Supporting Information

Thermometer or Freezer: Dual Functionality in a 2D Mixed-Anion Terbium (III) Oxide Carbodiimide

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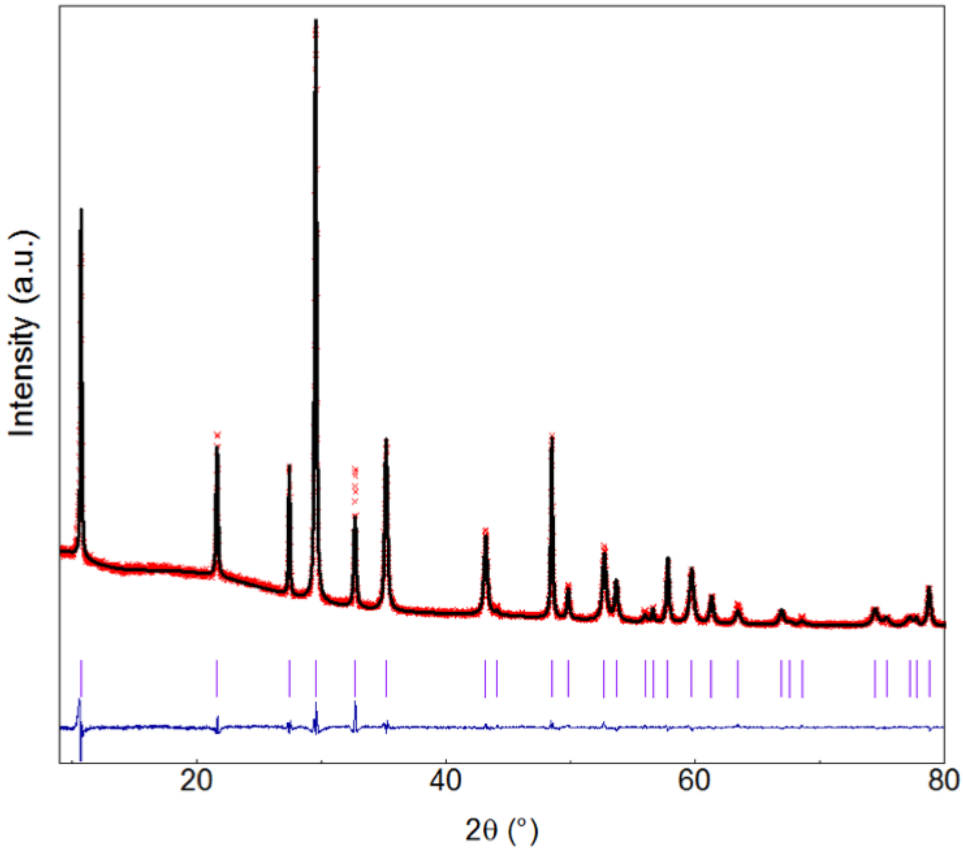

Figure S1. Rietveld fit of Tb_2O_2NCN to PXRD data, showing observed (red), calculated (black) and difference (blue) intensities. Bragg positions of Tb_2O_2NCN (violet) are denoted by vertical markers.

Table S1. Crystal data and structure refinement parameters of Tb_2O_2NCN

Empirical formula	Tb_2O_2NCN
Crystal system	Trigonal
Space Group	$P\bar{3}m1$, No. 164
Z	1
Unit cell dimensions	
a (Å)	3.7483(5)
c (Å)	8.1999(1)
V (Å^3)	99.7(7)

R_{wp} = 4.29 %, R_p = 2.75 %

Table S2. Fractional atomic coordinates for Tb_2O_2NCN. Standard deviations are given in parentheses.

atom		x	y	z	U_{iso} (10^2 Å^2)
Tb	2*d*	1/3	2/3	0.1814(1)	0.87(1)
C	1*b*	0	0	½	0.10(2)
O	2*d*	1/3	2/3	0.8833(1)	”
N	2*c*	0	0	0.3506(1)	”

Fitting parameters

Table S3. Fitting parameters of the ratiometric thermometry calibration using the Mott–Seitz model.

electronic transition	thermometric parameter (Δ)	Δ_0	α_1	$\Delta E_1/k_B$	α_2	$\Delta E_2/k_B$
$^5D_4 \rightarrow {}^7F_5$ and $^5D_4 \rightarrow {}^7F_4$	$I^{area}_{552\ nm} / I^{area}_{580\ nm}$	12.49	2.25	36.77	–	–
$^5D_4 \rightarrow {}^7F_4$	$I^{area}_{597\ nm} / I^{area}_{594\ nm}$	5.19	1.94	225.36	0.91	38.43
$^5D_4 \rightarrow {}^7F_5$ and $^5D_4 \rightarrow {}^7F_4$	$I_{552\ nm} / I_{580\ nm}$	15.14	6.28	75.76	0.62	1.48
$^5D_4 \rightarrow {}^7F_4$	$I_{597\ nm} / I_{594\ nm}$	6.10	5.84	77.94	0.71	1.72

Table S4. Fitting parameters (β_0 = intercept and β_1 = slope) of the linear ratiometric thermometry calibration.

thermometric parameter (Δ)	β_0	β_1	r^2
$I^{area}_{594\ nm} / I^{area}_{597\ nm}$	–108.4 ± 6.3	583.5 ± 21.0	0.99358
$I^{area}_{580\ nm} / I^{area}_{597\ nm}$	–169.3 ± 23.6	894.9 ± 67.8	0.9721
$I^{area}_{622\ nm} / I^{area}_{597\ nm}$	–38.3 ± 8.4	395.4 ± 11.4	0.99505

Table S5. Fitting parameters (β_0 = intercept and β_i = slopes) of the multivariate linear regression for the PCA-thermometry.

β_0	β_1	β_2	β_3	r^2
147.5 ± 3.9	–50.9 ± 2.6	92.4 ± 7.0	–7.02 ± 4.7	0.99544

Comments on the determination of performance parameters S_r and δT

For ratiometric thermometry, the thermometric parameter (Δ) used for calibration defined as $\Delta = I_2 / I_1$ has been fitted to the Mott–Seitz model according to:

$$\Delta_T = \frac{\Delta_0}{\left[1 + \alpha_1 \exp\left(-\frac{\Delta E_1}{k_B T}\right) + \alpha_2 \exp\left(-\frac{\Delta E_2}{k_B T}\right)\right]}$$

Thus, the relative thermal sensitivity (S_r) can be determined analytically according to:

$$S_r = \left|\frac{1}{\Delta_T}\left(\frac{\partial \Delta_T}{\partial T}\right)\right| = \frac{\alpha_1 \frac{\Delta E_1}{k_B T^2} \exp\left(-\frac{\Delta E_1}{k_B T}\right) + \alpha_2 \frac{\Delta E_2}{k_B T^2} \exp\left(-\frac{\Delta E_2}{k_B T}\right)}{\left[1 + \alpha_1 \exp\left(-\frac{\Delta E_1}{k_B T}\right) + \alpha_2 \exp\left(-\frac{\Delta E_2}{k_B T}\right)\right]}$$

The δT is calculated by:

$$\delta T = \frac{1}{S_r}\left(\frac{\delta \Delta}{\Delta}\right)$$

where $\delta\Delta$ is the uncertainty of Δ which can be estimated from Δ_{obs} and Δ_{calc} by the expression:

$$\delta\Delta = \sqrt{\frac{\sum(\Delta_{obs} - \Delta_{calc})^2}{(\sum \Delta_{obs})^2}}$$

This method can be applied for intensity- and area-based thermometry.

In the case of multivariable thermometry, the thermometric parameters are the principal components (*PC*) and the regression equation has been used as the basis for the calculations:

$$T = \beta_0 + \beta_1 PC_1 + \beta_2 PC_2 + \beta_3 PC_3$$

Then, the thermal sensitivity (S_r) has been calculated as follows:

$$S_r = \sqrt{\sum \left|\frac{1}{PC_i}\left(\frac{\partial PC_i}{\partial T}\right)\right|^2} = \sqrt{\sum \left|\frac{1}{PC_i}\left(\frac{1}{\beta_i}\right)\right|^2}$$

Since the values of the principal components can change from positive to negative, this can lead to values above 100% for S_r, so a different definition has been used for the calculation of an average value of the precision (δT) based on the number of observations (n) and the difference between the temperature according to the linear regression (T_{calc}) and the nominal temperature (T_{obs}). Thus, δT can be estimated as follows:

$$\delta T = \sqrt{\frac{1}{n(n-1)} \sum_{i=1}^{n} (T_{calc} - T_{obs})^2}$$

Applying this equation, we obtain the value of δT = 1.036 K.

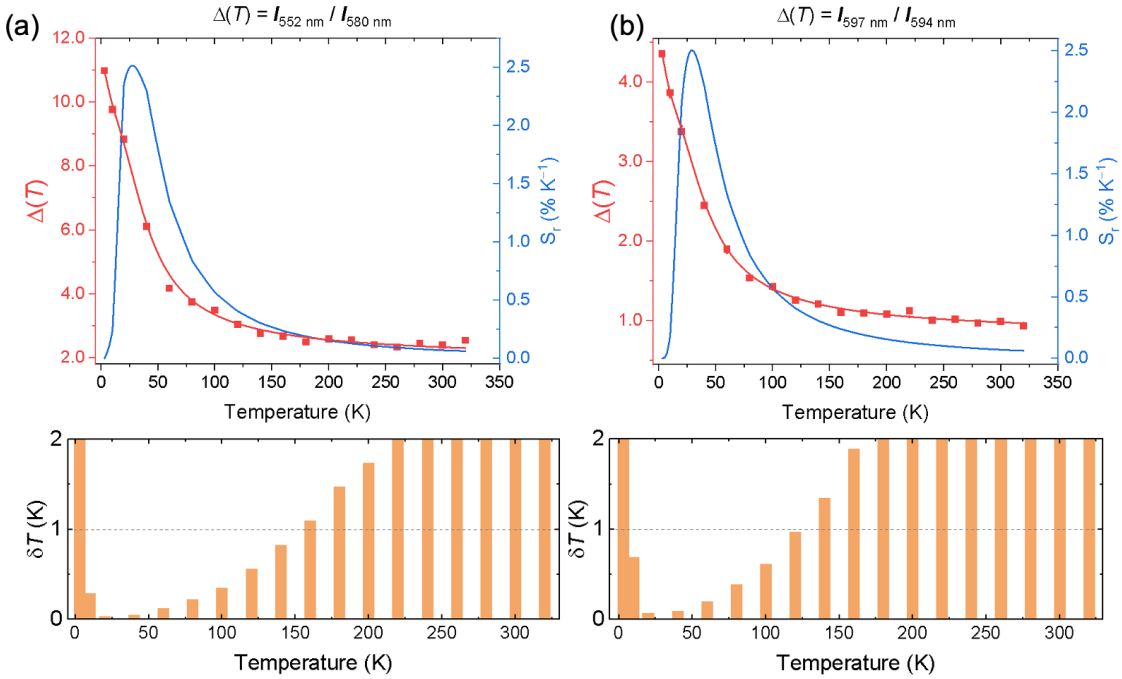

Figure S2. Top: Thermometric calibration curves $\Delta(T)$ involving the maximum of the emission for the peaks and their relative sensitivity dependence, $S_r(T)$. Red squares are the experimental data while solid curves are the best fit to the Mott–Seitz model. Bottom: temperature uncertainty curves $\delta T(T)$.

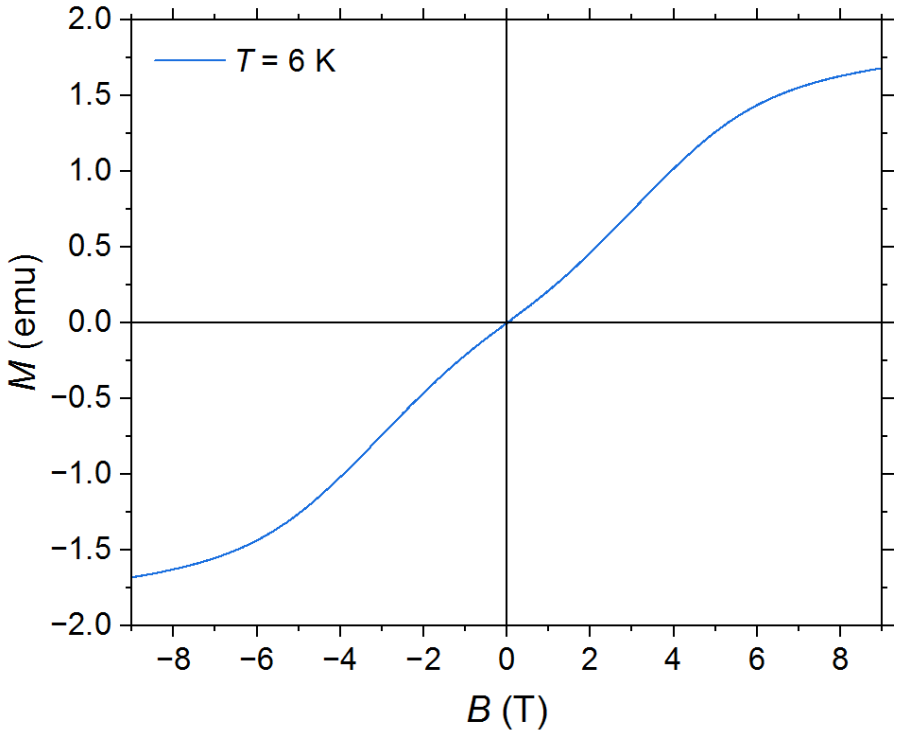

Figure S3. Magnetization hysteresis of Tb_2O_2NCN between –9 T and 9 T.

Comments on the determination of χ' and χ''

The generalized Debye model describes the frequency (ν) dependence of in-phase (χ') and out-of-phase (χ'') parts of the susceptibility as:

$$\chi'(\nu) = \chi_S + (\chi_T - \chi_S)\frac{1 + (2\pi\nu\tau_0)^{1-\alpha}\sin(\frac{\alpha\pi}{2})}{1 + 2(2\pi\nu\tau_0)^{1-\alpha}\sin\left(\frac{\alpha\pi}{2}\right) + (2\pi\nu\tau_0)^{2(1-\alpha)}}$$

$$\chi''(\nu) = (\chi_T - \chi_S)\frac{(2\pi\nu\tau_0)^{1-\alpha}\cos(\frac{\alpha\pi}{2})}{1 + 2(2\pi\nu\tau_0)^{1-\alpha}\sin\left(\frac{\alpha\pi}{2}\right) + (2\pi\nu\tau_0)^{2(1-\alpha)}}$$

Here, χ_T = is the isothermal susceptibility, χ_S = represents the adiabatic susceptibility, α = phenomenological parameter (0–1) and τ_0 is the average relaxation time.

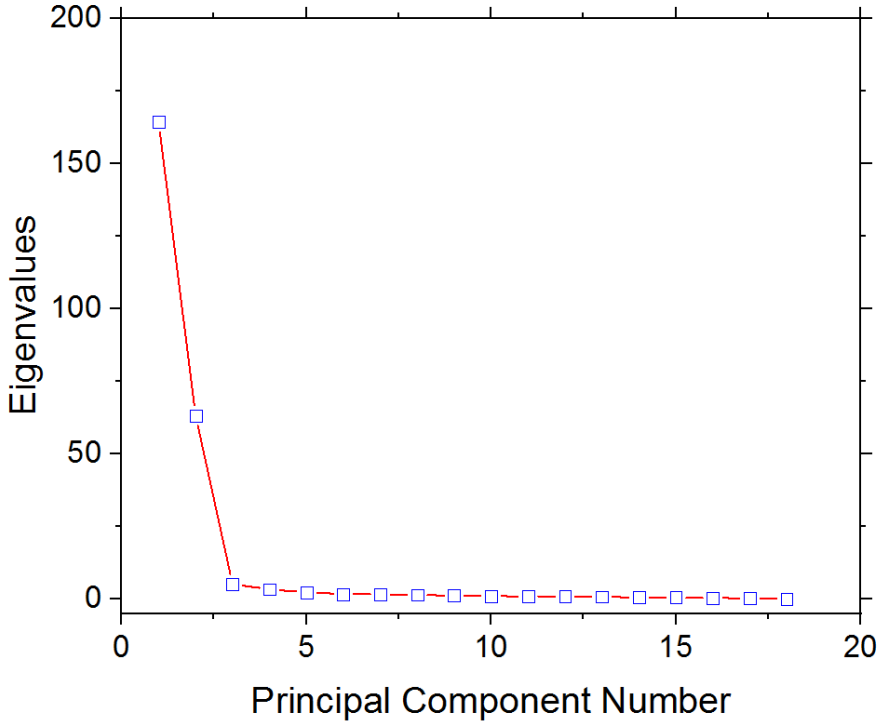

Figure S4. Scree plot showing the eigenvalues for the principal components.