

Electronic Supplementary Information (ESI)

Microscale hexagonal rods of a charge-assisted second-sphere coordination compound [Co(DABP)₃][Fe(CN)₆]

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S1. Materials and general methods

The ligand 5,5'-diamino-2,2'-bipyridine (DABP) and its complex [Co(DABP)₃]Cl₂ were prepared following previously published procedures.¹ All the other chemicals are commercially available and were used without further purification. In the reaction of [Co(DABP)₃]Cl₂ with K₃[Fe(CN)₆], it was found that the initial divalent [Co(DABP)₃]²⁺ was oxidized to [Co(DABP)₃]³⁺ in the product, presumably by [Fe(CN)₆]³⁻. Therefore, in the following experiments, H₂O₂ was used to generate the [Co(DABP)₃]³⁺ ion in the preparation of the samples for further characterization and morphology studies.

Elemental analyses were performed on a VarioEL instrument from Elementaranalysensysteme GmbH. IR spectra were recorded using a Nicolet AVATAR 360 FT-IR spectrometer as KBr disks. Powder X-ray

diffraction (PXRD) patterns were obtained with a D/max RB Diffractometer using Cu K α radiation. X-ray photoelectrons spectroscopy (XPS) measurements were carried out with a VG Scientific ESCALAB210-XPS photoelectron spectrometer with a Mg K α resource (The binding energy scale was calibrated to 285.0 eV for the main C1s peak). FE-SEM images were taken using a field-emission scanning electron microscope (JEOLJSM-6701F) operated at an accelerating voltage of 5 kV.

Single-crystal Diffraction data for the compound **1** was collected on a Bruker SMART APEX II diffractometer at room temperature (293 K) with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). An empirical absorption correction using SADABS was applied for all data.² The structures were solved by direct methods using the SHELXS program.³ All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 by the use of the program SHELXL.³ Hydrogen atoms bonded to carbon were included in idealized geometric positions with thermal parameters equivalent to 1.2 times those of the atom to which they were attached.

S2. Synthesis of [Co(DABP)₃][Fe(CN)₆] (**1**)

Single crystals of **1** were grown in a methanol/water/acetonitrile solution by a slow diffusion method using an H-shaped tube at room temperature. A solution of the [Co(DABP)₃]³⁺ complex (0.01 mmol, in situ prepared from [Co(DABP)₃]²⁺ and H₂O₂) in methanol/water (2:1 v:v, 2 mL) was placed to the bottom of one arm, and K₃[Fe(CN)₆] (4 mg, 0.012 mmol) was dissolved in water (3 mL) and added to the other arm. Then methanol/acetonitrile (4:1) was filled in the tube. Well-shaped dark brown crystals were obtained after several weeks. Yield: 3 mg (36%). M.p. > 300 °C.

Anal. Found: C, 50.38; H, 3.93; N, 29.66. Calcd for [Co(DABP)₃][Fe(CN)₆]·2H₂O: C, 49.95; H, 3.96; N, 29.13. FT-IR (KBr, ν/cm^{-1}): 3450, 3383, 3223, 3296, 3192, 3111, 3049, 2109, 2061, 1633, 1598, 1576, 1491, 1438, 1356, 1335, 1320, 1281, 1161, 1119, 1066, 1046, 1023, 883, 874, 849, 717, 669.

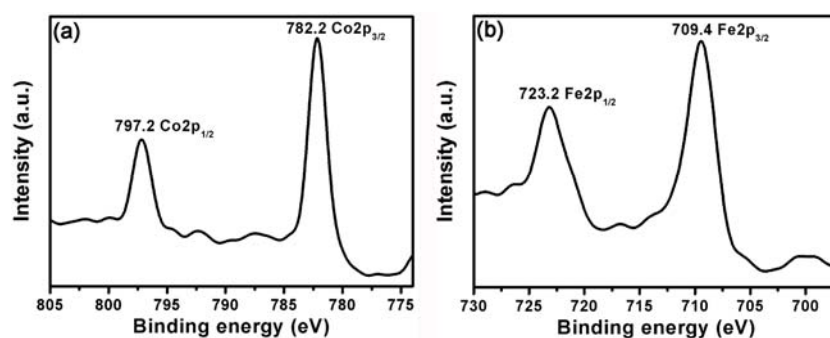


Fig. S1 XPS spectrum of compound **1**, (a) Co2p. (b) Fe2p.

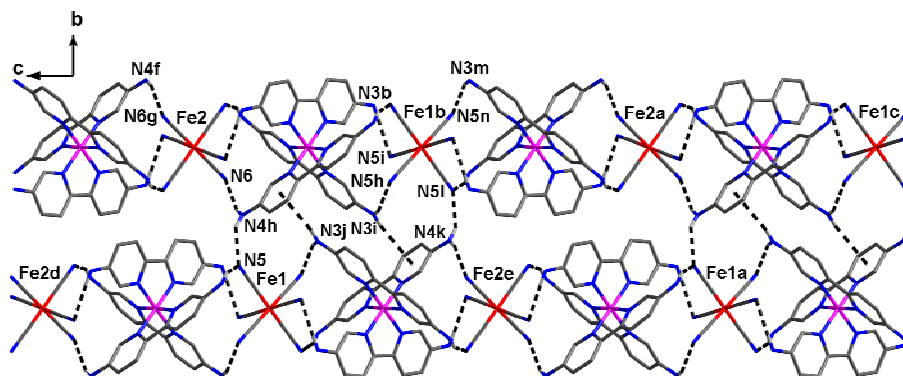


Fig. S2 The anions and cations are arranged alternately in the *c*-direction to a 1D linear chain linked by N–H(NH₂)⋯N(CN) hydrogen bonds, and adjacent 1D chains are linked through N–H⋯N and N–H⋯π interactions. Symmetry code: [a] *x*, *y*, $-1+z$; [b] $1/3+x$, $2/3+y$, $-1/3+z$; [c] $1/3+x$, $2/3+y$, $-4/3+z$; [d] $-1/3+x$, $-2/3+y$, $1/3+z$; [e] $-1/3+x$, $-2/3+y$, $-2/3+z$; [f] $1/3+x-y$, $2/3+x$, $2/3-z$; [g] $2/3-x$, $4/3-y$, $1/3-z$; [h] $1/3-x+y$, $2/3-x$, $-1/3+z$; [i] $1/3-y$, $2/3+x-y$, $-1/3+z$; [j] *y*, $-x+y$, $-z$; [k] $x-y$, *x*, $-z$; [l] $1/3-x$, $2/3-y$, $-1/3-z$; [m] $1/3+y$, $2/3-x+y$, $-1/3-z$; [n] $1/3+x-y$, $2/3+x$, $-1/3-z$.

Table S1 Hydrogen bonding parameters (Å, °) in **1**.

D–H⋯A	H⋯A	D⋯A	D⋯H	D–H⋯A	Symmetry code
N3–H3A⋯N5	2.30	3.058(5)	0.86	147.0	$-y, x-y, z$
N4–H4B⋯N6	2.26	3.025(5)	0.86	148.5	$-y+2/3, x-y+1/3, z+1/3$
N4–H4A⋯N5	2.18	2.914(5)	0.86	143.7	$-y+2/3, x-y+1/3, z+1/3$

S3. Fabrication of microrods of **1**

S3.1 Synthesis

In a typical synthesis of hexagonal microrod structures of [Co(DABP)₃][Fe(CN)₆], the complex [Co(DABP)₃]³⁺ (0.01 mmol) was added to a methanol solution (10 mL) containing 5 mg polyvinylpyrrolidone (PVP, K30, *M_w* ≈ 50000) as the surfactant, to which was added a K₃[Fe(CN)₆] (4 mg, 0.012 mmol) solution (10 mL) drop by drop. The resulting mixture was stirred at room temperature for 48 h. The samples for morphology and structure analysis were washed with acetone and water to remove excess PVP via centrifugation, and finally dissolved in ethanol. Yield: 6 mg (72 %). M.p. > 300 °C.

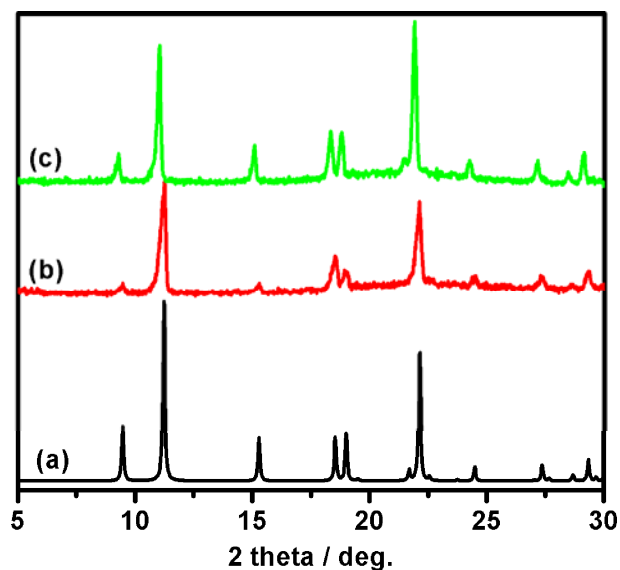


Fig. S3 PXR D patterns of compound **1**. (a) Simulated from single crystal X-ray diffraction of **1**. (b) Bulk crystals obtained using a slow diffusion method in an H-tube. (c) Hexagonal microrods synthesized using a PVP-assisted precipitation method.

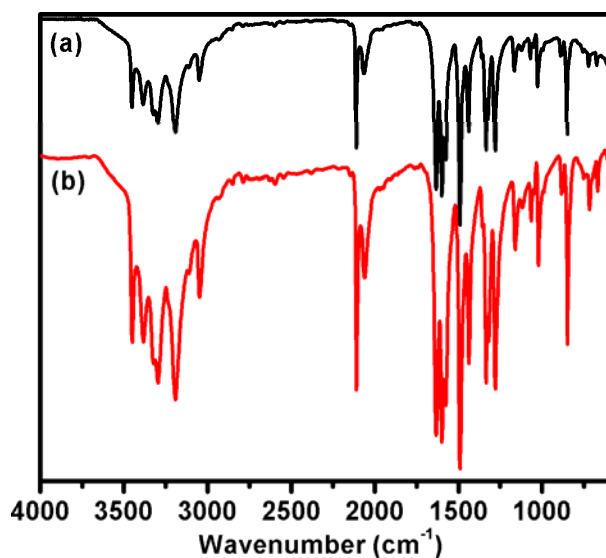


Fig. S4 FT-IR spectra of compound **1**. (a) Bulk crystals obtained using a slow diffusion method in an H-tube. (b) Hexagonal microrods synthesized using a PVP-assisted self-assembled precipitation method.

S3.2 Microstructural studies

The preparation of the microstructures of compound **1** in the presence of surfactant (PVP: 2 mg and 10 mg; or hexadecyltrimethylammonium bromide (CTAB): 4 mg, 0.01 mmol) was carried out following the above typical procedures (see S3.1).

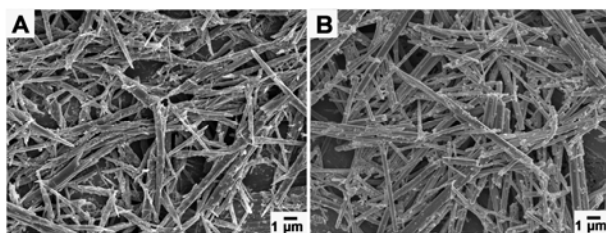


Fig. S5 FE-SEM images of compound **1** synthesized in the presence of PVP. (A) 2 mg; (B) 10 mg.

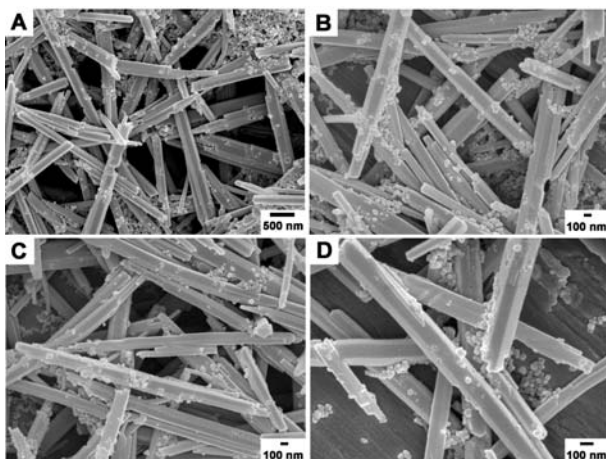


Fig. S6 FE-SEM images of compound **1** synthesized in the presence of surfactant CTAB. (A, B) Low-magnification images, and (C, D) High-magnification images.

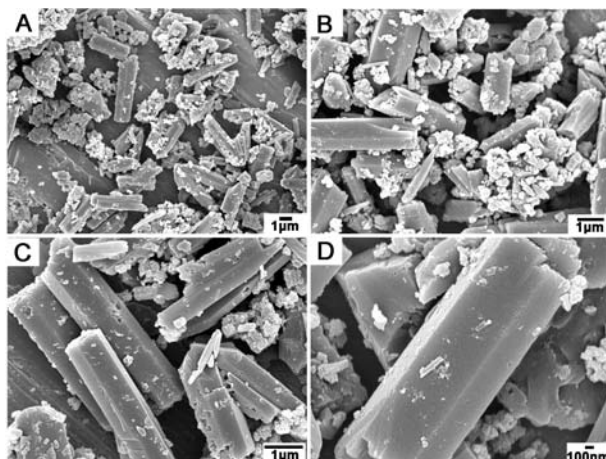


Fig. S7 FE-SEM images of compound **1** synthesized without any surfactant. (A, B) Low-magnification images, and (C, D) High-magnification images.

By fixing other reaction conditions, the effect of the surfactant concentration on the morphology and size of the as-prepared hexagonal rods was investigated. Although there is no obvious change in the morphology and size (Fig. S5) when the amount of PVP was changed from 2 mg to 10 mg, the hexagonal

rods of PVP 5 mg (Fig. 3) are relatively more uniform in size and shape than that with 2 mg and 10 mg. When hexadecyltrimethylammonium bromide (CTAB, 4 mg) was used as the surfactant, the hexagonal rods with diameters of 100–400 nm and lengths of 2–4 μm were obtained with a relatively wider size distribution (Fig. S6). In addition, some amorphous products were present. When compound **1** was synthesized without any surfactant, the yield of the desired microrods was low and some amorphous products were observed as shown in Figure S7. Less regular hexagonal rods with an average diameter of 1.3 μm and a length of 5 μm could be observed, which were obviously larger than the samples synthesized by using surfactant PVP or CTAB.

References:

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- 3 G. M. Sheldrick, *SHELXS-97, SHELXL-97, Programs for Crystal Structure Analysis*, 1997, University of Göttingen, Germany.