Designing Geometric Degrees of Freedom in ReO$_3$-Type Coordination Polymers

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ABSTRACT

Engineering the interplay of structural degrees of freedom that couple to external stimuli such as temperature and pressure is a powerful approach for material design. New structural degrees of freedom expand the potential of the concept, and coordination polymers as a chemically versatile material platform offer fascinating possibilities to address this challenge. Here we introduce a new class of hierarchically organized, perovskite-like AB$_2$X$_6$ coordination polymers based on a [BX$_3$]$^-$ ReO$_3$-type host network ([Mn(C$_2$N$_3$)$_3$]$^-$), in which the spatial orientation of divalent A$_2^+$ cations with separated charge centers that bridge adjacent ReO$_3$-cavities ([R$_3$N(CH$_2$)$_n$NR$_3$]$^{2+}$) is introduced as a new geometric degree of freedom. Herringbone and head-to-tail order pattern of [R$_3$N(CH$_2$)$_n$NR$_3$]$^{2+}$ cations are obtained by varying the separator length $n$ and, together with distortions of the pseudocubic [BX$_3$]$^-$ network, they determine the materials’ stimuli-responsive behavior such as counterintuitive large negative compressibility and uniaxial negative thermal expansion. This new family of coordination polymers highlights the chemists’ capabilities of designing matter on a molecular level to address macroscopic material functionality and underpins the opportunities of the design of structural degrees of freedom as a conceptual framework for rational material synthesis in the future.

Introduction

Dense and porous coordination polymers are a chemically versatile material platform and harbour a wealth of fascinating properties of academic and technological relevance. Recent examples are their application in next-generation water harvesting$^1$ and cooling technologies$^2$, the observation of counterintuitive material responses such as negative gas adsorption$^3$ and colossal negative linear compressibility$^4$, electric-field dependent gas separation properties$^5$ and enzyme-type molecular recognition$^6$ amongst many more. These examples illustrate the importance of fundamental research related to the materials’ stimuli-responsive behavior. It involves the study of material responsiveness for a knowledge-based improvement of existing material functionality, and provides the scientific basis for new material functions and potential next-generation technologies in the future.

In the pursuit to translate between synthetic chemistry and the underlying material’s free energy surface which defines material responsiveness$^7,8$, the decomposition of a material’s structure in terms of available structural and electronic degrees of freedom has proved powerful.$^9$ In coordination polymers, the available structural degrees of freedom, i.e. structural distortions that couple to external stimuli such as temperature and pressure, play the most prominent role due to relatively low densities and, when carefully engineered, can introduce new stimuli-responsive properties such as electric polarization that couples to
an electric field. In coordination polymers, the simple use of molecular scaffolds introduces new unconventional structural degrees of freedom compared to solid-state inorganics. Examples are orientational degrees of freedom related to order-disorder phase transitions in the barocaloric [(C₆H₇)₂N]Mn(C₂N₆)₂ and photovoltaic absorber \([\text{CH}_3\text{NH}_3]\text{PbI}_3\), large translational network deformations in the flexible metal-organic frameworks (MOFs) CUK-1 and DMOF-1 derivatives with potential in mechanical energy storage processes, and rotational molecular motions in amphidynamic MOFs as a basis for coordination polymer-based molecular machines. The concept conceptualizes current and past research progress related to stimuli-responsive properties in coordination polymers, and in looking forward, engineering the interplay of several structural degrees of freedom shows large promise in the design of materials with targeted and potentially new stimuli-responsive properties. Therefore, the search for new structural degrees of freedom and their synthetic integration to systematically direct material behavior is an active field of research, either explicitly or implicitly. The introduction of foldable nets, MOFs with frustrated metal-nodes and linker molecules with various internal conformations, geometry mismatch as a concept, the categorization of unconventional tilts and shifts in molecular perovskites, and the search for aperiodic MOFs are a few important examples in this context.

A subclass of coordination polymers that shows a number of unconventional structural degrees of freedom are ABX₄ molecular perovskites such as [(NH₂)₂CH]Mn(H₂PO₄)₂, [(C₆H₇)₂N]Mn(C₂N₆)₂, and [(CH₃)₂NH₂]Zn(HCO₂)₃. Their structures are based on the well-known perovskite motif where the molecular A-site cation sits in the void of a three dimensional [BX₃]⁻ ReO₃-like network. Compared to inorganic perovskites, the use of molecular A- and/or X-site ions introduces unconventional octahedral tilts and shifts, molecular order-disorder phase transitions as a function of temperature, and polymorphism based on conformational isomerism of the B-X connectivity, see Figure 1. Initially unconventional degrees of freedom in molecular perovskites were in the center of fundamental research, but recent developments in the area of barocalorics, multiferroics and improper ferroelectrics highlight their role in materials chemistry. When looking for synthetic strategies to integrate new structural degrees of freedom in molecular perovskites, it is important to emphasize that all current structural degrees of freedom originate from the use of molecular building units per sé rather than elaborate synthetic approaches.

Here we apply a crystal structure engineering strategy introducing novel geometric degrees of freedom in a ReO₃-type host network. The synthesis of hierarchically organized AB₂X₆ coordination polymers is reported, in which molecular A²⁺ cations with separated positive charges bridge two adjacent cavities of the host network, extending the structural chemistry of ReO₃-type networks with an additional geometric structural motif. The resulting AB₂X₆-materials are conceptually related to ABX₃ molecular perovskites which guides interpretation of their crystal chemistry. The A²⁺ cations’ order pattern depend on their chemical nature and act as property-directing factor, determining the materials’ mechanical properties such as thermal expansion behavior and compressibility.

Results and Discussion

Crystal Structure Engineering Methodology. In the pursuit to introduce new geometric degrees of freedom in a ReO₃-type network, the material [H₂dabco]Mn₂(H₂PO₄)₆ (\([\text{H}_2\text{dabco}]^{2+} = 1,4\text{-diazabicyclo}[2.2.2]\text{octane-1,4-diium}\)) is an important starting point. The use of the divalent cation [H₂dabco]²⁺ leads to a material in which half of the voids within the 3D ReO₃-type \([\text{Mn(H}_2\text{PO}_4)_2]^-\) cages are occupied, i.e. a perovskite-type structure with ordered A-site vacancies, see Figure 1d. Inspired by this example, the use of a divalent A-site cation with separated charge centers, suitable to bridge two pseudocubic [BX₃]⁻ cages, can be envisaged, which introduces an additional geometric degree of freedom related to the spatial
distribution of divalent A-site cations within the 3D [BX₃]⁻ host network.

The challenge in synthesizing an AB₂X₆ coordination polymer where the divalent A-site cation bridges two [BX₃]⁻ type cages is the identification of a suitable A-B-X permutation. We use [C₂N₃]⁻ as X-site anion and Mn²⁺ as B-site divalent metal, a combination that has proved robust for the synthesis of various molecular perovskites with comparably large A-site cations such as [(C₃H₇)₄N]Mn(C₂N₃)₂₁⁻, [(C₇H₁₇)(C₄H₉)₃N]Mn(C₂N₃)₃¹⁻ and [(C₃H₇)(CH₃)N]Mn(C₂N₃)₃²⁸⁻. On the A-site, a divalent cation must be chosen which exhibits two spatially separated positive charges that can bridge two ReO₃-type [Mn(C₂N₃)₃]⁻ cages. A divalent A-site cation fulfilling these requirements is the cation [R₃N(CH₂)ₙNR₃]²⁺, where n determines the charge separation distance, and R and R’ provide chemical control over the bulkiness of the cation through alkyl chain length. For the size of R and R’, a n-propyl group (R = -C₃H₇) seems suitable, resembling the situation in [(C₃H₇)₄N]Mn(C₂N₃)₃. Looking at the parameter n, a good separation between the charge centers is expected for n > 2. Therefore, [(C₃H₇)₃N(CH₂)₄N(C₃H₇)₃]²⁺ (= TPC₄TP²⁺) and [(C₃H₇)₃N(CH₂)₅N(C₃H₇)₃]²⁺ (= TPC₅TP²⁺) are promising divalent A-site cations. TPC₄TP²⁺ and TPC₅TP²⁺ were synthesized by standard nucleophilic substitution strategies, see Supporting Information Figure-S1. Subsequently, the synthesis of the coordination polymers [TPC₄TP]Mn₂(C₂N₃)₆ and [TPC₅TP]Mn₂(C₂N₃)₆ was performed by following an established slow crystallization procedure. For instance, in a typical reaction the precursors [TPC₄TP]Br₂, Mn(NO₃)₂·4H₂O and Na(C₂N₃) are mixed in
a water/ethanol mixture. After several days, the formation of single crystals can be observed, see Figure S-2 and Supporting Information for details.

**Structure and Pattern Analysis.** Single crystal and powder X-ray diffraction at 100 K were used for structure solution, see Table S-2, S-5 and Figure S-11, S-16 for details of data collection and full crystallographic data. Both compounds crystallize in the monoclinic crystal system and [TPC4TP]Mn₂(C₂N₃)₆ in a non-centrosymmetric space-group which was confirmed by second harmonic generation, see Supporting Information Figure S-34 for experimental details. Both materials adopt a three dimensional ReO₃-type \([\text{Mn}(\text{C}_2\text{N}_3)_3]^-\) coordination network where all Mn²⁺ atoms are octahedrally coordinated by N atoms and linked to its neighbouring Mn²⁺ atoms via six \(\mu-1,5-\text{[C}_2\text{N}_3^-\) bridges. The A-site cations TPC4TP²⁺ and TPC5TP²⁺ are incorporated into the 3D network for charge balance, with one positive charge sitting in each void of a ReO₃-type cage. Therefore, TPC4TP²⁺ and TPC5TP²⁺ bridge adjacent pseudocubic ReO₃-type cages, see Figure 2a and 2c. Similar to molecular perovskites, active rigid unit modes in the ReO₃ network are possible and a distortion mode analysis of the 3D \([\text{Mn}(\text{C}_2\text{N}_3)_3]^-\) network reveals the presence of primary order parameters distinctive for dicyanamide-based molecular perovskites. These include conventional and unconventional tilts and columnar shifts for both materials, including distortions with an uncommon distortion vector of \(\mathbf{k} = \left[\frac{1}{4}, \frac{1}{4}, \frac{1}{2}\right]\) for [TPC4TP]Mn₂(C₂N₃)₆²⁵, see Supporting Information for full details of the mode analysis.

![Crystal structures and A²⁺ cation order pattern in AB₂X₆ materials.](image)

An intuitive description of both compounds starts from an ABX₃ molecular perovskite where \(-(\text{CH}_2)_{n^-}\) is used to link two adjacent A-site cations. The introduction of such a \(-(\text{CH}_2)_{n^-}\) link as a spacer introduces the spatial orientation of the A²⁺ within the \([\text{Mn}(\text{C}_2\text{N}_3)_3]^-\) network as a new structural degree of freedom which is geometric in nature. For [TPC4TP]Mn₂(C₂N₃)₆ and [TPC5TP]Mn₂(C₂N₃)₆ both A²⁺ cations exhibit 2D order patterns within the 3D ReO₃-type network, i.e. they bridge \([\text{Mn}(\text{C}_2\text{N}_3)_3]^-\) cages in two dimensions but not in the third. In [TPC4TP]Mn₂(C₂N₃)₆ a herringbone-type order of TPC4TP²⁺ is observed with an AB stacking of individual 2D layers, where B is shifted one pseudocubic unit along one dimension of the 2D layer. For TPC5TP²⁺ in [TPC5TP]Mn₂(C₂N₃)₆ an order pattern is found that
which is the space diagonal of a 2x2x2 \[M(C\alpha A\alpha A)\].

Thermal Expansion Behavior and Compressibility. By drawing comparisons to materials with a herringbone motif and topologically related motifs such as \(\text{Ag}_2[\text{Co(CN)}_6]^{32}\), \(\text{KMn}[\text{Ag(CN)}_2]_3^{33}\), \(\text{[Zn(\text{fudbc})_2\text{dabc}]^{34}}\), \(\text{[Fe(dpdp)}_2(\text{NCS})_2\text{]}^{35}\text{py}\), \(\text{InH(\text{bdcc})}^{36}\) and \(\text{MeOH}_2\text{H}_{2}\text{O}\)^{37}, uniaxial negative thermal expansion (NTE) and negative linear compressibility (NLC) based on molecular hinging and rhombic network deformations can be anticipated. Variable temperature powder X-ray diffraction \((T=100-400\ \text{K})\) and high-pressure powder X-ray diffraction \((p=\text{ambient-0.4 GPa})\) were performed to obtain thermal expansion coefficients \((\alpha)\) and compressibilities \((\chi)\) for both materials, see Supporting Information Figure-22 to S-30 for details. For comparison reasons, lattice parameters were transformed into principal axes \(X_1\), \(X_2\) and \(X_3\), see Table 1 and Supporting Information Table-S8, S-10, S-13 and S-15. \(\alpha\) and \(\chi\) of both materials are in a similar magnitude with \([\text{TPC4TP}]\text{Mn}_{2}(C_2N_3)\_6\) showing a slightly larger responsiveness towards temperature and pressure changes compared to \([\text{TPC5TP}]\text{Mn}_{2}(C_2N_3)\_6\). This is ascribed to the lower packing density which agrees with the trend in bulk moduli, \(B_0=6.26\pm0.38\ \text{GPa}\) for \([\text{TPC4TP}]\text{Mn}_{2}(C_2N_3)\_6\) compared to \([\text{TPC5TP}]\text{Mn}_{2}(C_2N_3)\_6\) with \(B_0=8.83\pm0.35\ \text{GPa}\), see Supporting Information Table S-16 for details.

Looking at \([\text{TPC4TP}]\text{Mn}_{2}(C_2N_3)\_6\), large uniaxial NTE and NLC behavior is observed along \(X_1\) with \(\alpha_{X_1}=-71.63\pm2.65\ \text{MK}^{-1}\) and \(\chi_{X_1}=-11.73\pm1.13\ \text{TPa}^{-1}\). \(X_1\) points along [304] in the unit cell which is the space diagonal of a 2x2x2 \([\text{M}(C_2N_3)]\) unit and the direction in which counter-intuitive material response based on a 3D hinging of A-site cations is expected, see Figure 3e and Supporting Information Figure S-14 for a mechanistic illustration. For \(X_2\) and \(X_3\) uniaxial expansion and linear compressibility is observed, overall compensating for total framework deformation. This observation suggests that A-site hinging combined with a rhombic network distortion is suitable to rationalize uniaxial NTE and NLC behavior of \([\text{TPC4TP}]\text{Mn}_{2}(C_2N_3)\_6\). To further support this interpretation, temperature-dependent single crystal X-ray diffraction for \([\text{TPC4TP}]\text{Mn}_{2}(C_2N_3)\_6\) at 100 K, 205 K and 310 K was performed, see Supporting Information Table S-3. An increasing dihedral angle for two A-site cations \((\angle_{100K}=81.71(7)\ ^\circ\ \text{to}\ \angle_{310K}=83.8(3)\ ^\circ)\) and decreasing Mn-Mn distance along [304] are observed which
Figure 3. Temperature and pressure dependent structural behavior of AB$_2$X$_6$ coordination polymers. Shown are the evolution of principal axes as a function of temperature and pressure. For A = TPC4TP$^{2+}$, uniaxial NTE and NLC along X$_1$ is observed, whilst for A = TPC5TP$^{2+}$ uniaxial NTE and positive compressibilities with a slightly different set of principal axes are found. For temperature-dependent data, filled and open symbols represent heating and cooling, respectively. Panels (e) and (f) show a 2x2x2 perovskite-type unit with particular directions of propagation. Colorcode: green/dark blue: A-cation N, pink: Mn. Note that the black lines are only a guide to the eye to indicate the perovskite-type connectivity and do not represent real chemical bonds.

corroborates the interpretation of thermal and pressure responsiveness of [TPC4TP]Mn$_2$(C$_2$N$_3$)$_6$ based on a hinging mechanism. Importantly, it is the synergistic interplay of the A$^{2+}$ cations’ herringbone order pattern and the constraining [BX$_3$]$^-$ network that causes NTE and NLC based on a herringbone-based hinging mechanism in these framework materials. A herringbone motif alone is only an insufficient criteria as it was recently shown for the molecular crystals Cu(acac)$_2$ (acac$^2-$ = acetylacetonato)$^{38}$ and the series of linear acenes.$^{39}$ Comparing the sizes of $\alpha_X$ and $\chi_X$ of [TPC4TP]Mn$_2$(C$_2$N$_3$)$_6$ with other molecular perovskites and coordination polymers (Table 1), the observed NLC coefficients and uniaxial NTE coefficients are large and to our knowledge [TPC4TP]Mn$_2$(C$_2$N$_3$)$_6$ is the first ReO$_3$-type coordination polymer with a large NLC coefficient of the ambient phase.

In contrast, for [TPC5TP]Mn$_2$(C$_2$N$_3$)$_6$ we only find moderate uniaxial NTE along X$_1$ with $\alpha_X = -26.33 \pm 1.91$ MK$^{-1}$ which is the space-diagonal of one pseudocubic [Mn(C$_2$N$_3$)$_3$]$^-$ cage and close to zero linear compressibility along the long diagonal of a [Mn(C$_2$N$_3$)$_3$]$^-$ cage, $\chi_X = 6.64 \pm 2.01$ TPa$^{-1}$. Note, that the slightly different responsive behavior of [TPC5TP]Mn$_2$(C$_2$N$_3$)$_6$ towards temperature and pressure variation results in different directions of principal axes for [TPC5TP]Mn$_2$(C$_2$N$_3$)$_6$; however, this observation together with the principal axes’ directions, which involve only one pseudocubic [Mn(C$_2$N$_3$)$_3$]$^-$ cell, already points at a different underlying mechanism when compared to [TPC4TP]Mn$_2$(C$_2$N$_3$)$_6$. Uniaxial
NTE propagates perpendicular to the skewed head-to-tail arranged A-cations and might be based on a lamellar-type movement of the A-site molecules and a related rhombic distortion of the network. The absence of NLC behavior as a formally reversed structural distortion of uniaxial NTE is less clear; however, the different responses towards temperature and pressure changes illustrate that a clear mechanism that provides a well-defined minimum energy structural distortion is not provided by a head-to-tail arrangement of A-site cations when compared with a herringbone arrangement.

**Table 1.** Linear thermal expansion coefficients (MK$^{-1}$) and compressibilities (TPa$^{-1}$) of selected molecular framework materials in the ambient phase. Additionally, the calculated bulk moduli (GPa) are reported. Abbrev. dpp = dipyrido[3,2-$a$:2',3'-c]phenazine, py = pyridine, L$^1$ = 2,5-bis(2-methoxyethoxy)benzene-1,4-dicarboxylate, np = narrow pore. *recalculated from reported heating/compression lattice parameters using the software PASCar.$^{40}$

<table>
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<th>Material</th>
<th>$\alpha_{X1}$</th>
<th>$\alpha_{X2}$</th>
<th>$\alpha_{X3}$</th>
<th>$Z_{X1}$</th>
<th>$Z_{X2}$</th>
<th>$Z_{X3}$</th>
<th>$B_0$</th>
<th>Ref.</th>
</tr>
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<tr>
<td>[TPC4TP]Mn$_2$(C$_2$N$_3$)$_6$</td>
<td>−72(3)</td>
<td>113(7)</td>
<td>131(3)</td>
<td>−12(1)</td>
<td>58(2)</td>
<td>69(3)</td>
<td>6.3(5)</td>
<td>this work</td>
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<tr>
<td>[TPC5TP]Mn$_2$(C$_2$N$_3$)$_6$</td>
<td>−26(3)</td>
<td>70(3)</td>
<td>87(1)</td>
<td>7(2)</td>
<td>35(1)</td>
<td>53(1)</td>
<td>8.9(5)</td>
<td>this work</td>
</tr>
<tr>
<td>Ag$_3$(Co(CN)$_6$)</td>
<td>−126(1)*</td>
<td>138(1)*</td>
<td>138(1)*</td>
<td>−76(9)</td>
<td>115(8)</td>
<td>115(8)</td>
<td>6.5(3)</td>
<td>32, 41</td>
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<tr>
<td>KMn[Ag(CN)$_2$]$_3$</td>
<td>61(2)</td>
<td>61(2)</td>
<td>−60(3)</td>
<td>−12(1)</td>
<td>33(1)</td>
<td>33(1)</td>
<td>12.7(11)</td>
<td>33</td>
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<td>[Zn$_2$(fu-L$^1$)$_2$dabco] (np)</td>
<td>−94</td>
<td>373</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>34</td>
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<tr>
<td>[Fe(dpp)$_2$(NCS)$_2$]py</td>
<td>−85(1)*</td>
<td>20(1)*</td>
<td>231(1)*</td>
<td>−10(2)</td>
<td>12(3)</td>
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<td>12.9(6)</td>
<td>42, 43</td>
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<td>InH(bdc)$_2$</td>
<td>64(3)</td>
<td>64(3)</td>
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<td>102</td>
<td>−62</td>
<td>6.8</td>
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<td>MeOH·H$_2$O</td>
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<td>85(5)</td>
<td>230(19)</td>
<td>−3(2)</td>
<td>32(1)</td>
<td>108(1)</td>
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<td>[(C$_3$H$_2$)$_3$N]Mn(C$_2$N$_3$)$_3$</td>
<td>54(2)</td>
<td>54(2)</td>
<td>8(1)</td>
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<td></td>
<td></td>
<td></td>
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<td>[C(NH$_3$)$_3$]Cd(HCOO)$_3$</td>
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<td>−17(1)</td>
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<td>3(1)</td>
<td>3(1)</td>
<td>21(1)</td>
<td>25.7(17)</td>
<td>46, 47</td>
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</table>

**Conclusion**

In conclusion, we introduce a new family of AB$_2$X$_6$ coordination polymers based on a ReO$_3$-type network. The synthesis of two representatives is reported in which the divalent A-site cation bridges two pseudocubic [BX$_3$]$^-$ cages. This introduces the spatial orientation of divalent A$^{2+}$ cations as a geometric degree of freedom, while maintaining all structural degrees of freedom as known from molecular perovskites such as (unconventional) octahedral tilts and shifts, and a variable A-site cation chemistry. The type of A$^{2+}$ cation order pattern and its interplay with distortion modes of the three-dimensional network are suitable to rationalize the mechanical properties of the materials. For [TPC4TP]Mn$_2$(C$_2$N$_3$)$_6$, the herringbone motif couples with structural distortions of the three-dimensional network, providing a clear low-energy pathway for structural distortions as a function of temperature and pressure variation. In going forward, the chemical variability of divalent [R$'_3$N(CH$_2$)$_m$NR$_3$]$^{2+}$ cations is promising to impart new, yet unknown A$^{2+}$ order pattern and therewith coupling schemes that determine the stimuli-responsive material properties. In particular, the use of non-symmetric cations based on different R$'$ and R functionalities is intriguing, where the use of R = −H and R$'$ = −(C$_3$H$_7$) seems promising. Such an A-site cation incorporates one A-site end that is formally too small for forming a perovskite motif, which might introduce packing frustration coupled to extreme or counter-intuitive stimuli-responsive properties.

The herein presented materials are conceptually related to the work by S. Telfer$^{48}$, where geometric degrees of freedom were introduced by controlled interpenetration of MUF-9. This and many other examples highlight that decomposing a coordination networks’ structure into structural degrees of freedom is a material class overarching conceptualization to engineer stimuli-responsive material behavior. As a concept, it represents a natural development of rigid-body guidelines such as the reticular chemistry.
approach\textsuperscript{49} and the Goldschmidt Tolerance Factor approach for (molecular) perovskites\textsuperscript{50} to control responsive properties through crystal structure engineering. Importantly, when considering photoactive linker molecules or catalytically active structural entities in MOFs as chemical degrees of freedom, the combination of structural with chemical degrees of freedom seems intriguing to rationally synthesize multifunctional materials with potentially new properties. Research examples exist that can be rationalized within this framework such as switchable catalysts based on flexible MOFs\textsuperscript{51}, energy transfer processes in photoactive MOFs\textsuperscript{52}, and the geometric arrangement of redox-active linker molecules in electrically conductive MOFs\textsuperscript{53} amongst other examples. To advance this concept to a practically useful guideline, the identification of new structural degrees of freedom and to learn about their impact on stimuli-responsive properties is key, to which this work provides an important step.

**Methods**

All experimental and analytical data including a detailed description of synthesis procedures for the precursor compounds as well as details on structure determination can be found in the Supporting Information. This also includes experimental set-up for data collection at the synchrotron facilities Diamond Light Source Ltd., UK and DESY, Germany. The reported crystal structures are available through the Cambridge Crystallographic Database (CCDC) listed with the respective entry numbers as can be found in the Supporting Information.

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**Author contributions statement**

S.B. and G.K. designed the study, analyzed experimental outcomes and wrote the manuscript. K.H., P.V. and D.D. assisted in synchrotron data collection and interpretation of results. J.K.Z conducted the SHG measurements and D.M. assisted with single crystal diffraction. In addition to continuous scientific exchange, all authors contributed to proof-reading and revisions of the manuscript.

**References**


