Supporting information for:

Iron(II) thio- and selenocyanate coordination networks containing 3,3'-bipyridine.

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Figure S1: Powder patterns of 2D 3 and 4

- Figure S2: Powder patterns of *trans*-{Fe(NCS)₂(3,3'-bipy)₂(MeOH)₂} 1
- Figure S3: Powder patterns of *trans*-{Fe(NCSe)₂(3,3'-bipy)₂(MeOH)₂} **2**

Figure S4: Powder pattern of 3D 4

Figure S5: TGA of 1

Figure S6: TGA of 2



Figure S1: Powder patterns of the two-dimensional $\{Fe(NCS)_2(3,3'-bipy)_2\}$ grid 3: calculated from the crystal structure (pink), powder synthesised by dropwise addition in acetonitrile (blue), and by thermal decomposition of 1 at 150 °C overnight (green). Pattern of 4 synthesised by thermal decomposition of 2 for comparison (lilac).



Figure S2: Powder patterns of *trans*-{Fe(NCS)₂(3,3'-bipy)₂(MeOH)₂} **1**; calculated (brown), and by precipitation from methanol (blue).



Figure S3: Powder patterns of *trans*-{ $Fe(NCSe)_2(3,3'-bipy)_2(MeOH)_2$ } **2**; Calculated from the crystal structure (brown), and by precipitation from methanol (lilac)



Figure S4: Experimental powder pattern of 4 (blue) compared with a tetragonal model using the cell lengths a = b = 15.60, c = 19.02 Å and atom coordinates based on published structure of $\{Ni(NCS)_2(3,3'-bipy)_2\}$ (with Fe and Se replacing Ni and S respectively).



Figure S5: TGA of 1.



Figure S6: TGA of **2**.