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Response to "Comment on 'Theoretical design of molecular nanomagnets for magnetic refrigeration'" [Appl. Phys. Lett. 105, 046101 (2014)]

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Response to "Comment on 'Theoretical design of molecular nanomagnets for magnetic refrigeration'" [Appl. Phys. Lett. 105, 046101 (2014)]

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The Comment by Evangelisti and Lorusso[1] points out that weakly ferromagnetically coupled molecular nanomagnets (MNMs) (case (ii)) are the best candidates as magnetocaloric refrigerants in the temperature (T) range 1–4.2 K. We agree with this remark, which however does not concern the focus of our Letter. We aimed indeed at the identification of the best candidates in the broader T-range *between 10 K and the sub-Kelvin region*, which turned out to be strongly ferromagnetically coupled MNMs (case (iii)).[2]

The first point raised in the Comment involves the intermolecular dipolar field b, responsible for an increase of the base temperature. This effect does not affect our conclusions and it had already been pointed out in the last part of the Letter. After discussing Figures 3 and 4 of Ref. 2, where we had neglected dipole-dipole couplings and assumed the ideal value $T_{\rm cold} = 1$ mK, we stressed that *the presence of intermolecular dipolar interactions may limit the value of the achievable* T_{cold}. Using the formula reported in the Comment for $T_{\rm base}$ and the typical value of the dipolar field in dipolar MNMs (Ref. 1) $b \simeq 0.02$ T, one obtains $T_{\rm base} \simeq 0.03$ K (with $T_{\rm hot} = 10$ K, $B_{\rm hot} = 7$ T, and $B_{\rm cold} = 0$). Thus, there is no convincing reason to assume $T_{\rm base} = 1$ K, as done in the Comment. Even considering a possible dipolar phase transition, the ordering temperature $T_{\rm C}$ is typically well below 1 K, as stated by the authors of the Comment themselves. Furthermore, there are solutions besides spin dilution to further reduce the effect of dipolar interactions. For instance, in Ref. 3, the authors state that the *Fe_{17} MNM can potentially be employed as a sub-Kelvin magnetic refrigerant*. They found that in this high-spin system ($S = 35/2$) $T_{\rm C}$ can be reduced below 0.3 K by packing the molecules in crystallographic symmetries that minimize the dipolar energy.[4] In addition, in Ref. 5, authors suggest the use of bulkier ligands, thus allowing one to use MNMs as *coolers for ultra-low temperatures* ($T_{\rm base} < 10$ mK). Hence, the choice $T_{\rm cold} = 1$ K is too pessimistic, especially within the broad theoretical analysis reported in our Letter. Anyway, the conclusion of our Letter is unchanged if $B_{\rm cold} = b$, as shown by the results reported below.

As far as $T_{\rm hot}$ is concerned, no justification is supplied in the Comment for limiting it to 4.2 K. The authors themselves state that MNMs are proposed as magnetic refrigerants up to 10 K. We mention in passing that recently developed closed-cycle refrigerators can reach T as low as 1.5 K, with relatively small extra cost with respect to a 4 K cryocooler. Hence, the T-range from 1 K to 4 K does not appear to be the most interesting.

Figure 1 reports the calculated entropy variation $\Delta S_{cold} = \Delta S(T_{\rm cold})$ of the square-based pyramid model in a Carnot cycle with $T_{\rm cold} = 0.1$ K, $T_{\rm hot} = 10$ K, and

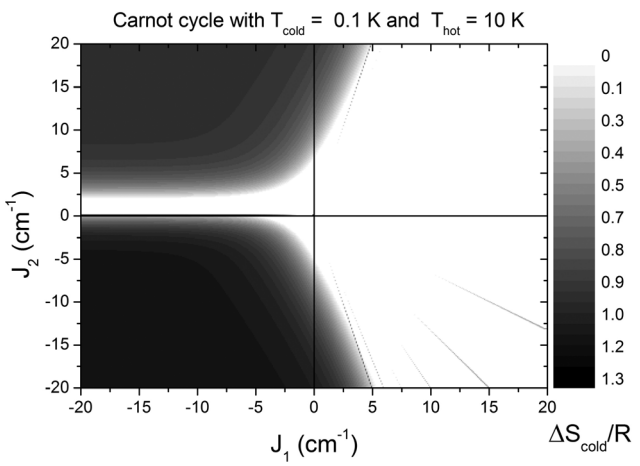

FIG. 1. Entropy variation of the square-based pyramid model for a Carnot cycle with $T_{\rm cold} = 0.1$ K, $T_{\rm hot} = 10$ K, and $B_{\rm cold} = 0.02$ T (darker means better). Negative exchange constants correspond to ferromagnetic coupling.

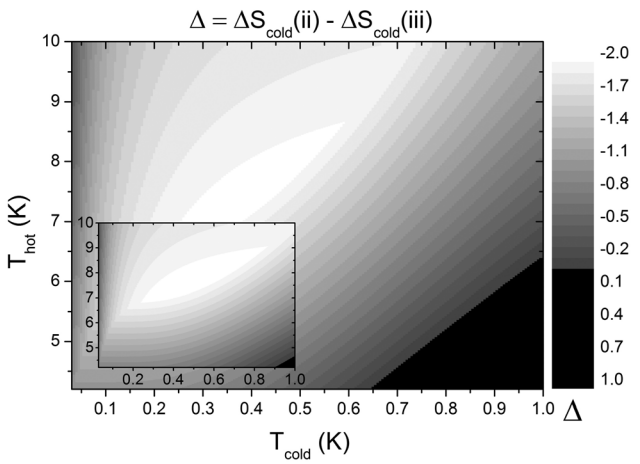

FIG. 2. The relative performance for cases (ii) and (iii) is shown by the color map of $\Delta \equiv \Delta S_{\rm cold}$ (ii) $- \Delta S_{\rm cold}$ (iii) as a function of $T_{\rm cold}$ and $T_{\rm hot}$, with $B_{\rm cold} = 0.02$ T. For case (iii), $J_1 = J_2 = -20\,{\rm cm}^{-1}$, whereas for case (ii), $J_1 = J_2 = -0.2\,{\rm cm}^{-1}$ or $J_1 = J_2 = -0.3\,{\rm cm}^{-1}$ (inset). Only in the narrow black regions case (ii), backed in the Comment, is better than case (iii).

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$B_{\mathrm{cold}} = 0.02\,\mathrm{T}$. It is evident that the heat absorbed in each cycle ($\propto \Delta S_{cold}$) is large when J_1 and J_2 are strong and ferromagnetic (case (iii)), confirming the conclusion of Ref. 2. In order to further substantiate our findings, in Figure 2, we directly compare the performances of Carnot cycles in cases (ii) and (iii) over a wide range of temperature spans. We report the quantity $\Delta = \Delta S_{\mathrm{cold}}$ (ii) $-\Delta S_{\mathrm{cold}}$ (iii) as a function of T_{cold} and T_{hot}, where in case (ii) $J_1 = J_2 = -0.2\,\mathrm{cm}^{-1}$ and in case (iii) $J_1 = J_2 = -20\,\mathrm{cm}^{-1}$. It is evident that $\Delta > 0$ (i.e., (ii) is better than (iii)) only in a narrow range with low T_{hot} and high T_{cold}. Moreover, the performance of (ii) is fragile with respect to J_1 and J_2, contrarily to (iii). For instance, if $J_1 = J_2 = -0.3\,\mathrm{cm}^{-1}$ (inset of Fig. 2), the temperature region where $\Delta > 0$ is further reduced.

At last, Fig. 2 of the Comment and the associated discussion are not truly relevant. Indeed, as Fig. 1 of the Comment shows the performances of the feasible Carnot cycles depend on the shapes of the zero-field and in-field entropy curves $S(T)$ and not merely on their difference $\Delta S_m(T)$ (which cannot be fully exploited in the cycle). Therefore, the curves reported in Fig. 2 do not determine the cooling power of the cycle ($\propto \Delta S_{\mathrm{cold}} \neq \Delta S_m(T_{\mathrm{cold}})$).

In conclusion, weakly ferromagnetically coupled MNMs (case (ii)) are the best candidates only in a narrow T-range close to that singled out in the Comment, whereas the best molecular refrigerants on ampler and hence more useful T-ranges are strongly ferromagnetically coupled MNMs (case (iii)).

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