Supporting Information to accompany:

Adapting (4,4) Networks Through Substituent effects and Conformationally Flexible 3,2':6',3"-Terpyridines

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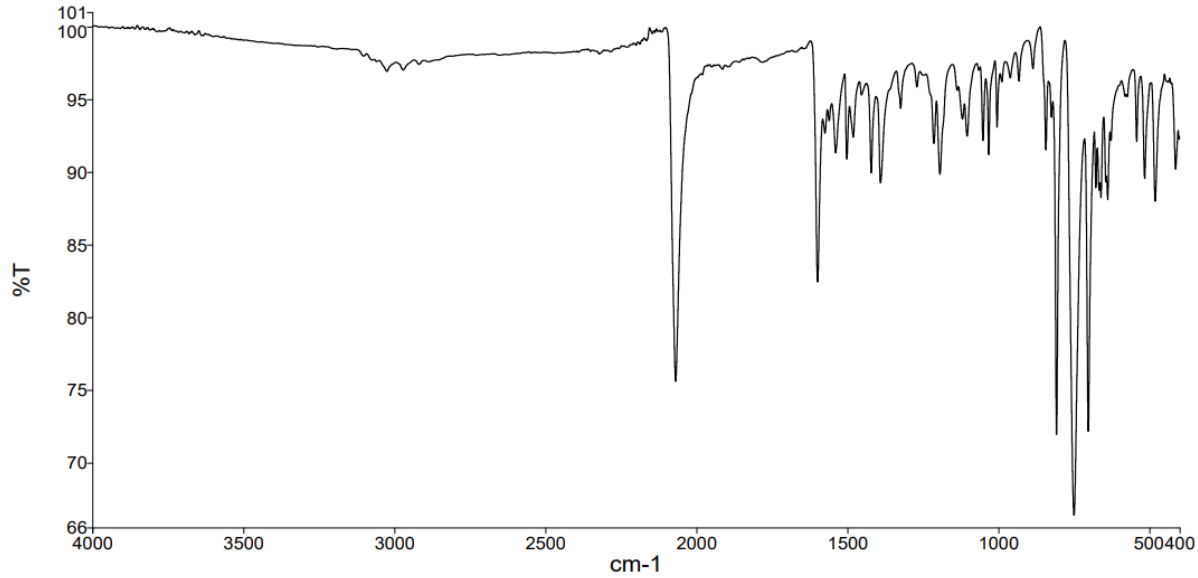

Fig. S1. Solid-state IR spectrum of $[Co(\mathbf{1})_2(NCS)_2]_n \cdot 4.5n CHCl_3$

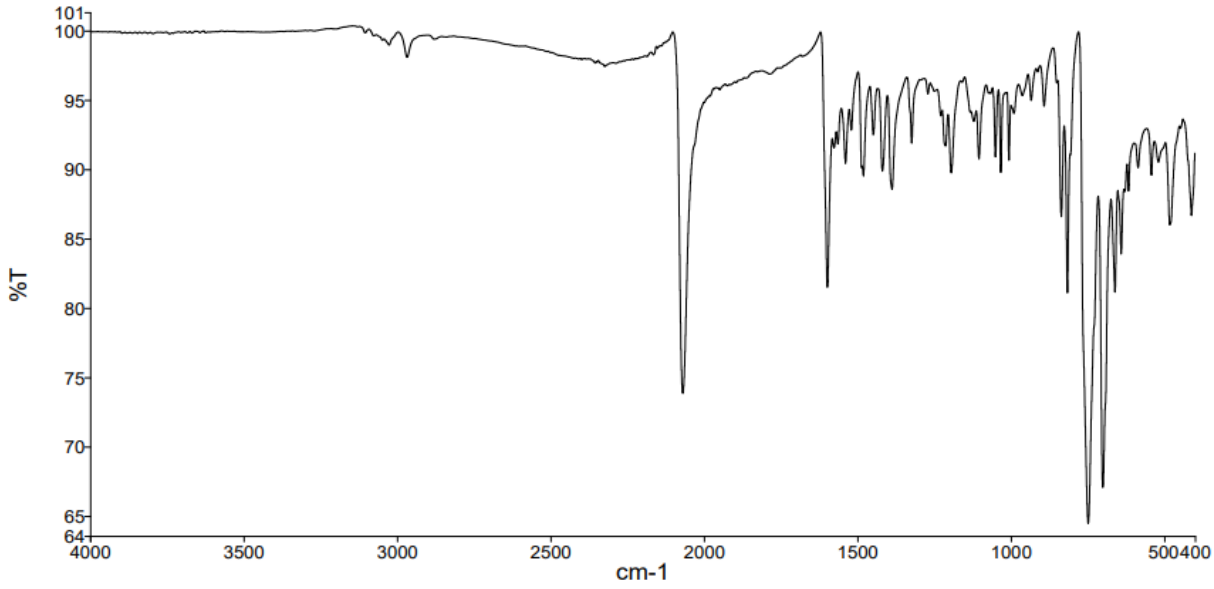

Fig. S2. Solid-state IR spectrum of $[Co(\mathbf{2})_2(NCS)_2]_n \cdot 4.3n CHCl_3$

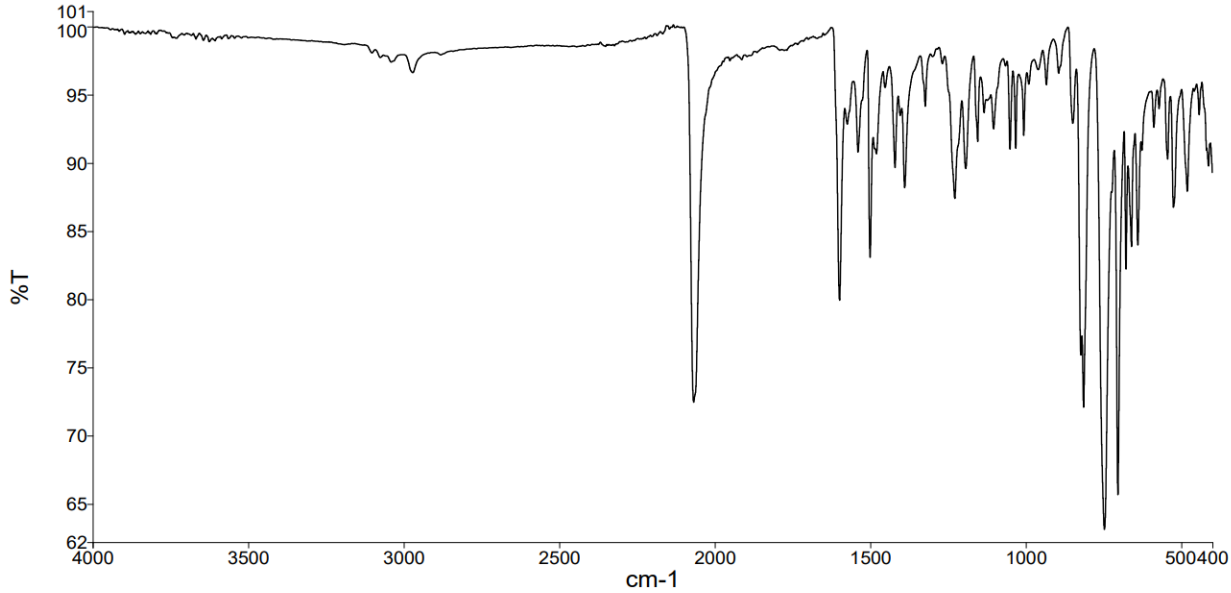

Fig. S3. Solid-state IR spectrum of $[Co(\mathbf{3})_2(NCS)_2]_n \cdot 4n CHCl_3$

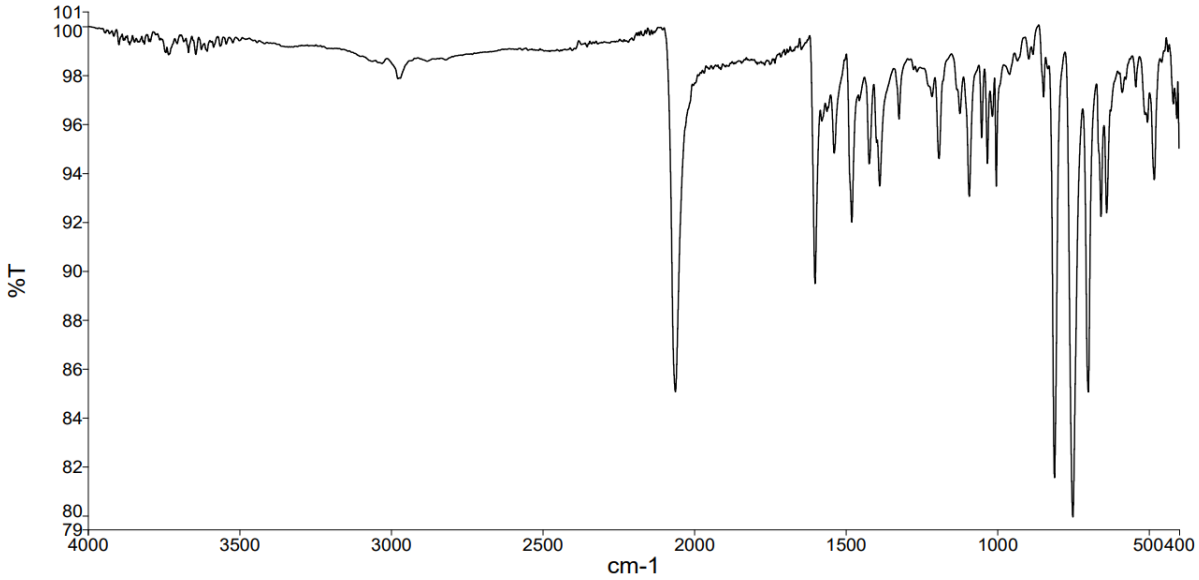

Fig. S4. Solid-state IR spectrum of $[Co(\mathbf{4})_2(NCS)_2]_n$

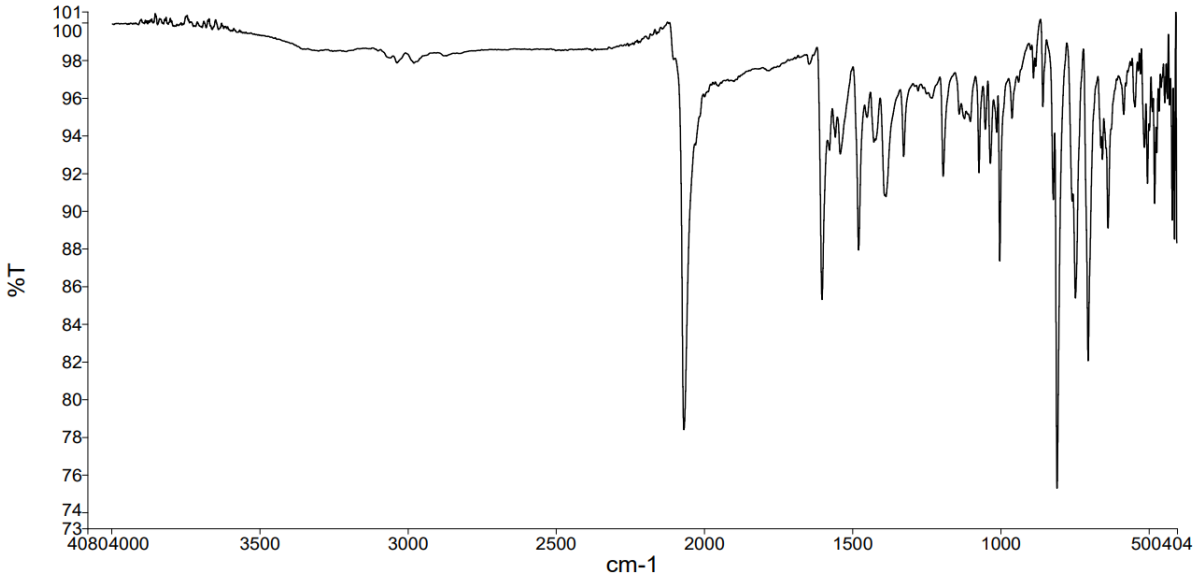

Fig. S5. Solid-state IR spectrum of $[Co(\mathbf{5})_2(NCS)_2]_n{\cdot}n CHCl_3$

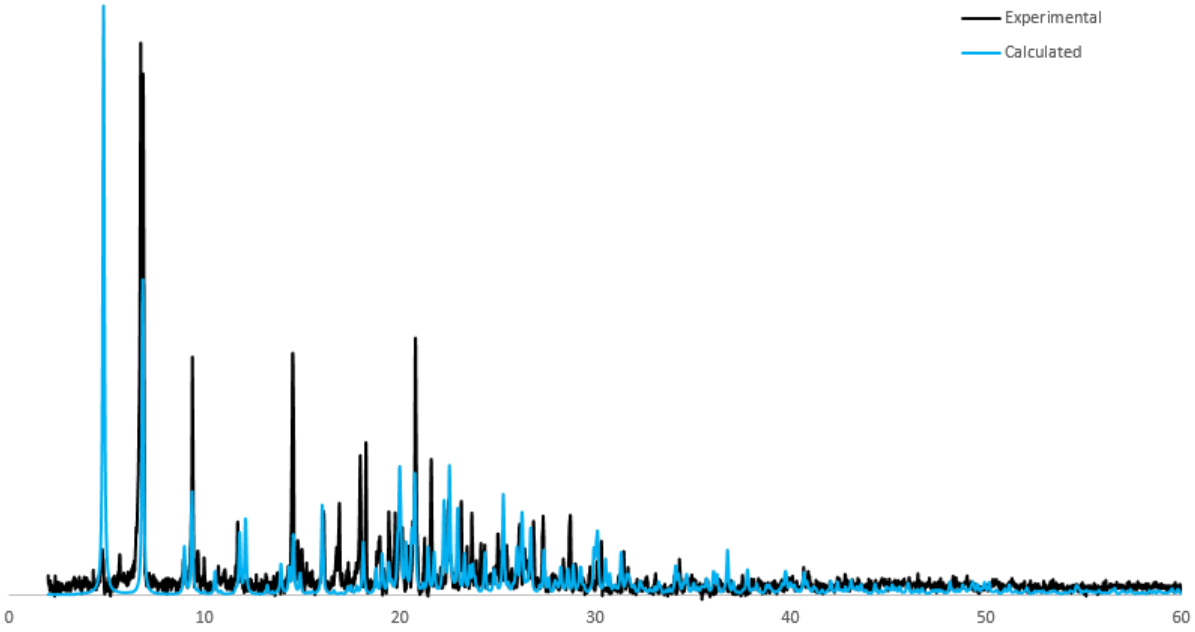

Fig. S6. Overlay of the experimental PXRD (298 K) for the bulk material and that predicted from the single crystal structure (150 K) of $[Co(\mathbf{2})_2(NCS)_2]_n{\cdot}4.3n CHCl_3$.

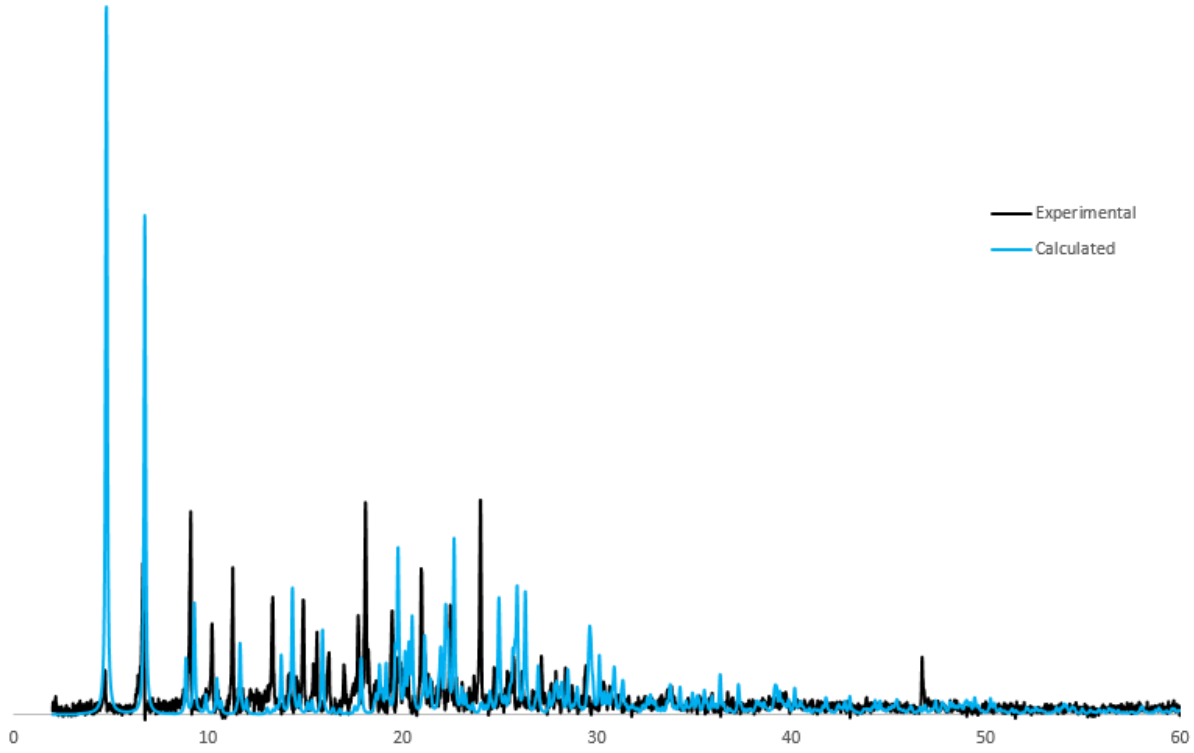

Fig. S7. Overlay of the experimental PXRD (298 K) for the bulk material and that predicted from the single crystal structure (150 K) of $[Co(\mathbf{1})_2(NCS)_2]_n \cdot 4.5n CHCl_3$.

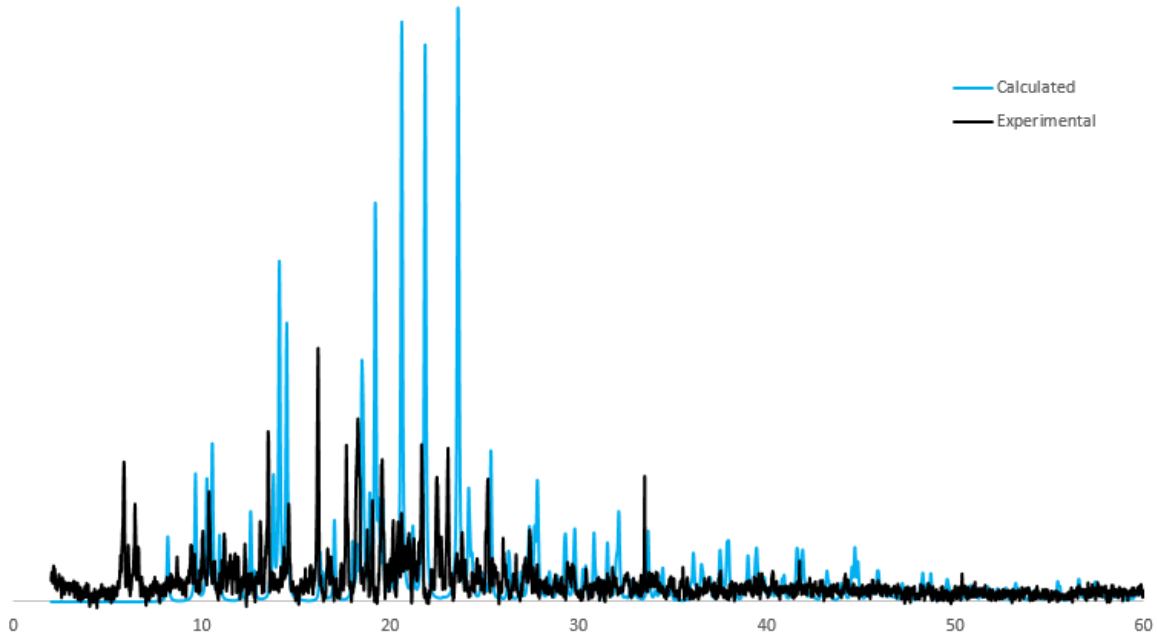

Fig. S8. Overlay of the experimental PXRD (298 K) for the bulk material and that predicted from the single crystal structure (150 K) of $[Co(\mathbf{4})_2(NCS)_2]_n$.

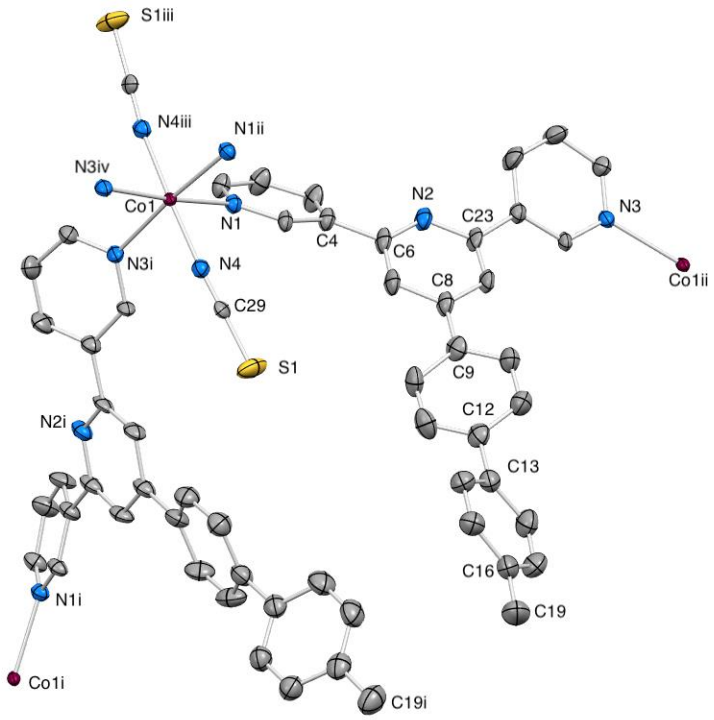

Fig. S9. Structure of the asymmetric unit in $[Co(\mathbf{1})_2(NCS)_2]_n \cdot 4.5n CHCl_3$ with symmetry related atoms. Symmetry codes: i = $^3/_2–y$, x, z; ii = y, $^3/_2–x$, z; iii = $1–y$, $1–x$, $^1/_2–z$; iv = $1–x$, $–^1/_2+y$, $^1/_2–z$. H atoms and solvent molecules are omitted. Ellipsoids are plotted at 40% probability level.

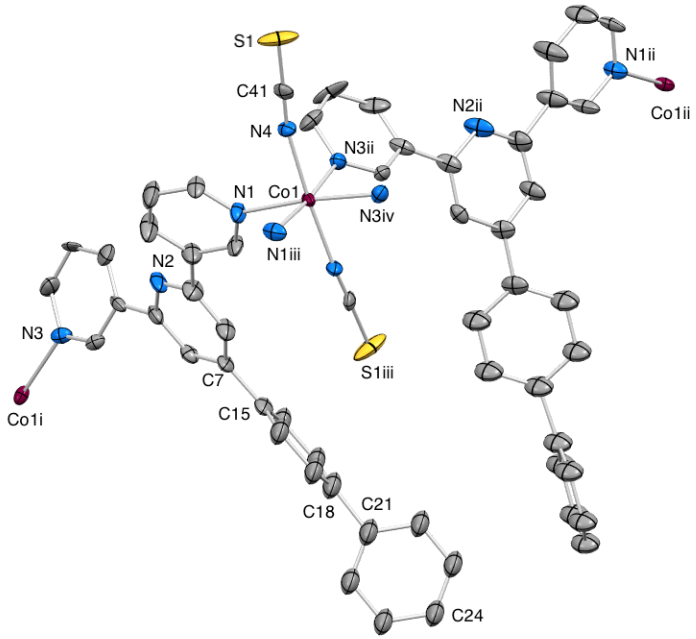

Fig. S10. Structure of the asymmetric unit in $[Co(\mathbf{2})_2(NCS)_2]_n \cdot 4.3n CHCl_3$ with symmetry related atoms. The biphenyl unit is disordered (see text) and only one position is shown. Symmetry codes: i = y, $^1/_2–x$, z; ii = $^1/_2–y$, x, z; iii = $–^1/_2+y$, $^1/_2+x$, $^3/_2–z$; iv = $–^1/_2+x$, $1–y$, $^3/_2–z$. H atoms and solvent molecules omitted. Ellipsoids are plotted at 40% probability level.

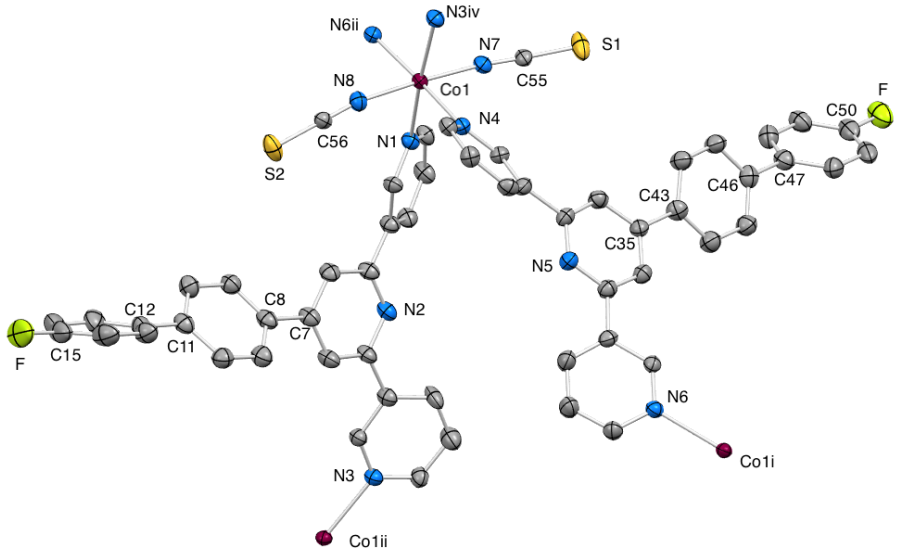

Fig. S11. Structure of the asymmetric unit in [Co(**3**)$_2$(NCS)$_2$]$_n$·4*n*CHCl$_3$ with symmetry related atoms. H atoms and solvent molecules omitted. Ellipsoids are plotted at 40% probability level. Symmetry codes: i = 1–*x*, –$^1/_2$+*y*, $^3/_2$–*z*; ii = $^1/_2$+*x*, 1–*y*, $^3/_2$–*z*; iii = 1–*x*, $^1/_2$+*y*, $^3/_2$–*z*; iv = –$^1/_2$+*x*, 1–*y*, $^3/_2$–*z*.

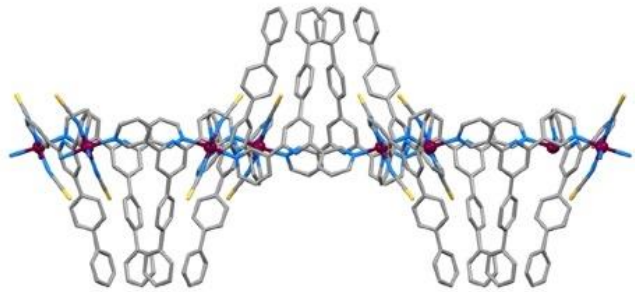

Fig. S12. Part of one 2D-sheet in [Co(**2**)$_2$(NCS)$_2$]$_n$·4.3*n*CHCl$_3$ showing cones above and below the plane containing the Co atoms. H atoms and solvnet molecules are omitted.

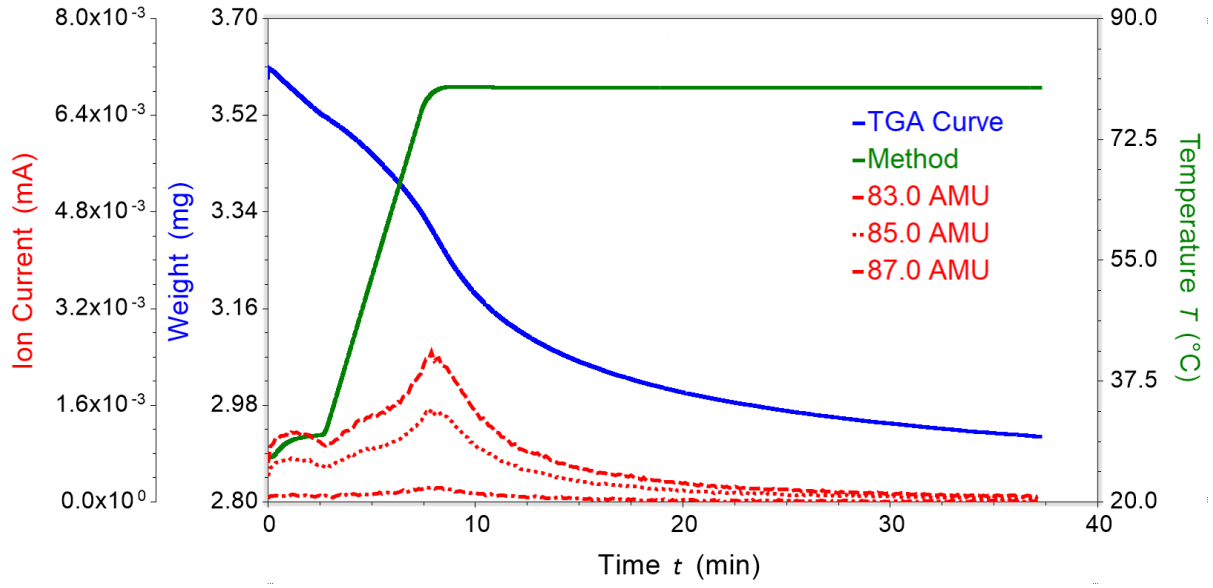

Fig. S13. TGA and mass spectrometric traces for the analysis of $[Co(\mathbf{3})_2(NCS)_2]_n{\cdot}4n CHCl_3$ (cycle 2: after 24 hour exposure to $CHCl_3$ vapor). Green: temperature vs. time; blue: weight of sample vs. time; red: mass detection for *m/z* 83.0 (most intense peak), 85.0 and 87.0. The initial mass of sample was 3.60 mg and a weight loss of 0.68 mg corresponds to ca. 19%.

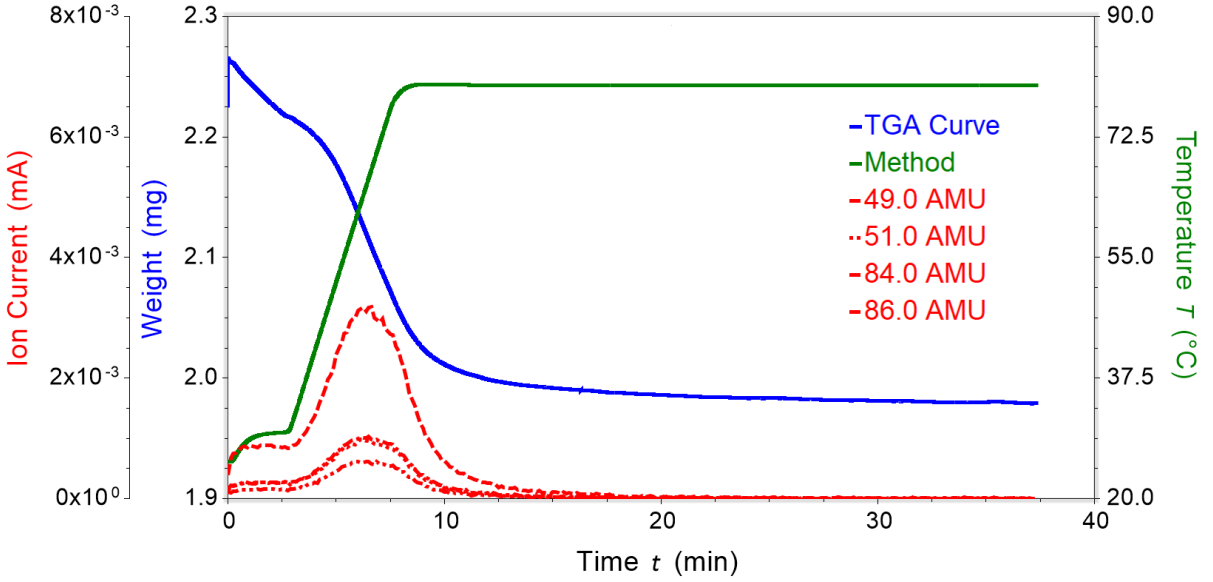

Fig. S14. TGA and mass spectrometric traces for the analysis of $[Co(\mathbf{3})_2(NCS)_2]_n{\cdot}2n CHCl_3{\cdot}2n CH_2Cl_2$ (cycle 4: after 24 hours exposure to CH_2Cl_2 vapor). Green: temperature vs. time; blue: weight of sample vs. time; red: mass detection for *m/z* 49.0, 51.0, 84.0, 86.0. The initial mass of sample was 2.26 mg and a weight loss of 0.28 mg corresponds to ca. 12%.

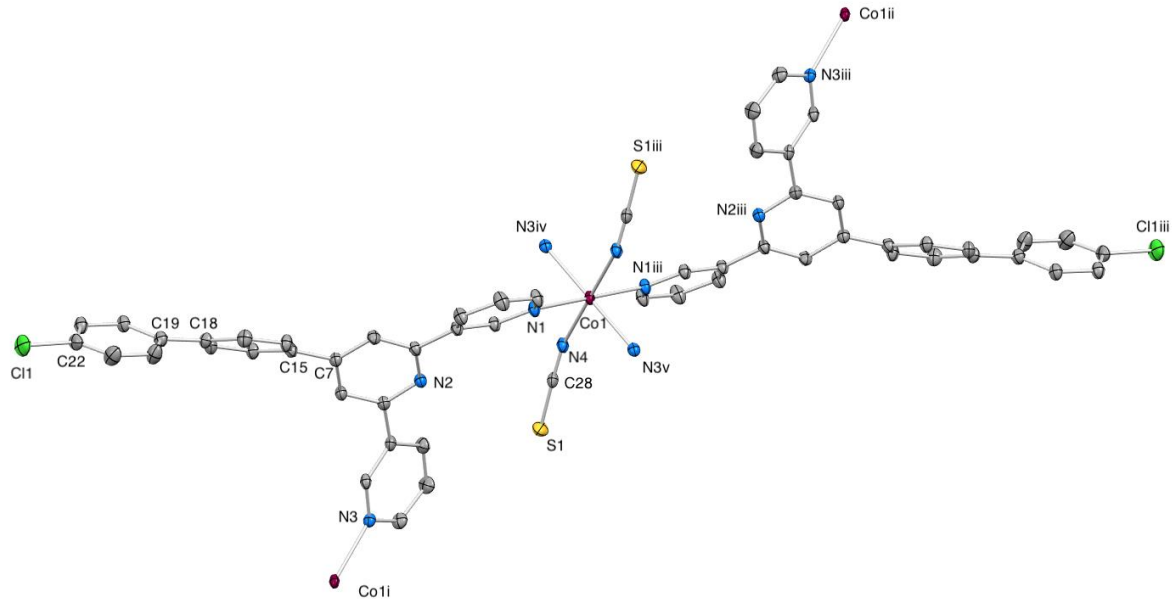

Fig. S15. Structure of the asymmetric unit in $[Co(\mathbf{4})_2(NCS)_2]_n$ with symmetry related atoms. H atoms and solvent molecules omitted. Ellipsoids are plotted at 40% probability level. Symmetry codes: i = $^1/_2+x$, $^1/_2+y$, $^3/_2-z$; ii = $-^1/_2-x$, $-^1/_2+y$, $^1/_2-z$; iii = $-x$, $-y$, $1-z$; iv = $-^1/_2+x$, $^1/_2-y$, $-^1/_2+z$; v = $^1/_2+x$, $-^1/_2+y$, $^3/_2-z$.

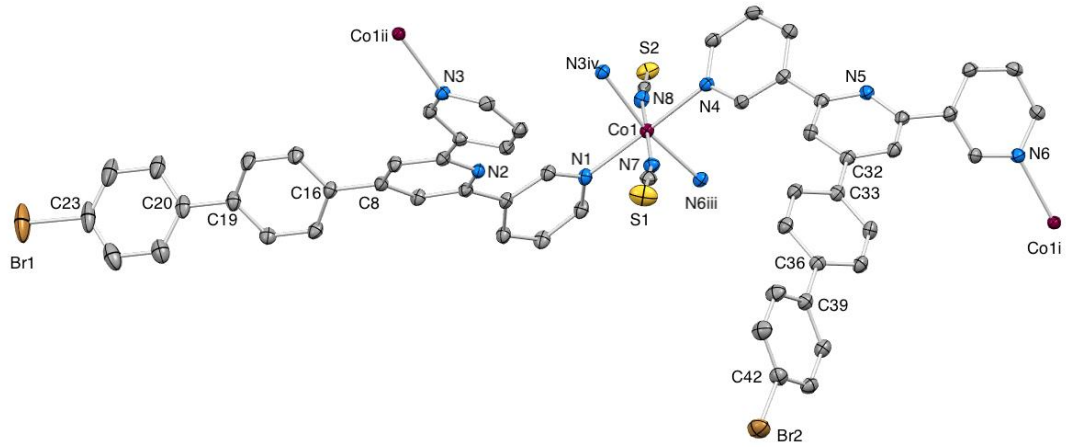

Fig. S16. Structure of the asymmetric unit in $[Co(\mathbf{5})_2(NCS)_2]_n{\cdot}n CHCl_3$ with symmetry related atoms. H atoms and solvent molecules omitted. Ellipsoids are plotted at 40% probability level. Symmetry codes: i = $^5/_2-x$, $^1/_2+y$, $^1/_2-z$; ii = $^3/_2-x$, $-^1/_2+y$, $^1/_2-z$; iii = $^5/_2-x$, $-^1/_2+y$, $^1/_2-z$; iv = $^3/_2-x$, $^1/_2+y$, $^1/_2-z$.