Supplementary information

1) SQUID magnetometry on Mn12- $L_{3,4,5\text{-}H6F6}$

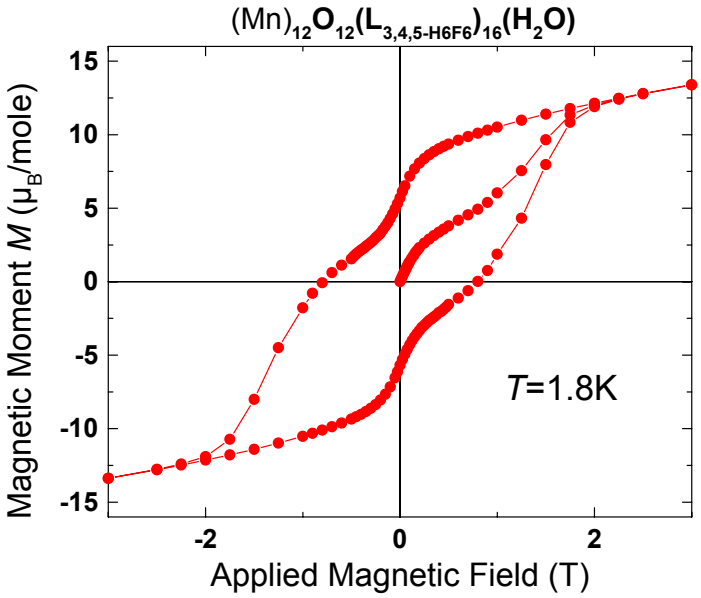
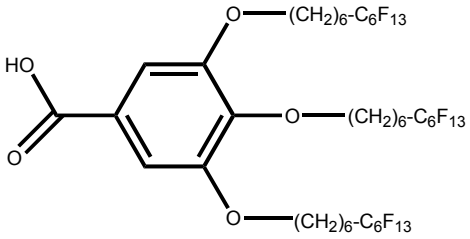


Figure S1. First magnetization and hysteresis curve of the compound under study.

The figure represents the variation of the magnetization as a function of the applied magnetic field at 1.8 K. The first magnetization curve is also given. The whole cycle ($\mu_0 H$ = 0 → +3 T → −3 T → +3 T) is recorded in ~2h. The usual features of Mn12-based SMM are present: open hysteresis cycle and temperature dependence of the *ac* relaxation. Even at high fields the magnetic moment does not saturate, this has already been reported for other compounds[1]. The step which is visible in the curve at $\mu_0 H$ ~0.5 T is not due to quantum tunneling of the magnetization, but most probably to the presence of two Jahn-Teller isomers, as already reported for various SMM. Analysis of the temperature dependence of the *ac* relaxation gives a blocking temperature of *ca*. 2.5 K (considering a relaxation time of 100 s). Fit of the data yields a spin ground state S = 10 if g = 1.86 and S = 9 if g = 2.05, the latter values being the more reasonable ones. Mn12-Ac and its derivatives are known for having a spin ground state S = 10 but smaller values have already been reported for Mn12-based SMM. (see Ref. (16) and references therein).

2) Molecular structure of the ligand $L_{3,4,5\text{-}H6F6}$

The 16 acetate ligands originally found in the canonical Mn12-OAc SMM have been all replaced by the gallate derivative[2], termed $L_{3,4,5\text{-}H6F6}$ and pictured hereafter:



Mw = 22926 g/mol

Figure S2. Molecular structure of the ligands.

3) UV-vis spectrum of Mn12- $L_{3,4,5\text{-}H6F6}$

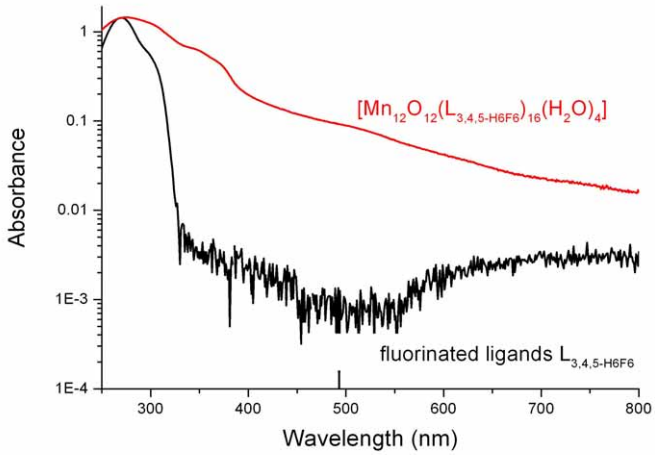


Figure S3. UV-vis absorption spetra of the ligands (*v.supra*) and of the compound under study.

Spectra have been recorded in 1,1,2-trichloro-1,2,2-trifluoroethane. It can be seen that most of the absorption is in the UV range and is due to the $L_{3,4,5\text{-}H6F6}$ ligand (black curve). Still, there are weak structures in the absorption spectrum of the title compound.

In the original Mn12-OAc, in spite of the lack of any strong absorption band, a number of charge transfer excitations have been detected, all being very weak and

broad. They consist mostly in charge transfers from the inner Mn ions towards the outer ones (at 521 and 376nm), and charge transfers from the oxygen *p*-orbitals towards the *d*-orbitals of inner and outer Mn ions (at 273 and 236nm)[3]. Low temperature measurements of the magnetic circular dichroism (MCD) also have been reported. Contrary to the previous ones, the spectra show a series of positive and negative broad bands, at 427, 472, 510 and 555nm, with the one at 472nm giving the largest MCD signal[4]. For applied fields below 1T the signals are independent of optical polarization, at higher fields the percentages of polarization have been computed by McInnes *et al.*

We tried irradiating at different wavelengths, in particular λ =510 nm and λ = 550 nm which correspond to MCD bands and λ = 480, 600, 650 & 700 nm which is outside the MCD bands without observing any change in the behaviour of our sample.

4) Chronogram of the magnetization at 2.0 K

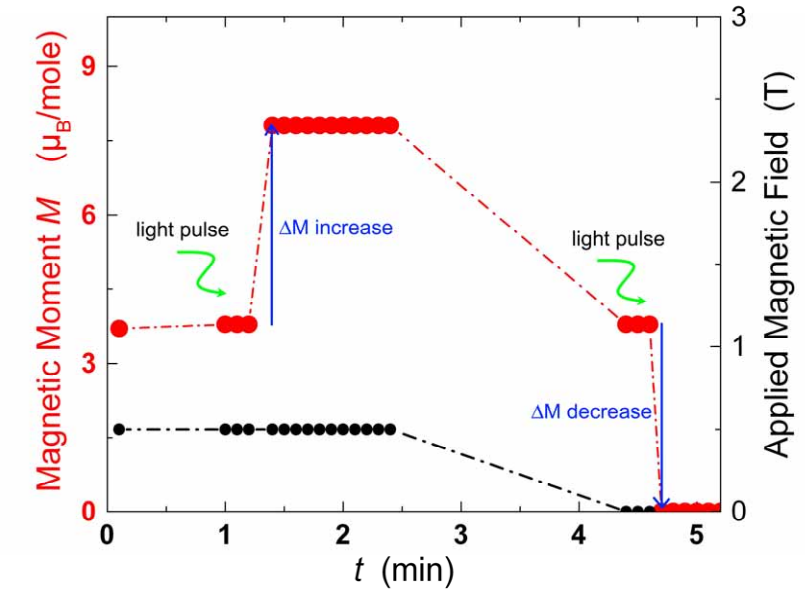


Figure S4. Chronogram of the magnetization at 2.0 K

Magnetization of the sample (red dots, left scale) and applied magnetic field (black dots, right scale) versus time. When the magnetized sample ($\mu_0 H$ = 0.5 T) is irradiated at t~1.2 min, a positive relative change of magnetization $\Delta M/M$ of 100% is induced, and the final state $M=M_{limit}$ is stable. H is then reduced to zero, hence the decrease of M ; a pulse of light sent at t~4.6 min can then trigger a drop of M to zero. The system can

therefore be considered as tri-state: $M = 0$, $M = M_{rem}$, $M = M_{limit}$, with the commutation between the states being driven by light and/or applied field. If the power of the incident light is reduced, both the increase and decrease of M also decrease.

5) XMCD - SQUID comparison

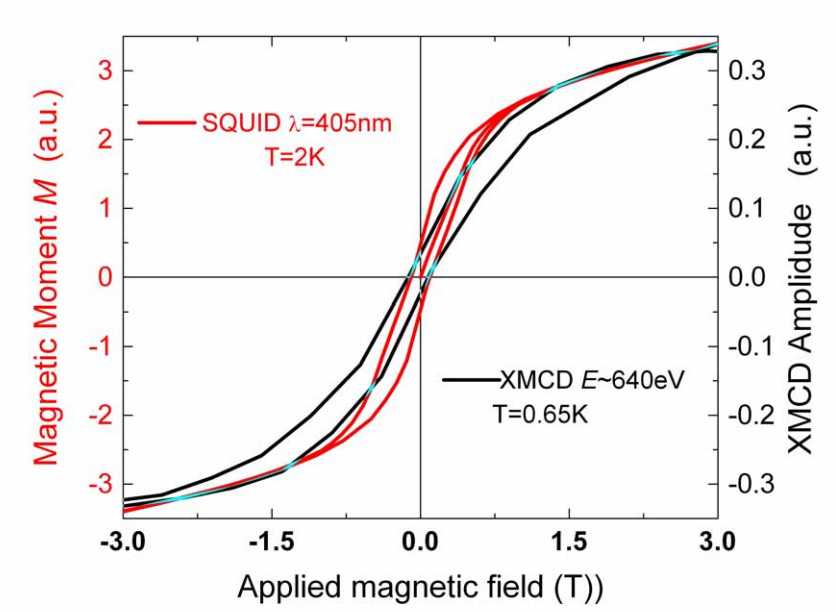


Figure S5. Comparison of the hysteresis curves recorded with XMCD and photo-SQUID.

Magnetization of Mn atoms in Mn_{12}-$L_{3,4,5\text{-}H6F6}$ (T=0.65 K) as deduced from the averaged XMCD signal at different energies (640.6, 641.2 and 642.4 eV, around the Mn-L_3 edge) as a function of the applied magnetic field, compared to the SQUID measurements under a continuous illumination λ=405 nm, at T=2.0 K. This figure shows that the irradiated samples exhibit a reduced hysteresis curve in both cases, as compared with the broad opening recorded with a regular SQUID (*see supplementary figure S1*). The difference in the overall shape of the curve maybe due to the fact that the XMCD sample is a monolayer whereas the SQUID sample is amorphous bulk.

6) Data acquired on Mn12-OAc

Some experiments have also been performed on Mn12-OAc, the "traditional" SMM compound, in polycrystalline powder. As can be seen in the following figure, the same behaviour is observed.

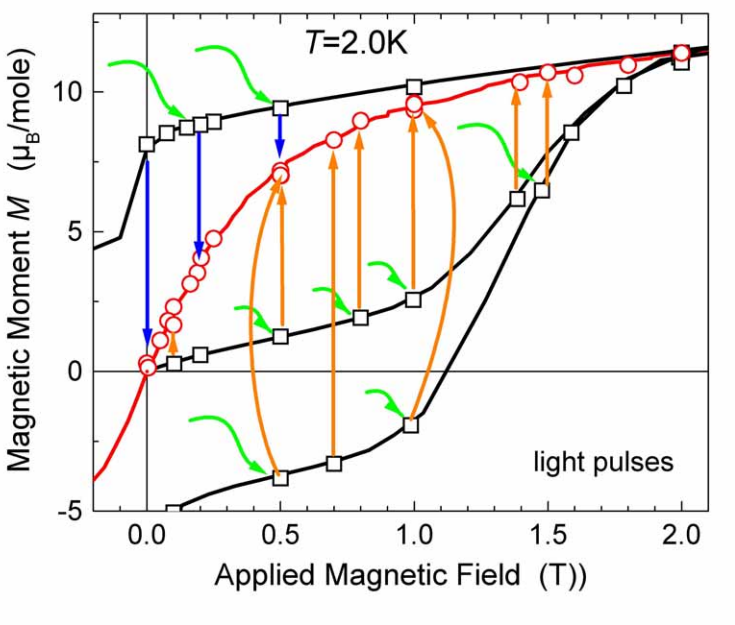


Figure S6. Behaviour of the magnetization of Mn12-OAc under light irradiation. Black solid curve : first magnetization curve and hysteresis for $H>0$. Red solid curve : $M(H)$ under continuous irradiation (643nm and 5mW/cm^2). Open black squares: initial value of M before the light pulse. Open red dots: final value of $M(H)$ at fixed H after illumination (λ = 532 nm, duration = 5 ns, energy = 0.2 mJ). Blue and orange arrows: ΔM jumps of the magnetic moment following light pulses (green wavy arrows) for various initial locations of M on the hysteresis curve. (Some arrows have not been drawn for clarity.)

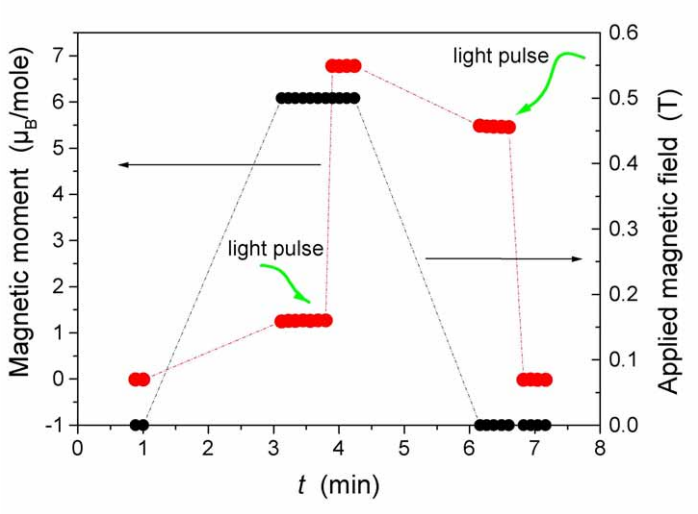


Figure S7. Chronogram of the magnetization at 2.0 K for Mn-OAc

Magnetization of the sample (red dots, left scale) and applied magnetic field (black dots, right scale) versus time. When the magnetized sample ($\mu_0 H$ = 0.5 T) is irradiated at t~3.8 min, a positive relative change of magnetization $\Delta M/M$ is induced, and the final state M=M_{limit} is stable. At t~4.3 min H is reduced to zero and M decreases accordingly ; a pulse of light can then trigger a drop of M to zero.

References

1- K. Awaga, Y. Suzuki, H. Hachisuka, K. Takeda, J. Magneto-structural correlation in the Jahn–Teller isomers of Mn_{12}, *J. Mater.Chem.*, 2006, **16**, 2516 – 2521

2- The gallic acid derivative was prepared according to the method described in : Johansson, G., Percec, V. Ungar, G. & Zhou, S.P. Fluorophobic Effect in the Self-Assembly of Polymers and Model Compounds Containing Tapered Groups into Supramolecular Columns, *Macromolecules*, 1996, **29**, 646-650

3- Oppenheimer, S.M., Sushkov, A.B., Musfeldt, J.L., Achey, R.M. & Dalal, N.S. Diffuse optical excitations in Mn_{12}-acetate., *Phys. Rev. B*, 2002, **65**, 054419.

4- McInnes, E.J.L., Pidcock, E., Oganesyan, V.S., Cheesman, M.R., Powell, A.K. & Thomson, A.J. Optical detection of spin polarization in single-molecule magnets $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$, *J. Am. Chem. Soc.*, 2002, **124**, 9219