Electronic Supplementary Information (ESI)

Structural and transport properties of neutral radical crystals of  $Co^{III}(tmp)(CN)_2$  (tmp = 5,10,15,20-tetramethylporphyrinato) and the CN-bridged polymer of  $[Co^{III}(tmp)(CN)]_n$ <sup>†</sup>

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Fig. S1 Powder X-ray diffraction pattern of Co(tmp)(CN)<sub>2</sub>

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**Fig. S1** Powder X-ray diffraction pattern of Co(tmp)(CN)<sub>2</sub> at 293 K. The lower panel indicates the simulated pattern using the results of single-crystal structure analysis of Co(tmp)(CN)<sub>2</sub> at 100 K.



Fig. S2 Cyclic voltammogram of the acetonitrile solution of TPP[Co(tmp)(CN)<sub>2</sub>]·1/2(acetone)·H<sub>2</sub>O (supporting electrolyte: 25 × 10<sup>-3</sup> M of tetra(*n*butyl)ammonium hexafluorophosphate). The experiments were performed using platinum wire (1 mm in diameter) working and counter electrodes, and the potential was measured against the Ag/AgCl reference electrode with a scan rate of 400 mV s<sup>-1</sup>. The potential is converted to the value vs. SCE.



**Fig. S3** ESR spectrum of Co(tmp) (randomly oriented polycrystals). The observed signal ((a); derivative form) and integration of the observed signal (b). The signal is not

symmetric. This is probably due to the anisotropy of the *g*-tensor. Though we performed the ESR measurements with the maximum scan range of our instrument, we could not cover the whole spectrum. Since the quantitative analysis requires the whole spectrum feature (more extended scan range), we did not perform quantitative analysis of the spectrum.