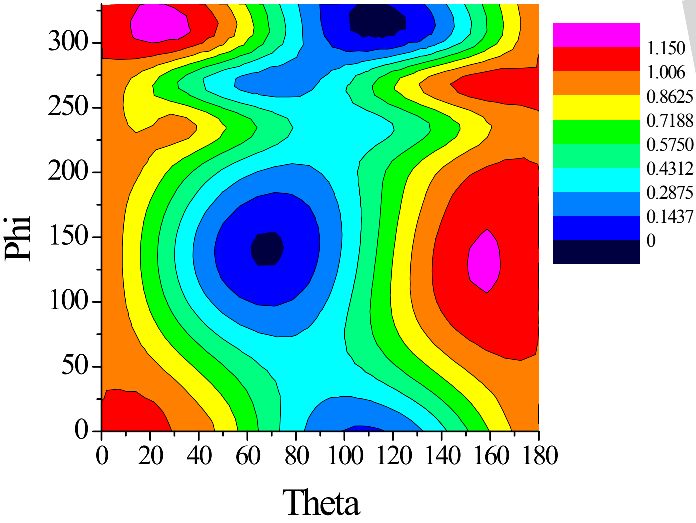


Figure S4. Optical absorption spectra of the Mn3-Benzoic acid complex with DMF molecules capping the cluster, with structure shown.



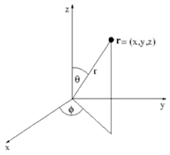


Figure S5. Energy landscape for the magnetization direction as a function of θ and ϕ obtained for the Mn3-Benzoic acid, DMF cluster.