Electronic supplementary information

Co\textsuperscript{II}, Mn\textsuperscript{II} and Cu\textsuperscript{II}-directed coordination polymers with mixed tetrazolate-dicarboxylate heterobridges exhibiting spin-canted, spin-frustrated antiferromagnetism and a slight spin-flop transition

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\begin{center}
\includegraphics[width=\textwidth]{Scheme_S1}
\end{center}

\textbf{Scheme S1} Possible binding modes of anionic atz' ligand.
Fig. S1 TG curves for 1 – 3.
Fig. S2 Simulated (red) and experimental (blue) X-ray powder diffraction patterns for 1 – 3.
Fig. S3 Local coordination environments of Co$^{II}$ atoms in 1 (Hydrogen atoms were omitted for clarity. Symmetry codes: A = 1 − x, 2 − y, 2 − z; B = 2 − x, 2 − y, 2 − z; C = x, 1 + y, z; D = x − 1, y, z).
Fig. S4 2D covalent layer of 1 jointly extended by atz' and nip^2 connectors (Terminal aqua ligands were omitted for clarity).
Fig. S5 3D supramolecular network of 1 formed by interlayer N–H···O hydrogen-bonding interactions.
### Table S1 Hydrogen-bonds distances (Å) and angles (°) for 1$^a$

<table>
<thead>
<tr>
<th>Donor – H···Acceptor</th>
<th>D – H</th>
<th>H ··· A</th>
<th>D···A</th>
<th>D – H···A</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(5)–H(5B)···O(1)$^{#1}$</td>
<td>0.86</td>
<td>2.41</td>
<td>2.947(3)</td>
<td>121</td>
</tr>
</tbody>
</table>

$^a$ Symmetry code: $^{#1} 1-x, 2-y, 1-z.$
**Fig. S6** The SBU of 2 with atom-numbering scheme in the asymmetric unit (H atoms were omitted for clarity. Symmetry code: A = 1 – x, 1 – y, 1 – z).

**Fig. S7** 3D supramolecular network of 2 formed by interlayer π···π stacking interactions.
Fig. S8 Plots of $\chi_M$ and $\chi_MT$ vs $T$ at different fields for 1.
**Fig. S9** Real ($\chi'$) and imaginary ($\chi''$) ac magnetic susceptibilities in zero applied dc field and an ac field of 3.5 Oe at different frequencies for 1.
Fig. S10 Field dependence of magnetization at 2 K for 1 (left) and 3 (right), respectively.
Fig. S11 Temperature dependence of $\chi_M$ for 2 under different dc fields.