Single-Chain Magnets

DOI: 10.1002/ange.201407628

Single-Chain Magnetic Behavior in a Hetero-Tri-Spin Complex Mediated by Supramolecular Interactions with $TCNQF^{\bullet-}$ Radicals**

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Abstract: *The self-assembly of organic* $TCNQF^{\bullet-}$ *radicals (2-fluoro-7,7,8,8-tetracyano-p-quinodimethane) and the anisotropic* $[Tb(valpn)Cu]^{3+}$ *dinuclear cations produced a single-chain magnet (SCM) involving stacking interactions of* $TCNQF^{\bullet-}$ *radicals (*H_2valpn *is the Schiff base from the condensation of o-vanillin with 1,3-diaminopropane). Static and dynamic magnetic characterizations reveal that the effective energy barrier for the reversal of the magnetization in this hetero-tri-spin SCM is significantly larger than the barrier of the isolated single-molecule magnet based on the {TbCu} dinuclear core.*

Organic electron acceptors, such as tetracyanoethylene (TCNE), 7,7,8,8-tetracyanoquinodimethane (TCNQ), and their derivatives, have been extensively studied for their magnetic, conducting, and electrical switching properties.[1] In particular, TCNQ radicals readily form columnar stacks which allows for excellent electron transport for the resulting materials. Moreover, as compared to diamagnetic linkers, the use of TCNQ radical anions as additional spin carriers can enhance magnetic exchange interactions between paramagnetic metal ions in the form of both bridging ligands and outer-sphere stacked radicals.[2] These characteristics of TCNQ radicals render them excellent candidates for the elaboration of magnetic and conducting bifunctional materials.[3]

Since the first observation of slow relaxation dynamics in well-isolated one-dimensional molecular materials, known as single-chain magnets (SCMs), the topic has received considerable attention owing to the potential for applications in quantum computing, spintronics, and high-density memory devices.[4] As compared to related single-molecule magnets (SMMs), SCMs typically exhibit an overall higher energy barrier for spin relaxation because of the presence of an additional correlation energy term which accounts for the intra-chain interactions.[5] Strategies for the design of these one-dimensional "super-paramagnets" are versatile and involve judicious choice of the source of anisotropy (e.g., mononuclear or polynuclear metal complexes), the auxiliary ligands on the individual units, and, finally, linkers that serve to promote one-dimensional magnetic exchange interactions. A particularly convenient method is to use single-molecule magnets themselves as the anisotropic building blocks but it is a challenge to align the SMMs to realize one-dimensional uniaxial anisotropy in the resulting materials.[4a,b,6]

Of particular relevance to the topic of the present study is the finding that organocyanide radicals have proven to be excellent bridging ligands for SCMs, for example, $[Mn(5\text{-}TMAMsaltmen)(\mu\text{-}TCNQ)][ClO_4]_2$,[7] [Mn(T*o*-FPP)-(TCNE)],[8] and [Mn(TBPP)(TCNE)].[5] Besides these well-studied SCMs that involve direct exchange interactions between the anisotropic building blocks, other examples of SCM behavior have been documented to be mediated by hydrogen bonding[9] and π-stacking.[4c,10] However, to our knowledge the specific case of SCM behavior originating from supramolecular stacking interactions of planar organic radicals is unprecedented.

With these considerations in mind, we chose the heterometallic family of compounds consisting of 3d–4f combinations, namely $[M^{II}(L)Ln^{III}]^{3+}$ (M^{II}, 3d metal ions; Ln^{III}, 4f lanthanide ions; L, a compartmental Schiff base ligand), members of which have been linked into SCMs through cyanide bridging units.[11] Also of pertinence to this work is the fact that one of us reported the trinuclear 4f–3d–2p heterospin compound $[\{Cu(valpn)\}_2Gd(TCNQ)_2]TCNQ$ which is composed of a supramolecular chain involving π–π stacking interactions between the coordinated and uncoordinated TCNQ radicals (H_2valpn = 1,3-propanediyl-bis(2-iminomethylene-6-methoxy-phenol)).[12] This strategy was later expanded to a series of 4f–3d–3p compounds with $[Ni(mnt)_2]$ radicals (mnt = cis-1,2-dicyano-1,2-ethylenedithiolate).[13] Herein, we report a new quasi-1D chain compound, namely $[(TCNQF)Cu(valpn)Tb(TCNQF)(H_2O)_4][TCNQF]\cdot CH_3OH\cdot 6H_2O$ (**1**), using the less explored radical of the 2-fluoro-7,7,8,8-tetracyano-*p*-quinodimethane

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[**] Z.-X.W. thanks the China Scholarship Council (No. 201206895004) and National Natural Science Foundation of China (No. 21171115) for financial support to visit Texas A&M. K.R.D. and Y.-Z.Z. thank the Department of Energy, Basic Energy Sciences Division (DE-FG02-02ER45999) for generous support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201407628.

(TCNQF) anion. This chain compound is a new type of heterospin SCM based on supramolecular π–π stacking interactions between the $TCNQF^{\bullet-}$ radicals. These results offer a new route for the design of low-dimensional magnetically bistable materials.

Slow diffusion of solutions of [Cu(valpn)(H_2O)] and $TbCl_3\cdot6H_2O$ in methanol into a solution of Li(TCNQF) in a mixture of methanol/water produced purple platelet crystals of **1** after 12 hours. A single-crystal X-ray diffraction study revealed that **1** crystallizes in the triclinic $P\bar{1}$ space group. The asymmetric unit consists of a dinuclear $[Cu(valpn)Tb]^{3+}$ moiety with two coordinated and one free $TCNQF^{\bullet-}$ radical anions, four coordinated and six interstitial water molecules, and one methanol molecule (Figure 1). The $[Cu(valpn)Tb]^{3+}$ moiety preserves the structural features of the $[Cu(L)Ln]^{3+}$ family of dinuclear complexes in which Cu^{II} and Tb^{III} ions are bridged by two μ_2-phenoxo oxygen atoms (O2 and O3). The Cu^{II} ion is in a distorted square pyramidal geometry with the "N_2O_2" environment comprising the basal plane and the apical site being occupied by a nitrogen atom from one $TCNQF^{\bullet-}$ group (Cu1–N3 2.352(5) Å). The Tb^{III} ion occupies the outer "O_4" cavity from the ligand in addition to four coordinated water molecules and one coordinated $TCNQF^{\bullet-}$ anion radical. The distance between the Cu and Tb centers within the dinuclear unit is 3.456(1) Å. For the coordinated valpn ligand, the two Tb–O bonds involving the methoxy side arms (2.559(3) and 2.624(4) Å) are longer than the ones from the phenolate oxygen atoms (2.320(4) and 2.356(4) Å). The four Tb–O (water) bond lengths vary from 2.342(4) to 2.437(4) Å, whereas the Tb–N bond measures 2.537(5) Å. The different TCNQF species are designated as A, B, and C for Cu and Tb centers, indicating coordinated (A and B) and free (C) $TCNQF^{\bullet-}$ radicals, respectively. The charges on the TCNQF moieties are estimated from the bond distances to be −0.9, −0.7, and −0.9 for A, B and C, respectively,[14] which, in conjunction with the FTIR $\nu(C\equiv N)$ spectral features at 2179 cm^{-1}, indicate that the TCNQF species are in their monoanionic radical states.

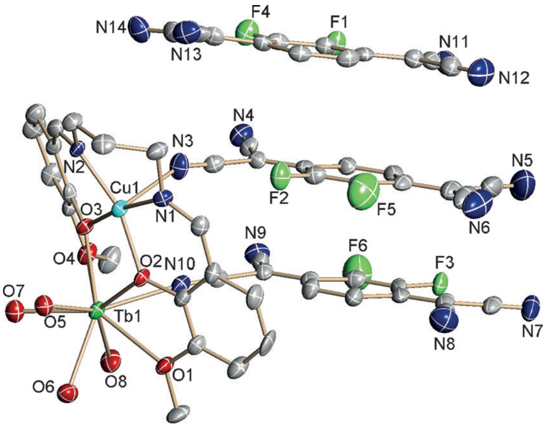


Figure 1. Thermal ellipsoid plot (displacement ellipsoids set at 50% probability) with selected atom labelling showing the molecular structure of **1**. Hydrogen atoms and free solvent molecules were omitted for clarity. Fluorine atoms are disordered over two positions on each of the TCNQF radicals.

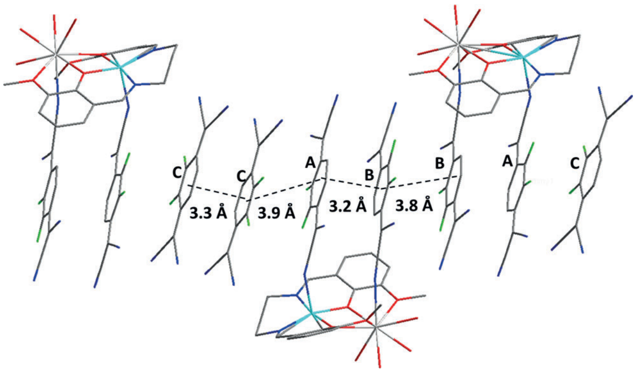


Figure 2. Side view of the quasi-1D chain showing the distances between adjacent TCNQF species (ring centroids) in the structure of compound **1** (A–B: 3.210(1) Å, B–B: 3.761(2) Å, A–C: 3.885(2) Å, C–C: 3.266(1) Å). Fluorine atoms are disordered in two positions on each of the TCNQF radicals.

The most intriguing structural characteristic in **1** is the packing arrangement which involves stacking interactions of the $TCNQF^{\bullet-}$ radical anions. As shown in Figure 2 and Figure S1 in the Supporting Information, two of the dinuclear $[Cu(valpn)Tb(TCNQF)_2(H_2O)_4]^+$ moieties interact with each other through the coordinated $TCNQF^{\bullet-}$ species in a slightly staggered fashion, and are further stitched together by two free $TCNQF^{\bullet-}$ species to form a quasi-one-dimensional chain along the *c*-axis. The stacking distances between the TCNQF quinoid ring centroids vary between 3.210(1) and 3.885(2) Å (Figure 2).

Variable-temperature magnetic susceptibility data for **1** were measured under a DC (direct current) field of 500 Oe (Figure 3). The $\chi_m T$ value of 12.0 $cm^3 mol^{-1} K$ at 300 K is smaller than the calculated 13.4 $cm^3 mol^{-1} K$ (Tb^{III}, $J=6$, $g=1.5$; Cu^{II}, $S=1/2$, $g=2.0$; $TCNQF^{\bullet-}$, $S=1/2$, $g=2$, $n=3$), but is very close to the value (12.2 $cm^3 mol^{-1} K$) without considering magnetic contributions from the dimerized $TCNQF^{\bullet-}$ radicals. Upon cooling, the $\chi_m T$ value gradually decreases to a minimum of 10.25 $cm^3 mol^{-1} K$ at 30 K and

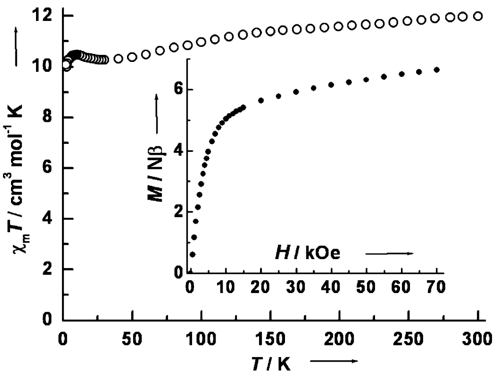
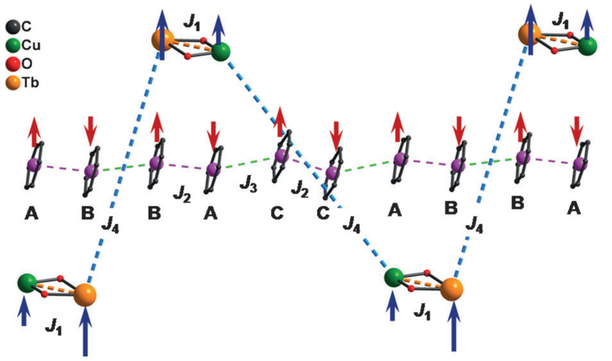


Figure 3. Variable-temperature DC magnetic susceptibility data of **1**, collected in an applied field of 500 Oe (where χ_m is the molar magnetic susceptibility). Inset: Plot of isothermal DC field-dependent magnetization at 1.8 K.

then increases to a maximum of 10.5 $cm^3 mol^{-1} K$ at 10 K before decreasing to 10.1 $cm^3 mol^{-1} K$ at 2 K. The profile of this curve suggests depopulation of Tb^{III} excited-state M_J levels and weak ferromagnetic Cu^{II}–Tb^{III} interactions (J_1), which have also been observed in other $[Cu(valpn)Tb]^{3+}$ systems.[15] It should be mentioned that antiferromagnetic (AF) coupling (J_2) was found previously in the case of two $TCNQ^{\bullet-}$ radicals that form $(TCNQ)_2^{2-}$ diamagnetic dimers.[12] In this regard, the pairs of $TCNQF^{\bullet-}$ radicals (A–B and C–C, with distances measuring 3.2–3.3 Å in Figure 2) in **1** also form an antiferromagnetically coupled chain along the *c*-axis (Scheme 1). This chain acts as a diamagnetic ligand to the neighboring $[Cu(valpn)Tb]^{3+}$ pairs which are weakly coupled (J_4) through the π–π stacking of the radicals. This conclusion is consistent with the lower room-temperature $\chi_m T$ value (see above). As a result of the unquenched orbital angular momentum of the Tb^{III} center, however, it is not practical to arrive at a quantitative analysis of the static magnetic properties.[15] The isothermal field-dependent magnetization (*M* versus *H*) was measured at 1.8 K (Figure 3 inset, and Figure S2) with a value of 6.64 Nβ at 70 kOe. The lack of saturation indicates significant anisotropy. It should be mentioned that no hysteresis loop was observed at 1.8 K which is the limit of our cryogenics (Figure S3).



Scheme 1. The possible magnetic interaction pathways in compound **1**.

To characterize the dynamics of the magnetization, variable-temperature (2–10 K) AC (alternating current) magnetic susceptibility measurements were performed with an oscillating field of 5 Oe and in a zero DC field. As depicted in Figure 4a, strong frequency dependence of both the in-phase (χ_m') and out-of-phase (χ_m'') components are clearly observed. The Mydosh parameter $\phi = (\Delta T_p/T_p)/\Delta(\log f)$, where T_P is the temperature of the peaks in χ_m' and *f* is the frequency, has a value of approximately 0.4, which is much larger than what is expected for typical glassy magnets (usually around 0.01), and falls into the category of superparamagnets (either SMMs or SCMs).[10a,17]

The relaxation time at $T > 3$ K plotted as $\ln(\tau)$ versus T^{-1} follows an Arrhenius law $\tau = \tau_0 \exp(\Delta/(k_B T))$ with $\Delta/k_B = 26.9$ K and $\tau_0 = 5.7 \times 10^{-7}$ s, where τ_0 is the pre-exponential factor, Δ the effective energy barrier of relaxation, and k_B the Boltzmann constant (Figure S4). It should be mentioned that application of a DC field of 1 kOe did not result in significant changes in the slow relaxation, with $\Delta_{eff}/k_B = 31.8$ K and $\tau_0 = 3.1 \times 10^{-7}$ s (Figure S5). The values are in good agreement with those reported for other SCMs.[6,18]

Variable-frequency AC magnetic susceptibility data collected from 2–5.75 K also show highly frequency dependent features (Figure 4b). Moreover, the relaxation time follows two thermally activated laws before and after the crossover temperature of $T^* = 3.4$ K, which we attribute to infinite-size and finite-size regimes for SCMs.[19] A fitting of the data to the Arrhenius law leads to: $\Delta_1/k_B = 25.9$ K, $\tau_1 = 9.7 \times 10^{-7}$ s; $\Delta_2/k_B = 12.9$ K, $\tau_2 = 4.6 \times 10^{-5}$ s. A generalized Debye model was used to fit the experimental AC susceptibility data and the best fit α values range from 0.20 to 0.45 for the Cole–Cole plot as the temperature varies from 5 to 2 K (Figure S6 and Table S1). This relatively wide distribution of relaxation times at low temperatures suggests multiple relaxation processes and polydispersity of the chain length, especially below 3.4 K, which corresponds well to the finite chain regime.[19]

It should be mentioned that the isolated Cu–Tb derivatives behave as SMMs with much lower energy barriers (about 13 K).[15b] Moreover, no out-of-phase peaks were observed in the absence of a DC field in its related compounds with $[Cu(valpn)Tb]^{3+}$ units bridged by long diarylethene ligands, through which the coupling is negligibly weak such that the system behaves as isolated $[Cu(valpn)Tb]^{3+}$ SMMs.[15c] These facts support our assumption that the 1D correlation of SMMs into SCMs by the supramolecular π–π stacking interactions of $TCNQF^{\bullet-}$ radicals significantly improves the energy barrier. In this regard,

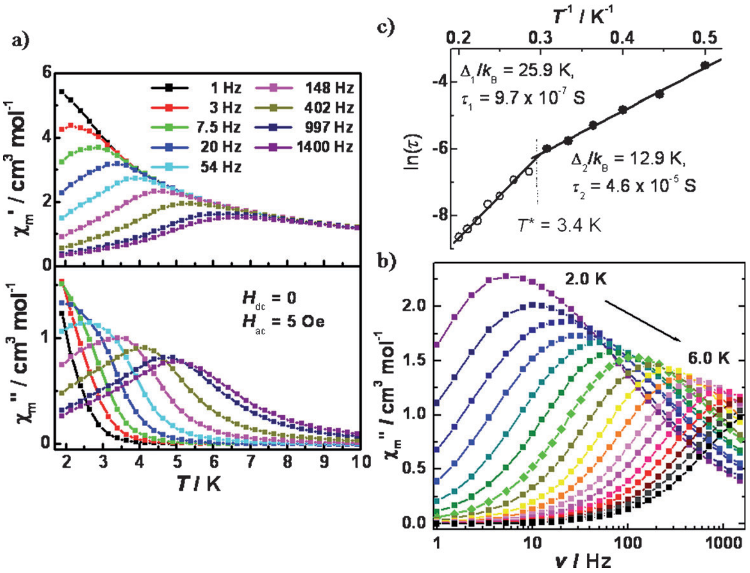


Figure 4. a) Variable-temperature in-phase (top) and out-of-phase (bottom) components of the AC magnetic susceptibility data for **1**, collected in a 5 Oe AC field oscillating at frequencies of 1–1400 Hz; b) Variable-frequency out-of-phase (χ_m'') AC magnetic susceptibility data, collected in a 5 Oe AC field oscillating at temperatures of 2.00–5.75 K. c) Arrhenius plot of the relaxation time, extracted from data plotted in (b).

we postulate that the weak ferromagnetic interactions between the $[Cu(valpn)Tb]^{3+}$ units through the π–π stacks in **1** (Scheme 1) gives rise to the SCM behavior. In comparison, a SCM with $[Cu(valpn)Tb]^{3+}$ bridged by $Fe(CN)_6^{3-}$ moieties exhibits only the beginning of out-of-phase AC signals at low temperatures.[11] Our results indicate that the stacking and magnetic exchange interactions of the $TCNQF^{\bullet-}$ radicals help to constrain the dimensionality of the system and enhance the overall uniaxial anisotropy of the system. Clearly such interactions in hetero-tri-spin systems deserve further investigation.

In summary, we have synthesized a heterospin single-chain magnet $[(valpn)CuTb(TCNQF)_2(H_2O)_4]$-$[TCNQF]\cdot CH_3OH\cdot 6H_2O$ which demonstrates that 1D magnetic bistability can be achieved through the supramolecular π-stacking interactions of planar radicals of the TCNQ type. This strategy offers a new route for the realization of SCMs. We plan to expand the series by employing the more anisotropic Ni^{II} center in place of Cu^{II} and by using other TCNQ radical derivatives to establish systematic control over the electronic and magnetic properties of these materials through supramolecular interactions.

Experimental Section

A solution of $[Cu(valpn)(H_2O)]$ (22.3 mg, 0.05 mmol) and $TbCl_3\cdot 6H_2O$ (18.7 mg, 0.05 mmol) in methanol (2 mL) was carefully layered onto a solution of LiTCNQF (5.6 mg, 0.025 mmol) in MeOH (1 mL) and H_2O (1 mL) in a 5 dram vial. Purple single crystals suitable for X-ray diffraction of **1** were obtained. IR: ν(C≡N): 2179 cm^{-1}.

Crystal data for **1**: $C_{56}H_{50}CuF_3N_{14}O_{15}Tb$, *f.w.* = 1441.58 $g\,mol^{-1}$, triclinic, space group $P\bar{1}$, $Z=2$, $a=10.006(5)$, $b=16.058(7)$, $c=20.522(9)$ Å, $\alpha=67.500(5)$, $\beta=85.188(6)$, $\gamma=85.846(6)°$, $V=3033(2)$ Å^3, $\rho=1.579\,g\,cm^{-3}$, $\mu=1.594\,mm^{-1}$, $R_1=0.0508$, $wR_2=0.1191$, $S=0.995$. CCDC 998664 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Received: July 25, 2014
Revised: August 3, 2014

Keywords: radical ions · single-chain magnets · TCNQ radicals · X-ray diffraction · π–π stacking interactions

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