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Synthesis, Structures, and Magnetic Properties of Two Coordination Assemblies of Mn(III) Single Molecule Magnets Bridged via Photochromic Diarylethene Ligands

Ahmed Fetoh,[†] Goulven Cosquer,[‡] Masakazu Morimoto,[§] Masahiro Irie,[§] Ola El-Gammal,[†] Gaber M. Abu El-Reash,[†] Brian K. Breedlove,[‡] and Masahiro Yamashita*[,‡,∥,⊥]

[†]Department of Chemistry, Faculty of Science, Mansoura University, Mansoura, Egypt

[‡]Department of Chemistry, Graduate School of Science, Tohoku University, 6-3 Aramaki-Aza-Aoba, Aoba-ku, Sendai 980-8578, Japan

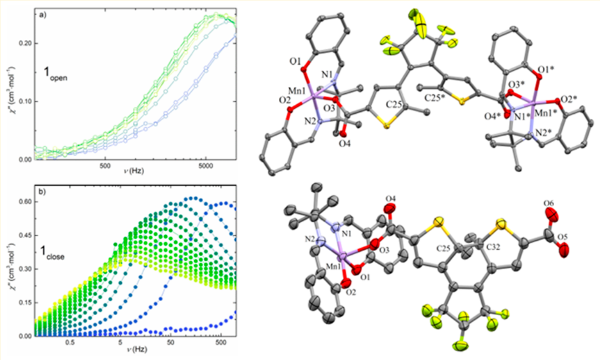
[§]Department of Chemistry and Research Center for Smart Molecules, Rikkyo University, Nishi-Ikebukuro 3-34-1, Toshima-ku, Tokyo, Japan

[∥]WPI, Advanced Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-Ku, Sendai 980-8577, Japan

[⊥]School of Materials Science and Engineering, Nankai University, Tianjin 300350, China

Supporting Information

ABSTRACT: Two new coordination assemblies were prepared by combining the open and close forms of 1,2-bis(5-carboxyl-2-methyl-3-thienyl)perfluorocyclopentene (H_2dae) with $[Mn_2(saltmen)_2(H_2O)_2](PF_6)_2$, where H_2saltmen = 2,2′-((1*E*,1′*E*)-((2,3-dimethylbutane-2,3-diyl)bis(azaneylylidene)) bis(methaneylylidene))diphenol. From X-ray diffraction analyses, the complexes had the following formula: $[Mn_2(saltmen)_2$(dae-open)] (**1**$_{open}$) and [Mn(saltmen)(dae-close)]·H_2O·Et_3N (**1**$_{close}$). Both complexes crystallized in the *C*2/*c* monoclinic space group. In **1**$_{open}$, dae-o^{2-} behaves as a bidentate ligand attached to the outer Mn-saltmen monomer via the oxygen atom of carboxylato groups, whereas in **1**$_{close}$, the dae-c^{2-} ligand behaves as a monodentate ligand attached to the external Mn-saltmen dimer by only one carboxylato group of the photochromic ligand. The complexes showed reversible photochromic responses to UV/vis light and showed single-molecule magnet-like behavior. The relaxation times and energy barriers of the metal complexes are clearly affected by UV/vis irradiation.



INTRODUCTION

Single-molecule magnets (SMMs) show characteristic magnetic properties, such as slow relaxation and molecular level magnetization. The magnetization is retained even in the absence of an applied field, and thus, SMMs can be utilized in information storage at the molecular level or in spintronic devices.[1] In order to improve the SMMs, their magnetic properties must be controllable by using various external stimuli, like light when a photochromic ligand is used.[2] Diarylethene (dae) molecules are favorable photochromic ligands due to their thermal stability in open and close forms, their fast photochromic responses, and their fatigue resistances.[3−5] Thus, dae is a promising candidate for use in optical storage and photonic switch devices.[6−11] By combining dae and various metal salts, a variety of supramolecular frameworks, of which photoresponsive performances can be controlled by changing the metal or the counteranion, can be obtained. Light irradiation generates a different isomer with different properties, which are related to the type of metal salt used and the topology of the newly formed complex.[12−16] In 2007, the magnetic properties of the first one-dimensional (1D) photoactive Co(II) complex with the dae derivatives ending with two carboxy groups were reported. However, the authors provide no evidence showing that the magnetic susceptibilities are affected by light irradiation.[17] In 2009, photoactivity of two other 1D assemblies of Mn_4 SMMs with *S* = 9 was investigated. When the assemblies are irradiated with visible light, generating the open form of the photochromic ligand, the magnetic properties change.[12] Three years later, two photoactive complexes with mixed metal Cu^{II}−Tb^{III} SMMs and the dae ligand were reported, and the magnetic properties of the closed isomer, which formed during light irradiation, were shown to be different than those of the open form.[13] Subsequently, for two two-dimensional (2D) coordination polymer complexes, in which Ln_2 units are bridged by

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the terminal carboxylato groups in grid-like frameworks, the quantum-tunneling relaxation mechanism is affected by photoisomerization.[18,19] Recently, the first reversible switching on and off of the SMM behavior, as a result of the combination of photoactive dae with an Mn(salen) complex, has been reported.[20] These advances have established the ability of the photochromic molecules to modulate the magnetic behavior of metal complexes.

To extend this work, we combined $[Mn(saltmen)(H_2O)]_2(PF_6)_2$, as the SMM unit, with the open and close forms of dae (referred as dae-o and dae-c, respectively) to yield $[Mn_2(saltmen)_2(dae\text{-}o)]$ ($\mathbf{1}_{open}$) and $[Mn(saltmen)(dae\text{-}c)]\cdot H_2O\cdot Et_3N$ ($\mathbf{1}_{close}$). In this study, we report the syntheses, crystal structures, magnetic properties, and photoswitchable behavior of $\mathbf{1}_{open}$ and $\mathbf{1}_{close}$ in the solid state.

EXPERIMENTAL SECTION

All chemicals and solvents were purchased from Tokyo Chemical Industry Co. Ltd. or Wako Pure Chemical Industries Ltd. and used as received. H_2dae-c, H_2dae-o, and $[Mn(saltmen)(H_2O)]_2(PF_6)_2$ were synthesized following published methods.[21,22] All experimental manipulations were done in the dark to prevent any photoisomerization.

Synthesis of ($\mathbf{1}_{open}$). To a solution of $[Mn(saltmen)(H_2O)]_2(PF_6)_2$ (92.90 mg, 0.086 mmol) in 10 mL of methanol, a solution of H_2dae-open (20 mg, 0.043 mmol) and triethylamine (4.34 mg, 0.2 mmol) in 5 mL of methanol was added. The resulting solution was stirred for 15 min at 50 °C and filtered. Dark-brown crystals of $\mathbf{1}_{open}$ suitable for X-ray structure determination were obtained by slow evaporation of the filtrate at room temperature over 4 weeks. The crystals were gathered by suction filtration. Anal. Calcd (%) for $C_{57}H_{52}N_4F_6Mn_2O_8S_2$: C 56.62; H 4.34; N 4.63. Found: C 56.56; H 4.28; N 4.58.

Synthesis of ($\mathbf{1}_{close}$). This synthesis follows the same procedure as that for $\mathbf{1}_{open}$ except that H_2dae-c (18.23 mg, 0.04 mmol) was used as the starting material instead of H_2dae-open. Dark-brown crystals of $\mathbf{1}_{close}$ suitable for X-ray single determination were obtained after 10 days. Anal. Calcd (%) for $C_{43}H_{47}N_3F_6MnO_7S_2$: C 54.31; H 4.98; N 4.42. Found: C 54.40; H 4.54; N 4.48.

Physical Measurements. Solid-state UV/vis absorption spectra were measured using a KBr matrix on a Shimadzu UV-3100 spectrophotometer. Magnetic susceptibilities of crunched crystal were measured on a Quantum Design MPMS-5S superconducting quantum interference device (SQUID) magnetometer in applied magnetic fields of 1000 Oe in the range of 1.8−300 K. Experimental data were corrected for the sample holder contribution, and the diamagnetic contribution of the sample was calculated from Pascal's constants.[23] Dynamic susceptibilities measurements were collected with a 3 Oe oscillating magnetic field with or without a static magnetic field. The dynamic susceptibilities of $\mathbf{1}_{open}$ were required on a Quantum Design PPMS-6000 physical property measurement system with an oscillating magnetic field amplitude of 3 Oe below 1000 Hz and 1 Oe over 1000 Hz with or without a static magnetic field. Freshly prepared crystalline samples were used for the magnetic measurements. Irradiation has been performed with a Asahi Spectra Max-303.

Single-Crystal X-ray Diffraction. Single-crystal crystallographic data were collected at 103 K on a Rigaku Saturn70 CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 nm) produced by a VariMax microfocus X-ray rotating anode source. Data processing was performed using the CrystalClear crystallographic software package.[24] The structures were solved by using direct methods via SIR-92 or SIR-2011[25] and refined using the full-matrix least-squares technique included in SHELXL-2013.[26] The final cycles of full-matrix least-squares refinements on F^2 converged with unweighted and weighted agreement factors of $R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$ ($I > 2.00\sigma(I)$ for R_1), and $wR_2 = [\Sigma w(F_0^2 - F_c^2)^2]/\Sigma w(F_0^2)^2]^{1/2}$ (all reflections), respectively. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms were set in calculated positions and refined using a riding model with a common fixed isotropic thermal parameter (excepted for solvent water). CCDC 1866760 and 1866761.

RESULTS AND DISCUSSION

Crystal Structure Analysis. $\mathbf{1}_{open}$ crystallized in the monoclinic $C2/c$ space group (Table 1) with one $[Mn(saltmen)]^+$ and a half dae-o^{2-} per asymmetric unit. The dae-o^{2-} behaves as a bridging ligand between two $[Mn(saltmen)]^+$ monomers (Figure 1). The Mn^{III} ion is coordinated by the

Table 1. Crystallographic Data for $\mathbf{1}_{open}$ and $\mathbf{1}_{close}$

	$\mathbf{1}_{open}$	$\mathbf{1}_{close}$
formula	$C_{57}H_{52}N_4F_6Mn_2O_8S_2$	$C_{43}H_{47}N_3F_6MnO_7S_2$
formula weight	1209.05	950.91
temperature (K)	103.15	103.15
crystal system	monoclinic	monoclinic
space group	$C2/c$	$C2/c$
a (Å)	21.131(12)	24.91(3)
b (Å)	19.599(11)	21.46(3)
c (Å)	13.925(8)	18.39(2)
α (deg)	90	90
β (deg)	112.732(6)	98.650(14)
γ (deg)	90	90
V (Å^3)	5319.02	9718.90
Z	4	8
D_{calc} (g/cm^3)	1.51	1.298
F_{000}	2488	3936
$\mu_{Mo-K\alpha}$ (mm^{-1})	0.635	0.428
data measured	15085	16622
data unique	5072	6317
number of variables	347	655
R_1	0.0537	0.0843
wR_2	0.1411	0.2223
goodness of fit	1.059	1.149

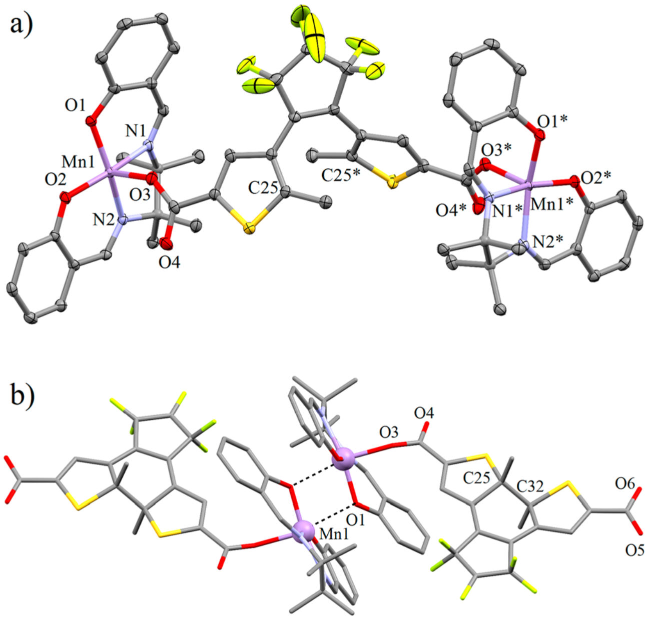

Figure 1. Diagram of (a) $\mathbf{1}_{open}$ and (b) $\mathbf{1}_{close}$. Hydrogen atoms and solvent molecules were omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $\mathbf{1}_{open}$ and $\mathbf{1}_{close}$

distances (Å)	$\mathbf{1}_{open}$	$\mathbf{1}_{close}$	angles (deg)	$\mathbf{1}_{open}$	$\mathbf{1}_{close}$
Mn1−O1	1.882(3)	1.986(5)	O1−Mn1−O2	91.4(1)	95.5(2)
Mn1−O2	1.875(3)	1.943(4)	O1−Mn1−O3	95.5(1)	90.0(2)
Mn1−O3	2.050(3)	2.170(5)	O1−Mn1−N1	90.1(1)	90.7(2)
Mn1−N1	1.991(3)	2.049(6)	O1−Mn1−N2	162.0(1)	166.2(2)
Mn1−N2	1.987(3)	2.056(5)	O2−Mn1−O3	100.1(1)	89.8(2)
C25···C25*	3.609(6)		O2−Mn1−N1	165.5(1)	173.6(2)
intramolecular $Mn^{III}\cdots Mn^{III}$	14.335(7)		O2−Mn1−N2	93.0(1)	92.8(2)
intermolecular $Mn^{III}\cdots Mn^{III}$	6.274(3)		O3−Mn1−N1	94.1(1)	91.8(2)
intradimer $Mn^{III}\cdots Mn^{III}$		3.531(3)	O3−Mn1−N2	100.9(1)	101.0(2)
intradimer $Mn^{III}\cdots O$		2.539(5)	N1−Mn1−N2	81.5(1)	80.9(2)

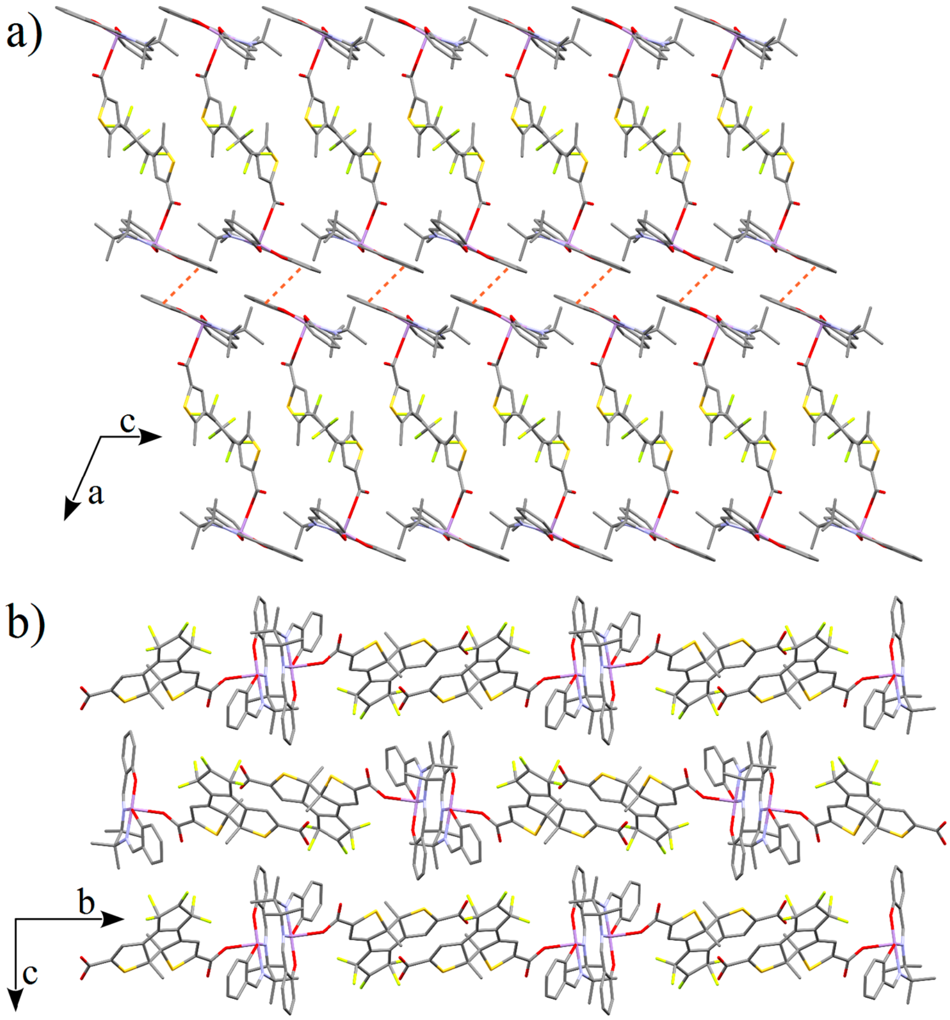

Figure 2. Packing diagram of (a) $\mathbf{1}_{open}$ with the dash lines representing the $\pi-\pi$ interactions and (b) $\mathbf{1}_{close}$. Hydrogen atoms and solvent molecules were omitted for clarity.

tetradentate saltmen^{2-} ligand and by one oxygen of the carboxylato group of the dae-o^{2-} ligand to form a square pyramidal coordination geometry. The Mn^{III} ion is located 0.259 Å out of the average plane of the square base of the coordination sphere (Table 2). The Mn−N and Mn−O bond lengths are consistent with a high-spin Mn^{III} ion.[27] The long Mn−O3 bond length (2.050(3) Å), compared to other Mn−O bonds (~1.88 Å), is due to Jahn−Teller distortion. The C25−C25* distance (3.609(6) Å) facilitates isomerization of the dae-o^{2-} ligand.[28] The molecules interact though $\pi-\pi$ interactions of the benzene rings (3.329(6) Å) without intermolecular Mn−O interactions (Figure 2). The intramolecular and shortest intermolecular $Mn^{III}\cdots Mn^{III}$ distances were calculated to be 14.335(7) and 6.274(3) Å.

$\mathbf{1}_{close}$ crystallized in the $C2/c$ space group with one $[Mn(saltmen)]^{+}$, one dae-c^{2-}, one protonated triethylamine, and one water molecule per asymmetric unit. Although both carboxylato groups of the dae-c^{2-} ligand are deprotonated, only one of them coordinates to the Mn^{III} ion. The Mn^{III} ion in $\mathbf{1}_{close}$ is hexa-coordinated with a distorted octahedral geometry with the square planar tetradentate saltmen ligand in the equatorial plan and dae-c^{2-} in the axial position. Intradimer

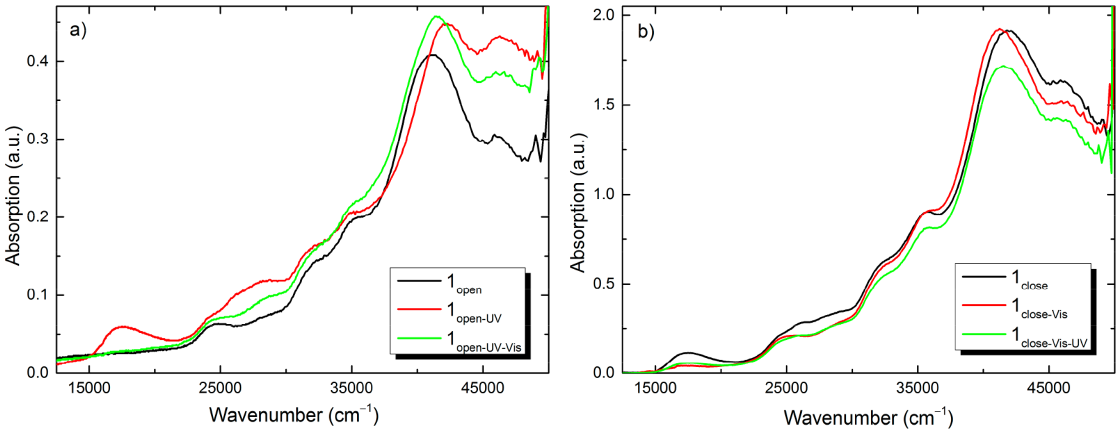

Figure 3. Solid UV−vis spectra of (a) $\mathbf{1}_{\mathbf{open}}$ and (b) $\mathbf{1}_{\mathbf{close}}$ before and after irradiating with UV light (λ = 365 nm) and visible light (λ > 480 nm).

$Mn^{III}\cdots O$ interactions (2.539(5) Å) between $[Mn(saltmen)]^+$ moieties and the phenoxo oxygen atom of the neighboring molecule complete the coordination sphere. The Mn^{III} ion is located 0.105 Å out of the average plane of the square base of the coordination sphere. Each $[Mn(saltmen)]^+$ dimer is separated from each other by dae-c^{2-} molecules. The hydrogen bonds among the triethylamine ligand, water molecule, and carboxylato group of the dae-c^{2-} ligand complete the structure.

Solid-State Optical Properties. The reversibility of the photoisomerization of the complexes was analyzed by using UV−vis spectroscopy as KBr pellets after irradiating with UV (λ = 365 nm) and visible lights (λ = 480 nm) (Figure 3). After irradiating $\mathbf{1}_{\mathbf{open}}$ with UV light (hereafter $\mathbf{1}_{\mathbf{open\text{-}UV}}$), the characteristic absorption of the close form around 17300 cm^{-1} was observed, and it disappeared after irradiation with visible light.[29] Similarly, the characteristic absorption for $\mathbf{1}_{\mathbf{close}}$ disappeared after irradiating it with visible light ($\mathbf{1}_{\mathbf{close\text{-}vis}}$), but it returned after UV irradiation. Both complexes can be reversibly photoisomerized in the solid state.

Magnetic Properties of $\mathbf{1}_{\mathbf{open}}$. The magnetic properties of freshly prepared crystalline samples of $\mathbf{1}_{\mathbf{open}}$ and $\mathbf{1}_{\mathbf{close}}$ were measured before and after light irradiation at room temperature for 24 h with 365 nm UV light and 480 nm visible light, respectively. χT values of grind polycrystalline samples of $\mathbf{1}_{\mathbf{open}}$ and $\mathbf{1}_{\mathbf{open\text{-}UV}}$ were measured in the temperature range of 2−300 K (Figure 4). The χT values of $\mathbf{1}_{\mathbf{open}}$ and $\mathbf{1}_{\mathbf{open\text{-}UV}}$ showed similar behavior. The χT values at 300 K of 6.42 and 6.57 $cm^3\cdot K\cdot mol^{-1}$, respectively, are slightly larger than the expected value for two noninteracting high-spin Mn^{III} ions (S = 2; 6.002 $cm^3\cdot K\cdot mol^{-1}$). This difference can be attributed to the presence of thermally independent paramagnetism, which can also explain the low slope observed between 25 and 300 K.[30] The drastic decrease in the χT value below 25 K was attributed to antiferromagnetic (AF) interactions between the ions. These AF interactions are more likely to be between the intermolecular Mn^{III} ions associated by π−π interactions ($Mn^{III}\cdots Mn^{III}$ = 6.3 A) than between the intramolecular ones linked by the long ligand ($Mn^{III}\cdots Mn^{III}$ = 14.3 A). The χT values for both complexes could be fitted with the Curie−Weiss law (eq 1). The Curie constants C were determined to be 6.410 and 6.534 $cm^3\cdot K\cdot mol^{-1}$, and the Weiss temperature θ was −0.55 and −0.52 K for $\mathbf{1}_{\mathbf{open}}$ and $\mathbf{1}_{\mathbf{open\text{-}UV}}$, respectively (Figure S1). The estimated values of C agree with the spin-only value for two high-spin Mn^{III} ions (6.11 $cm^3\cdot K\cdot mol^{-1}$), and the negative Weiss constant values indicates the presence of AF interactions. The magnetization of both complexes was the same with a spin-flip around 1.3 T and no saturation up to 5 T (Figure 5). This behavior is thought to be due to AF interactions or magnetic anisotropy. From the spin-flip field value (H_{ex}) in eq 2, the intensity of the mean interaction J was determined to be 0.749 and 0.752 K for $\mathbf{1}_{\mathbf{open}}$ and $\mathbf{1}_{\mathbf{open\text{-}UV}}$, respectively. These values are in the range of previously reported values (0.1−1.0 K).[31−35]

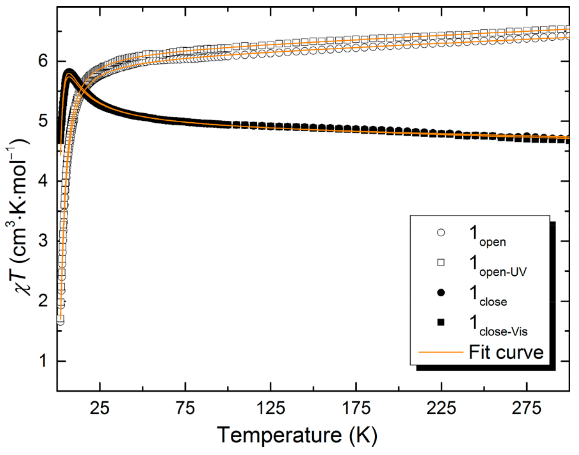

Figure 4. Comparison of the χT vs T plots.

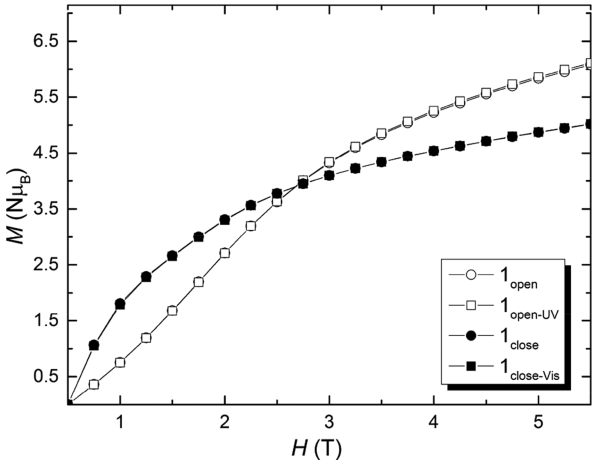

Figure 5. Comparison of the M vs H at 1.82 K.

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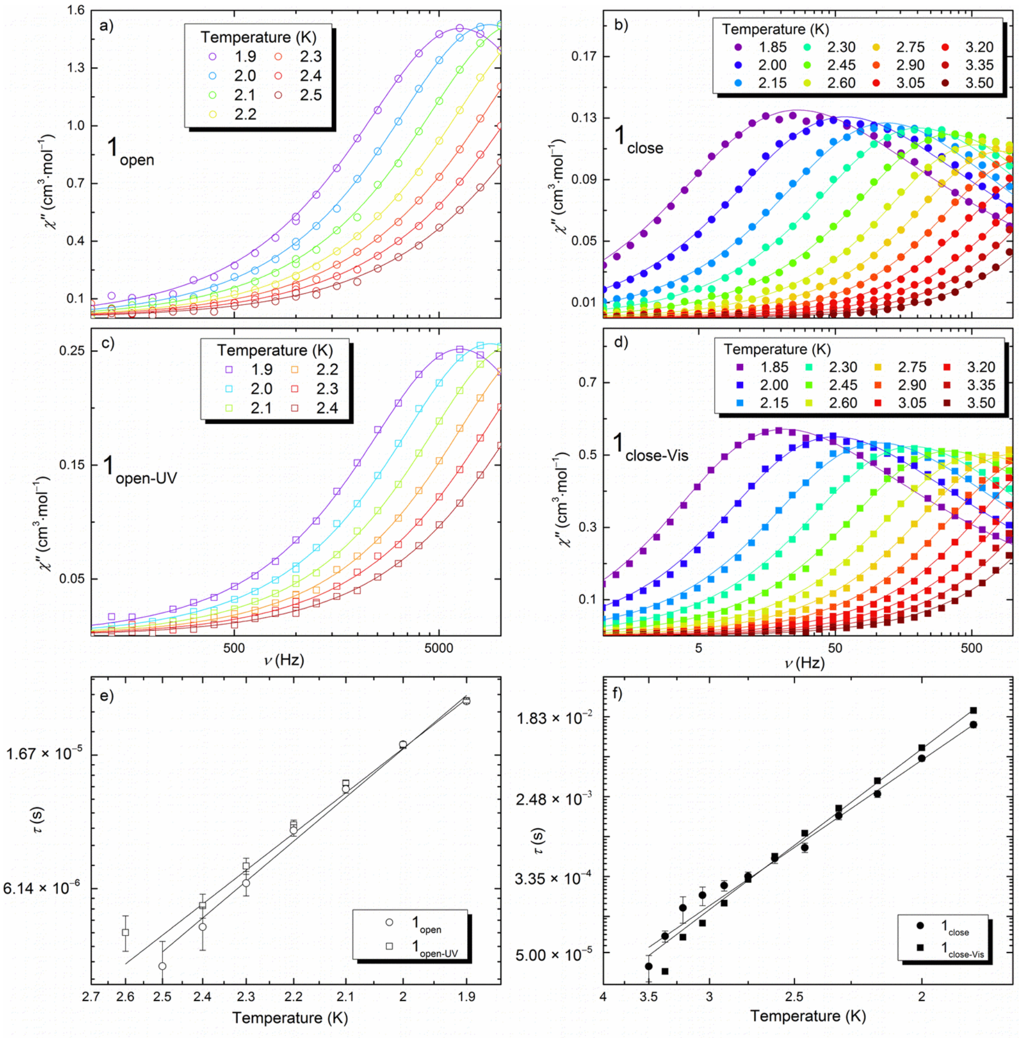

Figure 6. Frequency and temperature dependences of the out-of phase magnetic susceptibilities of (a) $\mathbf{1}_{\mathbf{open}}$, (b) $\mathbf{1}_{\mathbf{close}}$, (c) $\mathbf{1}_{\mathbf{open\text{-}UV}}$, and (d) $\mathbf{1}_{\mathbf{close\text{-}vis}}$. Arrhenius plots for (e) $\mathbf{1}_{\mathbf{open}}$ and $\mathbf{1}_{\mathbf{open\text{-}UV}}$ and (f) $\mathbf{1}_{\mathbf{close}}$ and $\mathbf{1}_{\mathbf{close\text{-}vis}}$. Fields of 1200 Oe for $\mathbf{1}_{\mathbf{open}}$ and $\mathbf{1}_{\mathbf{open\text{-}UV}}$ and 1000 Oe for $\mathbf{1}_{\mathbf{close}}$ and $\mathbf{1}_{\mathbf{close\text{-}vis}}$ were applied.

$$X = \frac{C}{T - \theta} \tag{1}$$

$$2|J|S^2 = gS\mu_B H_{ex} \tag{2}$$

The temperature dependence of the χT values of $\mathbf{1}_{\mathbf{close}}$ and $\mathbf{1}_{\mathbf{close\text{-}vis}}$ shows the same behavior. From the room temperature values of 4.71 and 4.68 cm^3·K·mol^{-1}, respectively, the χT values increased with a decrease in the temperature, reaching a maximum of 5.79 and 5.76 cm^3·K·mol^{-1}, respectively, at 7.5 K, and then decreased to 4.74 and 4.68 cm^3·K·mol^{-1}, respectively, at 2 K. This behavior is usual for $[\mathrm{Mn_2(saltmen)_2}]^{2+}$ units with ferromagnetic (F) coupling between the metal ions as well as zero-field splitting (ZFS) from the uniaxial anisotropy of the Mn$^{\mathrm{III}}$ ions.[21,36] Above 50 K, the magnetic data could be fitted with the Curie–Weiss law to afford C = 4.74 and 4.72 cm^3·K·mol^{-1} and θ = 0.52 and 0.54 K for $\mathbf{1}_{\mathbf{close}}$ and $\mathbf{1}_{\mathbf{close\text{-}vis}}$, respectively. The positive θ values indicate the presence of F coupling in these complexes. In magnetization versus field plots for $\mathbf{1}_{\mathbf{close}}$ and $\mathbf{1}_{\mathbf{close\text{-}vis}}$ at 1.82 K, neither spin-flipping nor saturation of the magnetization was observed. The absence of saturation was attributed to the magnetic anisotropy caused by Jahn–Teller distortion of the high-spin Mn$^{\mathrm{III}}$ coordination sphere.

In order to quantify the interactions, the magnetic susceptibilities were fitted by using the software PHI,[37] considering the two closest Mn$^{\mathrm{III}}$ ions as a dimer interacting through the Hamiltonian $H = -2J \cdot S_{\mathrm{Mn1}} \cdot S_{\mathrm{Mn2}}$, and a zJ' interaction between dimer and its environement. For $\mathbf{1}_{\mathbf{open}}$ and $\mathbf{1}_{\mathbf{open\text{-}UV}}$, g-factor values of 2.009 and 2.027, respectively, were obtained. Analysis showed that there were AF interactions with a J = −0.438 and −0.434 cm^{-1}, respectively, which are consistent with the values obtained using eq 2 and with the presence of a spin-flip around 1.3 T. For $\mathbf{1}_{\mathbf{close}}$ and $\mathbf{1}_{\mathbf{close\text{-}vis}}$, the g-factors were determined to be 1.797 and 1.803, respectively. The results showed that F interactions with J values of 0.651 and 0.617 cm^{-1}, respectively, were present. Small interdimer interactions (zJ') were included in the model for the complexes: AF interactions for $\mathbf{1}_{\mathbf{close}}$ and $\mathbf{1}_{\mathbf{close\text{-}vis}}$ (−0.051 and −0.053 cm^{-1}, respectively) and F ones for $\mathbf{1}_{\mathbf{open}}$ and $\mathbf{1}_{\mathbf{open\text{-}UV}}$ (0.057 and 0.058 cm^{-1}, respectively). This F interaction should be considered carefully as there is no other evidence of its presence. Using a more complex model may show a different result but also may result in an overfitting of the data.

Only a few examples of $(Mn^{III}-salen)_2$ clusters showing F interaction have been reported.[38−41] Bridging Mn−O−Mn angles of all $(Mn^{III}-salen)_2$ clusters are similar, meaning that they cannot be used to predict the nature of the magnetic interactions between the ions. The intradimer Mn···O distances (η) are longer when F interactions are present than they are when AF interactions are present. At the same time, F interactions occur in all Mn^{III} clusters with saltmen^{2-} ligands.[42−52] The F interactions can be understood by considering the degeneracy of the d orbitals of the Mn^{III} ions. The electronic configuration of the Mn^{III} ion with Jahn−Teller distortion is $(d_{xy})^1$, $(d_{yz})^1$, $(d_{xz})^1$, and $(d_{z2})^1$ which is a $^5B_1$ ground state.[53] The methyl group of the saltmen^{2-} ligand behaves as an electron donor and supports the Jahn−Teller orbital splitting. Thus, the F interactions between Mn^{III} ions are probably due to the orthogonality between the d_{z^2} and the dπ orbitals (d_{xy}, d_{yz}, and d_{xz}).

In Mn^{III} clusters with saltmen^{2-} ligands, the $Mn^{III}-O_{phen}$ distance (η) and the magnetic exchange parameter (J_F) are correlated by $J_F = 4.5724-1.1868\eta$.[54] With an η of 2.539 Å, F interactions with $J_F = 1.5591$ cm^{-1} were determined for $\mathbf{1}_{\mathbf{close}}$. This value is slightly larger than the value obtained by fitting the magnetic susceptibility data. When η was increased, the F interactions in the out-of-plane dimeric core decreased and disappeared when $\eta > 3.80$ Å.

Dynamic magnetic properties of microcrystalline samples of the complexes were performed. The susceptibilities were found to be frequency independent in the absence of an external static magnetic field (Figure S2), which was attributed to fast quantum tunneling of the magnetization (QTM). QTM could be suppressed by applying a magnetic field.[55] For $\mathbf{1}_{\mathbf{open}}$ and $\mathbf{1}_{\mathbf{close}}$, fields of 1200 and 1000 Oe, respectively, were applied to minimize QTM and direct relaxation processes (Figure S3). The relaxation times of the complexes basically did not change upon photoisomerization of the ligand (Figure 6). The complexes were determined to undergo Orbach magnetic relaxation processes (Table 3). The barrier for spin reversal (Δ_{eff}/k_B) and pre-exponential value (τ_0) obtained from Arrhenius plots are similar to other $[Mn^{III}_2]$ SMMs.[56−61] We concluded that UV light irradiation of the $\mathbf{1}_{\mathbf{open}}$ scarcely altered the magnetic behavior. However, the changes in Δ_{eff}/k_B and τ_0 reflect the change in the intermolecular environment caused by ring closure. Moreover, the π-conjugation of the dae moiety changed, affecting the superexchange cooperation between the two Mn^{III} ions. Upon photoisomerization the intensity of the out-of-phase and in-phase signal change with a larger signal for $\mathbf{1}_{\mathbf{open}}$ and $\mathbf{1}_{\mathbf{close\text{-}Vis}}$ than for $\mathbf{1}_{\mathbf{close}}$ and $\mathbf{1}_{\mathbf{open\text{-}UV}}$. The complexes with an open form of the ligand show a 4−6 times higher signal than complexes with a close form of the ligand. The reason for this difference remains unclear. Calculation could be necessary to explain such behavior.

Table 3. Summary for the Magnetic Relaxation Parameters

	$\mathbf{1}_{\mathbf{open}}$	$\mathbf{1}_{\mathbf{close}}$	$\mathbf{1}_{\mathbf{open\text{-}UV}}$	$\mathbf{1}_{\mathbf{close\text{-}vis}}$
field (Oe)	1200		1000	
	1200	1000		
Δ_{eff}/k_B (K)	15.89	18.10	13.96	19.91
τ_0 (s)	6.31×10^{-9}	2.59×10^{-7}	1.68×10^{-8}	1.16×10^{-7}

CONCLUSION

Two new complexes with open and close forms of a photochromic dae ligand and $[Mn_2(saltmen)_2(H_2O)_2](PF_6)_2$ were synthesized, and their properties were investigated by using UV/vis. spectroscopy and SQUID magnetometry. In $\mathbf{1}_{\mathbf{open}}$, the dae-o^{2-} behaves as a bridging ligand attached to two Mn-saltmen monomers via the oxygen atoms of carboxylato groups, whereas in $\mathbf{1}_{\mathbf{close}}$, the dae-c^{2-} ligand does not bridge but coordinates to only one Mn-saltmen unit via only one carboxylato group. These complexes showed a reversible photochromic response to UV and visible light irradiation, respectively. Antiferromagnetic interactions were observed in the case of $\mathbf{1}_{\mathbf{open}}$ and $\mathbf{1}_{\mathbf{open\text{-}UV}}$, and ferromagnetic interactions were present in the case of $\mathbf{1}_{\mathbf{close}}$ and $\mathbf{1}_{\mathbf{close\text{-}vis}}$. In an optimized external magnetic field, slow magnetic relaxation, characteristic of SMM behavior, were observed for both complexes. The photoisomerization of the ligand only slightly affected the magnetic relaxation behavior and energy barrier.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b02578.

> The details of the temperature dependence of χ^{-1}, summary for the magnetic properties, frequency, and temperature dependence of χ' and χ'', magnetic field dependence of χ'' vs ν at 1.85 K, frequency and temperature dependences of the magnetic susceptibilities in different magnetic fields (PDF)

Accession Codes

CCDC 1866760−1866761 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

*E-mail: yamasita.m@gmail.com.

ORCID

Ahmed Fetoh: 0000-0002-2879-3968
Goulven Cosquer: 0000-0003-2692-1230
Masahiro Irie: 0000-0002-5644-3818

Notes

The authors declare no competing financial interest.

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