Electronic Supplementary Information

Two-Dimensional Heterotriangulenes Based Manganese Organic Frameworks: Bipolar Magnetic and Half Semiconductor with Perpendicular Magnetocrystalline Anisotropy

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A. Computational Methods of nearest-neighbor exchange integral and anisotropy constant

The \( q = \sqrt{3} \times \sqrt{3} \) frustrated AFM state was calculated based on the \( XYZ \) Heisenberg Hamiltonian which is defined as

\[
H = -\sum_{\langle i,j \rangle} J(S_i^x S_j^x + S_i^y S_j^y + k_u S_i^z S_j^z)
\]

Where \( k_u \) is the anisotropy constant, \( 0 \leq k_u \leq 1 \). It becomes the \( XY \) model and isotropic Heisenberg model when \( k_u=0 \) and 1, respectively.\(^1\) The nearest-neighbor exchange integral \( J_i \) can be obtained through the formula:

\[
J_i = (E_{\text{AFM}} - E_{\text{FM}}) / (2|S|^2)
\]

The magnetic anisotropy energy \( E_{\text{MAE}} \) can be expressed as

\[
E_{\text{MAE}} = 8J |k_u - 1||S|^2
\]

The calculated results show that \( k_u \) is in the range of 0.3 to 0.7. According to the ground-state phase diagram deduced in a previous theoretical study,\(^2\) the ground state of the \( XTPA\)-Mn and \( XTPB\)-Mn (\( X=\text{M}, \text{C} \) and \( \text{O} \)) with \( S=5/2 \) and \( 0.3<k_u<0.7 \) is \( q=0 \) frustrated antiferromagnetic order.
Table S1 Lattice constant \( a \) (Å) of unit cell OTPA-Mn, energy difference \( \Delta E_{\text{FM-AFM}} \) and \( \Delta E_{\text{FIM-AFM}} \) (eV), magnetic moment \( M_{\text{Mn}} \) (\( \mu_B \)) of Mn atom and total magnetic moment \( M_{\text{FM}} \) and \( M_{\text{FIM}} \) (\( \mu_B \)) adopted with different effective \( U_{\text{eff}} \) (eV).

<table>
<thead>
<tr>
<th>( U_{\text{eff}} )</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a )</td>
<td>21.65</td>
<td>21.68</td>
<td>21.73</td>
<td>21.74</td>
<td>21.81</td>
</tr>
<tr>
<td>( \Delta E_{\text{FM-AFM}} )</td>
<td>44.93</td>
<td>28.66</td>
<td>17.67</td>
<td>8.6</td>
<td>7.41</td>
</tr>
<tr>
<td>( \Delta E_{\text{FIM-AFM}} )</td>
<td>7.19</td>
<td>5.2</td>
<td>3.82</td>
<td>3.6</td>
<td>2.55</td>
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<tr>
<td>( M_{\text{Mn}} )</td>
<td>4.31</td>
<td>4.40</td>
<td>4.48</td>
<td>4.53</td>
<td>4.60</td>
</tr>
<tr>
<td>( M_{\text{FM}} )</td>
<td>15.00</td>
<td>15.00</td>
<td>15.00</td>
<td>15.00</td>
<td>15.00</td>
</tr>
<tr>
<td>( M_{\text{FIM}} )</td>
<td>5.00</td>
<td>5.00</td>
<td>5.00</td>
<td>5.00</td>
<td>5.00</td>
</tr>
</tbody>
</table>
Table S2  Lattice constant ($a$) and band gap ($E_g$) of $X$TPA and $X$TPB ($X$=M, C and O).

<table>
<thead>
<tr>
<th></th>
<th>MTPA</th>
<th>CTPA</th>
<th>OTPA</th>
<th>MTPB</th>
<th>CTPB</th>
<th>OTPB</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>17.45</td>
<td>17.37</td>
<td>17.10</td>
<td>17.64</td>
<td>17.61</td>
<td>17.20</td>
</tr>
<tr>
<td>$E_g$ (eV)</td>
<td>1.67</td>
<td>1.74</td>
<td>1.09</td>
<td>2.14</td>
<td>1.30</td>
<td>2.07</td>
</tr>
</tbody>
</table>
Table S3  Calculated structure of XTPA-Mn and XTPB-Mn (X=M, C and O)

<table>
<thead>
<tr>
<th></th>
<th>MTPA-Mn</th>
<th>CTPA-Mn</th>
<th>OTPA-Mn</th>
<th>MTPB-Mn</th>
<th>CTPB-Mn</th>
<th>OTPB-Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_1$ (Å)</td>
<td>2.07</td>
<td>2.04</td>
<td>2.07</td>
<td>2.06</td>
<td>2.08</td>
<td>2.07</td>
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<tr>
<td>$d_2$ (Å)</td>
<td>1.42</td>
<td>1.41</td>
<td>1.39</td>
<td>1.52</td>
<td>1.52</td>
<td>1.47</td>
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<tr>
<td>$d_3$ (Å)</td>
<td></td>
<td>1.24</td>
<td>1.40</td>
<td></td>
<td>1.24</td>
<td>1.40</td>
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<tr>
<td>$d_4$ (Å)</td>
<td>1.10</td>
<td>1.09</td>
<td>1.09</td>
<td>1.10</td>
<td>1.09</td>
<td>1.09</td>
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<tr>
<td>$\theta_1$ (°)</td>
<td>120.00</td>
<td>120.00</td>
<td>119.88</td>
<td>119.95</td>
<td>120.00</td>
<td>119.90</td>
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<td>$\theta_2$ (°)</td>
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<td>119.98</td>
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<tr>
<td>$M_C$ ($\mu_B$)</td>
<td>-0.06</td>
<td>-0.06</td>
<td>-0.06</td>
<td>-0.06</td>
<td>-0.06</td>
<td>-0.06</td>
</tr>
</tbody>
</table>

Mn-C bond length ($d_1$), N/B-C bond length ($d_2$), O-C bond length ($d_3$), C-H bond length ($d_4$), Mn-Mn-Mn bond angle ($\theta_1$), C-N/B-C ($\theta_2$), magnetic moments of adjacent C atoms ($M_C$)
Figure S1  Test of (a) cutoff energy and (b) $k$-mesh for MTPB-Mn. The inset of (a) is the energy per atom around convergent cutoff energy.
Figure S2  The band and lattice structures of (a) MTPA, (b) MTPB, (c) CTPA, (d) CTPB, (e) OTPA and (f) OTPB, respectively.
Figure S3 $\sqrt{3} \times \sqrt{3}$ and q=0 spin configurations.
Figure S4  Top views of spin-polarized electron density for (a) MTPA-Mn, (b) MTPB-Mn, (c) CTPA-Mn, (d) CTPB-Mn, (e) OTPA-Mn and (f) OTPB-Mn in FM and FIM states, respectively. The isosurface value is 0.002 e/Bohr$^3$. Yellow and blue regions represent the positive and negative values, respectively.
Figure S5  The energy difference of (a) MTPA-Mn, (b) CTPA-Mn, (c) OTPA-Mn, (d) MTPB-Mn, (e) CTPB-Mn and (f) OTPB-Mn with SOC, respectively. The energy of AFM is set to zero.
Figure S6  The band structures around Fermi level, CB and VB for (a) MTPA-Mn, (b) OTPB-Mn, (c) CTPA-Mn and (d) CTPB-Mn in FM, FIM and AFM configurations, respectively. The Fermi level is set to zero. The red (blue) lines represent the spin-up (spin-down) channel.
Figure S7  The band structures around Fermi level, CB and VB for XTPA-Mn and XTPB-Mn ($X$=M, C and O) with SOC.
Figure S8  The local and total DOS of (a) MTPA-Mn, (b) CTPA-Mn, (c) OTPA-Mn, (d) MTPB-Mn, (e) CTPB-Mn and (f) OTPB-Mn in FM, FIM, AFM configurations, respectively. The positive and negative values represent the spin-up and spin-down channel, respectively.
Figure S9  The energy difference $\Delta E$ of (a) MTPA-Mn, (b) CTPA-Mn, (c) OTPA-Mn, (d) MTPB-Mn, (e) CTPB-Mn and (f) OTPB-Mn, respectively. FM, FIM with respect to the AFM under different biaxial strain. The energy of AFM is set to zero.
Figure S10  Strain-dependent band gap $\Delta E_g$ of $\chi$TPA-Mn and $\chi$TPB-Mn ($\chi$=M, C and O) in AFM state.
Figure S11  Evolution of the Monte Carlo averaged specific heat capacity for $\chi$TPA-Mn and $\chi$TPB-Mn ($\chi$=M, C and O) as a functional of temperature.
References
