Reversible Tuning of Luminescence and Magnetism in a Structurally Flexible Erbium-Anilato MOF

Noemi Monni, a,b,d José J. Baldovi, b Victor Garcia-Lopez, b Mariangela Oggianu, a,d Enzo Cadoni, a Francesco Quochi, c,d Miguel Clemente-León, b Maria Laura Mercuri*, a,d and Eugenio Coronado b

a Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Cagliari, Complesso Universitario di Monserrato, 09042 Monserrato, Italy.

b Instituto de Ciencia Molecular, Universitat de València, Catedrático José Beltrán 2, 46980 Paterna, Spain.

c Dipartimento di Fisica, Università degli Studi di Cagliari, Complesso Universitario di Monserrato, 09042 Monserrato, Italy

d INSTM, Via Giusti, 9 50121 Firenze, Italy

Supporting Informations

Index

1. Synthesis and Physical Measurements
2. X-Ray Diffraction
3. FT-IR Spectroscopy
4. Thermogravimetric Analysis
5. Magnetic Measurements
6. Theoretical Calculations
7. Photoluminescence Measurements
8. References
1. Synthesis and Physical Measurements

GENERAL REMARKS. The Ln precursors, NaOH in pellets and the solvents used were purchased from Alfa Aesar and Exacta Optech and used without further purification. Synthesis of ligand H_{2}trz_{2}An was performed according with literature. Elemental analyses (C, H, and N) were performed with a CE Instruments EA 1110 CHNS.

SYNTHESIS. [Er_{2}(trz_{2}An)_{3}(H_{2}O)_{4}]_{n}·10H_{2}O (1a) and [Er_{2}(trz_{2}An)_{3}(H_{2}O)_{4}]_{n}·7H_{2}O (1b). A 5 mL Teflon vial with a mixture of Er(NO_{3})_{3}·6H_{2}O (0.05 mmol; 22.2 mg), H_{2}trz_{2}An (0.05 mmol, 13.7 mg), NaOH (0.1 mmol, 4 mg) and water (5 mL) was heated at 130°C for 48 hours and then the vial was slowly cooled to room temperature. Two different types of crystals were obtained from the same batch, dark red-block crystals (phase a) and orange prismatic crystals (phase b), both of them were suitable for SC-XRD measurements. Their density's difference was exploited to separate them, using CH_{2}Cl_{2}/CH_{2}Br_{2} solvent mixture in the ratio 0.925/0.975, for all further measurements. Elemental analysis of 1a and 1b is reported below in Table 1. Both single crystals and polycrystalline powder of 1a were placed under vacuum in a vacuum line pump and then sealed in a glove box to obtain [Er_{2}(trz_{2}An)(H_{2}O)_{2}]_{n}·2H_{2}O (1a_{des}), whereas the same attempt on 1b produced no changes. Elemental analysis of 1a_{des} is not shown since it turns to the structure of 1a after two days in air (see below).

Figure S1. a) Optical microscope image of a mixture of crystals of phase a and b; b) crystals separations using the CH_{2}Cl_{2}/CH_{2}Br_{2} solution mix.
Table S1. Elemental analysis for all the compounds 1a and 1b.

|          | Calculated | Found |
|----------|------------|-------|
|          | %C         | %H    | %N    | %C  | %H  | %N   |
| 1a       |            |       |       |     |     |      |
| C₃₀H₄₀N₁₉O₂₆Er₂ | 25.68     | 2.87  | 17.97 | 25.37 | 2.81  | 17.86 |
| 1b       |            |       |       |     |     |      |
| C₃₀H₃₄N₁₉O₂₃Er₂ | 26.71     | 2.54  | 18.69 | 26.70 | 2.24  | 18.57 |

PHYSICAL MEASUREMENTS.

A detailed description of **X-Ray Diffraction** experimental setup and additional data is provided in paragraph 2.

**Thermogravimetric Analysis.** Thermogravimetric analyses were performed in alumina crucibles with the instrument STA-6000 under nitrogen flux (40 mL/min), in the 25-800°C temperature range at 10°C/min.

**Magnetic Measurements.** Magnetic measurements were performed with Quantum Design MPMS-XL-5 SQUID and PPMS-9 magnetometers on powdered polycrystalline samples measured with eicosane to avoid preferential orientations. In the case of 1a, it was necessary to protect the sample covering it with H₂O in a glass tube since the vacuum of the squid chamber caused desolvation and the formation of 1a_des. Thus, magnetic measurements of 1a in the absence of H₂O correspond to 1a_des.

**Theoretical Calculations.** For the theoretical modelling of the magnetic properties, we have used the SIMPRE computational package,² introducing the crystallographic atomic coordinates and the experimental magnetic properties of the compounds as an input. In order to fit the experimental data, we have varied the two parameters (D, and Zᵢ) of the REC model for each type of donor atom of the first coordination sphere.³ A detailed explanation is provided in paragraph 6.

**Photoluminescence Measurements.** Photoluminescence (PL) experiments were performed with pulsed laser irradiance at 355 nm wavelength. Finely ground powders were compacted between quartz slides for measurements in standard conditions, or attached to the cold finger of a continuous-flow cryostat (Janis ST-500) for measurements under controlled atmosphere (air, vacuum, N₂), fed with liquid N₂ for low-temperature measurements under vacuum conditions at
77K. For time-resolved measurements of the ligand-centered emissions, samples were excited by optical parametric amplifier (Light Conversion TOPAS-C) emitting ~200-fs-long pulses at the repetition frequency of 1 kHz and detected by a Vis streak camera (Hamamatsu C1091) connected to a single-grating spectrometer (Princeton Instruments Acton SpectraPro2300i). For all other PL experiments, samples were pumped by a passively Q-switched powerchip laser (Teem Photonics PNV-M02510) delivering ~350 ps pulses, centered at 355 nm wavelength, at 1 kHz. The PL signals were analyzed by a single-grating spectrometer (Princeton Instruments Acton SpectraPro 2300i) and acquired by thermoelectrically cooled detectors, namely, (a) a Vis CCD camera (Andor NewtonEM) for ligand-centered emission spectra, (b) a NIR array detector (Andor iDus InGaAs 1.7mm) for NIR PL spectra, and (c) a photomultiplier (Hamamatsu H10330A-75) connected to a 1 GHz digital oscilloscope (Tektronix TDS 5104) for NIR PL decay transients.

2. X-Ray Diffraction

Single crystal X-Ray diffraction was performed on 1a and 1b crystals, which were mounted on a glass fiber using a viscous hydrocarbon oil to coat the single crystal and then transferred directly to the cold nitrogen stream for data collection. X ray data were collected at 120 K for both samples. Furthermore, a single crystal of 1a was measured at 360 K (1a_des 360 K) and another one was measured at 120 K after being placed in vacuum under a vacuum line pump and were then opened in the glove box to be sealed and mounted on a glass fiber using a viscous hydrocarbon oil to coat the single crystal. Then, the sample was transferred to the cold nitrogen stream for data collection (1a_des vacuum). Measurements were performed on a Supernova diffractometer equipped with a graphite-monochromated Enhance (Mo) X-ray Source (λ = 0.71073 Å). The program CrysAlisPro, Oxford Diffraction Ltd., was used for unit cell determinations and data reduction. Empirical absorption correction was performed using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm. The structures were solved with the ShelXT structure solution program and refined with the SHELXL-2013 program, using Olex2. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions refined using idealized geometries (riding model) and assigned fixed isotropic displacement parameters. Single crystal diffraction data of 1a_Des are of very bad quality due to the loss of single crystallinity under vacuum or temperatures above 350 K but good enough to solve the structure. Dehydration caused structural damage of part of the crystal, which could be responsible of several A and B errors in the checkcif files. Crystallographic data of all the compounds are summarized in Table S2. Crystallographic data for the structures was deposited in the Cambridge Crystallographic Data Centre, deposition numbers CCDC 2130639-42. These data can be obtained
Powder X-ray diffraction (PXRD) patterns were performed using a 0.7 mm glass capillary filled with polycrystalline samples of the compounds and mounted and aligned on an Empyrean PANalytical powder diffractometer, using Cu Kα radiation (λ = 1.541 77 Å). A total of three scans were collected for each compound at room temperature in the 2θ range of 5–40°. Polycrystalline samples of 1a and 1b were further placed under vacuum in a vacuum line pump and were then opened in the glove box to be sealed in the 0.7 mm glass capillary.

Table S2. Crystallographic data for compound 1a, 1a_des and 1b.

|                  | 1a       | 1a_des (360 K) | 1a_des (vacuum) | 1b       |
|------------------|----------|----------------|-----------------|----------|
| Empirical formula| C₃₀H₂₈N₁₈O₂₅Er₂ | C₃₀H₁₄N₁₈O₁₇Er₂ | C₃₀H₁₆N₁₈O₁₇Er₂ | C₃₀H₂₈N₁₈O₂₀Er₂ |
| FW               | 1.3752   | 1203.12        | 1249.12         | 1295.22  |
| Crystal color    | Dark Purple | Purple        | Purple           | Orange   |
| Crystal size (mm³)| 0.24 × 0.15 × 0.07 | 0.19 × 0.18 × 0.11 | 0.29 × 0.24 × 0.12 | 0.24 × 0.15 × 0.13 |
| Temperature (K)  | 120      | 360            | 120             | 120      |
| Wavelength (Å)   | (MoKa) λ = 0.71073 | (MoKa) λ = 0.71073 | (MoKa) λ = 0.71073 | (MoKa) λ = 0.71073 |
| Crystal system   | triclinic | triclinic      | triclinic       | triclinic |
| Space group      | P-1      | P-1            | P-1             | P-1      |
| a (Å)            | 8.9555 (7) | 9.0051 (13)    | 9.013 (3)       | 8.6201 (3) |
| b (Å)            | 9.4191 (7) | 9.3427 (17)    | 9.200 (3)       | 10.4220 (4) |
| c (Å)            | 15.4553 (12) | 12.533 (2)     | 12.495 (3)      | 11.9887 (4) |
| a (°)            | 75.154 (7) | 93.979 (15)    | 94.90 (2)       | 80.139 (3) |
| b (°)            | 77.176 (7) | 97.759 (14)    | 98.10 (2)       | 79.145 (3) |
| g (°)            | 67.936 (7) | 115.991 (16)   | 115.67 (3)      | 82.373 (3) |
| V (Å³)           | 1156.33 (17) | 929.3 (3)      | 912.1 (5)       | 1036.52 (7) |
| ρcalc (g.cm⁻³)   | 1.975    | 2.150          | 2.274           | 2.075    |
| μ(MoKa) (mm⁻¹)   | 3.712    | 4.584          | 4.681           | 4.126    |
| 2θ range (°)     | 5.59 to 55.74 | 6.078 to 52.78 | 6.15 to 56.152  | 6.584 to 56.08 |
| Index ranges     | -11 ≤ h ≤ 11, -11 ≤ k ≤ 12, -17 ≤ l ≤ 20 | -10 ≤ h ≤ 11, -11 ≤ k ≤ 11, -12 ≤ k ≤ 11, -13 ≤ k ≤ 12, -15 ≤ l ≤ 15, -15 ≤ l ≤ 16, -15 ≤ l ≤ 14 |
| Reflections collected | 4608 [Rint = 0.0362, Rsigma = 0.0667] | 3640 [Rint = 0.1450, Rsigma = 0.1500] | 3881 [Rint = 0.1745, Rsigma = 0.2099] | 4366 [Rint = 0.0203, Rsigma = 0.0223] |
| Independent reflections | 7799 | 9454 | 10668 | 14194 |
| Data/restraints/parameters | 4608/0/339 | 3640/0/270 | 3881/2/272 | 4366/0/324 |
| Goodness-of-fit on F² | 1.046 | 1.111 | 1.090 | 1.055 |
| Final R indexes [I>2σ (I)] | R₁ = 0.0354, wR₁ = 0.0680 | R₁ = 0.1222, wR₁ = 0.2922 | R₁ = 0.1400, wR₁ = 0.298 | R₁ = 0.0155, wR₁ = 0.037 |
| Final R indexes [all data] | R₁ = 0.0414, wR₁ = 0.0735 | R₁ = 0.1678, wR₁ = 0.3317 | R₁ = 0.2072, wR₁ = 0.361 | R₁ = 0.0162, wR₁ = 0.037 |
| Largest diff. peak/hole/e Å⁻³ | 1.21/-1.47 | 3.73/-3.05 | 4.79/-2.83 | 0.88/-0.93 |
Table S3. Bond lengths (Å) in 1a.

| Bond Lengths (Å)       |       |       |       |
|------------------------|-------|-------|-------|
| Er1 O3                 | 2.319(3) | N1 C4 | 1.329(6) |
| Er1 O4\(^1\)           | 2.416(3) | N1 C2 | 1.429(6) |
| Er1 O7                 | 2.377(3) | C7 C8 | 1.385(7) |
| Er1 O5                 | 2.377(3) | C7 C6 | 1.396(6) |
| Er1 O1                 | 2.409(3) | C8 C6\(^1\) | 1.545(6) |
| Er1 O2\(^2\)           | 2.426(3) | N7 C12 | 1.435(6) |
| Er1 O8                 | 2.369(3) | N7 N8 | 1.377(5) |
| Er1 O6\(^3\)           | 2.433(3) | N7 C14 | 1.323(6) |
| Er1 N3\(^4\)           | 2.461(4) | N2 C5 | 1.313(6) |
| O3 C6                  | 1.247(6) | N6 C9 | 1.337(6) |
| O4 C8                  | 1.250(5) | N6 C10 | 1.342(7) |
| O5 C11                 | 1.254(6) | C12 C13 | 1.397(7) |
| O1 C1                  | 1.241(6) | C12 C11 | 1.395(7) |
| O2 C3                  | 1.268(6) | N9 C14 | 1.314(6) |
| O6 C13                 | 1.246(6) | N9 C15 | 1.356(7) |
| N3 C4                  | 1.331(6) | N5 C10 | 1.320(7) |
| N3 C5                  | 1.347(6) | N8 C15 | 1.318(6) |
| N4 C7                  | 1.438(6) | C2 C1 | 1.404(6) |
| N4 N5                  | 1.367(5) | C2 C3 | 1.386(7) |
| N4 C9                  | 1.326(6) | C13 C11\(^3\) | 1.530(6) |
| N1 N2                  | 1.369(6) | C1 C3\(^2\) | 1.532(6) |
| Bond Angles (°) |
|----------------|
| Bond Angles (°) |
| O3  Er1  O4$^1$ 66.19(10) C9  N4  C7  129.6(4) |
| O3  Er1  O7  87.90(11) C9  N4  N5  108.9(4) |
| O3  Er1  O5  72.95(11) N2  N1  C2  121.1(4) |
| O3  Er1  O1  69.95(11) C4  N1  N2  110.1(4) |
| O3  Er1  O2$^2$ 135.11(11) C4  N1  C2  128.8(4) |
| O3  Er1  O8  83.36(11) C8  C7  N4  122.0(4) |
| O3  Er1  O6$^3$ 134.50(11) C8  C7  C6  120.2(4) |
| O3  Er1  N3$^4$ 141.28(13) C6  C7  N4  117.8(4) |
| O4$^1$  Er1  O2$^2$ 137.35(11) O4  C8  C7  125.8(4) |
| O4$^1$  Er1  O6$^3$ 132.63(11) O4  C8  C6$^1$  114.5(4) |
| O4$^1$  Er1  N3$^4$ 75.13(12) C7  C8  C6$^1$  119.7(4) |
| O7  Er1  O4$^1$ 68.06(12) N8  N7  C12  122.0(4) |
| O7  Er1  O5  137.77(11) C14  N7  C12  127.9(4) |
| O7  Er1  O1  69.60(11) C14  N7  N8  110.1(4) |
| O7  Er1  O2$^2$  75.70(12) C5  N2  N1  101.9(4) |
| O7  Er1  O6$^3$ 135.81(12) C9  N6  C10  101.2(4) |
| O7  Er1  N3$^4$ 79.16(12) O3  C6  C7  125.2(4) |
| O5  Er1  O4$^1$ 130.45(11) O3  C6  C8$^1$  114.8(4) |
| O5  Er1  O1  68.53(12) C7  C6  C8$^1$  120.0(4) |
| O5  Er1  O2$^2$  91.64(12) C13  C12  N7  118.1(4) |
| O5  Er1  O6$^3$ 65.36(11) C11  C12  N7  119.5(4) |
| O5  Er1  N3$^4$ 137.59(12) C11  C12  C13  122.2(4) |
| O1  Er1  O4$^1$ 118.62(11) C14  N9  C15  103.0(4) |
| O1  Er1  O2$^2$ 65.18(10) N1  C4  N3  109.7(4) |
| O1  Er1  O6$^3$ 108.72(12) C10  N5  N4  101.9(4) |
| O1  Er1  N3$^4$ 135.17(12) C15  N8  N7  101.2(4) |
| Bond lengths (Å) in 1b. |
|------------------------|

| Bond lengths (Å)       |
|------------------------|
| C1    | C2     | 1.395(3) | C11   | C13$^3$ | 1.530(3) |
| C1    | C3$^1$ | 1.530(3) | C11   | O5      | 1.256(3) |
| C1    | O1     | 1.254(3) | C12   | C13     | 1.407(3) |
| C2    | C3     | 1.400(3) | C12   | N7      | 1.425(3) |
| C2    | N1     | 1.420(3) | C13   | O6      | 1.241(3) |

**Table S5.**
| C3  | O2       | 1.245(3) | C14 | N8       | 1.315(3) |
| C4  | N1       | 1.333(3) | C14 | N9       | 1.357(3) |
| C4  | N3       | 1.317(3) | C15 | N7       | 1.331(3) |
| C5  | N2       | 1.315(3) | C15 | N9       | 1.322(3) |
| C5  | N3       | 1.355(3) | Er1 | N6\textsuperscript{4} | 2.5317(19) |
| C6  | C7       | 1.397(3) | Er1 | O1       | 2.3648(15) |
| C6  | C8\textsuperscript{2} | 1.537(3) | Er1 | O2\textsuperscript{i} | 2.5060(16) |
| C6  | O3       | 1.256(3) | Er1 | O3       | 2.3505(15) |
| C7  | C8       | 1.403(3) | Er1 | O4\textsuperscript{2} | 2.3928(15) |
| C7  | N4       | 1.427(3) | Er1 | O5       | 2.3336(15) |
| C8  | O4       | 1.242(3) | Er1 | O6\textsuperscript{3} | 2.4919(15) |
| C9  | N4       | 1.332(3) | Er1 | O7       | 2.3245(15) |
| C9  | N6       | 1.320(3) | Er1 | O8       | 2.3423(16) |
| C10 | N5       | 1.310(3) | N1  | N2       | 1.368(3) |
| C10 | N6       | 1.356(3) | N4  | N5       | 1.369(3) |
| C11 | C12      | 1.393(3) | N7  | N8       | 1.370(3) |

**Table S6.** Bond angles (°) in 1b.

| Bond Angles (°) |
|-----------------|
| C2   | C1   | C3\textsuperscript{i} | 120.9(2) | O5   | Er1  | N6\textsuperscript{4} | 70.51(6) |
| O1   | C1   | C2   | 124.0(2) | O5   | Er1  | O1   | 137.48(5) |
| O1   | C1   | C3\textsuperscript{i} | 115.13(19) | O5   | Er1  | O2\textsuperscript{i} | 142.92(5) |
| C1   | C2   | C3   | 121.5(2) | O5   | Er1  | O3   | 135.83(5) |
| C1   | C2   | N1   | 116.9(2) | O5   | Er1  | O4\textsuperscript{2} | 91.72(5) |
| C3   | C2   | N1   | 121.6(2) | O5   | Er1  | O6\textsuperscript{3} | 65.68(5) |
| C2   | C3   | C1\textsuperscript{i} | 117.58(19) | O5   | Er1  | O8   | 77.04(6) |
| O2   | C3   | C1\textsuperscript{i} | 115.53(19) | O6\textsuperscript{3} | Er1  | N6\textsuperscript{4} | 117.29(6) |
| O2   | C3   | C2   | 126.9(2) | O6\textsuperscript{3} | Er1  | O2\textsuperscript{i} | 126.52(5) |
| Atom 1 | Atom 2 | Atom 3 | Bond Angle (°) | Distance (Å) |
|--------|--------|--------|----------------|-------------|
| N3     | C4     | N1     | 111.7(2)      | O7          | Er1       | N6         | 142.02(6)  |
| N2     | C5     | N3     | 115.8(2)      | O7          | Er1       | O1         | 137.57(6)  |
| C7     | C6     | C8^2   | 119.35(19)    | O7          | Er1       | O2^1       | 73.46(5)   |
| O3     | C6     | C7     | 124.4(2)      | O7          | Er1       | O3         | 87.57(5)   |
| O3     | C6     | C8^2   | 116.27(19)    | O7          | Er1       | O4^2       | 136.38(5)  |
| C6     | C7     | C8     | 122.5(2)      | O7          | Er1       | O5         | 81.29(6)   |
| C6     | C7     | N4     | 118.09(19)    | O7          | Er1       | O6^3       | 69.99(5)   |
| C8     | C7     | N4     | 119.44(19)    | O7          | Er1       | O8         | 76.67(6)   |
| C7     | C8     | C6^2   | 118.17(19)    | O8          | Er1       | N6^4       | 72.67(6)   |
| O4     | C8     | C6^2   | 116.60(19)    | O8          | Er1       | O1         | 93.86(6)   |
| O4     | C8     | C7     | 125.2(2)      | O8          | Er1       | O2^1       | 71.09(5)   |
| N6     | C9     | N4     | 110.48(19)    | O8          | Er1       | O3         | 141.17(6)  |
| N5     | C10    | N6     | 114.8(2)      | O8          | Er1       | O4^2       | 143.62(5)  |
| C12    | C11    | C13^3  | 119.83(19)    | O8          | Er1       | O6^3       | 132.66(5)  |
| O5     | C11    | C12    | 124.4(2)      | C4          | N1         | C2         | 127.2(2)   |
| O5     | C11    | C13^3  | 115.79(19)    | C4          | N1         | N2         | 108.81(19) |
| C11    | C12    | C13    | 122.2(2)      | N2          | N1         | C2         | 123.31(19) |
| C11    | C12    | N7     | 116.91(19)    | C5          | N2         | N1         | 102.0(2)   |
| C13    | C12    | N7     | 120.81(19)    | C4          | N3         | C5         | 101.6(2)   |
| C12    | C13    | C11^3  | 117.95(19)    | C9          | N4         | C7         | 129.33(19) |
| O6     | C13    | C11^3  | 115.98(19)    | C9          | N4         | N5         | 109.27(18) |
| O6     | C13    | C12    | 126.1(2)      | N5          | N4         | C7         | 121.24(18) |
| N8     | C14    | N9     | 114.4(2)      | C10         | N5         | N4         | 102.55(18) |
| N9     | C15    | N7     | 110.4(2)      | C9          | N6         | C10        | 102.90(19) |
| O1     | Er1    | N6^4   | 67.15(6)      | C9          | N6         | Er1^5      | 129.68(15) |
| O1     | Er1    | O2^1   | 64.42(5)      | C10         | N6         | Er1^5      | 126.94(15) |
| O1     | Er1    | O4^2   | 71.19(5)      | C15         | N7         | C12        | 129.08(19) |
| O1     | Er1    | O6^3   | 133.34(5)     | C15         | N7         | N8         | 109.30(18) |
| Bond lengths (Å) |
|-----------------|
| Er01 O002       | 2.264(17) | N00B C00V 1.37(3) |
| Er01 O003       | 2.430(16) | N00D C00N 1.28(3) |
| Er01 O004       | 2.388(14) | N00D C00O 1.36(3) |
| Er01 O005       | 2.285(16) | N00E N00L 1.36(3) |
| Er01 O006       | 2.264(17) | N00E C00T 1.30(3) |
| Er01 O0071      | 2.418(17) | N00E C00W 1.41(3) |
| Er01 O00A2      | 2.394(17) | N00G C00O 1.32(3) |
| Er01 N00B3      | 2.47(2)   | N00H C00V 1.34(3) |
| O002 C00S       | 1.25(2)   | C00I C00R 1.42(3) |
| O003 C00K       | 1.22(3)   | C00I C00U 1.40(3) |
| O004 C00M       | 1.25(3)   | C00J C00M 1.36(3) |
| O005 C00U       | 1.26(2)   | C00J C00P 1.38(3) |
| O007 C00P       | 1.23(3)   | C00K C00S 1.60(3) |
| N008 C00F       | 1.37(3)   | C00K C00W4 1.45(3) |
| N008 N00H       | 1.33(3)   | N00L C00X 1.33(3) |
| N008 C00J       | 1.45(3)   | C00M C00P5 1.57(3) |
| Bond Angles (°) |
|-----------------|
| O002 Er01 O003 66.3(5) C00V N00B Er01³ 131.5(15) |
| O002 Er01 O004 87.0(6) C00N N00D C00O 102(2) |
| O002 Er01 O005 148.5(5) N00L N00E C00W 121(2) |
| O002 Er01 O007¹ 76.8(6) C00T N00E N00L 110(2) |
| O002 Er01 O00A² 81.7(6) C00T N00E C00W 129(2) |
| O002 Er01 N00B³ 141.3(6) N00B C00F N008 107(2) |
| O003 Er01 N00B³ 75.0(6) C00O N00G N009 101.0(19) |
| O004 Er01 O003 66.3(5) N008 N00H C00V 103(2) |
| O004 Er01 O007¹ 64.2(5) N009 C00I C00R 118(2) |
| O004 Er01 O00A² 130.6(5) N009 C00I C00U 124(2) |
| O004 Er01 N00B³ 78.3(5) C00U C00I C00R 118(2) |
| O005 Er01 O003 144.5(6) C00M C00J N008 118(2) |
| O005 Er01 O004 109.8(6) C00M C00J C00P 124(2) |
| O005 Er01 O007¹ 86.8(6) C00P C00J N008 118(2) |
| O005 Er01 O00A² 67.1(6) O003 C00K C00S 116.7(17) |
| O005 Er01 N00B³ 69.8(6) O003 C00K C00W⁴ 125(2) |
| O006 Er01 O002 85.5(6) C00W⁴ C00K C00S 118.0(19) |
| O006 Er01 O003 77.1(5) C00X N00L N00E 101(2) |
| O006 Er01 O004 142.5(6) O004 C00M C00J 128(2) |

*Table S8.* Bond angles (°) in 1a des (vacuum).
| ID   | Type | ID   | Type | Value 1   | Type | Value 2   | Type | Value 3   |
|------|------|------|------|-----------|------|-----------|------|-----------|
| O006 | Er01 | O005 | 95.1(6) | O004  | C00M  | C00P^1   | 112.8(19) |
| O006 | Er01 | O007^1 | 147.5(6) | C00J | C00M  | C00P^1   | 119(2)  |
| O006 | Er01 | O00A^2 | 84.5(6) | N00D | C00N  | N009     | 114(2)  |
| O006 | Er01 | N00B^3 | 84.9(6) | N00G | C00O  | N00D     | 116(2)  |
| O007^1 | Er01 | O003 | 118.3(5) | O007  | C00P  | C00J     | 129(2)  |
| O007^1 | Er01 | N00B^3 | 125.5(6) | O007  | C00P  | C00M^1   | 114(2)  |
| O00A^2 | Er01 | O003 | 143.9(5) | C00J | C00P  | C00M^1   | 117(2)  |
| O00A^2 | Er01 | O007^1 | 66.4(5) | C00X | N00Q  | C00T     | 99(2)   |
| O00A^2 | Er01 | N00B^3 | 134.3(6) | O00A  | C00R  | C00I     | 125(2)  |
| C00S | O002 | Er01 | 124.4(14) | O00A  | C00R  | C00U^2   | 113.7(19)|
| C00K | O003 | Er01 | 116.6(13) | C00I  | C00R  | C00U^2   | 121(2)  |
| C00M | O004 | Er01 | 121.2(14) | O002  | C00S  | C00K     | 110.0(19)|
| C00U | O005 | Er01 | 120.2(16) | O002  | C00S  | C00W     | 130(2)  |
| C00P | O007 | Er01^1 | 121.0(14) | C00W  | C00S  | C00K     | 119.6(17)|
| C00F | N008 | C00J | 121.7(19) | N00E  | C00T  | N00Q     | 113(2)  |
| N00H | N008 | C00F | 112.3(19) | O005  | C00U  | C00I     | 123(2)  |
| N00H | N008 | C00J | 126(2) | O005  | C00U  | C00R^2   | 115(2)  |
| C00I | N009 | N00G | 120.3(19) | C00I  | C00U  | C00R^2   | 121.5(19)|
| C00N | N009 | N00G | 107.0(19) | N00H  | C00V  | N00B     | 113(2)  |
| C00N | N009 | C00I | 132.5(19) | N00E  | C00W  | C00K^4   | 119(2)  |
| C00R | O00A | Er01^2 | 116.0(15) | C00S  | C00W  | N00E     | 118.3(19)|
| C00F | N00B | Er01^3 | 123.5(17) | C00S  | C00W  | C00K^4   | 122(2)  |
| C00F | N00B | C00V | 105(2) | N00L  | C00X  | N00Q     | 118(2)  |
Table S9. Continuous SHAPE measurement (CShM) values of the 13 possible coordination geometries for the Er\textsuperscript{III} ion with coordination number 9 in 1a and 1b.\textsuperscript{7}

|     | 1a   | 1b   |
|-----|------|------|
| EP-9| 35.360 | 37.136 |
| OPY-9| 23.761 | 21.660 |
| HBPY-9| 19.013 | 19.640 |
| JTC-9| 15.518 | 15.966 |
| JCCU-9| 10.426 | 10.461 |
| CCU-9| 9.140  | 9.497  |
| JCSAPR-9| 1.676  | 1.672  |
| CSAPR-9| 0.565  | 0.976  |
| JTCTPR-9| 2.191  | 1.653  |
| TCTPR-9| 0.979  | 0.532  |
| JTDIC-9| 13.722 | 12.866 |
| HH-9| 11.792 | 11.302 |
| MFF-9| 0.590  | 1.384  |

EP-9 = Enneagon; OPY-9 = Octagonal pyramid; HBPY-9 = Heptagonal bipyramid; JTC-9 = Johnson triangular cupola J3; JCCU-9 = Capped cube J8; CCU-9 = Spherical-relaxed capped cube; JCSAPR-9 = Capped square antiprism J10; CSAPR-9 = Spherical capped square antiprism; JTCTPR-9 = Tricapped trigonal prism J51; TCTPR-9 = Spherical tricapped trigonal prism; JTDIC-9 = Tridiminished icosahedron J63; HH-9 = Hula-hoop; MFF-9 = Muffin
Table S10. Continuous SHAPE measurement (CShM) values of the 13 possible coordination geometries for the Er$^{III}$ ion with coordination number 8 in 1a_des.7

| Geometry | CShM Value |
|----------|------------|
| OP-8     | 30.477     |
| HPY-8    | 23.286     |
| HBPY-8   | 15.656     |
| CU-8     | 12.267     |
| SAPR-8   | 4.494      |
| TDD-8    | 1.887      |
| JGBF-8   | 12.433     |
| JETBPY-8 | 25.772     |
| JBTPR-8  | 2.803      |
| BTPR-8   | 2.103      |
| JSD-8    | 3.334      |
| TT-8     | 12.666     |
| ETBPY-8  | 22.346     |

OP-8 = Octagon; HPY-8 = Heptagonal pyramid; HBPY-8 = Hexagonal bipyramid; CU-8 = Cube; SAPR-8 = Square antiprism; TDD-8 = Triangular dodecahedron; JGBF-8 = Johnson gyrobiastigium J26; JETBPY-8 = Johnson elongated triangular bipyramid J14; JBTPR-8 = Biaugmented trigonal prism J50; BTPR-8 = Biaugmented trigonal prism; JSD-8 = Snub diphenoid J84; TT-8 = Triakis tetrahedron; ETBPY-8 = Elongated trigonal bipyramid.
Figure S2. View of (a) one hexagonal cavity of 1a, (b) one rectangular cavity of 1b and (c) one shrinked rectangular cavity of 1a_des.
Powder X-Ray Diffraction (PXRD)

Figure S3. Experimental powder XRD pattern (red) and calculated pattern (black) of compound 1a, in 2θ range of 5-40°.

Figure S4. Experimental powder XRD pattern (red) and calculated pattern (black) of compound 1b, in 2θ range of 5-40°.
Figure S5. PXRD patterns of 1b (black) and 1b under vacuum (red) in 2θ range of 5-40°.

Figure S6. Calculated (black) and experimental (red) PXRD patterns of 1a_des, in 2θ range of 5-40°.
3. FT-IR Spectroscopy

FT-IR spectra were collected using a Bruker Equinox 55 spectrometer, preparing the samples as KBr pellets.

The spectra of \(1\) and \(2\) were compared with \(\text{H}_2\text{trz}_2\text{An}\) spectrum. As shown in figure S1, the band at 1650 cm\(^{-1}\) of vCO of free ligand disappears and the broad band in the region around 1550 cm\(^{-1}\) is downshifted, due to the coordination of C-O in the frameworks.

![FT-IR spectra of \(\text{H}_2\text{trz}_2\text{An}\) (green), \(1\) (black) and \(2\) (red) in the 1800-400 cm\(^{-1}\) region.](image)

**Figure S7.** FT-IR spectra of \(\text{H}_2\text{trz}_2\text{An}\) (green), \(1\) (black) and \(2\) (red) in the 1800-400 cm\(^{-1}\) region.

FT-IR spectra of \(1\) and \(2\) appear very similar and show only slight differences in the bands. The characteristic bands with their assignments are shown in the following table.

|                  | 1a  | 1b  |
|------------------|-----|-----|
| v O-H            | 3388| 3438|
| v C=O           | 1605| 1589|
| v C=O + v C=C aromatic | 1513| 1506|
| v aromatic ring   | 1385| 1391|
| v C-N           | 1321| 1325|
| v N-N           | 1272| 1278|
| \(\delta\) C=C   | 1272| 1272|
| v Er-O          | 1183| 1181|
|                 | 835 | 835 |
|                 | 459 | 438 |
|                 | 446 |     |
4. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was performed in order to study the thermal stability of both 1a and 1b and to have complementary information about the dehydrated phase 1a_des. Thus, the first weight loss of 10 % from room temperature to 350 K is consistent with the change of chemical formula from $[\text{Er}_2(\text{trz}_2\text{An})_3(\text{H}_2\text{O})_4]_n\cdot10\text{H}_2\text{O}$ found in 1a by elemental analysis to $[\text{Er}_2(\text{trz}_2\text{An})_3(\text{H}_2\text{O})_2]_n\cdot2\text{H}_2\text{O}$ found in the structure of 1a_des. It was not possible to use elemental analysis to obtain the formula of this compound due to the fast rehydration of 1a_des in air.

![Thermogram of 1a in 25-800°C temperature range.](image)

**Figure S8.** Thermogram of 1a in 25-800°C temperature range. The percentages shown in the graph are referred to the previous weight loss.

1a thermogram shows a continuous weight loss of 10 % from room temperature to 77°C, which is close to the expected weight loss of 10 water molecules. Then in the 77-160°C temperature range a second weight loss is present, which is close to the expected weight loss for the remaining 2 solvate water molecules, leading to the formula $[\text{Er}_2(\text{trz}_2\text{An})_3(\text{H}_2\text{O})_2]_n$. Therefore, the first weigh loss in the 25-77°C corresponds to half of the coordinating water molecules and part of the solvate water molecules, while the one 77-160°C it could be due to the remaining solvate water molecules. Taking into account the crystallographic data, the first weight loss is consistent with the transition from the initial compound $([\text{Er}_2(\text{trz}_2\text{An})_3(\text{H}_2\text{O})_4]_n\cdot10\text{H}_2\text{O})$ to $[\text{Er}_2(\text{trz}_2\text{An})_3(\text{H}_2\text{O})_2]_n\cdot2\text{H}_2\text{O}$ of 1a_des. Then the second weight loss is close to the expected loss which lead to the formula $[\text{Er}_2(\text{trz}_2\text{An})_3(\text{H}_2\text{O})_2]_n$. 
Thermogram of 1b, reported in Figure S8, shows the first weight loss of 7.3% at 165°C, which correspond to 5.5 water molecules. At 213°C there is another weight loss of 2.7%, corresponding to 1.5 water molecules. As 1a, the compound is very stable, starting its decomposition above 400°C, after the ligand decomposition.

Figure S9. Thermogram of 1b in 25-800°C temperature range, showing the weightlosses at different temperatures. The percentages shown in the graph refer to the previous one weightloss.
5. Magnetic Measurements

Figure S10. Experimental (symbols), fitted (solid line) temperature-dependence of the magnetic susceptibility from 2 to 300 K of 1b (a); Calculated (black) and experimental (red) ground-$J$ multiplet energy levels (b). Further details are provided in Table S12.

Figure S11. Experimental (symbols) and predicted average (lines) of magnetization $M$ versus field $H$ for 1a (a) and 1a_{des} (b) at 2K (blue), 4 K (green), 6 K (orange) and 8 K (red).
Figure S12. Experimental (symbols) and predicted average (lines) of magnetization M versus field H for 1b at 2K (blue), 4 K (green), 6 K (orange) and 8 K (red).
Figure S13. Temperature dependence of $\chi'$ and $\chi''$ of 1a (a) and 1a\_des (b) in an applied dc field of 0.09 T at frequencies in the range 100 to 10000 Hz.
**Figure S14.** Frequency dependence of the in-of-phase component, \( \chi' \), in an applied dc field of 0.09 T of 1a (a) and 1a_des (b) at different temperatures. Solid lines in 1a_des represent the best fitting of the experimental data to a Debye function.
Figure S15. Cole-Cole plots of 1a (left) and 1a_des (right). Solid lines represent the best fitting of the experimental data to a Debye function.
Figure S16. Plot of Ln $\tau$ versus $1/T$ for 1a_des (left) and 1b (right).

Figure S17. Thermal dependence of the relaxation time of 1a_des (left) and 1b (right) and best fit from two terms mechanism described in text.
**Figure S18.** Temperature dependence of $\chi'$ and $\chi''$ of 1b in an applied dc field of 0.1 T at frequencies in the range 100 to 10000 Hz.

**Figure S19.** ac susceptibility in an applied dc field of 0.1 T of 1b measured as a function of the frequency at the different temperatures (2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5 and 6.0 K). Left: Real component. Right: Imaginary component. Solid lines represent the best fitting of the experimental data to a Cole-Cole function.
Figure S20. Cole-Cole plots of 1b under an applied dc field of 0.1 T. Solid lines represent the best fitting of the experimental data to a Debye function.
6. Theoretical Calculations

Radial Effective Charge (REC) model

Our calculations start with the crystallographic/non-idealized atomic coordinates of the first coordination sphere. These are introduced as an input for the portable fortran77 software code SIMPRE. This code parameterizes the electric field effect produced by the surrounding ligands, acting over the central ion, by using the following Crystal Field Hamiltonian expressed in terms of the Extended Stevens Operators (ESOs):

\[ H_{cf}(J) = \sum_{k=2,4,6} \sum_{q=-k}^{k} B_{k}^{q} O_{k}^{q} = \sum_{k=2,4,6} \sum_{q=-k}^{k} a_{k} (1 - \sigma_{k}) A_{k}^{q} \left\langle r^{k} \right\rangle O_{k}^{q} \]

(1)

where \( k \) is the order (also called rank or degree) and \( q \) is the operator range, that varies between \( k \) and \( -k \), of the Stevens operator equivalents \( O_{k}^{q} \) as defined by Ryabov in terms of the angular momentum operators \( J_{\pm} \) and \( J_{z} \), where the components \( O_{k}^{\xi(c)} \) and \( O_{k}^{\xi(s)} \) correspond to the ESOs with \( q \geq 0 \) and \( q < 0 \) respectively. Note that all the Stevens CF parameters \( B_{k}^{q} \) are real, whereas the matrix elements of \( O_{k}^{q} (q < 0) \) are imaginary. \( a_{k} \) are the \( \alpha, \beta \) and \( \gamma \) Stevens coefficients for \( k = 2, 4, 6 \), respectively, which are tabulated and depend on the number of \( f \) electrons. \( \sigma_{k} \) are the Sternheimer shielding parameters of the 4\( f \) electronic shell, and \( \left\langle r^{k} \right\rangle \) are the expectation values of the radius.

In SIMPRE, the \( A_{k}^{q} \) CF parameters are determined by the following relations:

\[ A_{k}^{0} = \frac{4\pi}{2k+1} \sum_{i=1}^{N} Z_{i} e^{2} R_{i}^{k+1} Z_{k0}^{c}(\theta_{i},\phi_{i}) p_{kl} \]  

(2.a)

\[ A_{k}^{q} = \frac{4\pi}{2k+1} \sum_{i=1}^{N} Z_{i} e^{2} R_{i}^{k+1} Z_{kq}^{c}(\theta_{i},\phi_{i}) p_{kl} \]  

(2.b)

\[ A_{k}^{q} = \frac{4\pi}{2k+1} \sum_{i=1}^{N} Z_{i} e^{2} R_{i}^{k+1} Z_{klq}^{c}(\theta_{i},\phi_{i}) p_{klq} \]  

(2.c)

In the REC model the ligand is modeled through an effective point charge situated between the lanthanoid and the coordinated atom at a distance \( R_{i} \) from the magnetic centre, which is smaller than the real metal-ligand distance \( (r_{i}) \). To account for the effect of covalent electron sharing, a radial displacement vector \( \mathbf{D}_{r} \) is defined, in which the polar coordinate \( r \) of each coordinated atom is varied, \( R_{i} = r_{i} - D_{r} \). The usual procedure is to obtain the \( D_{r} \) parameter of each kind of donor
atom from a collective fit of an observable (e.g. energy levels or magnetic properties) for a family of isostructural lanthanide complexes. At the same time, the charge value \( Z_i \) is scanned in order to achieve the minimum deviation between calculated and experimental data, whereas \( Z_i \) and \( \phi_i \) remain constant. In this work, we have kept fixed the value of \( D_r \) for the oxygen and nitrogen atoms, 0.98 Å and 1.20 Å, which have been taken from the literature (Chem. Sci., Inorg. Chem.) and offer a better approximation for the relative relation between \( k = 2, 4, 6 \), which is one of the main drawbacks of the point-charge electrostatic model. This strategy allows us to restrict the number of free parameters to 2, i.e. the effective charges of the nitrogen and oxygen atoms, \( Z_i \) (N) = 0.05 and \( Z_i \) (O) = 0.161, which have been obtained by a two-parameter fit of the \( \chi T \) product of both phases. Here it is worth to mention that these phenomenological parameters used by SIMPRE to predict the spin energy levels and wave functions do not pretend to simulate the actual charge distribution. In the fitting procedures, we define the relative error \( E \) as:

\[
E = \frac{1}{n} \sum_{i=1}^{n} \left[ \frac{\chi_{\text{theo},i} - \chi_{\text{exp},i}}{\chi_{\text{exp},i}} \right]^2
\]

where \( \chi_{\text{exp}} \) and \( \chi_{\text{theo}} \) are experimental and theoretical magnetic susceptibility, respectively, and \( n \) is the number of points.

To calculate the magnetic properties, SIMPRE introduces the interaction between the electron spin and an external magnetic field along the z-direction via a Zeeman term \( \tilde{H}_{ZEB} \):

\[
\tilde{H}_{ZEB} = g_j \mu_B B_z \cdot \hat{J}_z
\]

Where \( g_j \) is the Landé g-factor for the ground \( J \)-multiplet, \( \mu_B \) is the Bohr magneton, \( B_z \) is the external magnetic field along the z-direction and \( \hat{J}_z \) is the z-component of the total electronic angular momentum operator. Once we have the eigenvalues of the system at different magnetic fields or temperatures, one can evaluate the partition function \( Z \):

\[
Z = \sum_n \exp \left( -\frac{E_n}{kT} \right)
\]

where \( E_n \) are the eigenvalues of the system, \( T \) is temperature and \( k \) is the Boltzmann constant. Then, the macroscopic thermodynamic properties, such as magnetization and magnetic susceptibility, are calculated by summing the \( N \) microscopic magnetizations weighed by according
to the Boltzmann distribution law, via the following fundamental equations:

\[ M = NkT \frac{\partial \ln Z}{\partial H} \]

**Table S12.** Crystal field parameters \( A_k^q < r^k >; \) Stevens notation in cm\(^{-1}\) obtained for 1a, 1a\_des and 1b.

| \( k \) | \( q \) | 1a     | 1a\_des | 1b      |
|-----|-----|--------|---------|--------|
| 2   | 0   | -109.47| -4.31   | -235.64|
| 2   | 1   | 536.28 | -174.55 | -23.17 |
| 2   | -1  | 132.52 | 97.96   | 175.22 |
| 2   | 2   | -9.96  | 443.83  | -232.21|
| 2   | -2  | 1.21   | 156.58  | 47.37  |
| 2   | 4   | 53.25  | 177.50  | -23.76 |
| 4   | 0   | 133.83 | 256.23  | 58.08  |
| 4   | 1   | 126.58 | 58.57   | 411.70 |
| 4   | -1  | 280.14 | -351.37 | -287.91|
| 4   | 2   | 54.85  | 319.13  | 55.10  |
| 4   | -2  | 260.99 | 378.95  | 118.07 |
| 4   | 4   | 218.69 | 36.18   | 90.32  |
| 4   | -4  | -215.45| -114.76 | -443.98|
| 6   | 0   | 19.33  | -16.06  | 24.75  |
| 6   | 1   | 112.26 | 116.46  | -18.66 |
| 6   | -1  | 17.69  | 18.09   | 41.02  |
| 6   | 2   | 1.40   | 57.54   | -81.76 |
| 6   | -2  | 10.26  | 41.34   | 93.90  |
| 6   | 3   | -266.50| -39.74  | 17.48  |
| 6   | -3  | 121.33 | 292.07  | 77.70  |
| 6   | 4   | -232.96| 2.04    | 111.02 |
| 6   | -4  | 103.40 | 44.61   | 145.96 |
Table S13. Ground multiplet energy level scheme (Kramers doublets in cm\(^{-1}\)) and main \(|M_f>\) contributions to the wave function calculated for **1a** and **1a_des**. Red numbers in brackets: Main energy values estimated from PL spectrum of **1a_des** at 77K, assuming a zero-phonon transition wavelength of 1529 nm.

|       | **1a**        | **1a_des**     |
|-------|---------------|----------------|
|       | 6             | -              |                      |
|       | 5             | 732.41         | -346.65              | -623.85              |
|       | 6 -           | 249.20         | 431.47               | 65.11                |
|       | 5             | 167.56         | 16.77                | 123.27               |
|       | 6             | 193.08         | 10.26                | 225.20               |

Table S14. Ground multiplet energy level scheme (Kramers doublets in cm\(^{-1}\)) and main \(|M_f>\) contributions to the wave function calculated for **1b**. Red numbers in brackets: Main energy values estimated from the PL spectrum of **1b** at 77K, assuming a zero-phonon transition wavelength of 1524 nm.

|       | **1b**         |
|-------|----------------|
|       | 0              | 59.2% |±13/2> |
| 32    | (36)           | 33.4% |±11/2> + 29.7% |±15/2> + 12.3% |±1/2> + 10.4% |
| 89    |                | 16.9% |±5/2> + 16.4% |±3/2> + 13.1% |±3/2> + 11.6% |
| 127   |                | 22.5% |±15/2> + 19.7% |±0.50> + 17.4% |±3/2> + 13.4% |±1/2> |
7. Photoluminescence Measurements

Figure S21. Demonstration of reversible Er\textsuperscript{III}-centred NIR PL properties in hydration/dehydration cycles. #1(2): First(second) measurement in air (a), under vacuum (v) and N\textsubscript{2} atmosphere (n). (A) NIR PL spectra of phase 1a (in air) and 1a\_des (under vacuum and N\textsubscript{2}). (B) NIR PL decay transients. (C,D) Same as (A,B) but for 1b. All spectra and decay transient are normalized to their peak values for better clarity. Absolute PL intensities were reproduced within 5-10% after each cycle. At room temperature, all phases displayed the same integrated PL intensity within 10%. Cooling to 77K produced less than a factor of two increase in integrated PL intensity in both 1a\_des and 1b.
8. References

1. W. Gauß, H. Heitzer and S. Petersen, *Justus Liebig's Ann. Chem.*, 1973, **764**, 131–144.

2. J. J. Baldoví, S. Cardona-Serra, J. M. Clemente-Juan, E. Coronado, A. Gaita-Ariño and A. Palli, *J. Comput. Chem.*, 2013, **34**, 1961–1967.

3. J. J. Baldoví, J. J. Borrás-Almenar, J. M. Clemente-Juan, E. Coronado and A. Gaita-Ariño, *Dalt. Trans.*, 2012, **41**, 13705–13710.

4. G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Crystallogr.*, 2015, **71**, 3–8.

5. G. M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem.*, 2015, **71**, 3–8.

6. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.

7. M. Llunell, D. Casanova, J. Cirera, P. Alemany and S. Alvarez, *Univ. Barcelona Barcelona, Spain.*

8. F. M. A. Kerim, H. F. Aly and A. El-Agramy, *Proc. Indian Acad. Sci. - Sect. A*, 1977, **85**, 559–566.

9. M. K. Trivedi, R. M. Tallapragada, A. Branton, D. Trivedi, G. Nayak, R. K. Mishra and S. Jana, *J. Mol. Pharm. Org. Process Res.*, 2015, **03**, 1–6.

10. O. Roubeau, B. Agricole, R. Cle and S. Ravaine, *J. Phys. Chem. B*, 2004, **108**, 15110–15116.

11. Q. Deng, C. Tian, Z. Luo, Y. Zhou, B. Gou, H. Liu, Y. Ding and R. Yang, *Chem. Commun.*, 2020, **56**, 12234–12237.

12. C. Rudowicz, *J. Phys. C Solid State Phys.*, 1985, **18**, 3837.

13. C. Rudowicz and C. Y. Chung, *J. Phys. Condens. Matter*, 2004, **16**, 5825–5847.

14. I. D. Ryabov, *J. Magn. Reson.*, 1999, **140**, 141–145.

15. K. W. H. Stevens, *Proc. Phys. Soc. Sect. A*, 1952, **65**, 209–215.

16. S. Edvardsson and M. Klintenberg, *J. Alloys Compd.*, 1998, **275–277**, 230–233.