Low Temperature Structures and Magnetic Interactions in the Organic-based Ferromagnetic and Metamagnetic Polymorphs of Decamethylferrocenium 7,7,8,8-Tetracyano-p-quinodimethanide, [FeCp*2]⁺[TCNQ]⁻

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Dedicated to the memory of Professor Joel Bernstein (1941-2019), a pioneer of polymorphic materials, and also to Dedicated to Professors Jaume Veciana and Concepció Rovira for their sustained contributions for the development of molecule-based electronics and magnetism
Abstract

To identify the genesis of the differing magnetic behaviors for the ferro- (FO) and metamagnetic (MM) polymorphs of [FeCp*2][TCNQ] (Cp* = pentamethylcyclopentadienide; TCNQ = 7,7,8,8-tetracyano-p-quinodimethane) the low temperature (18 ± 1 K) structures of each polymorph were determined from high-resolution synchrotron powder diffraction data. Each polymorph possesses chains of alternating $S = 1/2$ [FeCp*2]$^{+}$ cations and $S = 1/2$ [TCNQ]$^{+}$, but with differing relative orientations. These as well as an additional paramagnetic polymorph do not thermally interconvert. In addition, the room and low (<70 ± 10 K) temperature structures of the MM polymorph, MM$_{RT}$ and MM$_{LT}$, respectively, differ from that previously reported at 167 K (-106 °C) MM structure, and no evidence of either phase transition was previously noted even from the magnetic data. This transition temperature and enthalpy of this phase transition for MM$_{RT} \rightleftharpoons$ MM was determined to be 226.5 ± 0.4 K (-46.7 ± 0.4 °C) and 0.68 ± 0.04 kJ/mol upon warming, respectively, from differential calorimetry studies (DSC). All three MM phases are triclinic ($\bar{P}i$) with the room temperature phase having a doubled unit cell relative to the other two. The lower temperature phase transition involves a small rearrangement of the molecular ions and shift in lattice parameters. These three MM and FO polymorphs have been characterized and form extended 1-D chains with alternating $S = 1/2$ [FeCp*2]$^{+}$ cations, and $S = 1/2$ [TCNQ]$^{+}$ anions, whereas the fifth, paramagnetic (P) polymorph possesses $S = 0 \pi$-[TCNQ]$_2^{-}$ dimers. At 18 ± 1 K the intrachain Fe$•••$Fe separations are 10.738(2) and 10.439(3) Å for the FO and MM$_{LT}$ polymorphs, respectively. The key structural differences between FO and MM$_{LT}$ at 18 ± 1 K are the 10% shorter interchain N$•••$N and the 2.8% shorter intrachain Fe$•••$Fe separation present for MM$_{LT}$. Computational analysis of all nearest-neighbor spin couplings for the 18-K structures of FO and MM$_{LT}$ indicates that the intrachain [FeCp*2]$^{+}$•••[TCNQ]$^{-}$ spin couplings ($H = -2S_i\cdot S_j$) are the strongest (4.95 and 6.5 cm$^{-1}$ for FO and MM$_{LT}$, respectively), as previously hypothesized, and are ferromagnetic due to their $S = 1/2$ spins residing in orthogonal orbitals. The change in relative [TCNQ]$^{-}$•••[TCNQ]$^{-}$ orientations leads to a computed change from the ferromagnetic interaction (0.2 cm$^{-1}$) for FO to an antiferromagnetic interaction (-0.1 cm$^{-1}$) for MM$_{LT}$ in accord with its observed antiferromagnetic ground state. Hence, the magnetic ground state cannot be solely described by the dominant magnetic interactions.
Introduction

Organic-based materials possessing bulk, cooperative physical properties are a contemporary research area that spans chemistry, materials science, and physics. Examples of organic-based magnets, superconductors, and ferroelectrics have been established. These materials have the common feature of having delocalized $\pi$-electrons that are essential for the physical property. $[\text{Fe}^{III}\text{Cp}^\ast_2]^+\text{[TCNQ]}^-$ (TCNQ = 7,7,8,8-tetracyano-$p$-quinodimethane; Cp* = pentamethylyclopentadienide, $C_5\text{Me}_5^-$) was reported to order as a metamagnet below 2.55 K, and by substitution of TCNQ with TCNE (tetracyanoethylene) led to the discovery of the first organic-based ferromagnet, $[\text{Fe}^{III}\text{Cp}^\ast_2]^+\text{[TCNE]}^-$, which has a similar structural motif, but magnetically orders as a bulk ferromagnet with a magnetic ordering temperature ($T_c$) of 4.8 K.

$[\text{FeCp}^\ast_2]\text{[TCNQ]}$ has been reported to form three different magnetic polymorphs, namely, a dimeric paramagnet (P), a ferromagnet (FO) ($T_c = 3.1$ K), and the aforementioned metamagnet (MM). The FO and MM polymorphs possess parallel $\cdots D^+A^+D^+A^+ \cdots$ 1-D chains ($D = \text{FeCp}^\ast_2$; $A = \text{TCNQ}$), which is similar to that reported for the ferromagnet $[\text{FeCp}^\ast_2]\text{[TCNQ]}$. Based upon their respective reported room temperature and 167 K (-106 °C) structures, only a few key structural differences exist, but these are sufficient to render the significantly different properties observed for differing polymorphs.

Note that the structure of the P polymorph along with the metamagnetic properties of MM were reported first. The structure of MM was subsequently reported, however, in a preliminary communication, the structure of the then-unknown FO polymorph was described.

The previous structural determinations of $[\text{FeCp}^\ast_2]\text{[TCNQ]}$ were performed significantly above $T_c$, where the cation $C_5\text{Me}_5^-$ (Cp*) rings are in an eclipsed conformation ($D_{5h}$) for FO, but staggered ($D_3$) for MM. Additionally, the interchain arrangements have some small, but notable differences: the [TCNQ]$^-$ anions in adjacent layers of MM in are arranged in the same direction, but zigzag for FO. Thus, the closest N$\cdots$N [TCNQ]$^-$···[TCNQ]$^-$ distance in MM is 4.080 Å vs. 4.337 Å for FO, albeit at different temperatures. Due to the closer distance in MM than in FO, the expectation that this interaction should lead to stronger antiferromagnetic coupling, and the antiferromagnetic ground state is expected for this configuration. Above the 1300 Oe critical field the MM polymorph switches to a ferromagnetic-like state. To understand the magnetic couplings, however, requires the knowledge of the structures at temperatures as close as feasible to where the magnetic ordering is observed.
To understand the subtle structural differences between the FO and MM polymorphs and how they affect the magnetic properties of this unique system, where different polymorphs have ferro- and antiferromagnetic ground states, very low temperature structures are herein reported (although still above than the magnetic ordering temperatures) for both phases. These form the basis for theoretical evaluations of the magnetic interactions with a very high degree of accuracy, aiming at providing benchmark results that will provide a solid foundation for the analysis and rationalization of the subtle spin coupling interactions that lead to the different magnetic ground states. In addition, although there is no evidence from the magnetic data, two reversible structural phase transitions MM phase were discovered; both at higher (MM ⇌ MM\(_{RT}\)) and at low temperature (MM ⇌ MM\(_{LT}\)) that have not been previously published.

**Experimental Section**

The purple-reflecting crystals of the MM and FO polymorphs were prepared as previously reported. Differential scanning calorimetry (DCS) studies utilized a TA Instruments Model 2910 DSC equipped with a LNCA liquid nitrogen cooling accessory enabling operation between of -150 to 550 °C using a 1 °C/min scan rate and ~5 mg samples. Consecutive heating and cooling cycles were performed to ensure reversibility and reproducibility of the phase transitions. Computational results were obtained as previously reported.

High resolution powder diffraction measurements for the Rietveld structure analysis for the MM and FO polymorphs at various temperatures were performed at Beam Line X16C of the National Synchrotron Light Source at Brookhaven National Laboratory. The powdered samples were held in 1.0 mm diameter thin-wall quartz capillaries. X-Rays of a single wavelength were selected by a Si(111) channel cut crystal. Diffracted X-rays were selected by a Ge(111) analyzer and detected by a NaI scintillation counter. Samples were cooled either by an Oxford Cryostream (T ≥ 100 K) or an APD closed cycle refrigerator (T < 100 K). To improve particle statistics, the sample was spun in the former case, and rocked in the latter, during data collection. The incident intensity was monitored by an ion chamber and used to normalize the measured signal. The TOPAS-Academic program was used to index, solve, and refine the crystal structures. Rietveld plots are given in Figures S1 - S3.

The single crystal structures of MM were determined on a Nonius KappaCCD diffractometer equipped with Mo Kα radiation All the reflections were merged and only those for
which \( I > 2\sigma(I) \) were included in the refinement, where \( \sigma(F_o)^2 \) is the standard deviation based on counting statistics. The data were integrated using the Bruker SAINT software program. The structures were solved by a combination of direct methods and heavy atom methods. Direct methods and the refinement by full-matrix least-squares methods using SHELXL-97 were used for the structures of MM at several temperatures. All the non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were assigned isotropic displacements \( U(H) = 1.2U(C) \), and their coordinates were allowed to ride on their respective carbons using SHELXL97.

**Results and Discussion**

A fundamental understanding as the genesis of the magnetic couplings for the FO and for the MM polymorphs of [FeCp*₂][TCNQ] that lead to their observed ferro- and antiferromagnetic ordering and their subtle differences has yet to be identified. Insight into this system will provide a salient understanding of the couplings and competition among couplings that led to net antiferromagnetic as well as ferromagnetic couplings and subsequently long range, bulk magnetic ordering. A computational study of the magnetic couplings requires the structure determination preferably at or below the ordering temperature. The structures of the MM and FO polymorphs [FeCp*₂][TCNQ] have been reported at 167 K and at room temperature, respectively, but herein they are redetermined via high-resolution powder X-ray diffraction (PXRD) data at 18 ± 1 K. As part of these studies the room temperature structures were also obtained. The unit cell of the FO phase at room temperature is in accord with that previously reported, Table 1.

In contrast, the unit cell at room temperature for the MM is doubled from that previously reported at 167 K, Table 1, suggesting a phase transition between 167 K and room temperature. Lattice parameter measurements upon cooling show the room temperature phase persisting to 215 K. Single crystal measurements at 230, 265, and 300 K, Table 1, confirm the structure of the doubled cell of MM and provide a significantly more precise view of the molecular geometry in the room temperature phase. To further understand this phase transition differential scanning calorimetry (DSC) data was obtained and evaluated for MM (vide infra). Studies of the related MnCp*₂ and [FeCp*₂][TCNE] revealed structural transitions at similar temperatures. The prior 165 K structure of MM has an inversion center on the Fe atom, which implies that the Cp* rings have a staggered configuration. The transition in [FeCp*₂][TCNE] is from a staggered phase
to a disordered phase, whereas that in MnCp*$_2$ is a rotation of the Cp* rings, which is therefore more similar to that observed for MM.

In addition, a rearrangement of the structure was observed between 60 and 80 K, emphasizing the importance of using data collected at or near the magnetic ordering temperature to interpret magnetic interactions in molecular solids. The evolution of the temperature dependence of the lattice parameters of the MM phase is shown in Figure 1. Selected powder diffraction patterns, including two-phase coexistence at both transitions are shown in Figure S4. The phase transitions are clearly noted from the abrupt change in several unit cell parameters, e.g. $b$, $c$, $\alpha$, $\beta$, and $\gamma$, over the entire temperature range, but the molar volume evolves continuously, Figure 1.

While the basic structure of the three MM phases consist of columns of alternating [FeCp*$_2$]$^{\pm}$ and [TCNQ]$^{-}$ radical ions in roughly a triangular arrangement, e.g. Figure S7, but there are significant differences in their local arrangements. Figure 2 compares the environments of the FO and the three MM phases about one fixed TCNQ, showing the extent of the rearrangements among them. These structures are described in more detail below.
Figure 1. Unit cell lattice parameters of MM (MM_{LT}, MM, and MM_{RT}) as a function of temperature through the two structural transitions. Blue circles and red triangles are different powder samples; black squares are results from single crystal measurements. Values plotted outside of the 80 to 215 K range are not the reduced (Breuger) cell with three shortest non-coplanar translation vectors but are those that most closely match the shape of the intermediate temperature cell.
Figure 2. Overlay of the structures of the three MM and the FO phases, referenced to one TCNQ. Top: along the chain direction; bottom: plane perpendicular to the chain direction. Red: MM (167 K, MCFETC02); green: MM$_{RT}$ (300 K, this work); cyan: MM$_{LT}$ (17 K, this work); grey: FO (19 K, this work).
Table 1. Summary of the unit cell parameters for the P, MM, and FO polymorphs of [FeCp*₂][TCNQ].

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<sup>a</sup> Room temperature, 295 K  <sup>b</sup> Single crystal  <sup>c</sup> Powder X-ray diffraction  <sup>d</sup> Unit cell only refined  <sup>e</sup> Intrachain  <sup>f</sup> Approximately, D<sub>5h</sub>
The structures of the FO and three MM polymorphs of $[\text{FeCp}^\ast_2][\text{TCNQ}]$ at all temperatures are generally similar to that of $[\text{FeCp}^\ast_2][\text{TCNE}]^{10,11}$ and possess parallel chains of alternating $[\text{FeCp}^\ast_2]^{\ast+}$ cations, and $[\text{A}]^-$ $($A = TCNQ, TCNE$)$ anions. As for the MM and FO polymorphs the structure of the $D_{2h}$ planar radical anionic $[\text{TCNQ}]^-$ are typical to those previously reported and are not discussed. Likewise, the structure of the $[\text{Fe}^{\text{III}}\text{Cp}^\ast_2]^+$ cations are those previously reported, and except for the relative orientation of the Cp* rings, and are not discussed in detail. Each of these chains is surrounded by six parallel chains, two of which are in-registry ($i.e.$ cations are near cations and anions are near anions in adjacent chains), and four of which are out-of-registry ($i.e.$ cations are near anions in adjacent chains) ($vide$ $infra$). The net magnetic coupling leading to magnetic ordering arises from the intra- and interchain couplings.

**Structure of FO**

The structure of the FO polymorph at 19 K is similar to that previously reported at room temperature,$^{15}$ but with a 3.5% volume contraction, and the intrachain Fe•••Fe separation decreases by 0.9% to 10.738 Å, Table 2. Each chain is surrounded by six parallel chains, Figure S5, forming two identical in-registry nearest neighbor chains, I-II and I-II' separated by 8.308 Å, as well as four out-of-registry nearest neighbor chains, I-III, I-III', I-IV and I-V separated by 8.260, 8.260, 8.553, and 10.285 Å, respectively, Figure S6 , Table 2. The shortest interchain Fe•••Fe, Fe•••N, and N•••N separations are 8.535, 4.789, and 4.143 Å, respectively, Table 2. The $[\text{Fe}^{\text{III}}\text{Cp}^\ast_2]^+$ cation has a Fe-C distance of 2.147 Å, and Fe•••C$_5$-ring centroid of 1.738 Å, with the two Cp* rings being eclipsed, Figure 3a. Thus, the FeC$_{10}$ core has approximate $D_{5h}$ symmetry.
Table 2. Summary of key Fe•••Fe, Fe•••N, N•••N intra- and interchain bond distances and separations (Å) for the six nearest neighbor chains present for the MM<sub>LT</sub> and FO polymorphs of [FeCp*<sub>2</sub>][TCNQ] at 18 ± 1 K, and [FeCp*<sub>2</sub>][TCNE] at 12 K.<sup>10</sup>

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<th>Compound</th>
<th>MM&lt;sub&gt;LT&lt;/sub&gt;</th>
<th>FO</th>
<th>[FeCp*&lt;sub&gt;2&lt;/sub&gt;][TCNE]</th>
<th>Difference, Å, % (FO) - [FeCp*&lt;sub&gt;2&lt;/sub&gt;][TCNE] (vs. FO)</th>
<th>Difference, Å, % (MM&lt;sub&gt;LT&lt;/sub&gt;) - [FeCp*&lt;sub&gt;2&lt;/sub&gt;][TCNE] (vs. MM&lt;sub&gt;LT&lt;/sub&gt;)</th>
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<td>19</td>
<td>12</td>
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<td>10.738</td>
<td>10.415</td>
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<td>9.656</td>
<td>9.355 x2</td>
<td>9.087 x2</td>
<td>-0.301, 3.22</td>
<td>0.268, 2.86</td>
</tr>
<tr>
<td>out-of-registry interchain separation, Å</td>
<td>8.389 x2</td>
<td>8.260 x2</td>
<td>7.359 x2</td>
<td>-0.129, -1.56</td>
<td>0.901, 10.9</td>
</tr>
</tbody>
</table>

Figure 3. Top view along the C<sub>5</sub> axis of [Fe<sup>III</sup>Cp*<sub>2</sub>]<sup>+</sup> for the FO polymorph at 19 K (a), the MM polymorph at 17 K (MM<sub>LT</sub>) (b) and 300 K (MM<sub>RT</sub>) (c), and for ferromagnetic [FeCp*<sub>2</sub>][TCNE] at 12 K<sup>10</sup> (d) that belong to the ~D<sub>5h</sub>, D<sub>5d</sub>, D<sub>5</sub>, and D<sub>5h</sub> point groups, respectively.

Structure of MM<sub>LT</sub>

The structure of MM at 17 K (MM<sub>LT</sub>) belongs to the same P<sub>i</sub> space group, it was not isomorphous with the previously reported 167-K structure for MM,<sup>6</sup> Table 1, and has a 1.9% volume contraction.
and the intrachain Fe⋯Fe separation decreases by 1.0% to 10.439 Å, Table 2. Each chain is surrounded by 6 parallel chains, Figure S7, forming two identical pairs out-of-registry nearest neighbor chains, I-II (and I-II') and I-III (and I-III') separated by 9.245 and 8.389 Å, respectively, and one pair of in-registry nearest neighbor chains I-IV (and I-IV') separated by 8.631 Å, Figure S7, Table 2. The shortest interchain Fe⋯Fe, Fe⋯N, and N⋯N separations are 8.631, 5.225, and 3.729 Å, respectively, Table 2. The [FeIII\text{Cp*}^2]^+ cation has a Fe-C distance of 2.125 Å, and Fe⋯C5-ring centroid of 1.731 Å, with the two Cp* rings being staggered, Figure 3b. Thus, the FeC_{10} core has $D_{5d}$ symmetry.

As part of the structural investigation of MM at low temperature, the room temperature unit cell was determined, and although MM_{RT} had the same P1 space group, it was not isomorphous with the previously reported 167-K structure for MM, Table 1. Above 226 K, the unit cell volume is double of that observed at low temperature because the Fe atom is no longer on an inversion site, and, the Cp* rings are crystallographically independent of one another because the irreducible cell includes all atoms of each molecule in the formula unit; at room temperature the Cp* rings are rotated by 15° relative to the eclipsed configuration. The [FeIII\text{Cp*}^2]^+ cation has a Fe-C distance of 2.096 Å, and Fe⋯C5-ring centroid of 1.733 Å, with the two Cp* rings being staggered with a 14.4° dihedral angle, Figure 3c. Thus, the FeC_{10} core has $D_5$ symmetry. The relative orientation between the [FeCp*^2]^+ and [TCNQ]^− differs for the room temperature MM_{RT} and low temperature FO and MM_{LT} structures, Figure 4. The most symmetric cation occurs for MM_{LT} at 17 K, Figure 4b.
Figure 4. Top (above) and side (below) views of for the chain motif for MM at 300 (MM_{RT}) (a) and 17 K (MM_{LT}) (b), for FO at 19 K (c, c'), and for [FeCp^*2][TCNE] (d). The TCNQ and Cp* planes are not perpendicular to the chain axis for (c), and (c') shows the side and top views looking normal to these planes. For (a), (b), and (c/c') the iron atoms are eclipsed and the exo-C-C TCNQ bonds are parallel to the top of the page when rotated by 90°.

Comparison of the low temperature FO, MM, and [FeCp^*2][TCNE] structures

FO, MM, and [FeCp^*2][TCNE] each possess chains of alternating cations and anions and each chain is surrounded by two in-registry and four out-of-registry chains as described above, Figures S5, S6, S7, S8, and 4. The main structural difference between FO and MM_{LT} polymorphs of [FeCp^*2][TCNQ] at low temperature occurs for the in-registry [TCNQ]^−•••[TCNQ]^− interactions, Figures S6 (I-II) and S8 (I-IV), with the MM_{LT} polymorph having a 10.0% shorter separation (3.729 Å) with respect to the FO polymorph (4.143 Å), Table 2. Also, the intrachain Fe•••Fe separation is 2.8% shorter for MM_{LT} (10.439 Å) than for FO (10.738 Å). While the N•••N separation in longer for FO, the in-registry interchain and Fe•••Fe separations are 3.8 and 1.0% shorter, respectively, for FO, Table 2. Likewise, the shortest out-of-registry interchain, Fe•••Fe, and Fe•••N separations are 1.6, 3.2, and 9.1% shorter, respectively, for FO.

The biggest difference between FO and [FeCp^*2][TCNE], of course, is that D_{2h} [TCNQ]^− is about twice the size of the almost square D_{2h} [TCNE]^−. Thus, reduced interchain separations
are anticipated for [FeCp*₂][TCNE]. While the reduced size of [TCNE]⁻ should not directly affect the intrachain separation, it however, it is 10.738 Å for FO; 3.0% longer with respect to [FeCp*₂][TCNE] (10.415 Å), and it is an 0.23% shorter than for MM_LT (10.439 Å). The smaller [TCNE]⁻ leads to a 17.8% decrease in the N•••N separation to 3.408 Å from 4.143 Å in FO, and 8.6% decrease with respect to MM_LT (3.729 Å), as expected. Likewise, the shortest out-of-registry interchain, Fe•••Fe, and Fe•••N separations are 1.6, 3.2, and 9.1% shorter, respectively, for FO. Each of the in- and out-of-registry Fe•••Fe and interchain separations for [FeCp*₂][TCNE] are reduced from 1.5 to 10.9% with respect to FO, and by 4.9 to 12.3% with respect to MM_LT. The out-of-registry Fe•••N separation increases from 4.789 Å by 5.3% to 5.042 Å for [FeCp*₂][TCNE], and this is attributed to the almost square nature of [TCNE]⁻ enabling it to adopt a differently rotated orientation; however, this separation decreases by 3.5% from the 5.225 Å observed for MM_LT.

**Thermal behavior of MM**

A DSC study confirmed the phase transition upon warming above -55 °C, Figure 5. The transition temperature ($T_{\text{warm}}$) was determined from extrapolation of the most linear portion of the onset of absorption in the heat flow to an approximated baseline established from the internal standard heat flow. A slight variation was observed in this value with that observed upon cooling ($T_{\text{cool}}$), and these differences were found to depend on the temperature scan rate and was determined to be an artifact of finite temperature scan rates. The $T_{\text{warm}}$ and enthalpy of transition were determined to be $226.5 \pm 0.4$ K (46.7 ± 0.4 °C) and 0.68 ± 0.04 kJ/mol (0.16 ± 0.01 kcal/mol), respectively, Figure 5. The transition was found to be robust under successive temperature cycles and for multiple samples. Calorimetric studies of the related MnCp*²⁶ and [FeCp*₂][TCNE]¹⁰⁻²⁷ revealed structural transitions at similar temperatures. While MnCp*₂ displayed an peak between 255 and 238 K, which was attributed to slipping of MnCp*₂ units within a chain,²⁶ [FeCp*₂][TCNE] exhibited anomalies in the adiabatic heat capacity at 248.7 and 281.8 K.²⁷ The structural similarities between [FeCp*₂][TCNE] and MM suggest that the transition, Figure 5, may be analogous to that observed for [FeCp*₂][TCNE]. The reported enthalpy for the [FeCp*₂][TCNE] transition (3.32 kJ/mol) is significantly larger than reported for MM, but includes the neighboring anomaly at 281.8 K, which adds substantially to the enthalpy.²⁷ The transition at 248.7 K for [FeCp*₂][TCNE] was classified as an order-disorder type on the basis of entropy,²⁷ which was
consistent with later temperature dependent diffraction studies.\textsuperscript{11} The absence of disorder in diffraction data of \textbf{MM} indicate that the behavior observed at 226.5 K is more likely to resemble that of \textit{MnCp*}_2.\textsuperscript{6} However, unlike for \textit{MnCp*}_2 where an anomaly occurs in the temperature dependent magnetic susceptibility data,\textsuperscript{6} there is no evidence of such a transition for either \textbf{MM} or \textit{[FeCp*}_2][TCNE]. The investigation of the 70 ± 10 K \textbf{MM} to \textbf{MM}\textsubscript{LT} phase transition was beyond the limits of our DSC and thus unfortunately could not be studied.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Heat_Flow.png}
\caption{Heat flow of a representative sample of \textbf{MM} upon warming.}
\end{figure}

Spin coupling analysis for the FO and MM polymorphs of \textit{[FeCp*}_2][TCNQ] and \textit{[FeCp*}_2][TCNE]

\textbf{Methodological details}

The spin-coupling interactions, \(J_{ij}\), between the nearest neighbor \textit{[FeCp}_2]\textsuperscript{+⋯}[TCNQ]\textsuperscript{−}, \textit{[FeCp}_2]\textsuperscript{+⋯}[FeCp}_2]\textsuperscript{+}, and \textit{[TCNQ]}\textsuperscript{−⋯}[TCNQ]\textsuperscript{−} radical pairs present in the FO and MM\textsubscript{LT} polymorphs were evaluated using the \(H = -2J_{ij}\mathbf{S}_i\mathbf{S}_j\) Heisenberg Hamiltonian. Since each of these
spin-containing units are doublets, values of $J_{ij}$ for all symmetry-unique pairs of spin-containing units were computed as $J_{ij} = (E(S)_{ij} - E(T)_{ij})/2$, where $E(S)_{ij}$ and $E(T)_{ij}$ are the energies of the lowest-energy singlet and triplet states for the ij pair. The wave-function based RASSCF methodology, as implemented in the MOLCAS package, was used to calculate these energies. To ensure the introduction of all correlation energy involved in the singlet-triplet gaps, all p and d orbitals (double-shell) in the restricted active space through orbital localization technique are included. In all energy calculations, the Madelung field effect has been incorporated introducing ~1500-point charges surrounding the ab-initio calculated dimer. Those charges were obtained for the [FeCp$_2$]$^+$ and [TCNQ]$^-$ ions at the DFT level.

The restricted active space used for the [FeCp$_2$]$^+$$\cdots$[TCNQ]$^-$ dimers is (34, 2, 2; 15, 3, 18) and it is based on a (34, 36) active space. (Figure S9 includes the scheme of the RASSCF methodology.) The orbitals included in the restricted active space are: (a) the five orbitals of [FeCp$_2$]$^+$ of dominating Fe character, which possess five electrons, (b) the [TCNQ]$^-$ SOMO orbital, (c) a second shell of empty d orbitals on Fe intended to allow the d-d correlation (d-doubling), and (d) all Cp* and [TCNQ]$^-$ $\pi$ orbitals. MOs for [FeCp$_2$]$^+$$\cdots$[TCNQ]$^-$ dimers are shown in Figure S10. In contrast, the restricted active space used for the [TCNQ]$^-$$$\cdots$[TCNQ]$^-$ dimers is (34, 2, 2; 16, 2, 14) and is based on a (34, 32) active space. The orbitals included are all of the [TCNQ]$^-$ $\pi$ orbitals (Figure S11). Finally, the restricted active space used to calculate the magnetic coupling between the [FeCp$_2$]$^+$$\cdots$[FeCp$_2$]$^+$ radical pairs is (34, 2, 2; 14, 4, 22), and is based on a (34,22) active space. The orbitals included are the d orbitals (double-shell) of the Fe atom and all $\pi$ orbitals of the Cp* units (Figure S12). Therefore, the three RAS active spaces are of similar accuracy. All RASSCF calculations were performed using the atomic natural orbital ANO-RCC basis sets. The contractions used were: [4s3p] for the C atoms of the Cp* rings, [5s4p] for the C and N atoms of the [TCNQ]$^-$, [6s4p3d1f] for the Fe atoms, and [2s] for the H atoms.

**SOMOs**

The ground state of [FeCp$_2$]$^+$ is a doublet that has a strong multi-referent character involving two degenerated d-dominated MOs of [FeCp$_2$]$^+$ (Figure 6a). It is thus a common practice to use state-average MCSCF computations for the [FeCp$_2$]$^+$ doublet considering two pseudo-degenerate states including all five Fe d orbitals with its electrons. This near degeneration dominated by
the d-MOs present in \([\text{FeCp}^*]_2\)\(^+\) doublet is maintained in the \([\text{FeCp}^*]_2\)\(^+\)···[TCNQ]\(^-\) pairs (Figure 6b). Indeed, an analysis of the occupation of the orbitals for a \([\text{FeCp}^*]_2\)\(^+\)···[TCNQ]\(^-\) pair excised from the stacks shows that three SOMOs have occupations of 1.5, 1.5 and 1.0 (Figure 7). The two SOMOs with occupations of 1.5 correspond to the non-bonding \(d_{xy}\) and \(d_{x^2-y^2}\) orbitals of Fe, while the remaining SOMO with an occupation of 1.0 corresponds to the bonding combination between of the \(d_{xz}\) orbital of Fe and the \(\pi^*\) orbital of [TCNQ]\(^-\) {and also in [TCNE]\(^-\)}\(^{10}\). Note that a 1.5, 1.5, 1.0 occupation is typical for a multireference wavefunction, where two configurations in which the three SOMOs of Figure 7 have occupations 2, 1, 1 and 1, 2, 1 and each are combined with a 50% weight.

As a consequence, two pseudo-degenerate singlets and two pseudo-degenerate triplets have to be considered. Likewise, four pseudo-degenerate singlets and four pseudo-degenerate triplets were considered for the \([\text{FeCp}^*]_2\)\(^+\)···[FeCp\(^*\)]\(^+\) radical pairs. Similar conclusions were obtained for the singlet and triplet states of \([\text{FeCp}^*]_2\)\(^+\)···[TCNQ]\(^-)\(^{10}\).
Figure 6. Qualitative MO diagram describing: (a) the state of lowest energy for the doublet (D1 and D2) [FeCp*₂]^+ radical cation; (b) the state of lowest energy for the doubly degenerate triplet states (T1 and T2) for [FeCp*₂]^+·[TCNQ]^-, two states that are more stable than their associated doubly degenerate S1 and S2 singlets states. The qualitative MO diagram for the [FeCp*₂]^+···[TCNE]^+ pair is similar to that computed here for the [FeCp*₂]^+···[TCNQ]^+ radical pair.
Figure 7. Shape of the three SOMOs computed at the B3LYP/6-31g(d) level for [FeCp*₂][TCNQ] (top) extracted from the FO and MM₇₈ structures (the same results are obtained in both cases) and for [FeCp*₂][TCNE] (bottom) (the isosurface of 0.02 atomic units is plotted, white for positive values and blue for negative values). Their electron occupation (left to right) is 1.5:1.5:1.0 atomic unit (electrons). The shape and occupation of the three [FeCp*₂][TCNE] SOMO orbitals are identical to that previously reported using the CASSCF(8,7) wave function¹⁰ (a different isosurface is presented for a clearer view of the nodal structure).

Results of the spin coupling analysis

The $J_{ij}$ values were evaluated for each symmetry-unique radical pair found in the crystal structures of the FO and MM₂₇₈ polymorphs of [FeCp*₂][TCNQ] determined at 18 ± 1 K. The five nearest neighbor interactions for which the associated $J_{ij}$ is different from zero in at least one of the polymorphs are shown in Table 3. The differences in the relative orientations present for the FO and MM₂₇₈ polymorphs is presented in Figure 8. All the $J_{ij}$ couplings between the nearest neighbor...
[FeCp*₂]^−•••[FeCp*₂]^+ pairs were computed to be negligible and will therefore not be further considered.

**Table 3.** Computed nearest-neighbor magnetic exchange interactions, $J_{ij}$ (cm$^{-1}$), for the [FeCp*₂]^+•••[TCNQ]^−, [FeCp*₂]^+•••[FeCp*₂]^+, and [TCNQ]^−•••[TCNQ]^− nearest-neighbor interactions present for the FO and MMₐₜ polymorphs of [FeCp*₂]^+[TCNQ]^− for which $|J_{ij}| \geq 0.1$ cm$^{-1}$ in at least one of the polymorphs. Note that none of the [FeCp*₂]^+•••[FeCp*₂]^+ have a $|J_{ij}| \geq 0.1$ cm$^{-1}$. Z is the number of equivalent interactions in the unit cell, and $C$ is the centroid of the ion.

<table>
<thead>
<tr>
<th>Interaction</th>
<th>FO [FeCp*₂][TCNQ]</th>
<th>MMₐₜ [FeCp*₂][TCNQ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J_1$</td>
<td>5.2</td>
<td>6.5</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>$J_1$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$J_2$</td>
<td>4.7</td>
<td>5.219 Å</td>
</tr>
<tr>
<td>$Z$</td>
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<td>2</td>
</tr>
<tr>
<td>$J_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$J_2$</td>
<td>= $J_1$</td>
<td></td>
</tr>
<tr>
<td>$J_2$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fe···C(TCNQ) = 5.311 Å
C(Cp*)···C(TCNQ) = 3.573 Å

Fe···C(TCNQ) = 5.219 Å
C(Cp*)···C(TCNQ) = 3.505 Å

Fe···C(TCNQ) = 5.667 Å
C(Cp*)···C(TCNQ) = 3.570 Å

Fe···C(TCNQ) = 5.219 Å
C(Cp*)···C(TCNQ) = 3.505 Å
<table>
<thead>
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<th>$J_3$</th>
<th>0.2</th>
<th>4</th>
<th>[ \text{N···H} = 2.820 \text{ Å} ]</th>
<th>-0.1</th>
<th>1</th>
<th>[ \text{N···H} = 2.465 \text{ Å} ]</th>
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<td>$J_4$</td>
<td>0.1</td>
<td>4</td>
<td>[ \text{Fe····C(TCNQ)} = 9.389 \text{ Å} ] [ \text{C(Cp*)····C(TCNQ)} = 3.732 \text{ Å} ]</td>
<td>0.0</td>
<td>[ \text{Fe····C(TCNQ)} = 9.245 \text{ Å} ] [ \text{C(Cp*)····C(TCNQ)} = 3.737 \text{ Å} ]</td>
<td></td>
</tr>
<tr>
<td>$J_5$</td>
<td>0.1</td>
<td>4</td>
<td>[ \text{N(TCNQ)····C(Cp*)} = 3.696 \text{ Å} ]</td>
<td>0.0</td>
<td>[ \text{N(TCNQ)····C(Cp*)} = 3.782 \text{ Å} ]</td>
<td></td>
</tr>
<tr>
<td>$J_1$</td>
<td><img src="image1.png" alt="Image" /></td>
<td></td>
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</tr>
<tr>
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<tr>
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</table>

**Figure 8.** Superposition of the [FeCp*$_2$]$^+$···[TCNQ]$^-$ interactions for both FO (black) and MM$_{LT}$ (red) polymorphs.

The alternating [FeCp*$_2$]$^+$ and [TCNQ]$^-$ ions present within each chain present for FO and MM$_{LT}$ (Figure 8) are computed to have ferromagnetic coupling, i.e. $J > 0$, and be the strongest nearest neighbor magnetic coupling for each polymorph. The average intrachain
[FeCp*₂]^−•••[TCNQ]^− interaction is computed to be 6.5 cm⁻¹ for MM₄LT, which on average is 24% lower for FO, Table 3. Note that the intrachain interaction for MM₄LT has higher symmetry than for FO; thus, the two different 5.2 and 4.7 cm⁻¹ interactions (J₁ and J₂) for FO become equivalent (6.5 cm⁻¹) for MM₄LT, Table 3. This, in part, is due to the 2.8% shorter separation for Fe•••Fe separation for MM₄LT with respect to FO, and differing orientations (Figure 8).

The MOs shown in Figures 7 and 9 provide a rationale for the ferromagnetic nature of the intrachain couplings. It should be noted that the degenerate SOMOs of ferrocenium, which are essentially localized on the dₓᵧ and dₓ₂₋ᵧ₂ orbitals of the Fe ion, are nearly orthogonal by symmetry to the SOMO of [TCNQ]^−. In fact, when the SOMOs of the intrachain [FeCp*₂]^−•••[TCNQ]^− pairs are plotted using a very small threshold for the electron density (see Figure 9) it is observed that the dₓᵧ and dₓ₂₋ᵧ₂-centered orbitals do not combine with the π* orbital of [TCNQ]^−. The vanishingly small overlap between the degenerate SOMOs of ferrocenium and the SOMO of [TCNQ]^− (Table 4) leads to a negligible antiferromagnetic component of the intrachain spin coupling. Second, the shape of the SOMO of the [FeCp*₂]^−•••[TCNQ]^− pair with an occupation of 1 displayed in Figure 9 explains the significant value of its ferromagnetic coupling. Specifically, this SOMO demonstrates that there is a partial charge transfer from the π* orbital of [TCNQ]^− to one of the degenerate virtual orbitals of [FeCp*₂]^+ (dₓz orbital). Such partial charge transfer is enabled by the delocalization of the dₓz orbital over the Cᵖ rings, which results in a non-negligible overlap between the SOMO of [TCNQ]^− and the dₓz orbital of the Fe ion (Table 4). The partial occupation of one of the virtual orbitals of ferrocenium favors the ferromagnetic coupling by virtue of Hund's rule.
Figure 9. RASSCF SOMO orbitals of $J_1$ (5.2 cm$^{-1}$) and $J_2$ (4.3 cm$^{-1}$) of the FO and $J_1$ (6.5 cm$^{-1}$) for MM$\text{LT}$. Triplet orbitals in all cases. All the orbitals have been plotted using a cutoff of 0.002.
Table 4. Overlap in atomic units between the [TCNQ]^− SOMO and: (a) one SOMO of [FeCp*₂]^+, (b) and (c) the two virtual antibonding Cp*-Fe(d) orbitals. The results are for the $J_1$ and $J_2$ dimers for both the FO and the MM_LT phases of [FeCp*₂][TCNQ]. The orbitals used are from a ROB3LYP/6-31g(d) calculation.

<table>
<thead>
<tr>
<th>Polymorph</th>
<th>$J_i$</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
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<tr>
<td>$J_1$ FO</td>
<td>5.2</td>
<td>0.00052</td>
<td>0.00119</td>
<td>-0.00904</td>
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<tr>
<td>$J_2$ FO</td>
<td>4.3</td>
<td>0.00245</td>
<td>0.00271</td>
<td>0.00935</td>
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<tr>
<td>$J_1 = J_2$ MM_LT</td>
<td>6.5</td>
<td>-0.04144</td>
<td>0.00914</td>
<td>-0.01104</td>
</tr>
</tbody>
</table>

In both of the MM_LT and FO polymorphs, there are 5 symmetry unique $J_n$ ($n = 1, 2, 3, 4, 5$) magnetic interactions (Table 3; Figure 8): (1) $J_1$, $J_2$, and $J_3$ are the three strongest magnetically coupled radical pairs and $J_4$ and $J_5$, whose average strength ($\sim 5$ cm$^{-1}$) is nearly twenty times weaker than that for $J_1$, $J_2$, and $J_3$, the latter are the dominating magnetic interactions. For MM_LT and FO the dominating interactions interconnect the [FeCp*₂]^•+ radical cations and [TCNQ]^− radical anions by a network of nearly parallel 1D chains, while the $J_4$ and $J_5$ interactions interconnect these 1D chains among their surrounding chains; thus, giving rise to a 3D network of magnetic interactions. None of the computed nearest neighbor couplings are negative, i.e. antiferromagnetic, and this is in agreement with observed ferromagnetic ground state for the FO polymorph. Furthermore, there are two [FeCp*₂]^•••[TCNQ]^− interactions computed to have a 0.1 cm$^{-1}$ ferromagnetic interaction for FO, which are reduced to 0.0 cm$^{-1}$ for MM_LT, Table 3.

As discussed above, the main structural difference between FO and MM_LT lies in the 10.0% shorter [TCNQ]^•••[TCNQ]^− ($J_3$) separations for MM_LT, Table 2. This along with the nominal change in relative orientations leads to a computed change from the ferromagnetic interaction (0.2 cm$^{-1}$) due to the near orbital orthogonality for FO (vide supra) to an antiferromagnetic interaction (-0.1 cm$^{-1}$) and is in accord with MM_LT having an antiferromagnetic ground state. The small values of the spin couplings due to weak lateral orbital interactions, together with the change in their sign in going from FO to MM_LT, indicate that the sign and value of the spin coupling in these pairs of radicals are governed by a delicate interplay of the overlap between SOMOs (which favors an antiferromagnetic coupling) and the exchange integral between SOMOs (which favors a ferromagnetic coupling). The antiferromagnetic interaction in the MM_LT...
polymorph is consistent with its shorter separations and the concomitant increase in the overlap between SOMOs (Figure 10), which results in the antiferromagnetic contribution of $J_3$ prevailing over the ferromagnetic contribution.

![Figure 10](image)

**Figure 10.** Top view of the bonding SOMO of the $[\text{TCNQ}]^\text{-}•••[\text{TCNQ}]^\text{-}$ pairs in the FO and MM$_{LT}$ polymorphs. The two SOMOs (resulting from a ROB3LYP/6-311+G(d) calculation) have been plotted using a cutoff of 0.0045.

While the $[\text{FeCp}^*]_2[\text{TCNQ}]$ (FO) and the $[\text{FeCp}^*]_2[\text{TCNE}]$ ferromagnets have differing magnetic topologies, Figure S13, both have a similar intrachain structure, Figure 4, and the two different ferromagnetic couplings (27.9 and 45.3 cm$^{-1}$) (Table 5) for $[\text{FeCp}^*]_2[\text{TCNE}]$ average 36.6 cm$^{-1}$, which is 7.4 times larger than for FO $[\text{FeCp}^*]_2[\text{TCNQ}]$. This enhanced ferromagnetic coupling is attributed to the smaller size and concomitant greater spin density for [TCNE]$^-$ with respect to [TCNQ]$^-$ (Figure 7), and a higher $T_c$ {4.8 K for $[\text{FeCp}^*]_2[\text{TCNE}]$; 3.1 K for FO} that cannot be accounted for from the $3\%$ reduced intrachain separation.

To explain the bulk magnetic behaviors for the FO and MM$_{LT}$ polymorphs of $[\text{FeCp}^*]_2[\text{TCNQ}]$ and $[\text{FeCp}^*]_2[\text{TCNE}]$, magnetic dipolar interactions may play an additional, but essential, contribution. Magnetic dipolar interactions should have magnitude similar to the extremely low interchain $J$ values, but the cooperative nature could strengthen their relevance.

**Table 5.** Computed nearest-neighbor magnetic exchange interactions, $J_{ij}$, for the $[\text{FeCp}^*]_2^+•••[\text{TCNE}]^-$, $[\text{FeCp}^*]_2^+•••[\text{FeCp}^*]_2^+$, and $[\text{TCNE}]^•••[\text{TCNE}]^-$ nearest neighbor pairs present for the ferromagnetic $[\text{FeCp}^*]_2^+•••[\text{TCNE}]^-$. $Z$ is the number of equivalent interactions in the unit cell and $C$ is the centroid of the ion. Except for the value of $J_3$, the rest of $J_{ij}$ values in the table

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correspond to the values reported in Ref. 10. $J_3$ has been recalculated using the same RASSCF methodology used herein.

<table>
<thead>
<tr>
<th>$J_{ij}$</th>
<th>$J_i$, cm$^{-1}$</th>
<th>$Z$</th>
<th>Ferromagnetic $[\text{FeCp*}_2][\text{TCNE}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J_1$</td>
<td>45.3</td>
<td>4</td>
<td><img src="image1" alt="Diagram" /></td>
</tr>
<tr>
<td></td>
<td>$\text{Fe}\cdots X(\text{TCNE}) = 5.323 \text{ Å}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$C(\text{Cp*})\cdots C(\text{TCNE}) = 3.650 \text{ Å}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$J_2$</td>
<td>27.9</td>
<td>4</td>
<td><img src="image2" alt="Diagram" /></td>
</tr>
<tr>
<td></td>
<td>$\text{Fe}\cdots C(\text{TCNE}) = 5.209 \text{ Å}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$C(\text{Cp*})\cdots C(\text{TCNE}) = 3.464 \text{ Å}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$J_3$</td>
<td>0.0</td>
<td>2</td>
<td><img src="image3" alt="Diagram" /></td>
</tr>
<tr>
<td></td>
<td>$\text{C(TCNE)}\cdots \text{C(TCNE)} = 8.321 \text{ Å}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$J_4$</td>
<td>0.2 cm$^{-1}$</td>
<td>4</td>
<td><img src="image4" alt="Diagram" /></td>
</tr>
<tr>
<td></td>
<td>$\text{Fe}\cdots \text{C(TCNE)} = 7.804 \text{ Å}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\text{C(\text{Cp*})}\cdots \text{C(\text{TCNE})} = 3.576 \text{ Å}$</td>
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</tr>
<tr>
<td>$J_5$</td>
<td>0.0</td>
<td>4</td>
<td><img src="image5" alt="Diagram" /></td>
</tr>
<tr>
<td></td>
<td>$\text{N(\text{TCNQ})}\cdots \text{C(\text{Cp*)}} = 3.890 \text{ Å}$</td>
<td></td>
<td></td>
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</tbody>
</table>
Conclusion

As summarized by Scheme 1, [FeCp*₂][TCNQ] forms five phases, namely, a paramagnet (P) possessing $S = 1/2$ [FeCp*₂]$^{1+}$ and $S = 0$ [TCNQ]$_2^{2-}$ ions, and FO and MM polymorphs with the latter having differing structures at room (MM$_{RT}$) and at low temperatures (MM$_{LT}$), than below 167 K; nonetheless, these four 1-D structures possess parallel ···[FeCp*₂]$^{1+}$··· [TCNQ]$^{-}$ ···[FeCp*₂]$^{1+}$··· [TCNQ]$^{-}$··· 1-D chains with differing relative orientations. The FO and three MM phases of [FeCp*₂][TCNQ] and ferromagnetic [FeCp*₂][TCNE] possess similar inter- and intrachain structures possessing alternating $S = 1/2$ [FeCp*₂]$^{1+}$ and $S = 1/2$ [TCNQ]$^-$/[TCNE]$^-$, but differing magnetic behaviors. Comparison of the structures and nearest neighbor spin couplings for MM$_{LT}$ ($T_c = 2.5$ K), FO ($T_c = 3.1$ K), and ferromagnetic [FeCp*₂][TCNE] ($T_c = 4.8$ K), albeit having an even shorter (17.8%) N···N separation with respect to FO, has significantly enhanced intrachain ferromagnetic coupling that is accord with the 55% greater $T_c$ for [FeCp*₂][TCNE] with respect to FO. This is attributed to the smaller size and concomitant greater spin density for [TCNE]$^-$ with respect to [TCNQ]$^-$ providing an enhanced ferromagnetic coupling and a higher $T_c$ that cannot be accounted for from the slightly reduced (3%) intrachain separation.

[FeCp*₂][TCNE], in contrast, only forms one polymorph at room temperature, however, upon cooling two additional phases reversibly form at 280 and 245 K, Scheme 1.$^{10,27}$ Furthermore, solvated pseudo polymorphs of [FeCp*₂][TCNE] have been reported,$^{11}$ which have yet to be reported for [FeCp*₂][TCNQ]. Based upon Kitaigorodskii’s principle$^{34}$ that the more stable polymorph has the higher density,$^{35}$ based on the room temperature structure, Table 1, P is the more stable than the MM$_{RT}$ and FO polymorphs. This is in accord with P also having extra stabilization arising from the intradimer π-[TCNQ]$_2^{2-}$ multicenter bonding,$^{36,37}$ in addition to the van der Waals interactions that are also present for MM$_{RT}$ and FO.
Scheme 1. Formation of the five (3 room temperature) forms of [FeCp*₂][TCNQ] (top) and three (1 room temperature) forms of [FeCp*₂][TCNE] (bottom).

A computational nearest-neighbor magnetic coupling analysis based upon the low temperature (18 ± 1 K) structures suggest dominating intrachain [FeCp*₂]**•••[TCNQ]•• ferromagnetic spin couplings (4.95 and 6.5 cm⁻¹ for FO and MM_LT, respectively) as a consequence of their spins (S = 1/2) residing in orthogonal orbitals. All of the nearest neighbor magnetic interactions are ferromagnetic (J_ij > 0) for the FO polymorph in accord with the observed ferromagnetically ordered ground state. Similar results were reported for ferromagnetic
Nonetheless, computational results indicate that in contrast to the FO polymorph, due to an orientational change and the shortest separation between nearest neighbor [TCNQ]•••[TCNQ]••• antiferromagnetic coupling is calculated for this interaction for the MM_{LT} polymorph that is consistent with its antiferromagnetic ground state. Thus, the magnetic ground state cannot be described from the dominant magnetic interactions. Furthermore, the MM_{RT} room temperature structure reversibly transforms to the MM structure at 226.5 K (-46.7 °C) with an enthalpy of transformation of 0.68 kJ/mol. At 70 ± 10 K, the MM structure reversibly transforms to the MM_{LT} structure that exhibits metamagnetic behavior. Hence, MM_{RT}, MM, and MM_{LT} result from displacive phase transitions, while MM, P, and FO do not.

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**Supporting Material**
The CCDC deposition numbers for FO, MM at 17 (MM_{LT}), 230, and 295 (MM_{RT}) K, are 2069077, 2069078, 2069829, and 2069080, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).
References

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http://www.bruker-axs.de. TOPAS-Academic is available at www.topas-academic.net


(24) (a) Saint Plus, v. 6.02; Bruker Analytical X-ray: Madison, WI 1999. (b) G. M. Sheldrick SADABS; University of Göttingen: Göttingen, Germany, 1996.

(25) G. M. Sheldrick *SHELXL97*, program for the crystal structure refinement, University of Göttingen, Germany, 1997


(30) The restricted active space is defined as the number of electrons in all RAS space, maximum number of holes in RAS1, maximum number of particles in RAS3; orbitals in RAS1, orbitals in RAS2, orbitals in RAS3 (see Figure S9 for further information)


(35) Since the density of $P$ exceeds the densities of the MM$_{RT}$ and FO by more than 1%, this assessment is deemed to be more than 90% reliable; A. Burger, R. Ramburger, *Microchem. Acta* **1979**, *II*, 273.


Low Temperature Structures and Magnetic Interactions in the Organic-based Ferromagnetic and Metamagnetic Polymorphs of Decamethyl-ferrocenium 7,7,8,8-Tetracyano-p-quinodimethanide, [FeCp₂⁺][TCNQ]⁻

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