Spin Frustration in the Triradical Trianion of a Naphthalenediimide Molecular Triangle

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S *Supporting Information*

ABSTRACT: Crystalline supramolecular frameworks consisting of charged molecules, held together by hydrogen bonds and Coulomb interactions, have attracted great interest because of their unusual structural, chemical, electronic, and magnetic properties. Herein, we report the preparation, structure, and magnetic properties of the triradical trianion of a shape-persistent chiral equilateral molecular triangle having three naphthalene-1,4:5,8-bis(dicarboximide)s ((+)-NDI-$\Delta^{3(-\bullet)}$). Single-crystal X-ray diffraction of its tris(cobaltocenium) salt ([(+)-NDI-$\Delta^{3(-\bullet)}(CoCp_2^+)_3$]) reveals accessible one-dimensional tubular cavities, and variable-temperature electron paramagnetic resonance spectroscopy shows that a dilute solution of [(+)-NDI-$\Delta^{3(-\bullet)}(CoCp_2^+)_3$] in an organic glass has a spin-frustrated doublet ground state and a thermally accessible quartet state. Furthermore, SQUID magnetometry from 5 to 300 K of solid [(+)-NDI-$\Delta^{3(-\bullet)}(CoCp_2^+)_3$] shows ferromagnetic ordering with a Curie temperature T_C = 20 K. The successful preparation of hybrid ionic materials comprising macrocyclic triradical trianions with spin-frustrated ground states and accessible 1D pores offers routes to new organic spintronic materials.

The ever-expanding opportunities offered by the broad scope of organic synthesis has led to new areas of molecular science such as organic electronics[1] and spintronics,[2] as well as molecular magnetism.[3] The concept of spin frustration was first proposed by Wannier in 1950[4] and Anderson in 1956,[5] who realized that the Ising model on an antiferromagnetic polychlore lattice maps onto Pauling's model of proton disorder in ice. The simplest example of spin frustration is given by attempting to place three antiferromagnetically coupled spins on a triangular lattice (Figure 1).[4] One can see by simple inspection that for any two paired spins on this lattice, the third spin must necessarily align parallel with one of the others, thereby being unable to minimize its exchange energy with the two competing interactions. Most research to date in this area has focused on inorganic crystals, where the rigid lattice allows strict control of the magnetic exchange interactions and long-range order.[6] There have been comparatively few examples of spin frustration in crystals of organic radicals[7] or small organic molecules,[8] but renewed interest in such systems has been triggered by interest in spin liquid phenomena.[9] Interest in magnetic frustration is also
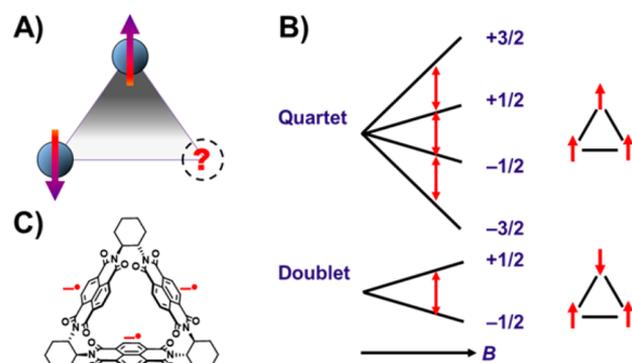
Figure 1. (A) Three coupled spins on a triangular lattice. (B) Allowed EPR transitions between doublet and quartet states. (C) Chemical structure of (+)-NDI-$\Delta^{3(-\bullet)}$.

motivated by its potential to explain conduction mechanisms in high Curie temperature (T_C) cuprate superconductors.[10]

Herein, we report the successful preparation and characterization of the structural and magnetic properties of the triradical trianion of a shape-persistent chiral equilateral molecular triangle having three naphthalene-1,4:5,8-bis(dicarboximide)s ((+)-NDI-$\Delta^{3(-\bullet)}$, Figure 1C). The tris(cobaltocenium salt of (+)-NDI-$\Delta^{3(-\bullet)}$ ([(+)-NDI-$\Delta^{3(-\bullet)}(CoCp_2^+)_3$]) has been characterized by single-crystal X-ray diffraction (XRD), optical circular dichroism (CD) spectroscopy, UV/vis absorption spectroscopy, electron paramagnetic resonance (EPR) spectroscopy, and SQUID magnetometry. We demonstrate that [(+)-NDI-$\Delta^{3(-\bullet)}(CoCp_2^+)_3$] displays spin frustration behavior using EPR spectroscopy as well as magnetic ordering by SQUID measurements.

Reaction of a concentrated solution of (+)-NDI-Δ[11] and 3 equiv of cobaltocene (CoCp₂) in dichloromethane (DCM) in a nitrogen-filled glovebox resulted in the formation of [(+)-NDI-$\Delta^{3(-\bullet)}(CoCp_2^+)_3$] as a dark brown precipitate, which was collected by filtration and washed with a minimal amount of DCM. The resulting material was dried under vacuum, and a yield >80% was routinely obtained. Single crystals of the product were grown by slow vapor diffusion of *n*-hexane into a saturated MeCN solution over 7 days. These black crystals are stable under an inert atmosphere. The structure was determined by XRD at 100 K. Crystallographic data are shown in Table S1 and a CIF file; a labeled figure and space-
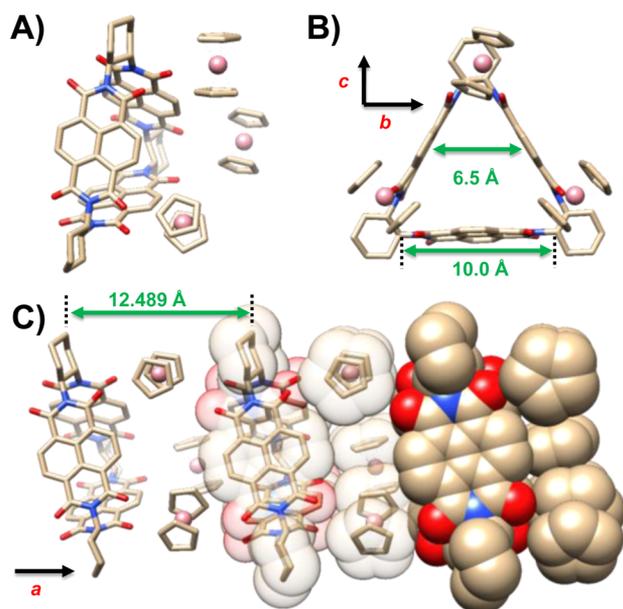
Figure 2. (A) Side view and (B) top view of a tubular representation of the crystal structure of $[(+)-NDI-\Delta^{3(-\bullet)}(CoCp^{2+})_3]$. The hydrogen atoms and residual solvent molecules are omitted for the sake of clarity. (C) A blend of tubular and space-filling representations of the solid-state superstructures of $[(+)-NDI-\Delta^{3(-\bullet)}(CoCp^{2+})_3]$ showing the tubular alignment along the a-axis.

Figure 3. (A) CV and (B) DPV of $(+)-NDI-\Delta$ (1.0 mM in DMF, 100 mM TBAPF$_6$, 50 mV·s^{-1}, 295 K). (C) UV/vis absorption and (D) CD spectra of $(+)-NDI-\Delta$ (0.38 mM in DMF, 1 mm, 295 K) upon addition of up to 3.5 equiv of cobaltocene (CoCp$_2$).

$$(+)-NDI-\Delta \leftrightarrows (+)-NDI-\Delta^{-\bullet}$$
$$\leftrightarrows (+)-NDI-\Delta^{2(-\bullet)}$$
$$\leftrightarrows (+)-NDI-\Delta^{3(-\bullet)} \qquad (1)$$

filling stereoviews are shown in Figure 2. $[(+)-NDI-\Delta^{3(-\bullet)}-(CoCp_2^+)_3]$ crystallizes in the monoclinic space group $P2_1$ and contains discrete units with no imposed symmetry. Inspection of Figure 2 shows that $[(+)-NDI-\Delta^{3(-\bullet)}(CoCp_2^+)_3]$ can be conveniently described as an organic triangular triradical trianion intimately associated with three cobaltocenium (CoCp$_2^+$) cations by means of both electrostatic forces and a multitude of intermolecular $[C-H\cdots O=C]$ interactions (closest $d_{C-H\cdots O=C}$ = 2.29 Å, $d_{C\cdots O=C}$ = 3.05 Å, $\angle_{C-H\cdots O=C}$ = 136°) between aromatic protons of cobaltocenium and the carbonyl O atoms (C=O) in the $(+)-NDI-\Delta^{3(-\bullet)}$ trianion. The overall triradical trianion $(+)-NDI-\Delta^{3(-\bullet)}$ has approximate D_3 symmetry and has bond distances very similar to those seen in the neutral $(+)-NDI-\Delta$, with only a small shortening of the imide C−N bond from an average value of 1.51 to 1.49 Å. The observed small structural perturbation is in line with the ability of NDIs to delocalize and stabilize the unpaired electrons over a large π-surface. $[(+)-NDI-\Delta^{3(-\bullet)}(CoCp_2^+)_3]$ molecules stack along the a-axis, forming infinite coaxial channels filled with residual solvent molecules (Figure 2). Bundles of these nanostructures are then tightly packed to form well-ordered arrays that constitute the single crystal.

Electrochemical studies (Figure 3A,B) on $(+)-NDI-\Delta$ in dimethylformamide (DMF) solution were performed using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). There are three redox couples on the reduction side and none on the oxidation side within the electrochemical window of the solvent. All three waves are reversible one-electron processes, corresponding to the sequential reduction of each NDI subunit to its radical anion, and give linear i_p vs $\nu^{1/2}$ plots (i_p = CV peak current) in the scan rate (ν) range 20−1800 mV/s, indicating diffusion-controlled processes (e.g., see Figure S4). The electrochemical results can be summarized by eq 1.
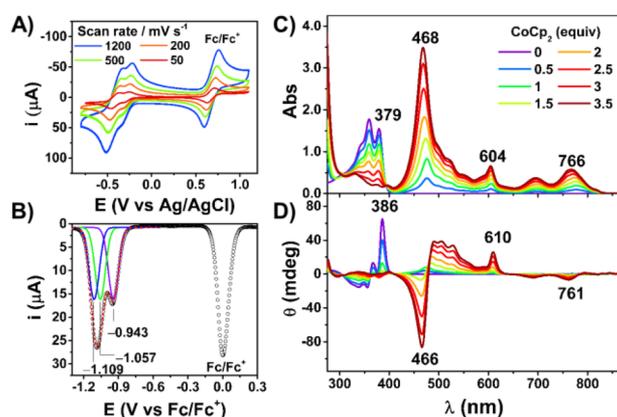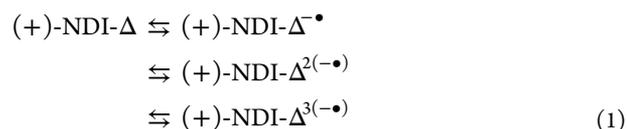
The optical properties associated with the redox process were investigated by UV/vis absorption (Figure 3C) and electronic CD (Figure 3D) spectroscopy, which show progressive disappearance of the features assigned to the neutral state (300−400 nm) accompanied by the growth of distinctive bands of radical anion state in the visible region (400−800 nm). The CD spectra display several bands having positive exciton-type Cotton effects, which reflect the rigid positive gauche torsional angle of the N−C−C−N bond system of the (S,S)-trans-1,2-cyclohexanediamine linker. A dilute solution of $[(+)-NDI-\Delta^{3(-\bullet)}(CoCp_2^+)_3]$ crystals dissolved in DMF yields absorption and CD spectra identical to those obtained by stepwise chemical reduction−titration, which further supports its triply reduced nature.

Continuous-wave (CW) EPR spectra of $(+)-NDI-\Delta^{3(-\bullet)}$ in DMF recorded at X-band from 7 to 75 K are shown in Figure 4A. At 7 K, $(+)-NDI-\Delta^{3(-\bullet)}$ exists in a doublet spin state, as evidenced by the single narrow line observed; however, when the temperature is raised above ~15 K, the broad features associated with a quartet state are observed. Unambiguous assignment of the spectral features observed in the CW-EPR spectrum to a doublet or quartet spin state were made using electron spin nutation spectroscopy.[12] Figure 4B shows the transient nutation frequency spectra for $(+)-NDI-\Delta^{3(-\bullet)}$ acquired at 350.3 mT at 7, 25, and 45 K and 347.5 mT at 45 K. In order to be confident in the assignment of the spin state, the nutation frequency was normalized to the frequency of a α,γ-bisdiphenylene-β-phenylallyl (BDPA) radical standard, so that the normalized ω_{NUT} = 1 for $S = {}^1/_2$. The nutation spectra clearly show that $(+)-NDI-\Delta^{3(-\bullet)}$ exists in an $S = {}^1/_2$ spin state at 7 K. Upon raising the temperature, a second frequency is observed growing in at $\omega_{NUT} = 2$, corresponding to $m_s = -{}^1/_2 \rightarrow m_s = {}^1/_2$ transition in a quartet spin system. A second indication of a quartet spin system can be seen at 347.5 mT, where a normalized nutation frequency, $\omega_{NUT} = \sqrt{3}$, clearly results from the $m_s = -{}^3/_2 \rightarrow m_s = -{}^1/_2$ or the $m_s = {}^1/_2 \rightarrow m_s = {}^3/_2$ transitions.
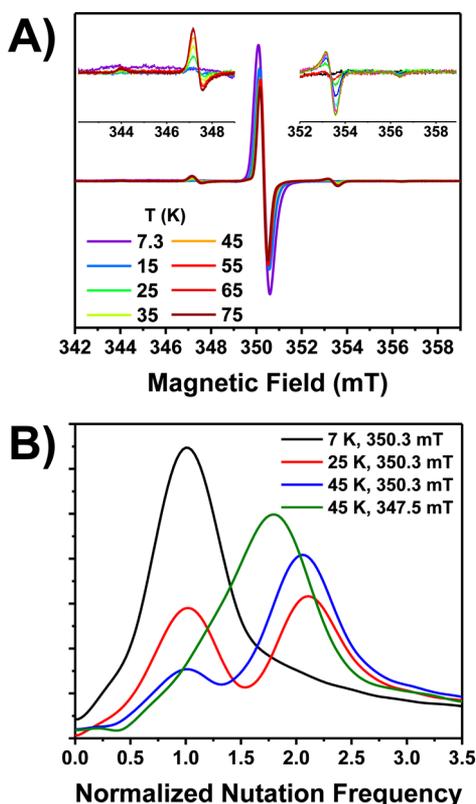
Figure 4. (A) X-band CW-EPR spectra of $[(+)\text{-NDI-}\Delta^{3(-\bullet)}\text{-}(CoCp^{2+})_3]$ at the indicated temperatures in DMF. (B) Transient nutation data for $[(+)\text{-NDI-}\Delta^{3(-\bullet)}(CoCp^{2+})_3]$.

In order to characterize the EPR spectrum of (+)-NDI-$\Delta^{3(-\bullet)}$ more thoroughly, nutation frequency-selective EPR measurements were performed at W-band at 7 and 30 K (Figure 5A,B). A combination of high-field EPR and a nutation frequency-selective spectrum provides the opportunity to both elucidate the orientation of the g-tensor relative to the zero-field-splitting tensor and assign the spectral features to the allowed transitions. Figure 5A shows the cross section at normalized $\omega_{NUT} = 1$ at 7 K, and the corresponding simulation. The spectrum was simulated as an $S = \frac{1}{2}$ species using the g-tensor, $g = [2.00472, 2.00472, 2.00268]$. Figure 5C shows the cross sections at normalized $\omega_{NUT} = 2$ and $\omega_{NUT} = \sqrt{3}$ at 30 K, and their corresponding simulations. The spectrum was treated as a pure $S = \frac{3}{2}$ system, and was fit using an effective g-tensor, $g = [2.0037, 2.0037, 2.00472]$, and a zero field splitting of $D = 84$ MHz, which has Euler angles of $[0°, 20°, 60°]$ relating the principal axis of the zero-field-splitting tensor to the principal axis of the g-tensor.

Magnetic susceptibility data were collected on a polycrystalline powder sample of $[(+)\text{-NDI-}\Delta^{3(-\bullet)}(CoCp_2^+)_3]$ at an applied magnetic field of 100 Oe on a SQUID magnetometer (Figure 6A). Fitting the high-temperature inverse susceptibility data (110−315 K) yields $\Theta_{CW} = -194$ K, which suggests that the mean superexchange interaction is antiferromagnetic. The plot of χ_m vs T (Figure 6A) shows a sharp increase at 20 K, and the corresponding plot of $\chi_m T$ vs T (Figure 6A, inset) shows very similar behavior. These data are suggestive of the onset of a ferromagnetic ordering transition at $T_C = 20$ K. Additional evidence for a ferromagnetic ordering transition is provided by the plot of the magnetization vs field measured at 5 K (Figure 6B). This figure shows a small hysteresis loop, indicative of a
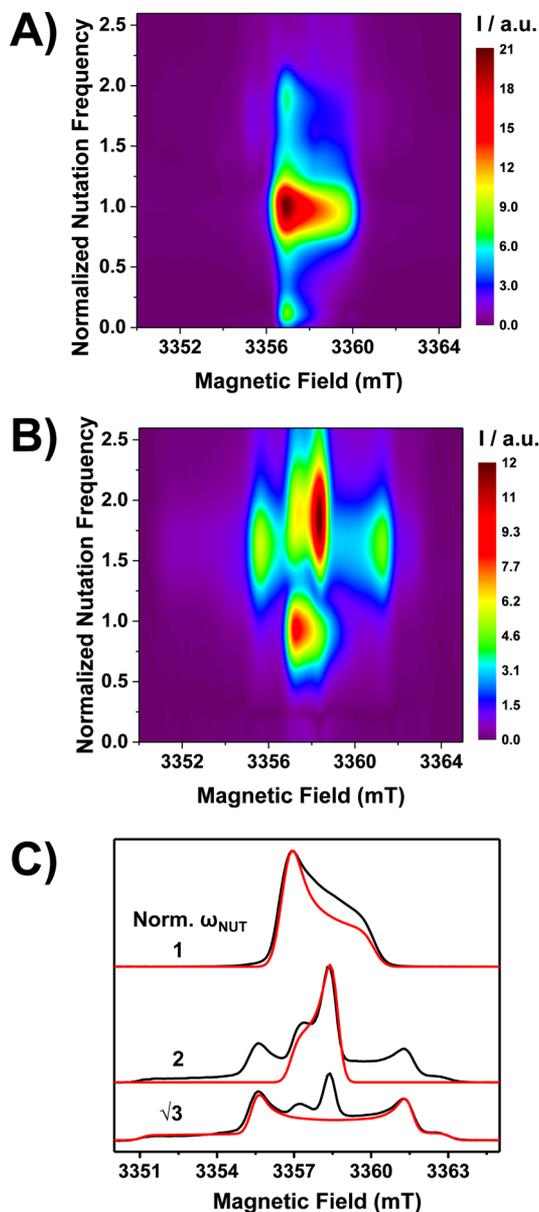
Figure 5. (A) Contour plots of W-band 2D pulse electron spin nutation spectra of $[(+)\text{-NDI-}\Delta^{3(-\bullet)}(CoCp_2^+)_3]$ complex in frozen DMF at (A) 7 K and (B) 30 K. (C) Plot of cross sections at normalized $\omega_{NUT} = 2$ and $\omega_{NUT} = \sqrt{3}$ at 30 K, and their corresponding simulations.

very soft ferromagnet with a coercive field of 50 Oe and a remanence of 10.3 emu Oe mol^{-1}. The bulk magnetic data suggest spin-frustrated behavior of $[(+)\text{-NDI-}\Delta^{3(-\bullet)}(CoCp_2^+)_3]$ in the solid state. A measure of spin frustration was provided by Ramirez by defining $f = |\Theta_{CW}|/T_C$, where Θ_{CW} is the Weiss constant, with $f > 10$ representing a strong effect.[13] According to this definition, $[(+)\text{-NDI-}\Delta^{3(-\bullet)}(CoCp_2^+)_3]$ is indeed spin frustrated, with a value of $f = 9.7$. Intramolecular superexchange between the NDI radical anion units bridged by cyclohexyl bridges is antiferromagnetic, as demonstrated by the EPR results. The origin of ferromagnetic behavior is likely derived from intermolecular superexchange through the cobaltocenium counterions, similar to the donor−acceptor co-crystals reported by Miller and Epstein,[3g] where the exchange interactions
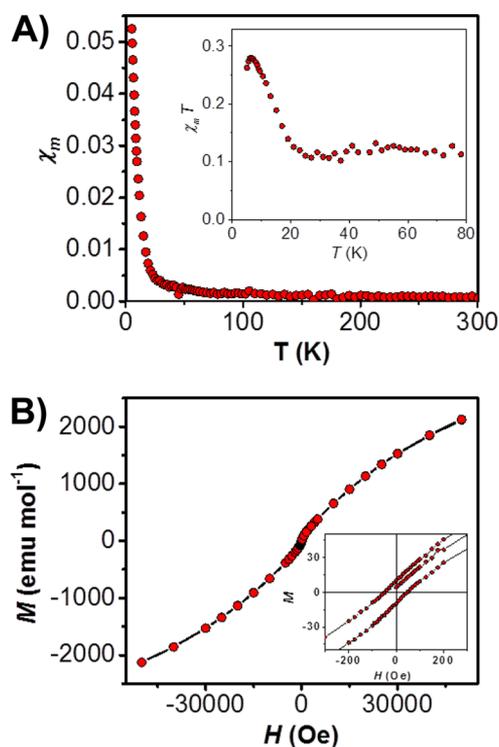
Figure 6. (A) Temperature dependence of χ_m and $\chi_m T$ (inset) of $[(+)\text{-NDI-}\Delta^{3(-\bullet)}(CoCp^{2+})_3]$ at a constant field of 100 Oe. (B) Hysteretic $M(H)$ for $[(+)\text{-NDI-}\Delta^{3(-\bullet)}(CoCp^{2+})_3]$ at 5 K.

between stacks dictate their overall magnetic ordering at low temperature.

In summary, we have characterized the shape-persistent chiral equilateral triradical trianion molecular triangle $[(+)\text{-NDI-}\Delta^{3(-\bullet)}(CoCp_2^+)_3]$ by means of both molecular spectroscopic tools and single-crystal X-ray diffraction analysis. $[(+)\text{-NDI-}\Delta^{3(-\bullet)}(CoCp_2^+)_3]$ shows spin frustration at the individual molecule level and magnetic ordering in the solid state. We envision that these magnetic properties combined with the accessible cavity of $[(+)\text{-NDI-}\Delta^{3(-\bullet)}(CoCp_2^+)_3]$ could be potentially useful for unconventional sensing, molecular memory, and quantum information applications.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b00515.

> Synthesis, NMR and MS characterization, and X-ray and EPR data, including Table S1 and Figures S1−S4 (PDF)
> X-ray crystallographic data for $[(+)\text{-NDI-}\Delta^{3(-\bullet)}(CoCp_2^+)_3]$ (CIF)

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Notes
The authors declare no competing financial interest.

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