Electronic Supporting Information (ESI):

Generating new magnetic properties in organic-inorganic hybrids

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Preparation procedure for the $CoCl_4(C_5H_6CH_2CH_2NH_3)_2$ and $MnCl_4(C_5H_6CH_2CH_2NH_3)_2$ bulk hybrids

To prepare the $CoCl_4(C_5H_6CH_2CH_2NH_3)_2$ and $MnCl_4(C_5H_6CH_2CH_2NH_3)_2$ bulk hybrids 2phenylethylammoniumchloride was mixed with $MCl_2.xH_2O$ ($M = Co^{2+}$ or Mn^{2+}) in stoichiometric ratio. The mixture was heated in a water bath at 50 °C, the solvent water was added until the mixture was dissolved. When the solution was then cooled to room temperature small crystals formed. The crystals was filtered and recrystallized three times.



Fig. S1 Crystal structures of the bulk hybrids; (a) the cobalt-based organic-inorganic hybrid consists of free standing CoCl₄ in organic matrix held together by a hydrogen bond network; (b) the manganese-based bulk hybrid comprises 2-dimensional inorganic MnCl₄ sheets of corner-sharing octahedra interleaved by organic layers.[1]

Structure and magnetic properties of the $CoCl_4(C_5H_6CH_2CH_2NH_3)_2$ and $MnCl_4(C_5H_6CH_2CH_2NH_3)_2$ bulk hybrids

The structure of the bulk hybrids of CoCl₄(C₅H₆CH₂CH₂NH₃)₂ and MnCl₄(C₅H₆CH₂CH₂NH₃)₂ was determined by means of single crystal diffraction on a three-circle Bruker Apex diffractometer equipped with a CCD detector and operating with Mo Kα radiation. The inorganic component of CoCl₄-based bulk hybrid forms tetrahedra arranged in planes but connected only indirectly by hydrogen bonds via the ammonium group from the organic component. The nearest neighbour Co ions are 6.533 Å apart.^[1] The composition of the MnCl₄-based bulk hybrid is similar to the CoCl₄-based bulk hybrid. However the inorganic component forms octahedra, instead of tetrahedra. The nearest neighbour Mn ions are 5.082 Å apart.^[1]



Fig. S2 The inverse magnetization (zero-field-cooling (ZFC)) versus temperature measured at 0.2 T for the $CoCl_4$ -based hybrid LB film (a) and at 0.05 T for the $MnCl_4$ -based hybrid LB film (b).

The in-plane zero field cooled magnetization versus temperature for both $CoCl_4$ -based and $MnCl_4$ based hybrid LB films are shown in figure S2. The high temperature region can be fitted with Curie-Weiss law. The Weiss temperature (θ_{cw}) can be derived from the fitting. θ_{cw} is an indication for the magnetic correlations in the material: it is zero when the magnetic interactions are absent or cancel out, positive for ferromagnetic interactions and negative for antiferromagnetic interactions. For both the CoCl₄-based and MnCl₄-based hybrid LB films, the value of θ_{cw} is negative, pointing to antiferromagnetic interactions.



UV/visible spectrum of a CoCl₄-based hybrid LB film

Fig. S3 UV/visible spectrum of a CoCl₄-based hybrid LB film.

The UV/visible absorption spectrum of an 80-layer-thick $CoCl_4$ -based hybrid LB film is shown in figure S3. An absorption band at 476 nm,[2] can be identified as due to Co^{2+} in an octahedral environment. Since to the energy separation between e_g and t_{2g} in the tetrahedral field is less than that in the octahedral one, the UV/visible spectra of Co^{2+} in tetrahedral symmetry exhibit bands at wavelengths of 524 nm, 610 nm and 660 nm.[3]

References

[1] A. H. Arkenbout, Organic-inorganic hybrids: a Route Towards Soluble Magnetic Electronics; University of Groningen, *PhD Thesis*, 2010.

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