

**Fig. S1** Powder XRD (Cu Kα) for Fe(phen)<sub>2</sub>(NCS)<sub>2</sub> powder. Top: Spectrum simulated using single crystal x-ray diffraction structure at 293 K from reference 34. Bottom: Synthesized.



Fig. S2 Full FT-IR spectra normalized to the N-CS stretch. Assignments are the same as those in Fig. 2.



**Fig. S3** Spin-crossover of bulk Fe(phen)<sub>2</sub>(NCS)<sub>2</sub> powder observed by variation of  $(\chi_m T)$  with temperature measured by SQUID magnetometry (H = 1 kOe) for approximately 10 mg.

[Fe(phen) <sub>3</sub> ](SCN) <sub>2</sub>		Fe(phen) <sub>2</sub> (NCS) <sub>2</sub>		red film		purple film		
IR	Raman	IR	Raman	$\mathrm{IR}^a$	Raman <sup>b</sup>	$IR^{c}$	Raman <sup>d</sup>	Assignment <sup>e</sup>
		2102 w		2103 w		2101 w		
	2068 w	2072 s	2070 s			2072 s	2070 s	v(SC-N)
2048 s	2053 w	2058 s		2053 s		2060 s		v(SC-N)
		2040 sh						v(S <sup>13</sup> C-N)
		2019 w				2020 w		v(S <sup>13</sup> C-N)
2004 sh						2000 w		
1976 sh		1974 w						
1631 m				1629 w				
		1623 m	1626 w	1621 sh		1623 w		
1601 m	1599 m		1601 w	1602 w	1603 m		1597 m	v(C-C), v(C-N)
		1590 m	1590 w			1590 w		
1577 m	1575 s	1574 m	1575 m	1577 w	1581 s	1574 w	1577 s	
				1561 w		1558 w		
						1541 w		
1510 m	1510 s	1512 m	1512 s	1513 m	1515 s	1512 m	1512 s	
1492 m		1493 m		1494 w		1492 m		
						1474 w		
1456 w	1451 s			1453 w	1456 s	1456 w		
		1447 w	1448 s			1448 w	1449 s	
					1434 w			
1422 s	1428 w	1422 s	1419 s	1424 s		1423 s	1420 s	
1408 s	1416 m	1413 m		1413 sh		1414 sh		
1388 sh								
1338 m	1337 w	1340 m	1340 m	1342 m	1345 w	1340 w	1341 m	
1311 m		1314 w		1312 w		1314 w		
1297 w	1295 s		1299 s		1301 m		1300 s	
		1268 w						
1250 w	1249 w			1252 w	1254 w			
1224 m	1224 w	1221 w	1226 w	1223 w		1223 w	1224 w	
1204 m	1206 s	1208 w	1212 m	1207 w	1212 m	1208 w	1210 m	
1141 m	1144 m	1138 w	1145 m	1142 m	1144 w	1138 w	1144 m	δ(С-Н)
1105 w	1105 w	1100 w	1101 w	1102 w	1107 w	1101 w		
1092 m	1092 w	1091 w		1094 w		1092 w		δ(С-Н)
1056 m	1055 m	1053 w	1053 s	1056 w	1057 w		1054 s	
1042 w				1040 w				
1007 w								

## Table S1. All observed FT-IR and Raman peaks (in wavenumbers) and assignments for powders and films.

990 w								
982 w								
		972 w				972 w		
946 w		952 w				954 w		
925 w								
913 w	912 m				913 w			
			902 w				905 w	
877 w	876 w				878 w			
		865 m	865 m	865 w		865 w	865 m	
842 s		845 s		843 s		845 s		carbocyclic ring deformation
804 w		804 w	808 w	809 w		805 w	808 w	v(NC-S)
				801 w				
		792 w						v(NC-S)
779 m				773 m				
768 m		764 m				763 w		
736 w	737 s			734 w	738 s			
722 s	723 m	723 s	725 s	724 s	724 m	724 s	725 s	heterocyclic ring deformation
	645 w				645 w			
			636 w				636 w	
					619 w			
					583 w			
	560 m				561 m		559 w	
	495 m				495 w			δ(NCS)
	464 w							
	435 w				436 w			
	419 w		419 m				419 m	
	407 w		406 w				406 w	
	368 w				369 w			v(Fe-N(phen))
	314 w				314 w			
	296 w				296 w			
	281 w		282 m				282 s	
			257 w				258 w	v(Fe-NCS)
			217 m				218 m	v(Fe-N(phen))
	177 w		177 s				179 s	
	154 w		155 w		153 m		154 w	
			131 w				132 m	

<sup>*a*</sup> A red film vapor deposited onto KBr. <sup>*b*</sup> A red film vapor deposited onto glass. <sup>*c*</sup> A purple film on KBr made by annealing a red film. <sup>*d*</sup> A purple film on glass made by annealing a red film. <sup>*e*</sup> Assignments drawn from references 29, 39, 64.