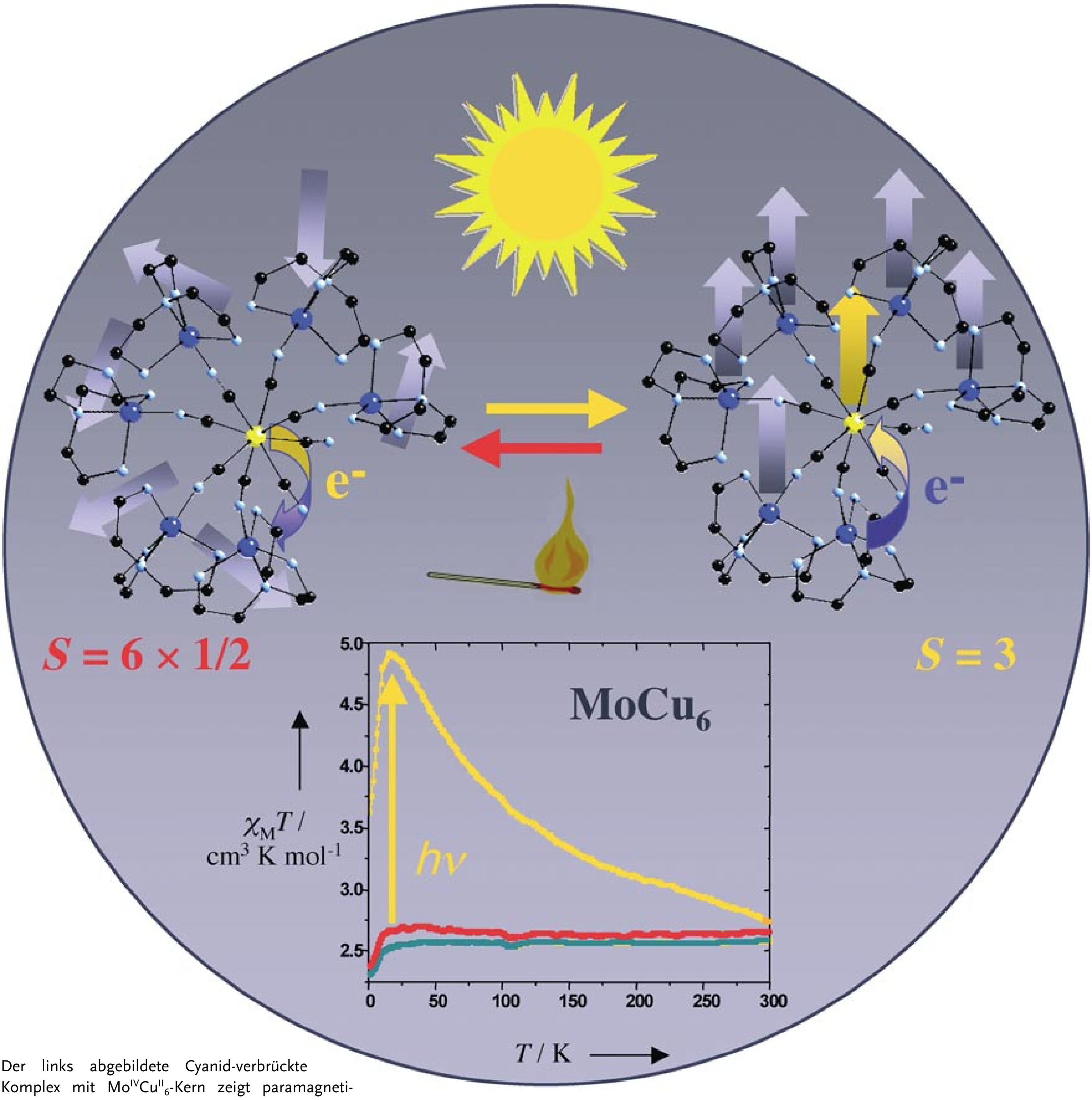
Zuschriften



Der links abgebildete Cyanid-verbrückte Komplex mit $Mo^{IV}Cu^{II}_6$-Kern zeigt paramagnetisches Verhalten mit $S = 6 \times 1/2$ und geht bei Bestrahlung mit Licht durch intramolekularen Elektronentransfer in einen High-Spin-Komplex mit $Mo^{V}Cu^{I}Cu^{II}_5$-Kern und $S = 3$ über. Dieser Zustand ist bis 280 K metastabil, und der photomagnetische Effekt ist thermisch reversibel. Weiteres erfahren Sie in der Zuschrift von V. Marvaud, C. Mathonière et al. auf den folgenden Seiten.

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Single-Molecule Magnets

Reversible Photoinduced Magnetic Properties in the Heptanuclear Complex $[Mo^{IV}(CN)_2(CN{-}CuL)_6]^{8+}$: A Photomagnetic High-Spin Molecule**

*Juan Manuel Herrera, Valérie Marvaud,**
Michel Verdaguer, Jérôme Marrot, Marguerite Kalisz,
*and Corine Mathonière**

Dedicated to Professor Jean-Pierre Launay
on the occasion of his 60th Birthday

Switching effects operating at the molecular level are currently subject to intense research efforts.[1] Amongst the various triggering media usually considered, light is assuredly one of the most often utilized.[2] Amongst possible physical molecular properties that may be switched, magnetism[3] is one of the most common.[4] Basic photoinduced processes mostly involved in photomagnetic materials are Light-Induced Excited Spin-State Trapping (LIESST)[5] or spin alignment,[6] changes in intramolecular exchange interactions,[7] spin crossover resulting from electron transfers (Co–Fe Prussian blue analogues[8]), or peripheral ligand(s) isomerization (Ligand-Driven Light-Induced Spin Change, LD–LISC).[9] Recent works have also been devoted to photomagnetic materials based on octacyanometalate precursors,[10] well known since the 1960s for their photoreactivity.[11] Herein we report the first photomagnetic high-spin molecule, which was obtained by combining the two following approaches. Some of us (Mathonière and co-workers) have previously suggested the possibility of photoinduced electron transfers within mixed Mo^{IV}/Cu^{II} compounds[12] while the others (Marvaud et al.) have demonstrated the feasibility of designing and synthesizing hetero-polynuclear complexes of controlled shape (anisotropy), nuclearity, and magnetic properties.[13] The resulting compound (**1**; see below) is of main interest in the field of single-molecule magnets (SMM).[14] Indeed, anisotropic high-spin species are appealing candidates to study the reversal of the magnetization in a magnetic field and might be used, in future, as new components for information storage at the molecular scale. These new species can also be viewed as model compounds to better understand related 3D photomagnetic materials, by evaluating the exchange coupling. It is worth noting that, up to now, the most important photomagnetic effect ever observed in such a type of compounds was in a Co–Fe Prussian blue analogues,[8] with a relaxation temperature of 120 K.

In the continuation of the synthetic strategy previously described for polynuclear complexes based on hexacyanometalate chemistry,[13,15] we have selectively obtained a heptanuclear complex built from an octacyanomolybdate(IV) core and Cu^{II} building blocks. This $[Mo(CN)_2(CN{-}CuL)_6]^{8+}$ polynuclear complex, **1**, was formed by treating potassium octacyanomolybdate(IV) with a mononuclear copper(II) complex generated in situ from the tris(2-aminoethyl)amine terminal ligand L and Cu^{II} perchlorate salt. Partial evaporation of mother liquor led to green needles soluble in water and common organic solvents.

The complex has been fully characterized and its identity confirmed. On the IR spectrum, the intense distinctive bands of ClO_4^- (around $1090\,cm^{-1}$) revealed the presence of cationic complexes. In the range of $2200–2000\,cm^{-1}$, two types of cyanide asymmetric stretching bands are observed: a strong band at $2158\,cm^{-1}$, assigned to bridging cyanides and a weak band at $2128\,cm^{-1}$, attributed to singly bound cyanides. The ESMS spectrum showed major peaks at $m/z = 1079.7$ and 490.1 ascribed to $\{[Mo(CN)_2(CN{-}CuL)_6](ClO_4)_6\}^{2+}$ and $\{[Mo(CN)_2(CN{-}CuL)_6](ClO_4)_4\}^{4+}$ respectively, which also indicates that the complex is stable in solution.

X-ray analysis reveals that **1** crystallizes in monoclinic space group, Pn ($Z = 2$). Two heptanuclear complexes (Figure 1), 16 perchlorate ions and 9 water molecules are present in the asymmetric unit, which corresponds to 255 non-hydrogen atoms. Each $[Mo(CN)_2(CN{-}CuL)_6]^{8+}$ entity is formed by the octacyanomolybdate core, the molydenum center being in an dodecahedral environment with six copper(II) ions bounded to six cyanide nitrogen atoms. Two cyanide ligands are end-on coordinated. The copper ions are in a trigonal-bipyramid environment, in which L plays the role of blocking ligand. Cyano bridges appear distorted with Mo-C-N angles ranging from 170.0° to 179.0°, and the C-N-Cu angles range from 149.3° to 172.5°. The shortest Mo–Mo distance between two neighboring molecules is 13.05 Å.

UV/Vis spectra recorded both in the solid state and for aqueous solution show similar features, including the following bands (λ nm [$\varepsilon\,M^{-1}\,cm^{-1}$]) at 242 [36000], 270 [27800], 680 [410] and 844 [1075]. These features, characteristic of the two individual $[CuL]^{2+}$ and $[Mo(CN)_8]^{4-}$ chromophoric fragments,[16] are attributed to d–d and metal-to-ligand charge transfer (MLCT) electronic transitions. Of note, an additional band at 440 nm ($\varepsilon = 660\,M^{-1}\,cm^{-1}$) is detected and assigned to an intervalence Mo–Cu transition (metal-to-metal charge

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[*] J. M. Herrera, Dr. V. Marvaud, Prof. M. Verdaguer
Laboratoire de Chimie Inorganique et Matériaux Moléculaires
CNRS, UMR 7071
Université Pierre et Marie Curie
75252 Paris Cedex 05 (France)
Fax: (+33) 144-273-841
E-mail: marvaud@ccr.jussieu.fr

M. Kalisz, Dr. C. Mathonière
Institut de Chimie de la Matière Condensée de Bordeaux
CNRS UPR 9048
87, avenue du Docteur Albert Schweitzer, 33 608 Pessac (France)
Fax: (+33) 556-842-649
E-mail: mathon@icmcb.u-bordeaux.fr

Dr. J. Marrot
Institut Lavoisier
Université Versailles Saint-Quentin
45, avenue des Etats-Unis, 78035 Versailles (France)

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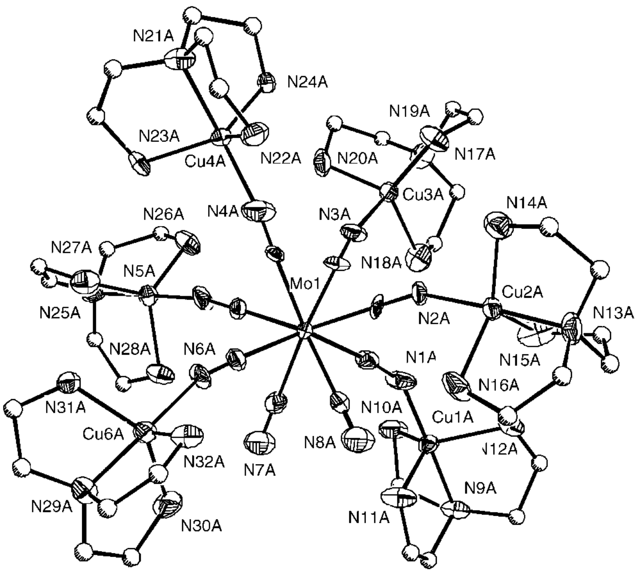

Figure 1. X-ray crystal structure (ORTEP drawing) of one of the two $[Mo(CN)_2(CN{-}CuL)_6]^{8+}$ entities with thermal ellipsoids set at 30%. Hydrogen atoms, crystallization solvents and counterions are omitted for clarity.

transfer, MMCT). These results are consistent with electrochemical data. Thus, the reversible oxidation of the molybdenum(IV/V) core within **1** is observed at +0.70 V versus the saturated calomel electrode (SCE) in acetonitrile, close to that obtained for the $[Mo(CN)_8]^{4-}$ precursor (+0.78 V vs SCE). The difference can be rationalized in terms of an increased electron-pair donation from Cu^{II} fragments to the molybdenum. In the reduction part of the cyclic voltammogram, no wave characteristic of the $Cu^{II/I}$ and $Mo^{IV/III}$ couples could be detected in the potential range investigated (limited by copper deposition).

The magnetic properties of compound **1** show that the $[Mo^{IV}(CN)_2(CN\text{-}Cu^{II}L)_6)]^{8+}$ complex, behave as six isolated paramagnetic centers, as expected for a diamagnetic Mo^{IV} center surrounded by six Cu^{II} cations. $\chi_M T$ is constant (2.5 $cm^3 mol^{-1} K$ down to 20 K; χ_M is the molar magnetic susceptibility) in agreement with six isolated Cu^{II} (the theoretical value is 2.48 for six independent spin 1/2 and $g = 2.2$; g is the g factor). At low temperature, below 20 K, the curve decreases, which indicates antiferromagnetic intramolecular interactions between the spin carriers, as observed in $\{CoCu_6\}$ or related compounds.[13] Upon irradiation with blue light (406–415 nm), magnetic susceptibility progressively changed: after 10 h of irradiation at 10 K, the $\chi_M T$ value increased up to 4.8 $cm^3 mol^{-1} K$. The light was then switched off. In heating mode, $\chi_M T$ first increased in the range from 5 to 16 K until it reached a plateau value of 5 $cm^3 mol^{-1} K$; this value decreased continuously as the temperature was raised to 300 K, with values always higher than those obtained for the nonirradiated compound. The two $\chi_M T$ versus T curves join at a temperature close to 300 K. After 1 h at room temperature, χ_M was measured in cooling mode. A constant $\chi_M T$ value was observed (2.6 $cm^3 mol^{-1} K$), thus showing unambiguously that the process is thermally reversible (Figure 2).

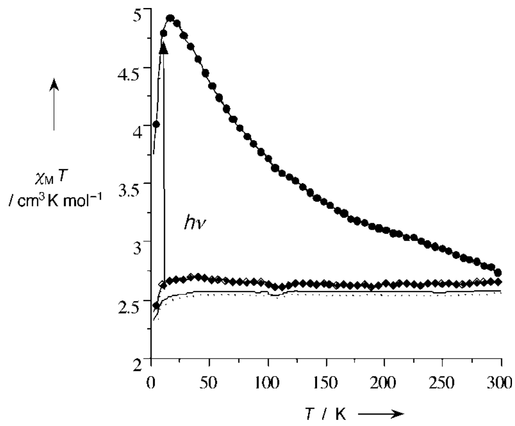

Figure 2. Thermal dependence of the $\chi_M T$ product for **1**: (·) before irradiation, (●) after irradiation, (◆) after irradiation and $T > 300$ K.

The photomagnetic effect may be observed as well in the magnetization curves, performed at 5 K and shown in Figure 3. Before irradiation, the data correspond to six isolated spin $S = 1/2$ (Cu^{II} ions). After irradiation, the magnetization data shows a value at 5 μ_B at 50 kOe. After reaching $T = 300$ K and cooling, the magnetization curve is similar to that obtained for the nonirradiated species, giving a further demonstration of the switching effect.

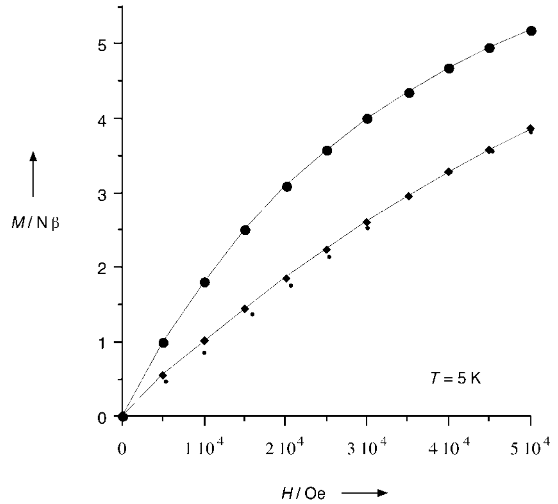

Figure 3. Field dependence of the magnetization of **1** at 5 K: (·) before irradiation, (●) after irradiation, (◆) after irradiation and $T > 300$ K.

These results are explained by the photoinduced formation of a high-spin molecule with ferromagnetic interaction between the spin carriers. Agreement between experimental data after irradiation and the calculated Brillouin function is obtained for $S = 3$, assuming that the ground state only is populated at $T = 5$ K and that 75% of the product has been transformed. This spectacular effect may be rationalized by an electron transfer from Mo^{IV} to Cu^{II} and the formation of paramagnetic centered (Mo^V) species: $Mo^V Cu^I Cu^{II}_5$. Irradiation by using wavelengths close to the intervalence band

(MMCT) photoinduces an electron transfer from the diamagnetic Mo^{IV} center (d^2, $S=0$) to one of the peripheral Cu^{II} ions. This electron transfer generates a paramagnetic Mo^{V} (d^1, $S=1/2$) center and one diamagnetic Cu^{I} (d^{10}, $S=0$) ion. Thus, cyano-mediated ferromagnetic interactions are switched on between the Mo^{V}, $S=1/2$, and the remaining five Cu^{II}, spin 1/2, in the photo-induced species Mo^{V}Cu^{I}Cu$^{II}{}_5$, which leads to a high-spin molecule with $S=3$. The photoinduced magnetic effect is thermally reversible and reproducible (Figure 4). The complete return to the initial state operates at temperatures close to room temperature. The high relaxation temperature indicates that the photoinduced metastable state is related to significant local reorganization of the coordination sphere around the Cu^{I} ion. This is relevant considering the usual geometry of the Cu^{I} ion (tetrahedral) compared to Cu^{II} ion (trigonal-bipyramid) and the flexibility of the L ligand.

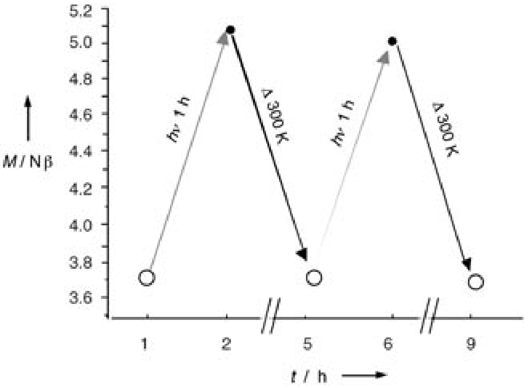

Figure 4. Study of the reversibility: variation of the magnetization of **1** ($H=50\,000$ Oe): ● after irradiation and ○ after irridation and thermal treatment ($T>300$ K).

In summary, **1** is the first photoinduced high-spin molecule. Calculations are in progress to evaluate the exchange coupling parameter while taking into account the thermal depopulation of the metastable state. Preliminary results obtained by using the isotropic Heisenberg Hamiltonian $\mathcal{H} = -J_{\mathrm{Mo/Cu}}\, S_{\mathrm{Mo}} \sum i\, S_i$ (i ranges from 1 to 5) give an exchange coupling value $J>100\ \mathrm{cm}^{-1}$ and a Landé factor $g=2.08$. The J value is higher than that of the {CrCu$_6$} compound ($J=+45\ \mathrm{cm}^{-1}$)[13] as predicted for compounds of second- and third-row transition-metal cations with diffuse d valence orbitals.[17] Other work is planned to obtain more convincing evidence of the presence of the Cu^{I} and Mo^{V} ions (such as X-Ray diffraction on an irradiated single crystal, Polarized Neutron diffraction, optic and vibrational spectroscopy). We shall study the optical reversibility and the SMM behavior and evaluate the photomagnetic properties of other complexes of the octacyanometalate family, specially the {WCu$_6$} analogue. The present study opens the field of photomagnetic high-spin molecules (higher than 3) and opens the way to photomagnetic single-molecule magnets.

Experimental Section

A solution of tris(2-amino)ethylamine (0.95 g, 6.5 mmol) in water/acetonitrile (1:1, 10 mL) was added to a solution of copper perchlorate (2.29 g, 6 mmol) in water (10 mL). The mixture was stirred for less than 5 min before the addition of hexacyanomolybate(IV) potassium salt (0.497 g, 1 mmol) dissolved in a minimum of water. After filtration, the solution was left standing for 24 h, which lead the formation of green needles. Yield 52 %. Elemental analysis calcd (%) for $C_{44}H_{118}MoCu_6N_{32}Cl_8O_{37}$: C 21.12, H 4.60, N 17.65, Mo 3.83, Cu 14.22, Cl 11.81; found: C 21.58, H 4.86, N 18.31, Mo 3.92, Cu 15.57, Cl 11.58. IR (KBr) 2158 and 2128 cm^{-1} (CN asymmetric stretching).

Crystal data and structure refinements for **1**: A green needle ($0.50\times0.30\times0.10$ mm) was analyzed with a Siemens SMART three-circle diffractometer equipped with a CCD bidimensional detector with Mo$_{K\alpha}$ monochromatized radiation ($\lambda=0.71073$ Å). Monoclinic, space group Pn, $a=24.7473(3)$ Å, $b=14.4050(1)$ Å, $c=30.0287(2)$ Å, $\beta=108.742(1)°$, $V=10\,137.15(16)$ Å^3, $Z=2$, $\rho_{\chi\mathrm{alc}}=1.598\ \mathrm{g\,cm^{-3}}$, $\mu(\mathrm{Mo_{K\alpha}})=1.653\ \mathrm{mm}^{-1}$, $F(000)=4996$, 46 001 reflections measured, of which 21 204 were independent, 1501 refined parameters, $R_{1=}0.0845$, $wR_{2=}0.2092.$, GOF = 0.963; max/min residual electron density 1.030/−0.587 e Å^{-3}. Data reduction was performed with the SAINT software. The absorption correction was based on multiple and symmetry-equivalent reflections in the data set by using the SADABS[18] program based on the method of Blessing. The structures were solved by direct methods and refined by full-matrix least-squares by using the SHELX-TL program.[19] CCCDC-203098 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

Magnetic studies were carried out with a Quantum Design MPMS-5S magnetometer working in the dc mode. The measurements were performed in the 5–300 K range with a magnetic field of 20 000 Oe. The photomagnetic experiments were performed with a Kr$^+$ laser coupled through an optical fiber directed into the cavity of the superconductivity quantum interference induction device (SQUID). Powdered samples were laid down on a diamagnetic sample holder (Magnetization (emu) = -2.62×10^{-4}) as thin layers (weight 0.68 mg) to avoid surface effects during illumination. The diamagnetic contribution and the weight were estimated by comparing the magnetization curves (5 K and versus temperature) before irradiation with the curves recorded in a routine magnetic experiment (20 mg of sample loaded into gel caps). The samples were irradiated continuously by using different multilines (406–415 nm and 337–356 nm) under a magnetic field of 20 kOe at 10 K. The effective power of the laser light received by the sample was measured at 3 mW cm^{-2} for $\lambda=337$–356 nm and 7 mW cm^{-2} for $\lambda=406$–415 nm. Magnetic properties were recorded before and after irradiation, in each case the light was turned off to avoid thermal inhomogeneities. The cycle in temperature corresponds to a complete study with different steps: 1) magnetization at 5 K first, and then measurement with the sample is warmed to 300 K, 2) cooling of the sample to 10 K in one hour and half with no measure, 3) new magnetization at 5 K.

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