Supplementary Information

Magnetic properties and magnetocaloric effect of Ln=Dy, Tb carborane-based metal-organic frameworks

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S1. Structural characterization: supplementary Figures

S2. Magnetization field-dependence modeling

S3. Corrected sum rules for lanthanide Ln^{3+}ions
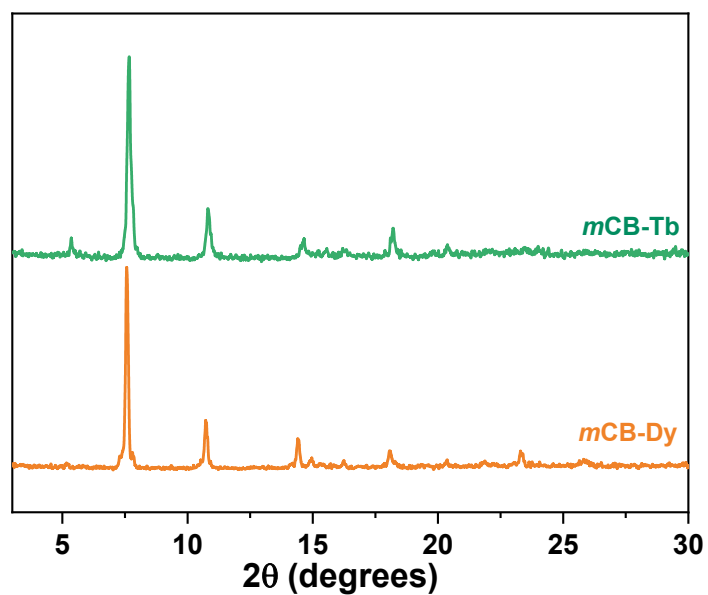
S1. Structural characterization: supplementary Figures

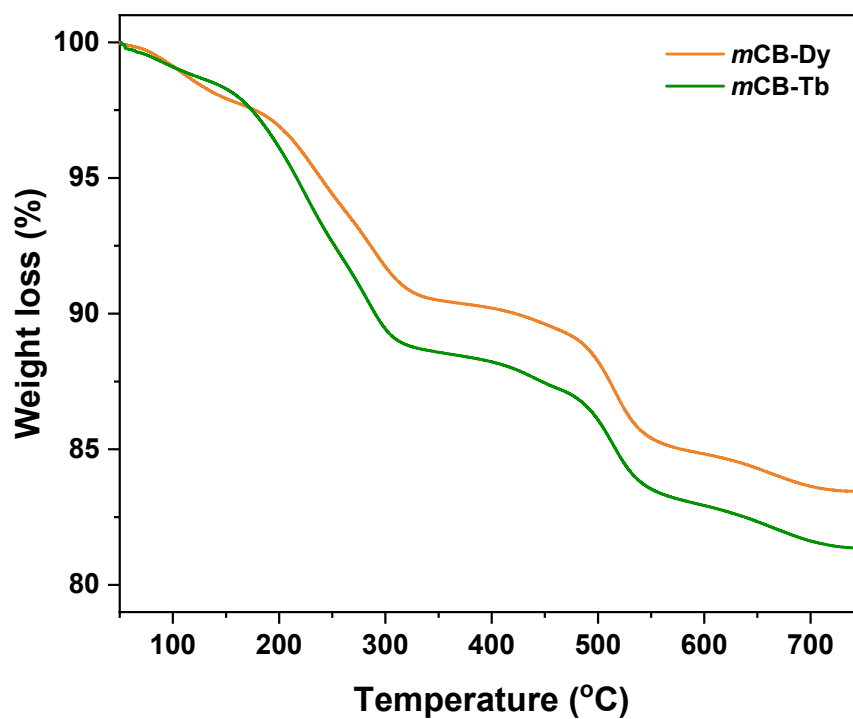**Figure S1.** PXRD patterns for individual *m*CB-Dy and *m*CB-Tb.

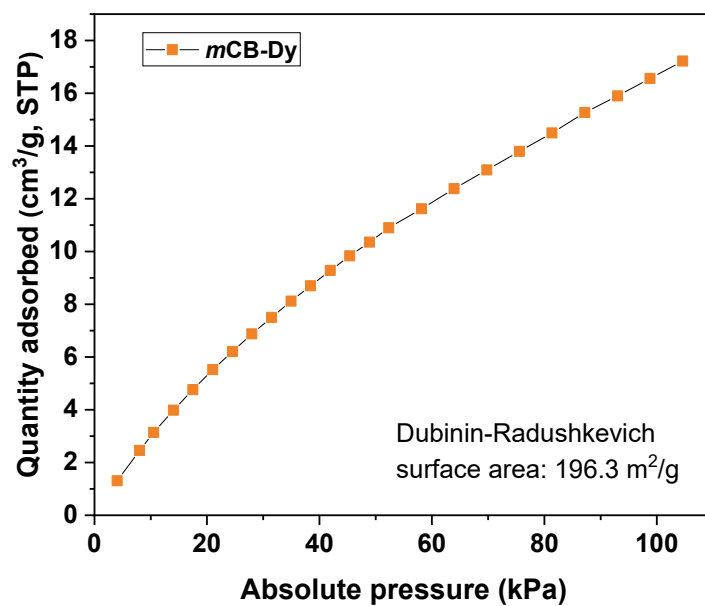

Figure S2. Comparison of the TGA for *m*CB-Dy and *m*CB-Tb.

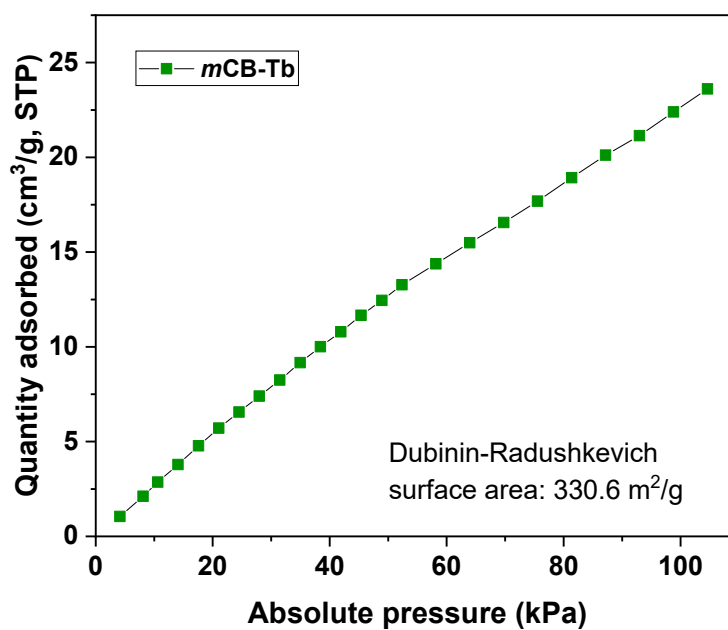**Figure S3.** CO_2 sorption isotherms for ***m*CB-Dy**.

Figure S4. CO_2 sorption isotherms for ***m*CB-Tb**.

S2. Magnetization field-dependence modeling

The magnetic properties of *m*CB-Dy and *m*CB-Tb at temperatures between 20 K-3.4 K could be modelled considering a single-ion Hamiltonian:

$$H_{si} = H_{CF} - \mu_B \vec{\hat{J}} \hat{g}_J \vec{H}$$

[1]

acting on the $|J, {}^{m_J}\rangle$ electronic states, assuming negligible Ln-Ln interactions. The first term accounts for the effect of the crystal field surrounding the Ln ion, and the second is the Zeeman splitting in the presence of a magnetic field $\vec{H}$, where $\hat{g}_J$ is the anisotropic *g*-tensor.

Dy(III) free-ion has a structure [Xe]4f^9, thus it is a Kramers ion with half-integer spin $S = 5/2$ and large orbital spin $L = 5$. The ground state $J = 15/2$ is split by the crystal field (CF) into 8 Kramers doublets (KDs). For Dy(III) with strong uniaxial anisotropy, the ground state doublet is often predominantly made of $|J, M_J\rangle = |15/2, \pm15/2\rangle$, and the first excited KD lies well above, at an energy Δ/k_B.

On the other hand, Tb(III) free-ion has a structure [Xe]4f^6, thus is a non-Kramers ion with integer spin $S = 3$ and orbital spin $L = 3$. The $J = 6$ ground-state contains 2J+1=13 degenerate $|J, M_J\rangle$ electronic states. The CF splits the $^7F_6$ ground state into 13 substates, $\{|\xi_i\rangle\}$, which can be described in terms of the electronic states as, $|\xi_i\rangle = \sum_{M=-J}^{J} C^i_{J,M_J} |J, M_J\rangle$. Typically, for strongly anisotropic Tb(III) the ground state $|\xi_0\rangle$, and the first excited state $|\xi_1\rangle$ are primarily composed of a combination of states, $|J, M_J\rangle = |6, \pm 6\rangle$, with possibly some minor admixture from other $|6, \pm M_J\rangle$ states. $|\xi_0\rangle$, and $|\xi_1\rangle$ are separated only by a very small energy gap, Δ'/k_B; thus, the ground state can be considered as a non-Kramers "quasi-doublet", well separated from the next levels of the multiplet. (For Tb(III), with a nuclear spin I=3/2, at very low T and under strong magnetic fields, one should also consider in the Hamiltonian the hyperfine and nuclear dipolar interaction contributions to the single-ion Hamiltonian, $H^*_n = A^* I S^*_z - \mu_N g_N I_z H_z$, where g_N=1.342 is the nuclear gyromagnetic factor).

Therefore, for both ions, at low temperatures of a few K, only the ground doublet is thermally occupied, and the system behavior can be approximately described by an "effective" Hamiltonian, acting on the wavefunctions $|S^* = 1/2, \pm S^*_z = 1/2\rangle$, which in the case of strong uniaxial anisotropy (Ising approximation, $g^*_z >> g^*_x, g^*_y$) reduces to:

$$H^*_{si} = H^*_z = -\mu_B S^*_z g^*_z H_z$$

[2]

The field-dependent magnetization curves $M(H)$ of *m*CB-Dy and *m*CB-Tb between 0 – 5 T at temperatures between 20 K-3.4 K could be fitted considering the effective S*=1/2 Hamiltonian in Eq. [2], with gyromagnetic factor g_z^*=18.5 (Dy), g_z^*=17.3 (Tb), $g_x^* = g_y^*$=0, with an additional small linear term in the field, $M_{VV} = \chi_{TIP} H$. This term accounts for positive temperature-independent paramagnetism (TIP), derived by Van Vleck as a second, perturbative correction to the Zeeman interaction, due to the mixing of ground doublet with excited doublets.[1] It is noted that although the SBU of these MOFs consists of three Ln with slightly different coordination environments, a similar "average" gyromagnetic value was considered for the three, to avoid overparametrization.

To fit the $M(H)$ curve at the lowest temperature, T=1.8 K, interactions had to be included. Given the structure of these MOFs (Fig. 1a), intra-chain interactions are plausibly dominant;

they were modeled using a simple dimer Hamiltonian, $H^*_{int,z} = -2\sum_{1,2} J^*_z S^*_{1,z} S^*_{2,z}$, yielding a small, ferromagnetic anisotropic coupling constant, $J^*_z/k_B = +0.45$ K (+0.50 K), for **mCB-Dy** (**mCB-Tb**) respectively.

S3. Corrected sum rules for lanthanide Ln^{3+} ions

The orbital moment (m_L), spin moment (m_s) and total magnetic moment ($m_{TOT} = m_L + m_s$) for Dy^{3+} and Tb^{3+} in, respectively, **mCB-Dy** and **mCB-Tb** were determined from the XAS and XMCD spectra measured at the $M_{4,5}$ edge of each ion, using the corrected sum rules for lanthanides, following the procedure described by S. Tripahi[2] as follows:

1. The uncorrected sum rules developed by Thole and Carra[3,4] are first applied to obtain the experimental expectation values of the orbital operator projection along the z (photon beam) direction, $\langle L_{z,exp} \rangle$, and effective spin operator projection along the z –direction $\langle S^{eff}_{z,exp} \rangle$:

$$\langle L_{z,\text{exp}} \rangle = -\frac{q}{r} n_h,$$

$$\langle S^{eff}_{z,\text{exp}} \rangle = -\frac{(5p-3q)}{4r} n_h = \langle S_z \rangle + 3 \langle T_z \rangle,$$

   where n_h is the number of holes, p is the integral of the XMCD spectrum across the M_5 edge, q is the integral of the XMCD spectrum across $M_4 + M_5$ edges, and r is the integral of the (background subtracted) XAS spectrum. The effective spin $\langle S^{eff}_{z,exp} \rangle$ relates the expectation value of the spin $\langle S_z \rangle$ and the magnetic dipolar term $\langle T_z \rangle$.

2. To correct for the effect of the $3d_{5/2} - 3d_{3/2}$ mixing, which can be strong for Ln^{3+} ions, the experimental effective spin must be divided by a correcting factor X_I/X_E (Table S1):

$$\langle S^{eff,corrMix}_{z,\text{exp}} \rangle = \frac{\langle S^{eff}_{z,\text{exp}} \rangle}{(X_I / X_E)}.$$

3. To obtain the corrected spin operator projection along the z–direction $\langle S^{corr}_z \rangle$, the experimental value of the magnetic dipole term should be known. However, $\langle T_z \rangle$ can be only estimated via theoretical calculations, which provide the expectation value when the magnetic moment is in saturation condition. A way to circumvent the problem is to calculate the *Reduction* that should be applied to the theoretical value, $\langle T_{z,Takeo} \rangle$, calculated in Ref. [5] (Table S1):

$$\text{Reduction} = \frac{\langle S^{eff}_{z,LFM} \rangle}{\langle S^{eff}_{z,\text{exp}} \rangle},$$

   this is, the ratio between the effective spin moment calculated from sum rules applied to ligand field multiplet (LFM)-simulated spectra, $\langle S^{eff}_{z,LFM} \rangle$, and the experimental effective spin, $\langle S^{eff}_{z,exp} \rangle$. Thus, the corrected spin operator is determined as:

$$\left\langle S_z^{corr} \right\rangle = \left\langle S_{z,\text{exp}}^{eff,corrMix} \right\rangle - \frac{3\left\langle T_{z,Takeo} \right\rangle}{\text{Reduction}} .$$

4. Finally, we calculate the spin moment $m_s = 2\left\langle S_z^{corr} \right\rangle$, the orbital moment $m_L = \left\langle L_{z,exp} \right\rangle$, and the total magnetic moment $m_{\text{TOT}} = m_{\text{L}} + m_{\text{s}}$.

Table S1. Correction factor (X_I/X_E), effective spin moment calculated from sum rules applied to LMF-simulated spectra, $\left\langle S_{z,LFM}^{eff} \right\rangle$, and theoretical dipolar term magnetic dipole, $\left\langle T_{z,Takeo} \right\rangle$, required for the application of the corrected sum rules for Ln^{3+}ions ions contained in ***m*CB-Dy** and ***m*CB-Tb.**

Ln ion	Number of holes (n_{h})	Correction factor X_I/X_E	$\left\langle S_{z,LFM}^{eff} \right\rangle$	$\left\langle T_{z,Takeo} \right\rangle$
Dy^{3+}	5	0.923	-1.877	0.139
Tb^{3+}	6	0.871	-1.928	0.253

References
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