

Supporting Information

Structural isomers of iron(III) *N*-methyl diethanolamine as sol-gel precursors for iron-based oxide nanomaterials

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Experimental

General Procedures. All manipulations were performed under argon atmosphere using Schlenk tube and vacuum line techniques. Solvents were purified on an MB SPS-800 instrument and amino alcohols (Aldrich) were stored over molecular sieves. The $[\text{Fe}_2(\text{O}^t\text{Bu})_6]$ [1] and $[\text{Bi}_2(\text{mdea})_2(\text{mdeaH})_2]$ [2] were prepared as reported in the literature. FT-IR spectra were recorded either as Nujol mulls (derivatives **1**, **A** and **B**) or KBr pellets (powders obtained after hydrolysis of precursors) on a Bruker Vector 22 spectrometer. TGA/DTA data of hydrolyzed products were collected on a Setaram 92 system in air with a thermal ramp of 5 °C

min⁻¹. Powder X-ray diffraction data were obtained with a Siemens D 5000 diffractometer using CuK α radiation. Particle sizes were measured in isopropanol solution with a Coulter N4 Plus submicron particle sizer. Cells were filled with isopropanol and 30-40 drops of the hydrolyzed solutions (0.06-0.3 M) were added to achieve a scattering intensity of 5×10^4 – 1×10^6 counts s⁻¹. SEM images were collected on Hitachi S800 spectrometers.

Syntheses

Chair-shaped [Fe₄(mdea)₆] \cdot 6CHCl₃ (1a**):** This isomer was obtained while attempting to prepare Fe-Bi heterometallics for FeBiO₃ nanomaterials. The bismuth complex [Bi₂(mdea)₂(mdeaH)₂] [2] containing residual hydroxyl functionality on *N*-methyldiethanolamine ligand seemed to be a perfect choice for anchoring iron metal. Such an approach has been previously demonstrated by Hubert-Pfalzgraf *et al* who obtained the heterometallic [La(TEA)₂{Nb(OPr^{*i*})₄}₃] (where TEA = anion of triethanolamine) from the 1:3 reaction of [La(TEA)₂H₃] _{∞} and [Nb(OPr^{*i*})₅] [3]. However, the reaction mixture containing [Bi₂(mdea)₂(mdeaH)₂] (0.63 g, 0.7 mmol) and [Fe(OBu^{*t*})₃] (0.39 g, 0.7 mmol) in CHCl₃ afforded, after usual work-up, the chair-shaped [Fe₄(mdea)₆] \cdot 6CHCl₃ (**1a**) as a redistribution product. Yield, 0.46 g (79% wrt iron(III) tert-butoxide). IR (cm⁻¹): 1452s, 1369s, 1280m, 1193w, 1140m, 1080s, 1040m, 991s, 918m, 887s, 740s, 645m, 577m, 501s, 471s, 420m.

Star-shaped [Fe₄(mdea)₆] \cdot 6CHCl₃ (1b**):** 1 ml of *N*-methyldiethanolamine (mdeaH₂) was added in the toluene solution of [Fe(OBu^{*t*})₃] (1.48 g, 5.37 mmol). The colour changed from dark green to yellowish green immediately. After stirring at room temperature for 4 h, the volatiles were removed under vacuum. The solid obtained was crystallization from chloroform at r.t. as light green coloured crystals (2.05 g, 93%). **1b** was soluble in all standard organic solvents. Anal.: calcd for C₃₀H₆₆Fe₄N₆O₁₂ \cdot 6CHCl₃ (1642.5): C 21.91, H 4.01, N 5.11; found C

22.0, H 4.06, N 5.17%. IR (cm⁻¹): 1455s, 1371s, 1282m, 1197w, 1138m, 1083s, 1038m, 989s, 915m, 890s, 742s, 642m, 578m, 503s, 469s, 419m.

[Fe₂(dmea)₆] (A). *N, N*-dimethylethanolamine (dmeaH) (0.40 ml, 3.97 mmol) was added to [Fe(OBu^t)₃] (0.362g, 1.31 mmol) in toluene (10 ml). After stirring first at r.t. for 4 h and then under reflux for 1h, solvents were removed under vacuum to give a dark brown solid, which was crystallized from concentrated toluene solution at -20 °C. Yield, 0.29 g, 69%. Anal.: calcd for C₁₂H₃₀O₃N₃Fe (319.8): C 45.08, H 9.38, N 13.13%; found: C 44.87, H 9.12, N 13.0%. IR (Nujol, cm⁻¹): 1749w, 1459, 1377s, 1621w, 1582w, 1269m, 1087m, 1032m, 944m, 900m, 846m, 777m, 719m, 630m, 503m.

[Fe₆(tea)₆] (B): To a toluene (10 ml) solution of [Fe(OBu^t)₃] (0.263g, 0.95 mmol), was added 0.13 ml (0.97 mmol) of triethanolamine (teaH₃). The resulting reaction mixture was first stirred at r.t. for 4 h and then refluxed for 2 h. The precipitated yellow solid (0.46 g, 96%) was separated by filtration. As the product was poorly soluble in common organic solvents, it was purified by washing repeatedly with hexane. Anal.: calcd for C₃₆H₇₂Fe₆N₆O₁₈ (1211): C 35.67, H 5.94, N 6.93%; found: C 36.10, H 6.05, N 7.0%. IR (Nujol, cm⁻¹): 1460s, 1376s, 1297w, 1253w, 1165w, 1096s, 1084s, 1037s, 1013s, 929w, 915w, 898s, 797w, 753w, 718w, 640m, 620w, 601w, 581w, 558m, 505m, 454m, 419m.

The crystalline solids of the derivatives **1**, **A** and **B** are green, dark-brown and orange in colour, respectively. The *N, N*-dimethylethanolamine and *N*-methyldiethanolamine derivatives **A**, **1a** and **1b** were soluble in THF, diethyl ether, toluene, aliphatic hydrocarbons and the parent alcohol but triethanol derivative **B** was soluble only in hot acetonitrile and methanol.

X-ray quality crystals of **1a** and **1b** were grown from chloroform at room temperature. As our efforts to get X-ray quality crystals of the **A** were unsuccessful, its formulation as a dimer is based on dimeric structure known for the indium analogue of **A** [4]. For **B**, we did obtain suitable crystals by cooling its hot methanol solution to r.t. in 45% yield. Even though the X-ray structure establishes its hexanuclear structure where the planar Fe₆ wheel is stabilized by six *N*-triethanolamine ligands bonded in a $\mu_3\text{-}\eta^2,\eta^2,\eta^1$ fashion and positioned alternately above and below the plane (Fig. S4), overall data are not good. In view of poor quality of this structure and its similarity to some of the six-membered ‘metalla-coronands’ described for iron and some other trivalent transition or main group metals [5], we are not submitting the structure in CCDC.

X-Ray crystallography of 1a and 1b. A suitable crystal of **1a** was mounted on an Oxford XCALIBUR diffractometer. Cell parameters were refined using CrysAlis RED [6]. Absorption correction was applied with the Blessing Method [7]. The structure was solved using SHELXS97 [8] and refined on F^2 by least squares using SHELXL97 [9]. All non-H atoms were refined anisotropically. Hydrogen atoms positions were calculated and refined but Uiso was fixed at 1.2 times that of the parent atom. A suitable crystal of **1b** was mounted on a Nonius Kappa CCD diffractometer. Intensities were collected by means of the COLLECT software [10]. Reflection indexing, Lorentz-polarization correction, peak integration and background determination were carried out with DENZO [11]. Frame scaling and unit-cell parameters refinement were made with SCALEPACK [11]. An analytical absorption correction was applied using the modeled faces of the crystal [12]. The structure was solved by direct methods with SIR97 [13]. The structure refinement was carried out with CRYSTALS [14].

References

- [1] S. Mathur, M. Veith, V. Sivakov, H. Shen, V. Huch, U. Hartmann and H. B. Gao, *Chem. Vap. Depos.* 2002, **8**, 277.
- [2] J. Lebaris, L. G. Hubert-Pfalzgraf, S. Daniele and J. Vaissermann, *Inorg. Chem. Commun.* 2007, **10**, 80.
- [3] V. G. Kessler, L. G. Hubert-Pfalzgraf, S. Halut and J.-C. Daran, *J. Chem. Soc., Chem. Commun.* 1994, 705.
- [4] S. Daniele, D. Tchekobokov, L. G. Hubert-Pfalzgraf and S. Lecocq, *Inorg. Chem. Commun.*, 2002, **5**, 347.
- [5] (a) A. Baniodeh, Y. Liang, C. E. Anson, N. Magnani, A. K. Powell, A.-N. Unterreiner, S. Seyfferle, M. Slota, M. Dressel, L. Bogani and K. Goß, *Adv. Funct. Mater.* 2014, **24**, 6280; (b) S.-J. Liu, S.-D. Han, J.-M. Jia, L. Xue, Y. Cui, S.-M. Zhang and Z. Chang, *CrystEngComm* 2014, **16**, 5212; (c) J. Kreitlow, J. Litterst, S. Sulow and B. Pilawa, *Hyperfine Interaction* 2006, **168**, 1197; (d) R. W. Saalfrank, C. Deutscher, S. Sperner, T. Nakajima, A. M. Ako, E. Uller, F. Hampel and F. W. Heinemann, *Inorg. Chem.* 2004, **43**, 4372; (e) E. M. Rumberger, L. N. Zakharov, A. L. Rheingold and D. N. Hendrickson, *Inorg. Chem.* 2004, **43**, 6531; (f) O. Waldmann, R. Koch, S. Schromm, J. Schülein, P. Müller, I. Bernt, R. W. Saalfrank, F. Hampel and E. Balthes, *Inorg. Chem.* 2001, **40**, 2986.
- [6] CrysAlis CCD and CrysAlis RED, Versions 1.71.26. Oxford Diffraction Ltd. Abingdon. Oxfordshire, England (2005).
- [7] R. H. Blessing, An empirical correction for absorption anisotropy, *Acta Crystallogr.*, 1995, **A51**, 33.
- [8] G. M. Sheldrick, SHELXS97. Program for Crystal Structure Solution, University of Göttingen, Germany (1997).
- [9] G. M. Sheldrick, SHELXL97. Program for Crystal Structure Refinement, University of Göttingen, Germany (1997).
- [10] B. V. Nonius, *COLLECT*, Nonius, Delft, The Netherlands (1997-2001).
- [11] Z. Otwinowski and W. Minor, *Methods in Enzymology*, Eds.: C. W. Carter, Jr. and R. M. Sweet, Academic Press, New York, 1997, Vol. 276, pp. 307.
- [12] J. de Meulenaar and H. Tompa, *Acta Crystallogr.*, 1965, **A19**, 1014.

[13] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Cryst.* 1999, **32**, 115.

[14] D. J. Watkin, C. K. Prout and L. J. Pearce, *CAMERON*, Chemical Crystallography Laboratory, OXFORD, UK (1996).

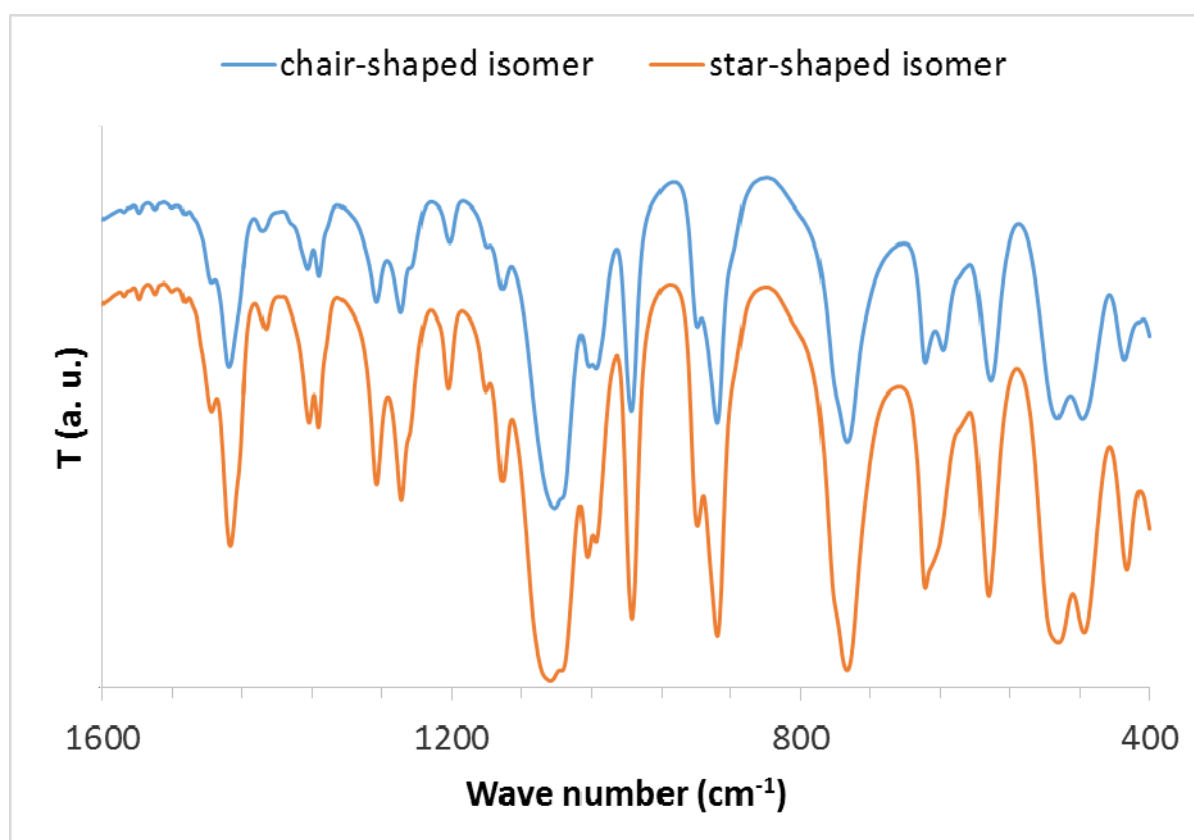


Fig. S1 FT-IR spectra of two isomers of $[\text{Fe}_4(\text{mdea})_6] \cdot 6 \text{CHCl}_3$ in nujol.

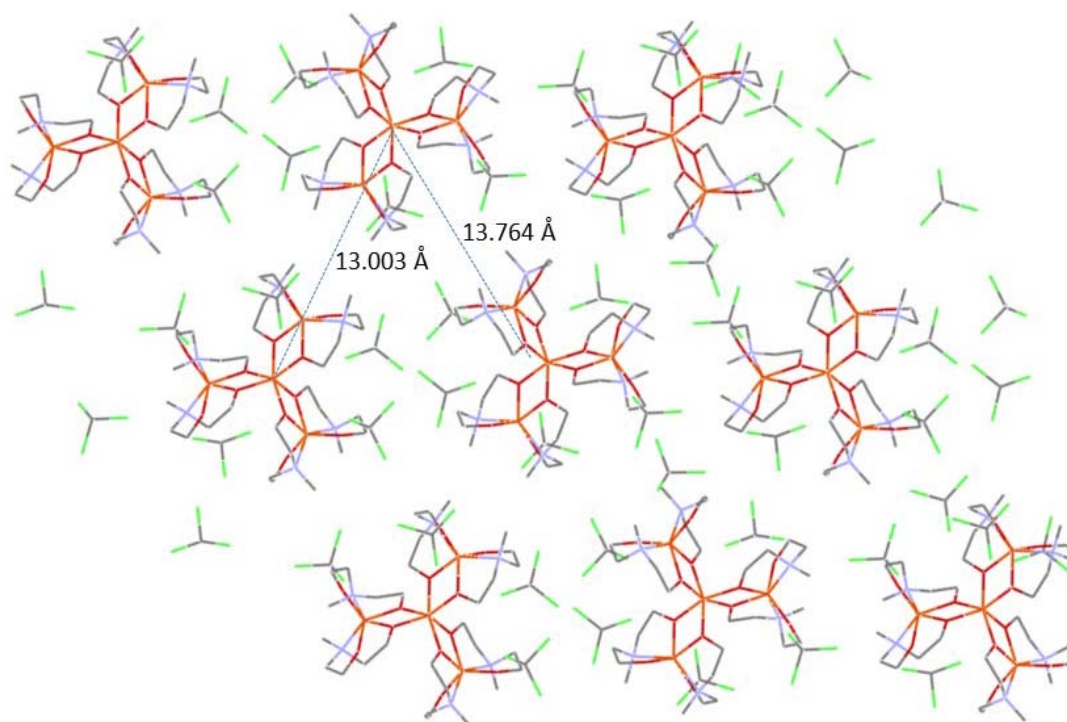


Fig. S2 Molecular packing in star-shaped $[\text{Fe}_4(\text{mdea})_6] \cdot 6 \text{CHCl}_3$ (**1b**).

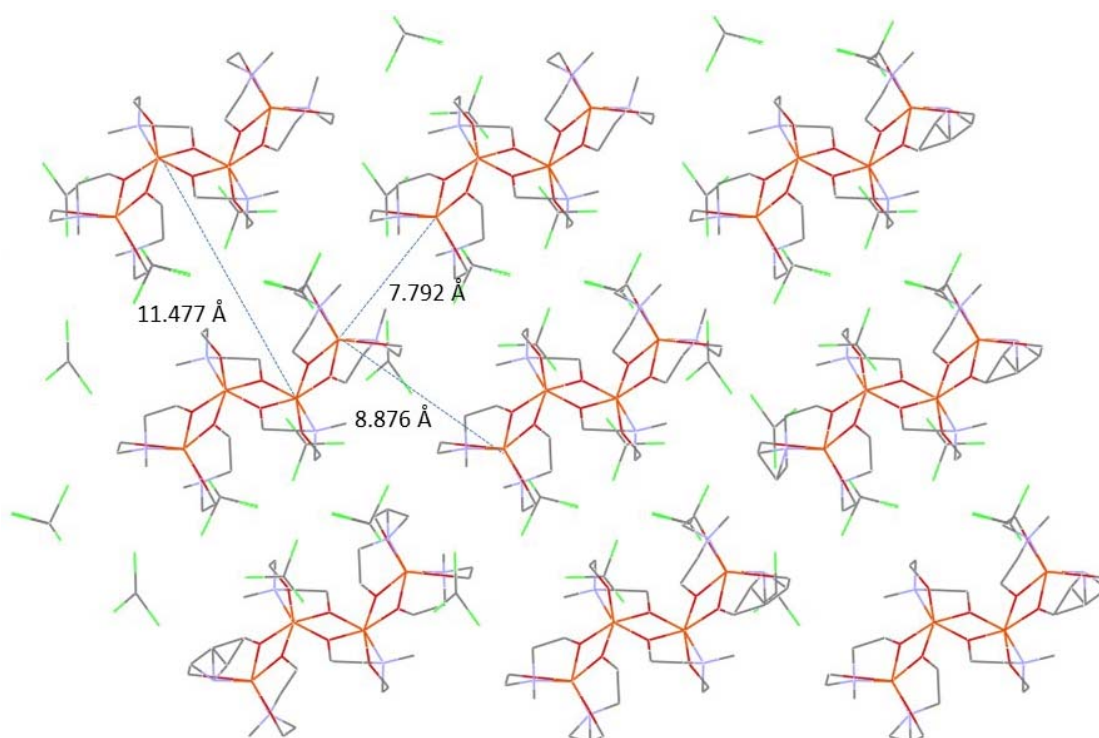


Fig. S3 Molecular packing in chair-shaped $[\text{Fe}_4(\text{mdea})_6] \cdot 6 \text{CHCl}_3$ (**1a**).

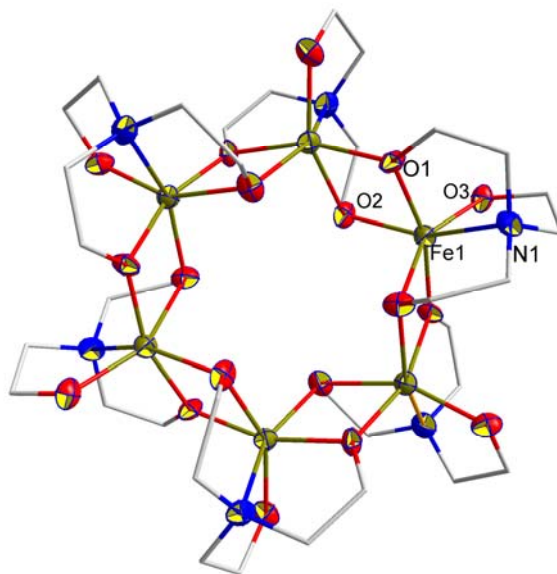


Fig. S4 Perspective view of the hexanuclear ring of $[\text{Fe}_6(\text{tea})_6]$ (**B**). As solvent molecules could not be refined, they are omitted here.

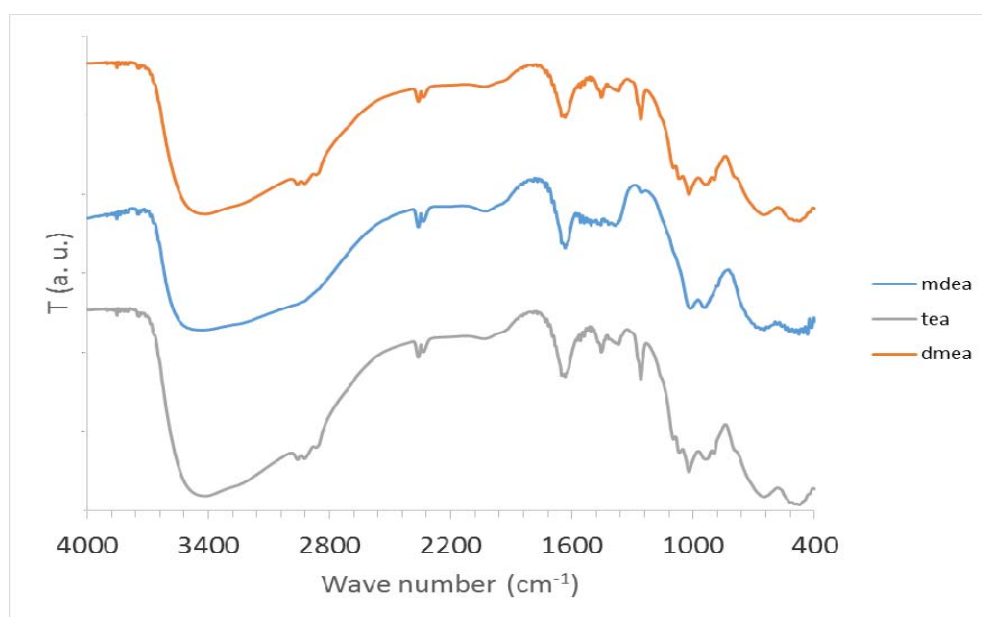
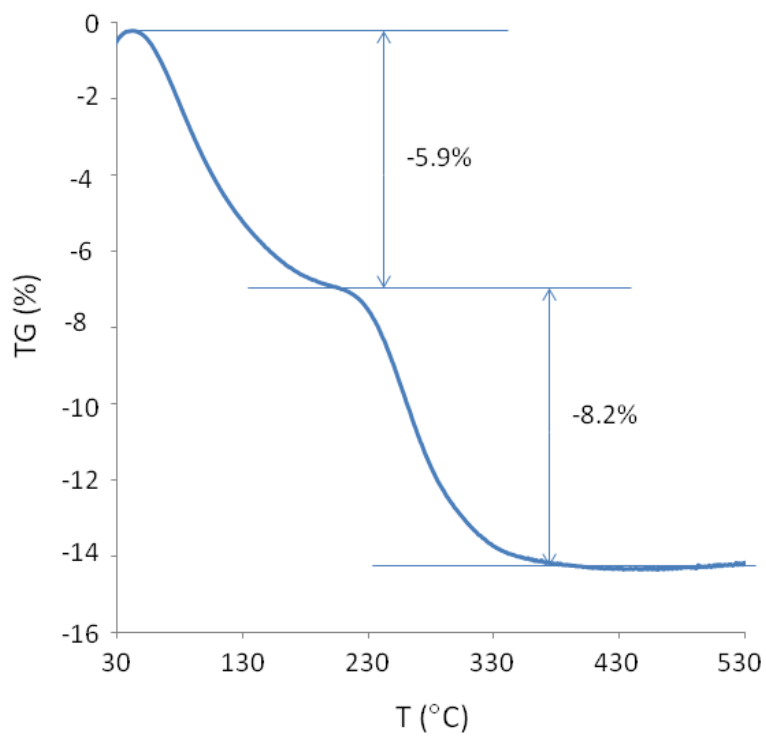
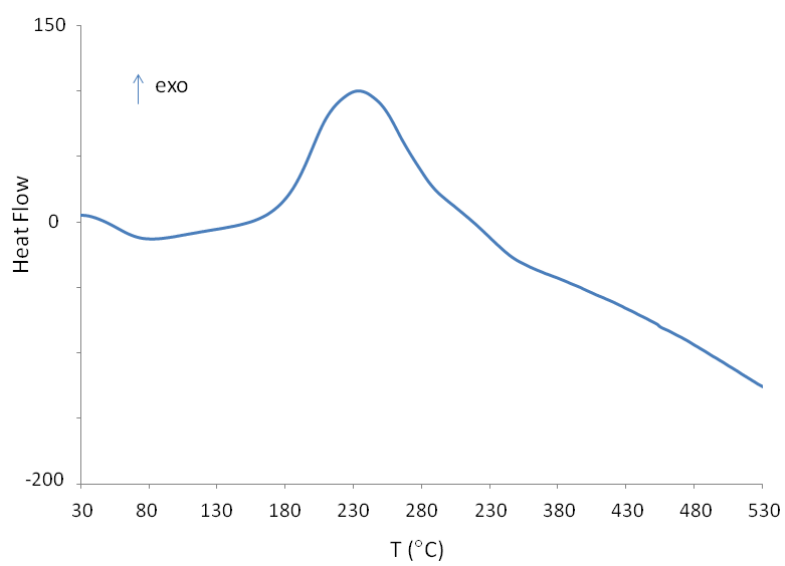


Fig. S5 FT-IR spectra of the as-prepared powders obtained after the hydrolysis of $\text{Fe}_4(\text{mdea})_6$ (**1**), $[\text{Fe}_2(\text{dmea})_6]$ (**A**) and $[\text{Fe}_6(\text{tea})_6]$ (**B**).



a)



b)

Fig. S6 TG (a) and DTA (b) curves of the as-prepared powder obtained after the hydrolysis of **1**.

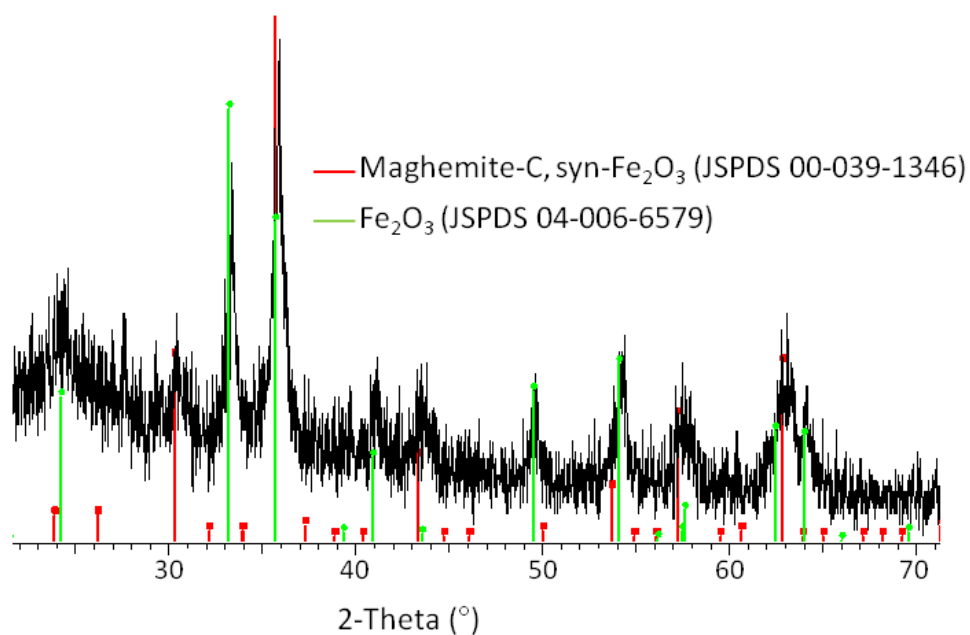


Fig. S7 XRD pattern of the powder obtained after the hydrolysis of **1** in the presence of ^tBu₄NBr followed by calcination at 500 °C.

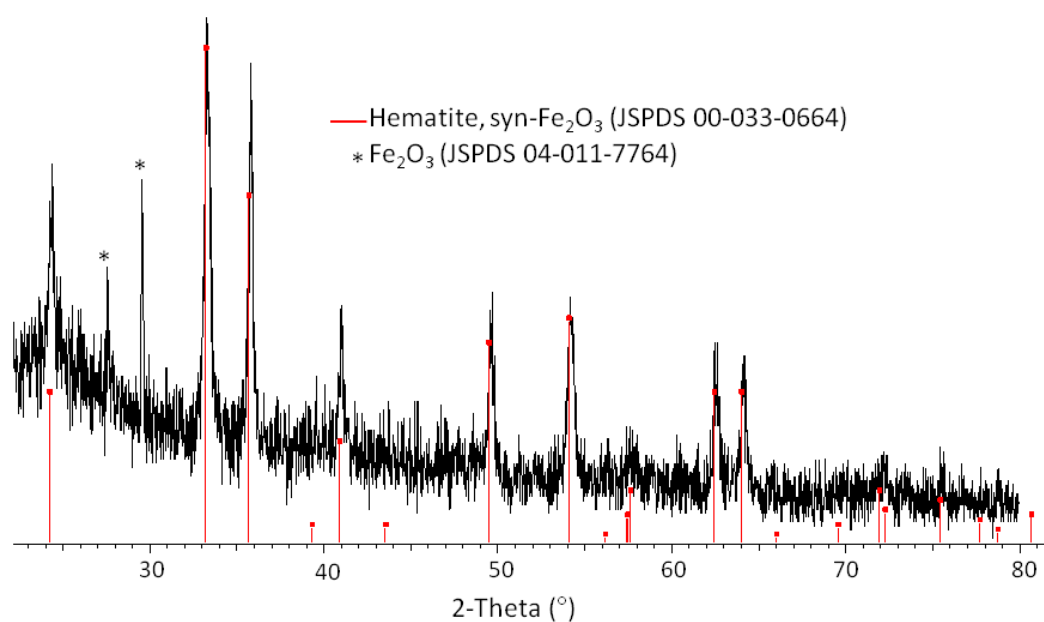


Fig. S8 XRD pattern of the powder obtained after the hydrolysis of **A** followed by calcination at 500 °C.

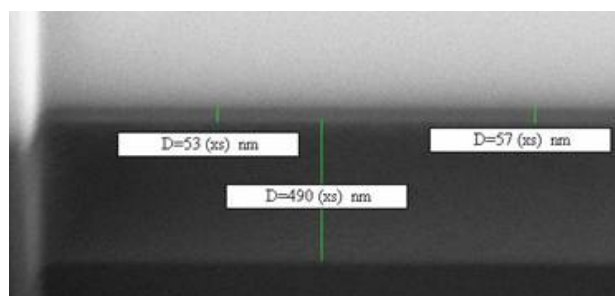


Fig. S9 Cross-sectional SEM image of Fe_2O_3 films deposited by spin-coating of the sol obtained from the precursor **1** on SiO_2 substrate and calcination at $400\text{ }^\circ\text{C}$.

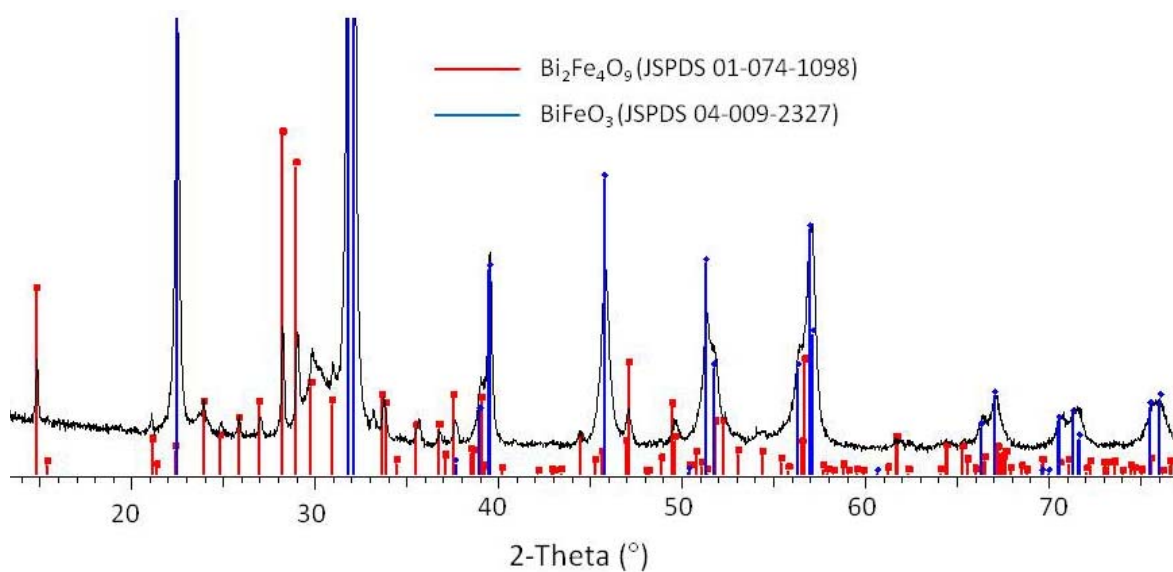


Fig. S10 XRD powder pattern of the BiFeO_3 NPs obtained after the calcination of monolithic xerogel (obtained from **1** and $[\text{Bi}_2(\text{mdea})_2(\text{mdeaH})_2]$) at $600\text{ }^\circ\text{C}$.