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## Spin-reorientation-induced magnetodielectric coupling effects in two layered perovskite magnets

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Spin-reorientation-induced magnetodielectric coupling effects were disclosed in two layered perovskite magnets, [C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>3</sub>]<sub>2</sub>[MCl<sub>4</sub>] (M = Mn<sup>2+</sup>, Cu<sup>2+</sup>), by isothermally magnetodielectric measurements on single-crystal samples. Specifically, peak-like dielectric anomaly and spin-flop transition appear simultaneously at around ±34 kOe for the canted antiferromagnet (M = Mn<sup>2+</sup>) at below 44.3 K, and a low-field (1 kOe) controlled magnetodielectric effect was observed in the “soft” ferromagnet (M = Cu<sup>2+</sup>) at below 9.5 K. These isothermal magnetodielectric effects are highly reproducible and synchronous with the field-induced magnetization at different temperatures, well confirming the essential role of spin reorientation on inducing the magnetodielectric coupling effect. These findings strongly implied that the layered perovskite magnets are new promising organic-inorganic hybrid systems to host magnetodielectric coupling effects.

### Introduction

The studies of coupling effect between two different physical parameters in molecular materials not only contribute to new perspectives in fundamental understanding of novel materials, but also provide extra dimensions for designing multifunctional devices.<sup>1</sup> The magnetodielectric coupling effect, defined as the dielectric properties controlled by an applied magnetic field, is important for understanding the coupled ferroelectric and magnetic properties in multiferroics as well as designing new generation of magnetodielectric devices.<sup>2,3</sup>

The progress of studying magnetodielectric coupling effect in the single-phase materials was very slow for a long time after the first experimental realization in Cr<sub>2</sub>O<sub>3</sub> in 1960s,<sup>4</sup> until the strong magnetodielectric effects were discovered in TbMnO<sub>3</sub> in 2003.<sup>5</sup> Since then, many efforts have been devoted to search new magnetodielectric materials in different systems of inorganic oxides, and have achieved numerous advances.<sup>6-12</sup> For instance, a highly-reproducible polarization switching by magnetic fields was observed in the orthorhombic TbMn<sub>2</sub>O<sub>5</sub>,<sup>13</sup> a gigantic magnetodielectric effect was found in the perovskite-type YMnO<sub>3</sub>,<sup>14</sup> and a low-field magnetodielectric effect was found in a Z-type hexaferrite Sr<sub>3</sub>Co<sub>2</sub>Fe<sub>24</sub>O<sub>41</sub>.<sup>15</sup> These outstanding discoveries promoted the researches of magnetodielectric coupling effect to the forefront of

condensed matter physics and material science.

Parallel to the intensive studies on inorganic oxides, the explorations of magnetodielectric coupling effect in the past decade have been extended to the organic-inorganic hybrid materials, taking their advantages of light weight, mechanical flexibility, environmentally benign synthesis and structural tunability.<sup>16,17</sup> To date, the major research interests in organic-inorganic hybrid materials were limited in the three-dimensional metal-formate frameworks, among which not a few compounds reveal interesting coexistence of ferroelectric and antiferromagnetic orders,<sup>18-21</sup> however, only five compounds, [NH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>][Fe<sup>III</sup>Fe<sup>II</sup><sub>(1-x)</sub>Ni<sup>II</sup><sub>x</sub>(HCOO)<sub>6</sub>] (x ≈ 0.63–0.69),<sup>22</sup> [(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>][Mn(HCOO)<sub>3</sub>],<sup>23</sup> [(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>][Fe(HCOO)<sub>3</sub>],<sup>24</sup> (CH<sub>3</sub>NH<sub>3</sub>)[Co(HCOO)<sub>3</sub>]<sup>26</sup>, and [NH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>][Fe<sup>III</sup>Fe<sup>II</sup>(HCOO)<sub>6</sub>],<sup>27</sup> were well identified exhibiting magnetodielectric coupling effects. In this sense, there is still huge room for progressing the magnetodielectric coupling effect in numerous organic-inorganic hybrid materials,<sup>28-31</sup> and it is in urgent need to investigate more hybrid material systems for exploring stronger magnetodielectric coupling effects.

As a unique family of organic-inorganic hybrids, the two-dimensional layered perovskite-type compounds have a general formula of A<sub>2</sub>MX<sub>4</sub> (the valence ratio of the cation A, metal ion M, and anionic halogen X components is 1:2:1), and structurally consist of infinite inorganic layers of corner-sharing MX<sub>6</sub> octahedra interleaved by bilayers of organic ammonium layers. The comprehensive studies on their magnetisms have well disclosed that, the long-range magnetic ordering could be established in the inorganic layers *via* the intra- and inter- layer magnetic interactions. Moreover, the magnetic types are strongly depending on the metal ion M, meanwhile the amplitude of magnetic interactions could be influenced by the halogen ion X together with the organic

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Electronic Supplementary Information (ESI) available: photos of crystals, powder XRD patterns, illustration of hydrogen bonds, magnetodielectric effect at different temperatures of PEA-Cu, and other magnetic properties of PEA-Mn and PEA-Cu. See DOI: 10.1039/x0xx00000x



cation A.<sup>32-34</sup> For instance, the layered perovskite-type compounds based on Jahn-Teller active  $\text{Cr}^{2+}$  and  $\text{Cu}^{2+}$  ions are typically Heisenberg ferromagnets,<sup>35, 36</sup> while the layered perovskites based on  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  ions are typically antiferromagnets,<sup>37-39</sup> including some canted antiferromagnets exhibiting spin-flop transition (*vide infra*) at low temperature.<sup>34</sup> It was generally believed that the ferromagnetic ordering could host stronger magnetodielectric interactions than the antiferromagnetic one. Therefore the ferromagnetic  $\text{Cu}^{2+}$ -based layered perovskites attracted more attentions, and some of them have been assigned as type-I multiferroic materials,<sup>33, 40, 41</sup> though none of them has been verified possessing magnetodielectric coupling effect. In contrast, the spin-flop transition, a field-induced magnetic transition concerning the antiferromagnetic ordering, has rarely been studied on its potentiality to induce magnetodielectric effect in organic-inorganic hybrid materials.<sup>26</sup>

In our previous studies on the multiferroic materials based on a ferromagnetic layered perovskite,  $(\text{C}_6\text{H}_5(\text{CH}_2)_4\text{NH}_3)_2[\text{CuCl}_4]$ , we found a coexistence of magnetic and dielectric bistabilities in the vicinity of both ferroelectric and ferroelastic structural phase transitions, arising from the buckling of the octahedra together with the freezing of the organic cations.<sup>41</sup> Such coexistence of both magnetic and dielectric bistabilities strongly implicates that, the unique hydrogen-bonding interaction between the inorganic layers and the organic cations may mediate the magnetic and dielectric properties to achieve a coupling effect.

To explore the magnetodielectric coupling effect in layered perovskites, we focused on two known layered-perovskite magnets, a canted antiferromagnet  $(\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_3)_2[\text{MnCl}_4]$  (PEA-Mn) and a ferromagnet  $(\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_3)_2[\text{CuCl}_4]$  (PEA-Cu). PEA-Mn and PEA-Cu are isomorphous, both of them crystallize in the centrosymmetric space group *Pbca* at room temperature.<sup>33,34</sup> Their structures consist of inorganic layers constructed by corner-sharing  $\text{MCl}_6$  octahedra ( $\text{M} = \text{Mn}^{2+}$  and  $\text{Cu}^{2+}$ ). The intralayer cavities between the octahedra are occupied by two  $-\text{NH}_3$  groups of two organic  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_3^+$  cations from the up and down sides, respectively (Fig. 1a). Notably, such a hybrid structure is stabilized by the  $\text{N}-\text{H}\cdots\text{Cl}$  hydrogen-bonding interactions (Fig. S3). These hybrid layers are further packed into a three-dimensional structure through Van der Waals forces along the *c*-axis.

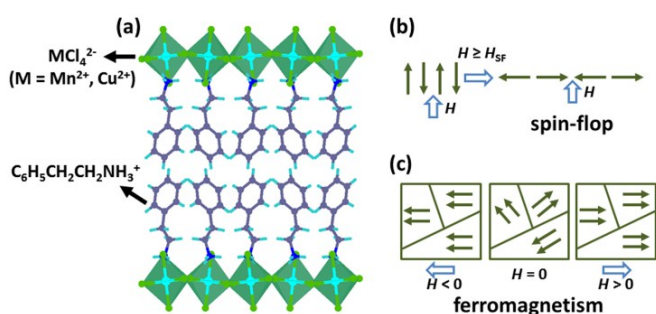


Fig. 1 Schematic diagram of crystal structure for PEA-Mn and PEA-Cu (a), spin-flop transition in canted antiferromagnetic PEA-Mn (b), and spin reorientation in “soft” ferromagnetic PEA-Cu (c).

PEA-Mn is a canted antiferromagnet and shows weak ferromagnetism below the ordering temperature of 44.3 K ( $T_C$ ).<sup>34</sup> Below  $T_C$ , the isothermal magnetization along the *c*-axis (normal to the inorganic layers) reveals a spin-flop transition. As illustrated by Fig. 1b, the spin-flop is a field-induced transition that a magnetic field parallel to the easy axis of an antiferromagnet causes the spins to flop to the direction perpendicular to the field, and the critical magnetic field is called spin-flop field ( $H_{sf}$ ).<sup>42</sup> For PEA-Cu, it shows ferromagnetic order below 9.5 K (Fig. S4), and is a “soft” ferromagnet with very small residual magnetization. Namely, as illustrated in Fig. 1c, the spin orientations of ferromagnetic domains are being randomly-oriented when  $H = 0$ , and could rapidly follow the direction of  $H$  when  $H > 0$  or  $H < 0$ . In addition, the field-induced spin-flop transition in PEA-Mn and the magnetization in PEA-Cu become more pronounced with decreasing temperature (Fig. S5), indicating the spin reorientation in both PEA-Mn and PEA-Cu are temperature dependent.

Herein, we carefully cultivated the large-enough and high-quality single crystals for PEA-Mn and PEA-Cu, and systematically studied their magnetodielectric coupling properties by applying magnetic and electric field on the specified face of their single crystals. We demonstrated that, for the first time, the spin reorientation in layered-perovskite magnets could induce a highly-reproducible magnetodielectric coupling effect, providing a promising way to design more advanced magnetodielectric materials based on layered perovskites.

## Experimental

### Synthetic procedures

In order to improve the sensitivity and accuracy of the results in the magnetodielectric measurements, large-enough and high-quality single crystals are particularly necessary. For this purpose, we increase the amounts of raw materials:<sup>33, 34</sup> 50 mmol 2-phenethylamine, 25 mmol manganese chloride dihydrate for PEA-Mn (25 mmol cupric chloride dihydrate for PEA-Cu), and 50 mmol hydrochloric acid were dissolved in an aqueous solution, stirred for 20 min and then kept the clear solution in a quiet environment without destabilization for slow evaporation at room temperature. After about one month, a number of high quality rectangular crystals as large as several millimetres were obtained (Fig. S1). Experimental powder X-ray patterns match well with the simulated one, confirming the phase purity for PEA-Mn and PEA-Cu. Besides, X-ray patterns measured on the largest faces of single crystals indicated the largest face is the (001) plane normal to the *c*-axis (Fig. S2).

### Physical measurements

The silver electrodes were carefully painted on the largest faces of the single crystals. The measurements of magnetization were performed on a Quantum Design physical property measurement system (PPMS) by applying magnetic field on a single crystal along its *c*-axis. The dielectric constant



( $\epsilon'$ ) at different magnetic fields and different temperatures were measured by using a combination of Tonghui TH2828A LCR meter ( $E//c$ ) and PPMS ( $H//c$ ) through a modified multifunctional probe with shielded cables (Quantum Design).

## Results and discussion

### Magnetodielectric effect in PEA-Mn and PEA-Cu

To probe the magnetodielectric coupling effect in PEA-Mn and PEA-Cu, we investigated the dielectric constant (10–1000 kHz) as a function of scanning magnetic field ( $E//c$ ,  $H//c$ ) by using single-crystal samples at 3 K. For PEA-Mn, as shown in Fig. 2a, with scanning magnetic field ( $-70 \rightarrow 0 \rightarrow 70$  kOe), the dielectric constant ( $\epsilon'$ ) for all the experimental frequencies reveal a pair of peaks accompanying with spin-flop transition at around  $H_{SF}$  ( $\pm 34$  kOe). Defining the magnetodielectric ratio as  $MD = [\epsilon'(H) - \epsilon'(0)]/\epsilon'(0)$ , we can obtain the maximum MD of about 0.34% at  $H_{SF}$ . Among the known single-phase compounds exhibiting isothermal magnetodielectric effect, the MD of PEA-Mn is smaller than those of the outstanding inorganic oxides such as  $TbMnO_3$ <sup>5</sup> and  $DyMnO_3$ ,<sup>14</sup> but is comparable with  $BiMnO_3$  and a dysprosium-based single-molecule magnet,<sup>6, 30</sup> and is much larger than  $Mn_3O_4$ ,<sup>43</sup>  $TbFe_3(BO_3)_4$ <sup>44</sup> and the metal-formate framework  $[(CH_3)_2NH_2][Fe(HCOO)_3]$ .<sup>25</sup>

For PEA-Cu, as showed in Fig. 2b, when the magnetic field scanning from  $-20 \rightarrow 0 \rightarrow 20$  kOe at 3 K,  $\epsilon'$  maintains unchanged until about  $-1$  kOe, then quickly decreases to the minimum value at 0 kOe, after that it increases to the former

value when  $H > 1$  kOe. The anomalies appeared at around 0 kOe, which is the critical field of magnetization changing from negative to positive (Fig. 1c), indicating the orientation of spins in the “soft” ferromagnet PEA-Cu effectively alter the dielectric property to induce a magnetodielectric coupling effect. It is interesting to find that the canted antiferromagnetic PEA-Mn only shows the maximum MD at  $H_{SF}$  ( $\pm 34$  kOe), while the ferromagnetic PEA-Cu reaches the maximum MD (0.21 %) at a large range of about  $H > 1$  kOe and  $H < -1$  kOe. The maximum MD of PEA-Cu is comparable to that of PEA-Mn, but its applied magnetic field of about 1 kOe is much smaller than that of PEA-Mn (34 kOe), demonstrating an advantage of “soft” ferromagnetism for realizing the low-field controllable magnetodielectric materials.

As implicated by the coexistence of magnetic and dielectric bistabilities arising from the buckling of inorganic octahedra together with the freezing of organic cations during the thermal-induced phase transitions in  $(C_6H_5(CH_2)_4NH_3)_2[CuCl_4]$ ,<sup>41</sup> a possible mechanism for the observed magnetodielectric effect in PEA-Mn and PEA-Cu could be proposed. The process of spin-reorientation in layered perovskite magnets could affect the buckling of the inorganic octahedra, then lead to a slight alternation of polar organic cations *via* the hydrogen-bonding interactions, and thus induce the dielectric anomalies. Notably, as no significant change of atomic positions occurs between the magnetic phases before and after the field-induced spin-reorientation, the dielectric anomalies observed in PEA-Mn and PEA-Cu are field-dependent phenomena, *i.e.*, showing a peak at the critical field, rather than the temperature-dependent phenomena commonly-observed in the thermal-induced phase transition, *i.e.*, changing between two plateaus.<sup>41</sup>

### Magnetodielectric effect at different temperatures

To further understanding the origin of the coupled magnetic and dielectric properties, the isothermal magnetodielectric effects at different temperatures were investigated. For PEA-Mn, as shown in Fig. 3a, the magnetodielectric anomalies appeared below 50 K and become stronger with decreasing temperature. The maximum magnetodielectric ratios at  $H_{SF}$  for 3, 10, 20, 30, 40 and 50 K are about 0.34%, 0.25%, 0.12%, 0.06%, 0.02% and 0%, respectively. As showed in the inset of Fig. 3a, the slowly increase of MD with decreasing temperature are synchronous with the field-induced magnetizations during the spin-flop transitions (Fig. S5a), further confirming the indispensable role of spin reorientation on inducing the magnetodielectric coupling effect. For PEA-Cu, the effects at different temperatures are similar to PEA-Mn, *i.e.*, field-induced dielectric anomalies are observed below its magnetic ordering temperature of 9.5 K and become stronger with decreasing temperature (Fig. 3b). The maximum MD ratios at 3, 5, 7, 9 and 11 K are about 0.21%, 0.07%, 0.05%, 0.02% and 0%, respectively, and the MD shows temperature dependence in multiferroic phase, *i.e.*, being stronger at lower temperature, similar to the behaviour of field-induced magnetizations (Fig. S5b). These results indicated that magnetodielectric coupling

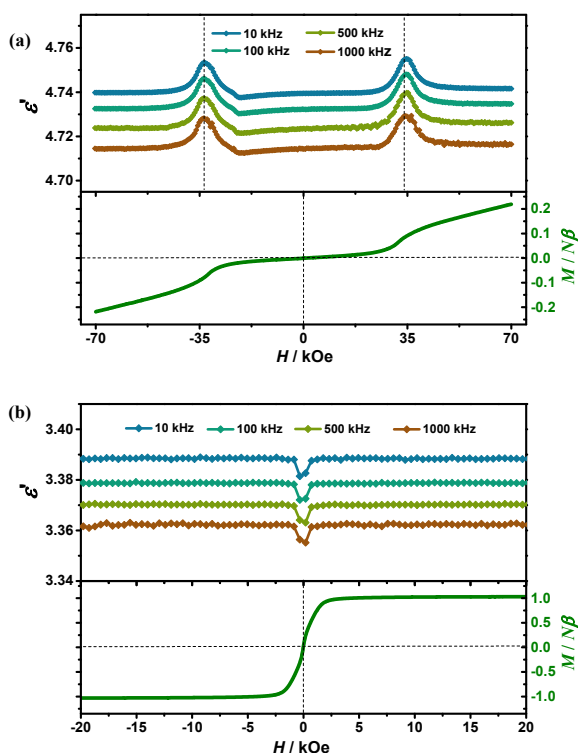


Fig. 2 Dielectric constant ( $\epsilon'$ ) and magnetization ( $M$ ) measured along the  $c$ -axis as a function of scanning magnetic field ( $H$ ) at 3 K for PEA-Mn (a) and PEA-Cu (b).





effect in both of PEA-Mn and PEA-Cu is induced by the spin reorientation. As such effect is synchronization with the field-induced spin orientation, which may provide another way to probe/monitor the spin-reorientation by a simple dielectric measurement.

### Highly reproducible magnetodielectric effect

To exclude the fake signals and confirm the intrinsic coupled dielectric and magnetic properties, it is very essential to detect the reproducibility of the magnetodielectric effect. However, the studies about reproducible magnetodielectric effect are rare, even some outstanding magnetodielectric materials such as  $\text{TbMnO}_3$ ,<sup>5</sup>  $\text{DyMnO}_3$ ,<sup>14</sup> and  $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ <sup>45</sup> exhibit obvious difference between descending and ascending process of the magnetic field. In this sense, the exploration of the fatigue phenomenon is particularly necessary and the highly reproducible magnetodielectric effect would be especially desired.

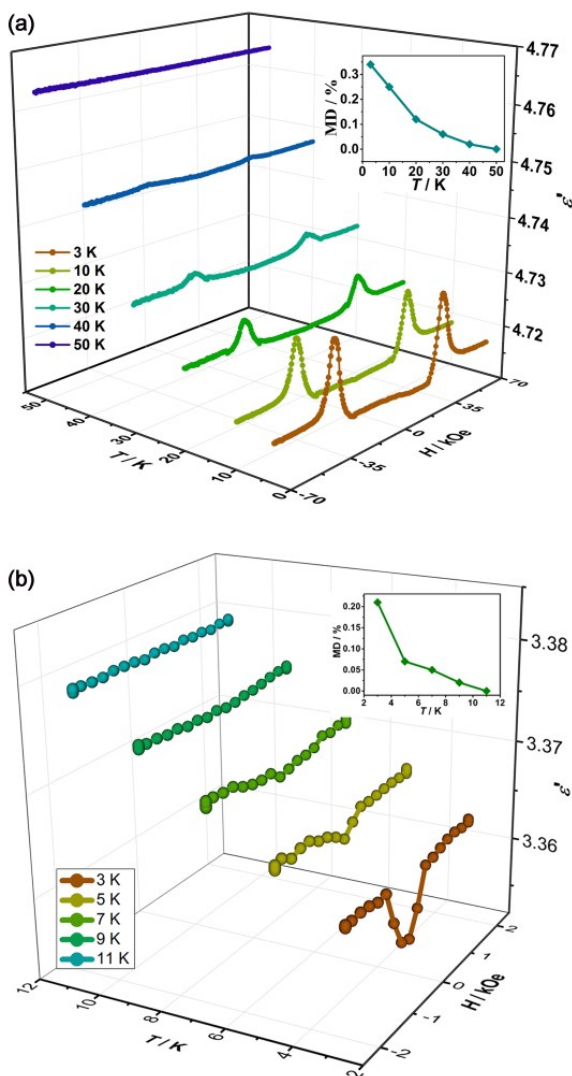


Fig. 3 Dielectric constant ( $\epsilon'$ , 1000 kHz) vs. magnetic field measured at different temperatures for PEA-Mn (a) and PEA-Cu (b). Inset: the maximum magnetodielectric ratios (MD) at different temperatures.

To demonstrate the reproducibility and stability of the magnetodielectric coupling effect, we set the procedure as follows: for PEA-Mn, temperature was set at 3 K, magnetic fields were alternately set as 0 and 34 kOe, and the dielectric constant was measured along its  $c$ -axis. For comparison, the magnetization was measured with the same procedure. As shown in Fig. 4a, accompanying with the alteration of the magnetic field, the step-like dielectric constant ( $\epsilon'$ ) and magnetization ( $M$ ) are synchronously observed, which can be regarded as “on” and “off” states of dielectric and magnetic bi-switches, and thus providing an extra dimension to design multifunctional device. Moreover, it shows almost no fatigue phenomenon along the whole experimental process, indicating the magnetodielectric coupling effect in PEA-Mn is highly reproducible. For PEA-Cu, its experimental procedure is similar to that of PEA-Mn, but the magnetic fields were alternately set as 0 and 1 kOe. Similar to PEA-Mn, altering magnetic field can switch both dielectric constant and magnetization in PEA-Cu (Fig. 4b), confirming its highly reproducible low-field (1 kOe) controllable magnetodielectric coupling effect. It is worth noting that, as the magnetodielectric coupling effect controlled by a low magnetic field is very desired but still extremely rare,<sup>15, 22</sup> the presented magnetodielectric coupling achieved by “soft” ferromagnetism in multiferroic PEA-Cu provides a new clue to search advanced materials for achieving low-field magnetodielectric coupling effect.

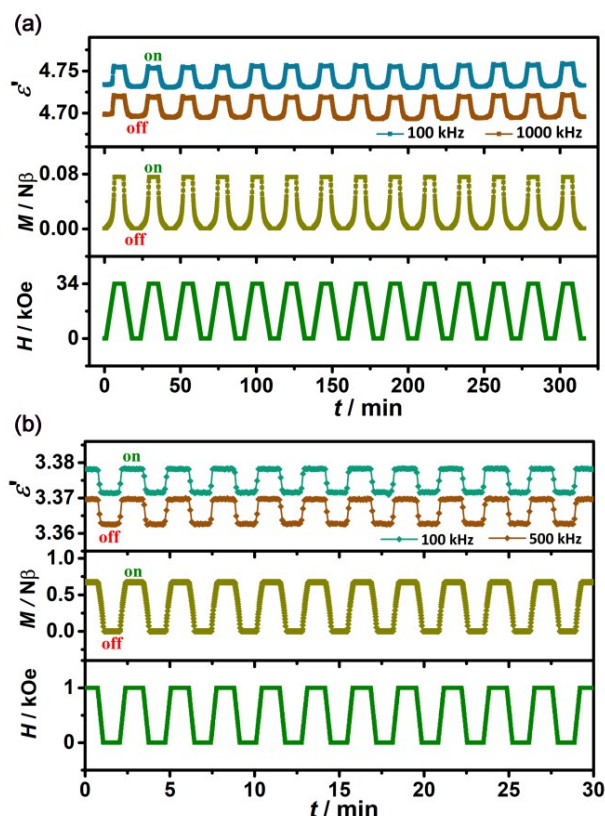


Fig. 4 Dielectric constant ( $\epsilon'$ ) and magnetization ( $M$ ) for PEA-Mn (a) and PEA-Cu (b) measured at different magnetic fields ( $H$ ) at 3 K. The magnetic fields for PEA-Mn were alternately set as 0 and 34 kOe, and the magnetic fields for PEA-Cu were alternately set as 0 and 1 kOe.



## Conclusions

In summary, the magnetodielectric coupling effects were disclosed in two organic-inorganic hybrid layered perovskite compounds, *i.e.*, PEA-Mn and PEA-Cu. The dielectric anomalies appear at around  $\pm 34$  kOe for the canted antiferromagnet PEA-Mn and 0 kOe for the “soft” ferromagnet PEA-Cu, respectively. Moreover, such isothermal magnetodielectric effects in both layered perovskite magnets are highly reproducible, and synchronize with the field-induced magnetizations at different temperatures. Therefore, the coupled magnetic and dielectric properties in both layered perovskite magnets could be ascribed to the field-induced spin reorientations originating from the spin-flop transition in PEA-Mn and magnetization reversal in PEA-Cu, respectively. The magnetodielectric coupling effects observed in PEA-Mn and PEA-Cu strongly implied that the organic-inorganic layered perovskite magnets are new promising hybrid material systems to host magnetodielectric coupling effects, probably owing to their unique hydrogen-bonding interactions between the inorganic magnetic layers and the organic layers. Moreover, considering the existence of the large family of organic-inorganic layered perovskite magnets, the discovery of magnetodielectric coupling effect in PEA-Mn and PEA-Cu not only open up a promising way to design more advanced magnetodielectric materials, but also promote the continued efforts to the applications of coupled dielectric and magnetic properties based on molecular materials.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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## Journal Name

## ARTICLE

Spin-reorientation-induced magnetodielectric effects were disclosed in two layered perovskite magnets,  $(\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_3)_2[\text{MCl}_4]$  ( $\text{M} = \text{Mn}^{2+}, \text{Cu}^{2+}$ ) by their highly-reproducible isothermal magnetodielectric measurements on single-crystal samples, well demonstrating that the organic-inorganic layered perovskite magnets are new promising hybrid material systems to host magnetodielectric coupling effects.

