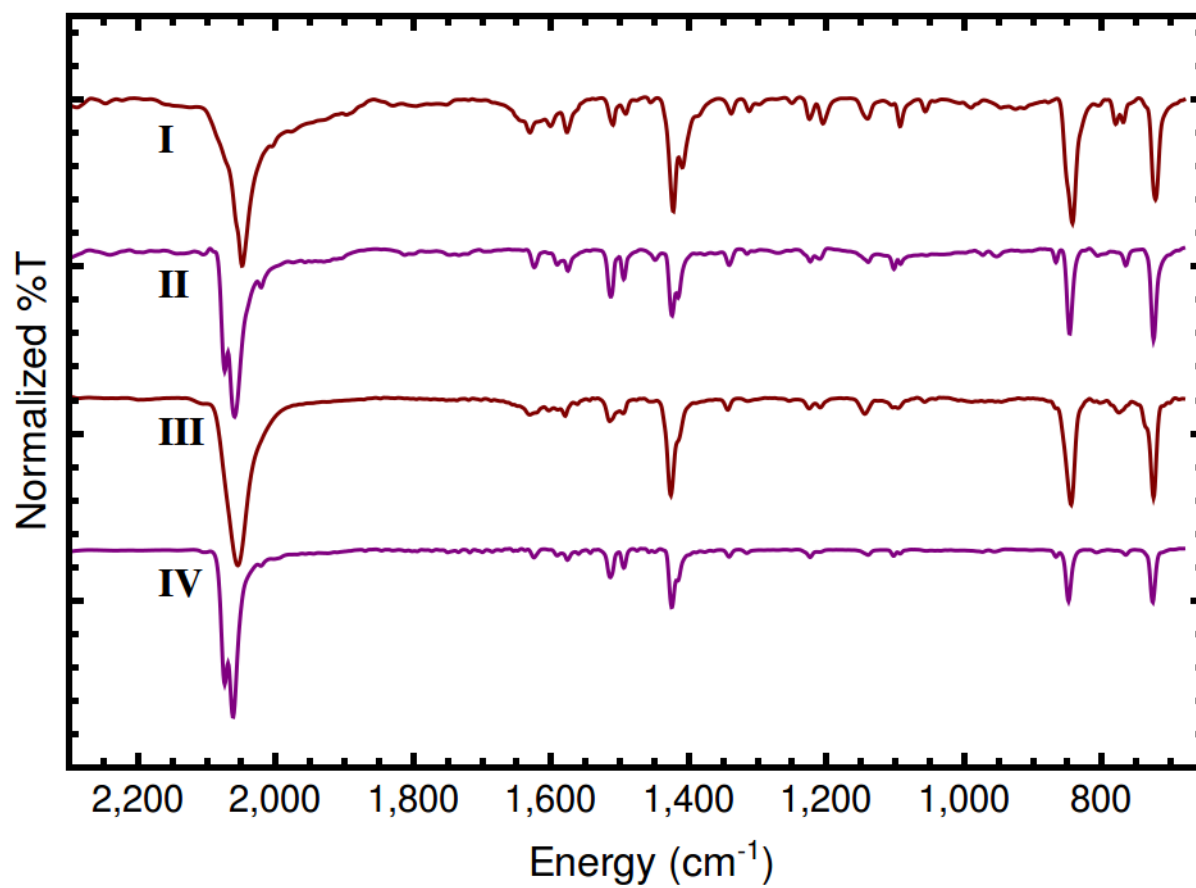
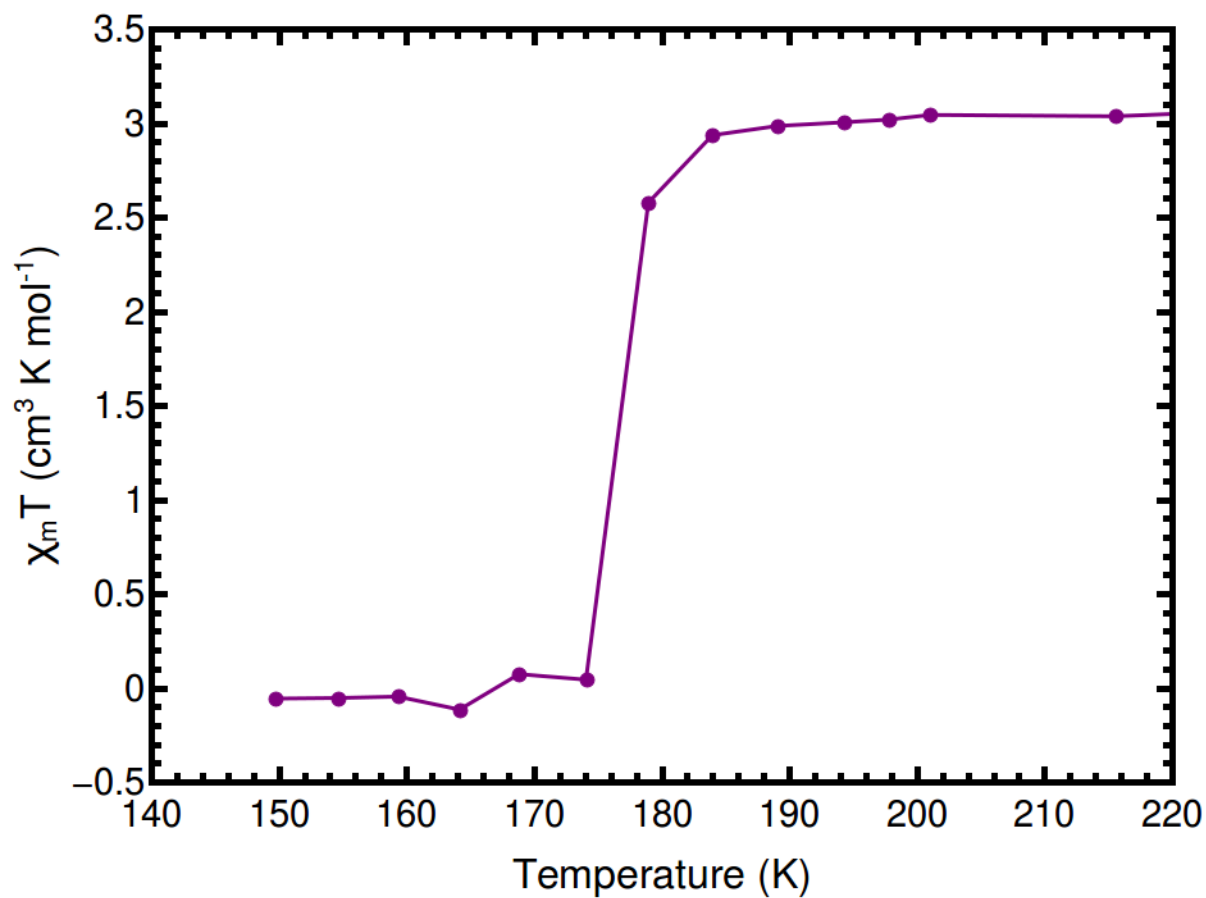


**Fig. S1** Powder XRD (Cu K $\alpha$ ) for Fe(phen)<sub>2</sub>(NCS)<sub>2</sub> powder. Top: Spectrum simulated using single crystal x-ray diffraction structure at 293 K from reference 34. Bottom: Synthesized.



**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  $\text{Fe}(\text{phen})_2(\text{NCS})_2$  powder observed by variation of ( $\chi_m T$ ) with temperature measured by SQUID magnetometry ( $H = 1 \text{ kOe}$ ) for approximately 10 mg.



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.