Electronic Supplementary Material (ESI) for Chemical Communications
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Electronic Supplementary Information

Molecular Cable of 1-D Iodic Spiral Chains Covered with Triple Helices Stabilized in Guest-Included Chiral Porous Framework

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1. Preparation of [Pr(DMAF)]I and Crystal 1

Preparation of [Pr(DMAF)]I: Dimethyl ferrocenylmethyl amine (DMAF) (0.53 g, 2.20 mmol/ *d* 1.228) and ^{n}PrI (5.08 g , 29.9 mmol/ *d* 1.743) were added to acetone (5 cm^3), and brown microcrystalline solids were deposited from the red solution, after stirred for 2 hours at room temperature. The precipitates was filtrated and washed by diethyl ether. (0.78 g, 86.6%) Calcd for [Pr(DMAF)]I ($C_{16}H_{24}FeNI$): C, 46.52%, H, 5.86%, N, 3.39%; Found: C, 46.45%, H, 5.94%, N, 3.38%, M/z = 286 ([^{n}Pr-DMAF]$^{+}$), ^{1}H-NMR(*ppm*) / $CDCl_3$: 4.88 (2H, *s*, Cp-CH_2-N), 4.54 (2H, *m,* Cp ring), 4.32 (7H, *s*, Cp ring), 3.32 (2H, *m*, N-CH_2Cp CH_3), 3.18 (6H, *s*, N-CH_3), 1.77 (2H, *m*, N-CH_2C$H_2$$CH_3$), 1.02 (3H, *t*, N-$CH_2CH_2CH_3$), IR(ATR/$cm^{-1}$): 3070, 3001, 2970, 2939, 1487, 1469, 1458, 1441, 1105, 1001, 912, 866, 840, 813, 746, 484.

Preparation of Crystal 1: A suspension of H_2bim (0.07 g, 0.52 mmol), [Pr(DMFA)]I (0.11 g, 0.26 mmol) and LiOMe (0.09 g, 2.42 mmol) was added to MeOH (10 cm^3) and heated under reflux until the ligand dissolved. $NiCl_2 \cdot 6H_2O$ (0.06 g, 0.26 mmol) in MeOH (10 cm^3) was added dropwise to the resulting solution, and the mixture was heated under reflux for 15 min. The insoluble components were removed by filtration, and the filtrate was allowed to stand at room temperature. Orange hexagonal prisms were obtained from the filtrate after a week. (0.05 g, 50.0%) Elemental analysis: Calcd for {[Pr(DMFA)]$_3$[Ni(Hbim)$_3$]$_2$I} ($C_{84}H_{102}N_{27}Fe_3Ni_2I$): C, 53.05%; H, 5.41%; N, 19.89%; Found: C, 52.66%; H, 5.61%; N, 19.77%. IR (ATR/cm^{-1}) 3103, 3078, 2968, 2947, 2881, 2595 (*br*, ν (NH)), 1905 (*br*, 2γ (NH)), 1597, 1479, 1402, 1128, 1105, 945, 706, 511.

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2. X-ray Analysis of Crystal 1

Crystal data for 1: $C_{84}H_{102}N_{27}Fe_3Ni_2$, *FW* = 1901.80, *T* = 173 K, *Hexagonal*, space group $P6_5$ (No.170) with *a* = 18.0024(14) Å, *c* = 46.984(4) Å, *V* = 13186.8(18) $Å^3$, *Z* = 6, D_{calcd} = 1.437 g/cm^3, F(000) = 5892.00. 1048 parameters, R_1 = 0.1058 ($I > 2\sigma(I)$), R_W = 0.2710 (all data) and *GOF* = 1.435, absolute structure parameter 0.05(3) for μ(MoKα) = 13.15 cm^{-1}; 17631 (R_{int} = 0.1646) independent reflections collected; the values of the minimum and maximum residual electron densities are –1.428 $e/Å^3$ and 4.251 $e/Å^3$, respectively. The data collections for crystal 1 are performed by a Burker SMART APEX 2000 CCD X-ray diffractometer using Lorenz-polarization corrections and graphite monochromatic Mo-Kα (λ = 0.071073 Å) for all crystals. Then, their structures were solved using direct method techniques with the SHELXL-97 [1] and Full-matrix least-squares (SHELX-97) refinement [2]. The C(37), C(38) , C(39) , C(40), and C(41) of the Cp ring of $[Pr(DMFA)]^+$ and the hydrogen atom positions were fixed. Because the Cp ring is disordering due to the rotation. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-862728 (**1**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ (fax: Int. Code (+44)1223/336-033; e-mail: deposit@chemcrys.cam. ac.Uk).

[1] G. M. Sheldeick, SHELEXS, 1997, University of Goettingen.

[2] G. M. Sheldeick, T. R. Schneider, SHELEXL, High-Resolution 1997, Method in Enzymology 277.

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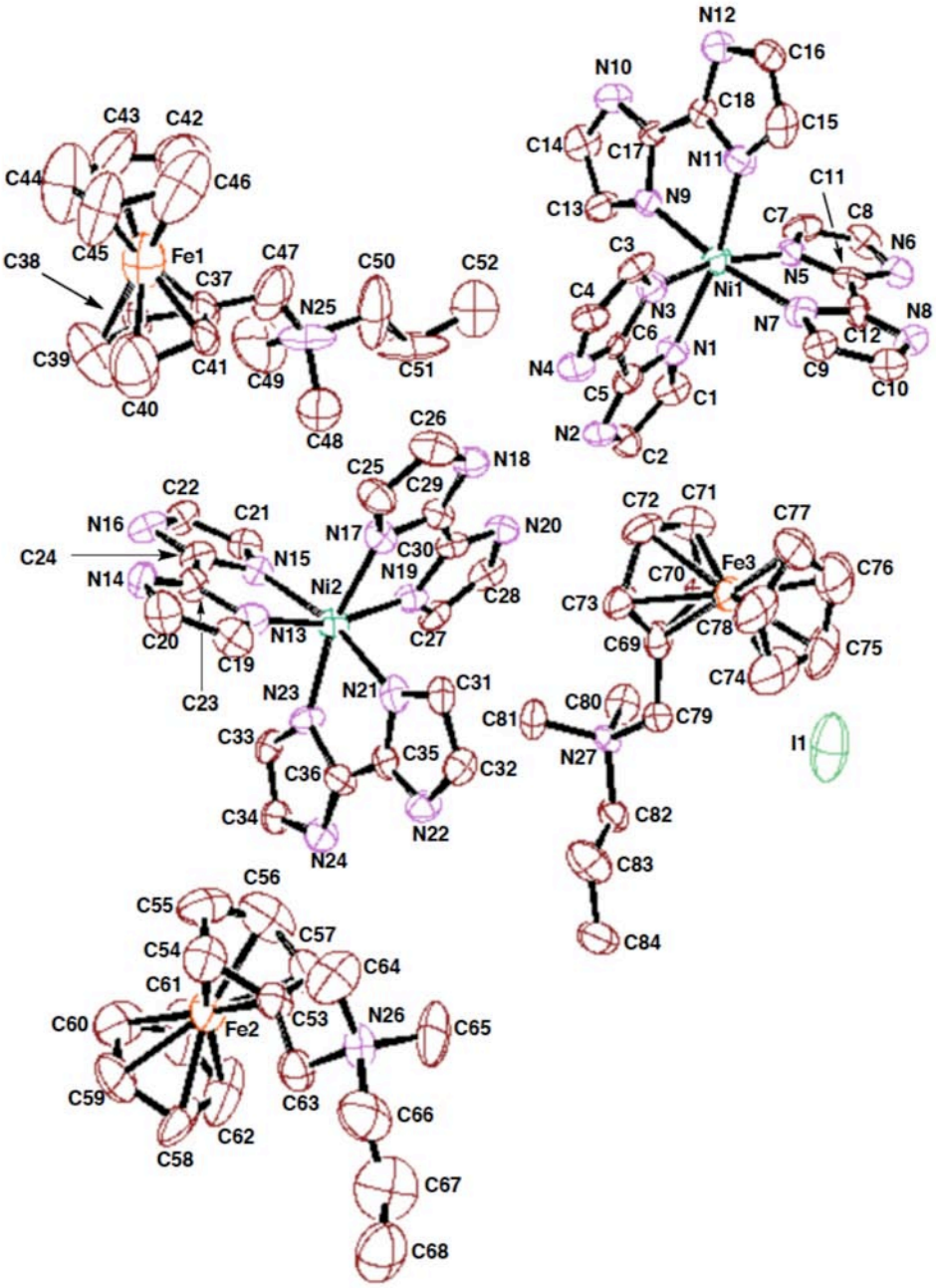

Fig. 1S

ORTEP image of crystal 1 with the numbering schemes

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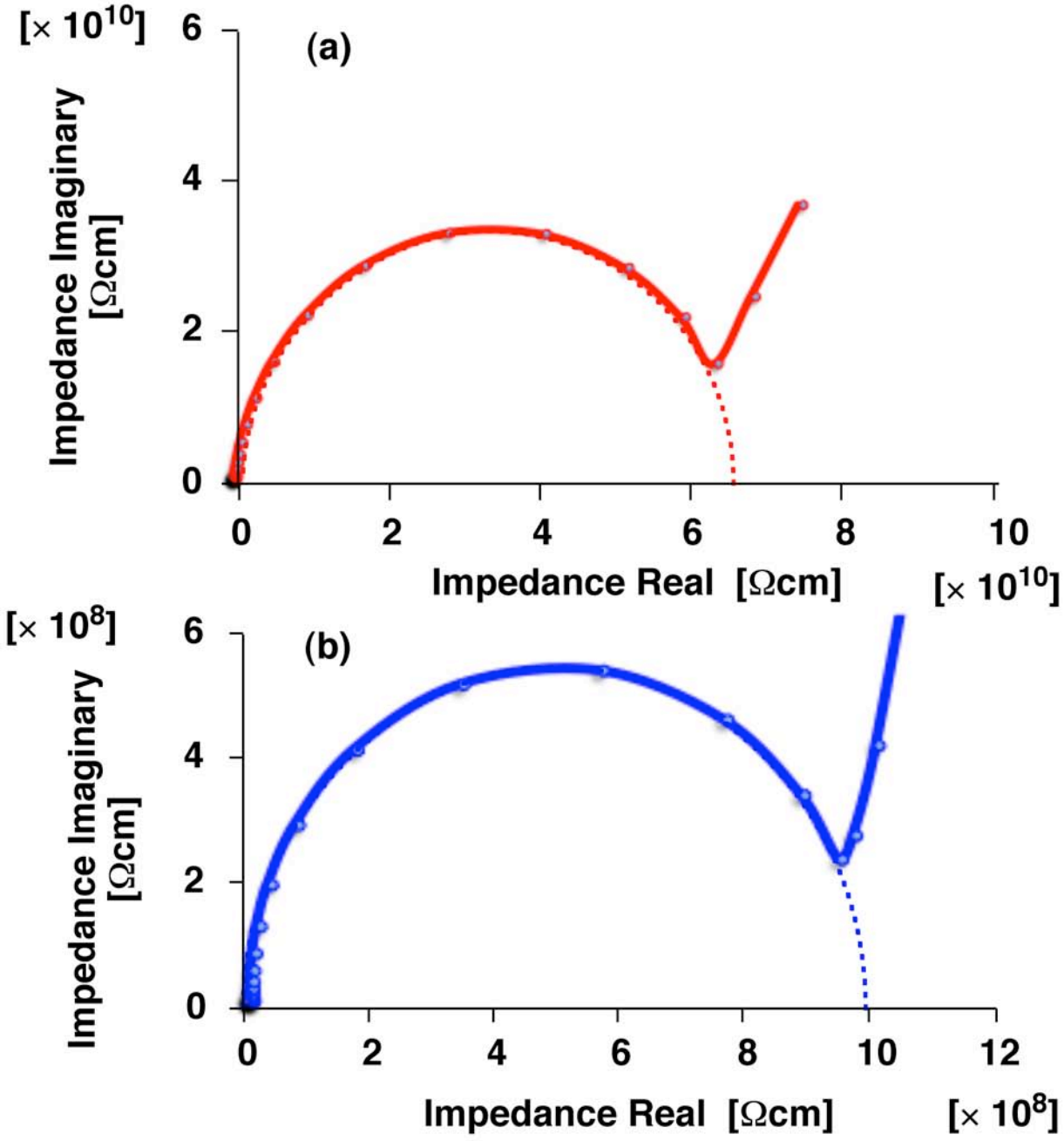

Fig. 2S

Two Nyquist plots for the AC conductivity on anisotropic ion-conductivity of 1 are observed as higher conductivity parallel to I– chains (b) at one order of magnitude than that perpendicular to the chains (a).

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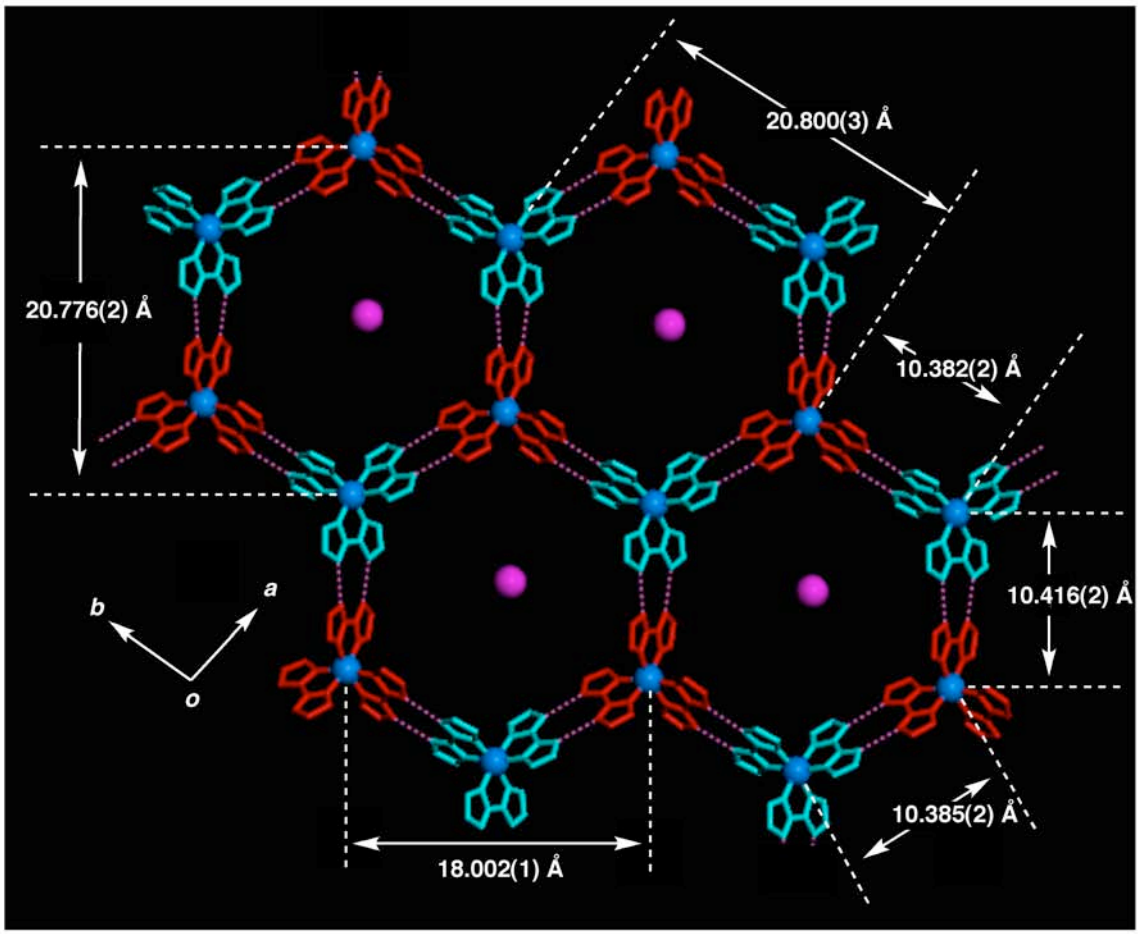

Fig. 3S

View showing the crystal structure of a honeycomb sheet constructed from alternating dual NH···N H-bonds between the D- (red lines) and L- (light blue lines) optical isomers of $[Ni^{II}(Hbim)_3]^-$. The coordinated Ni^{2+} ions and the I^- ions in the center of the hexagonal cavity are represented by blue and magenta spheres, respectively. Each labeled distance represents the distance between intermolecular Ni^{2+} ions of $[Ni^{II}(Hbim)_3]^-$ in the hexagonal cavity.

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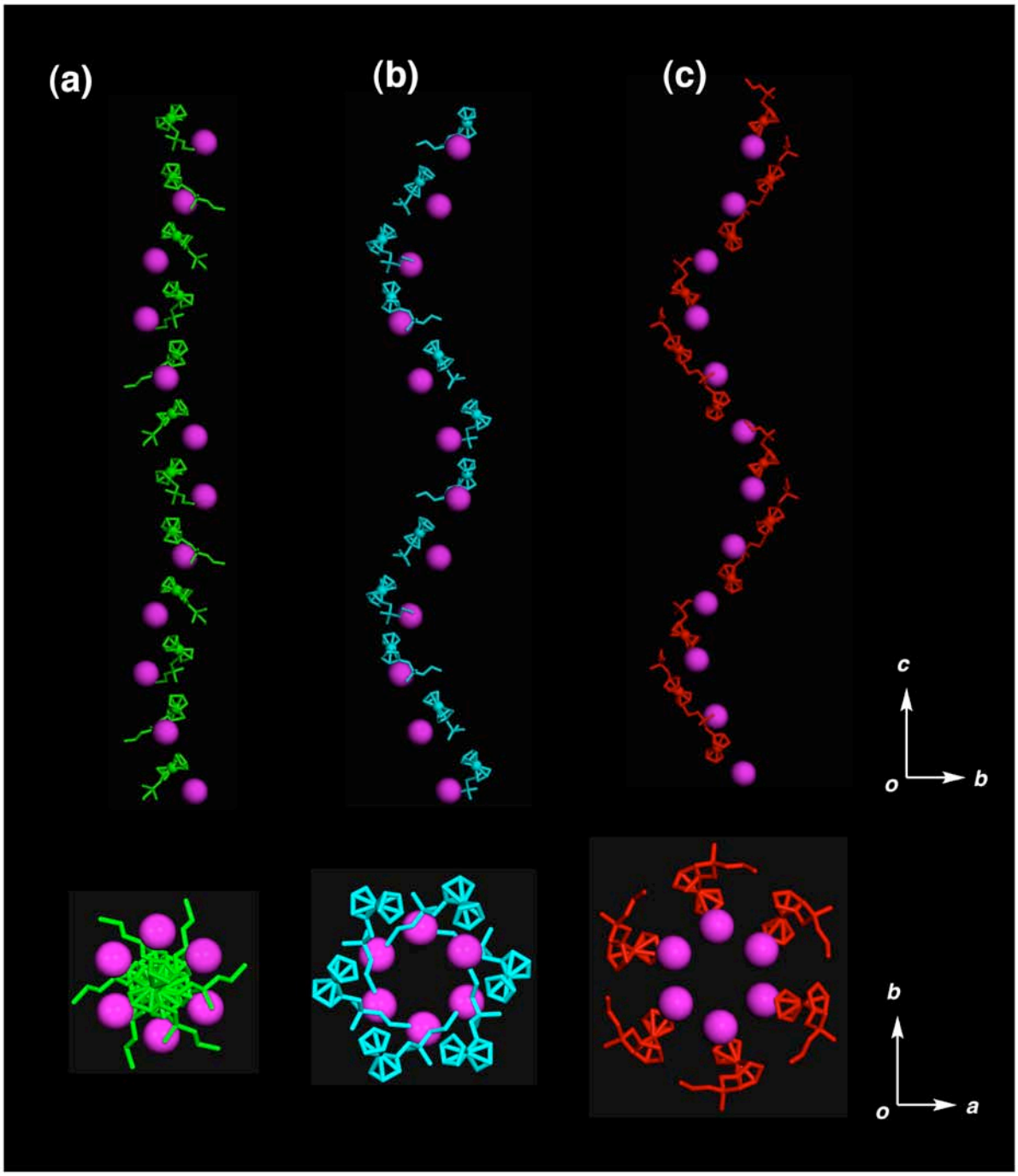

Fig. 4S

Stick-mage crystal structures of three separated 6^5 spiral chains (**a**, **b**, and **c**), contained in a triple-helix tubular structure of $\{([Pr(DMFA)]_3I)^{2+}\}_n$, with an I^- chain represented by the magenta ball images. The top and bottom panels show the perspective views through the *a* and *b* axes, respectively. **a**: a 6^5 spiral array with the green $[Pr(DMAF)]^+$ is located around the center of the tubular structure. **b** and **c**: each spiral array with blue and red images is located on the outside of the I^- spiral chain. The three bottom views along the *c* axis can be understood by the rotation on the base of the hexagonal arrays.

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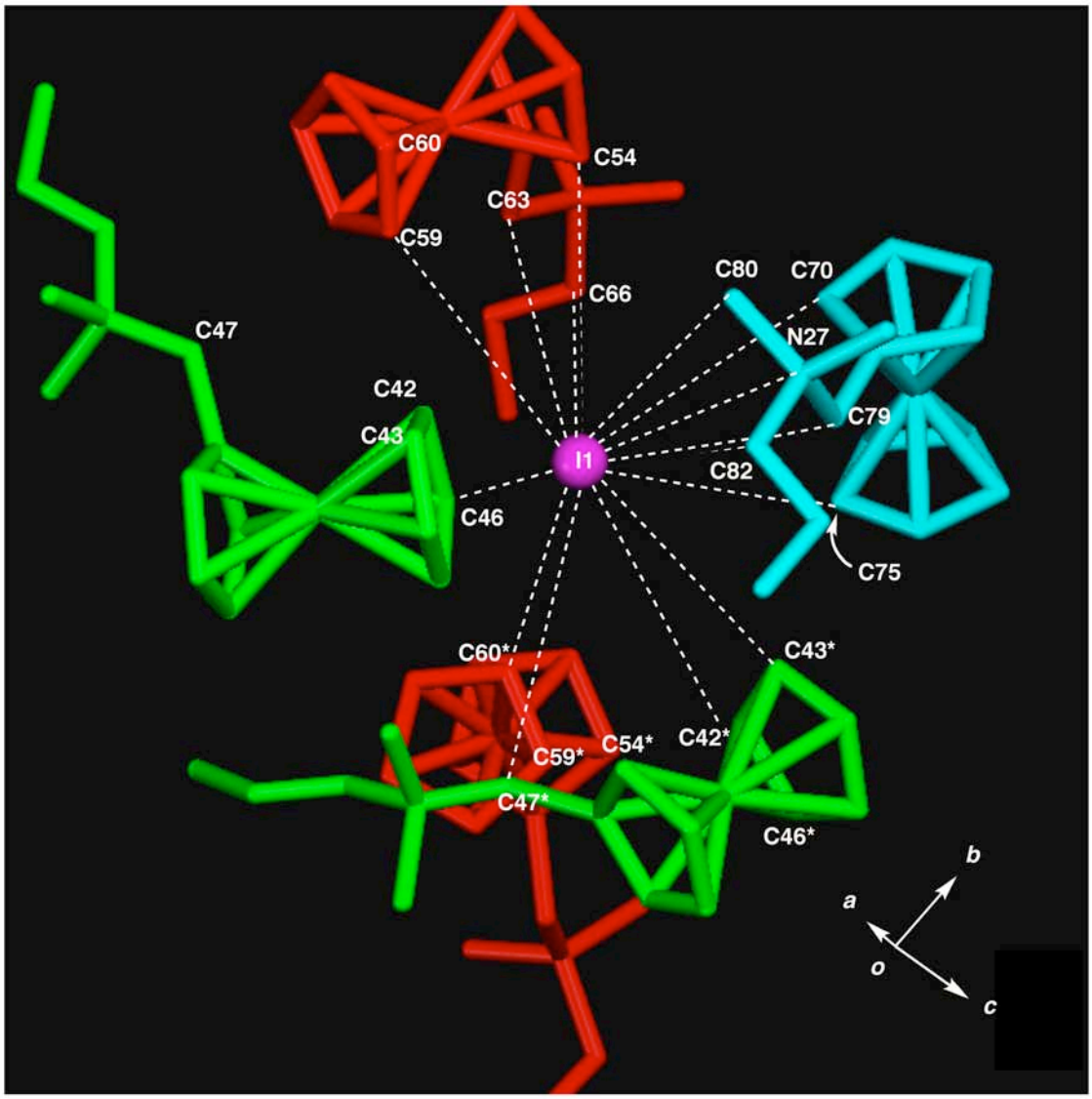

Fig. 5S

View of a CH···I^- contact structure around an I^- ion. The I^- ion is connected with aliphatic –CH– groups of alkylammonium cations and aromatic –CH– groups of cyclopentadienyl (Cp) moieties by weak CH···I^- contact interactions and an electrostatic interaction $-N^+\cdots I^-$ between I(1) and N(27). In two green and two red $[Pr(DMAF)]^+$ molecules, those with the color combinations in this figure correspond to those in Figures 3 and 4, respectively.

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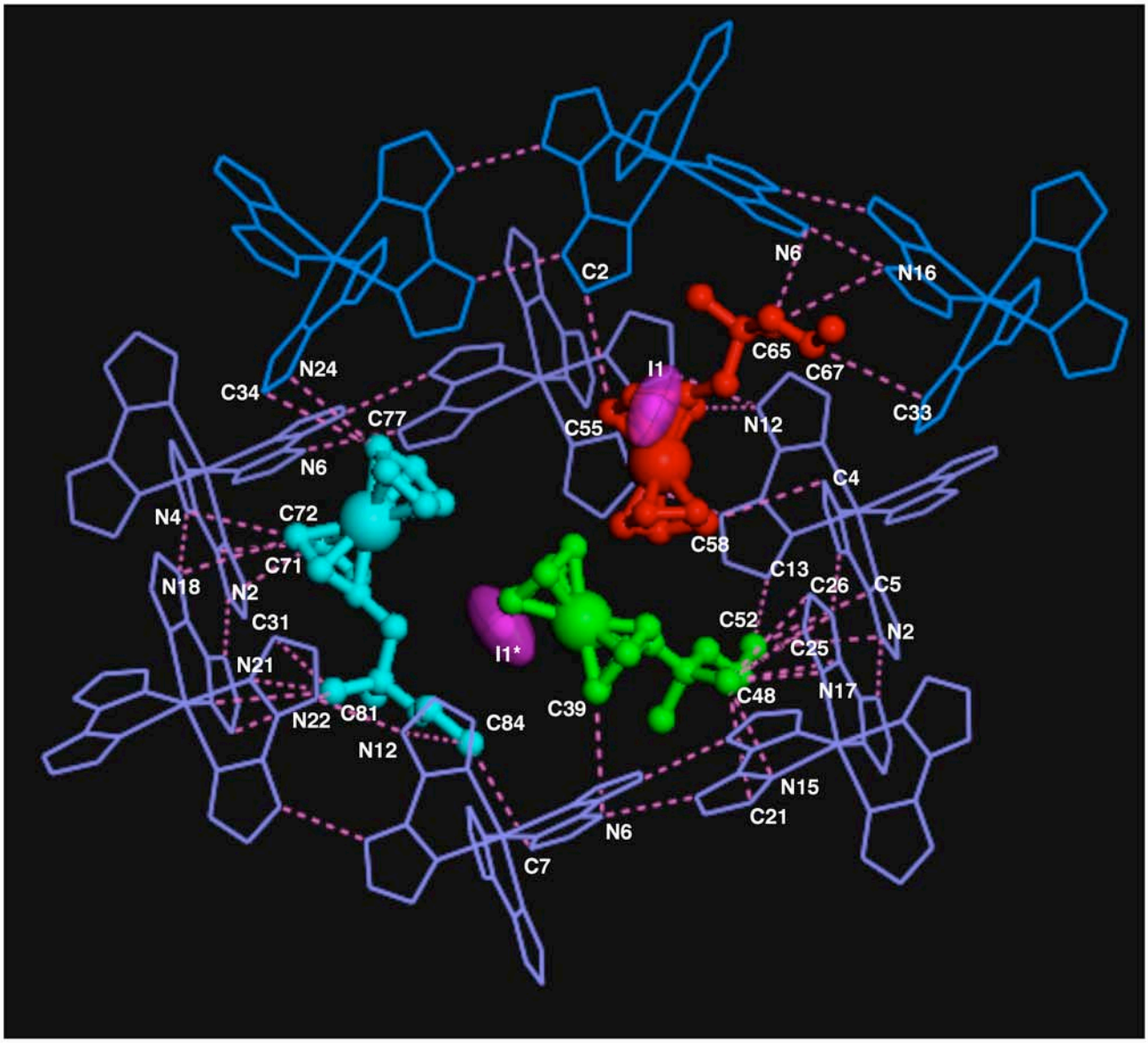

Figure 6S

$[Pr(DMFA)]^{+}$ molecules drawn by ball and stick images are located at hexagonal cavities of the honeycomb sheets (drawn in violet and blue lines) by an electrostatic interaction. (The blue moiety and violet moiety differ in that the former belongs to an upper layer.) The interactions of three $[Pr(DMFA)]^{+}$ molecules with $[Ni^{II}(Hbim)_3]^{-}$ forming a nanoporous framework are separated into two weak contacts: CH$\cdots\pi$ interactions between ammonium aliphatic CH groups of $[Pr(DMFA)]^{+}$ and imidazole aromatic rings of $[Ni(Hbim)_3]^{-}$, and between aromatic CH groups of Cp rings and imidazole rings. (Contacts less than 3.6 Å in distance are denoted as weak.)

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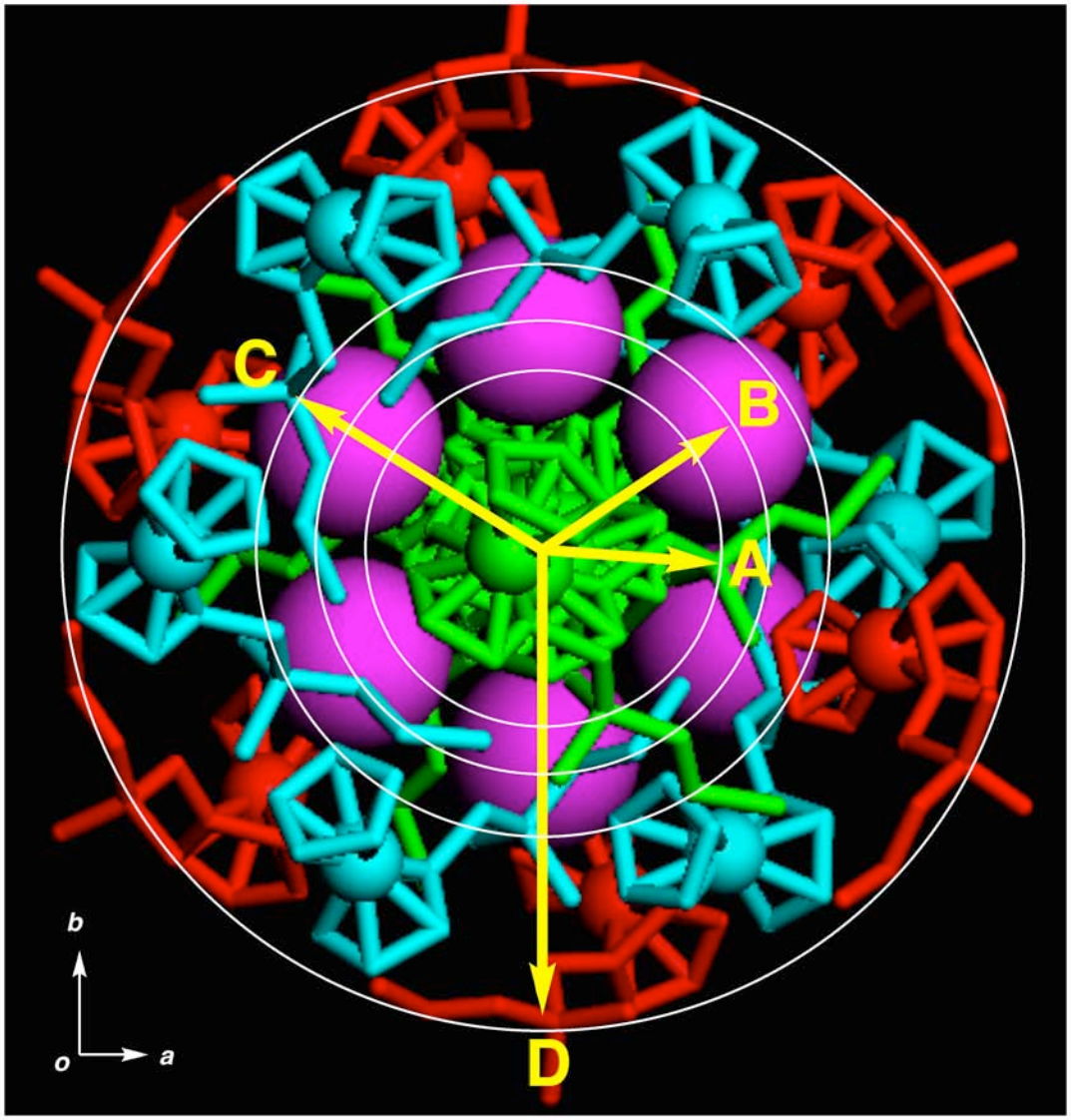

Fig. 7S

Each spiral radius ω is represented as the distance between ammonium N atom of each $[Pr(DMFA)]^{+}$ or I^{-} ion centers, and a circle center of each a spiral drawn by the down view through the c axis: A: the spiral radius ω between ammonium N atom of the green one is 3.35 Å, C and D: those spiral radii ω between ammonium N atoms of the blue and red ones, and the center are 5.23 Å and 8.77 Å, respectively. B: the spiral radius ω between I^{-} ions and the center is 3.88 Å.

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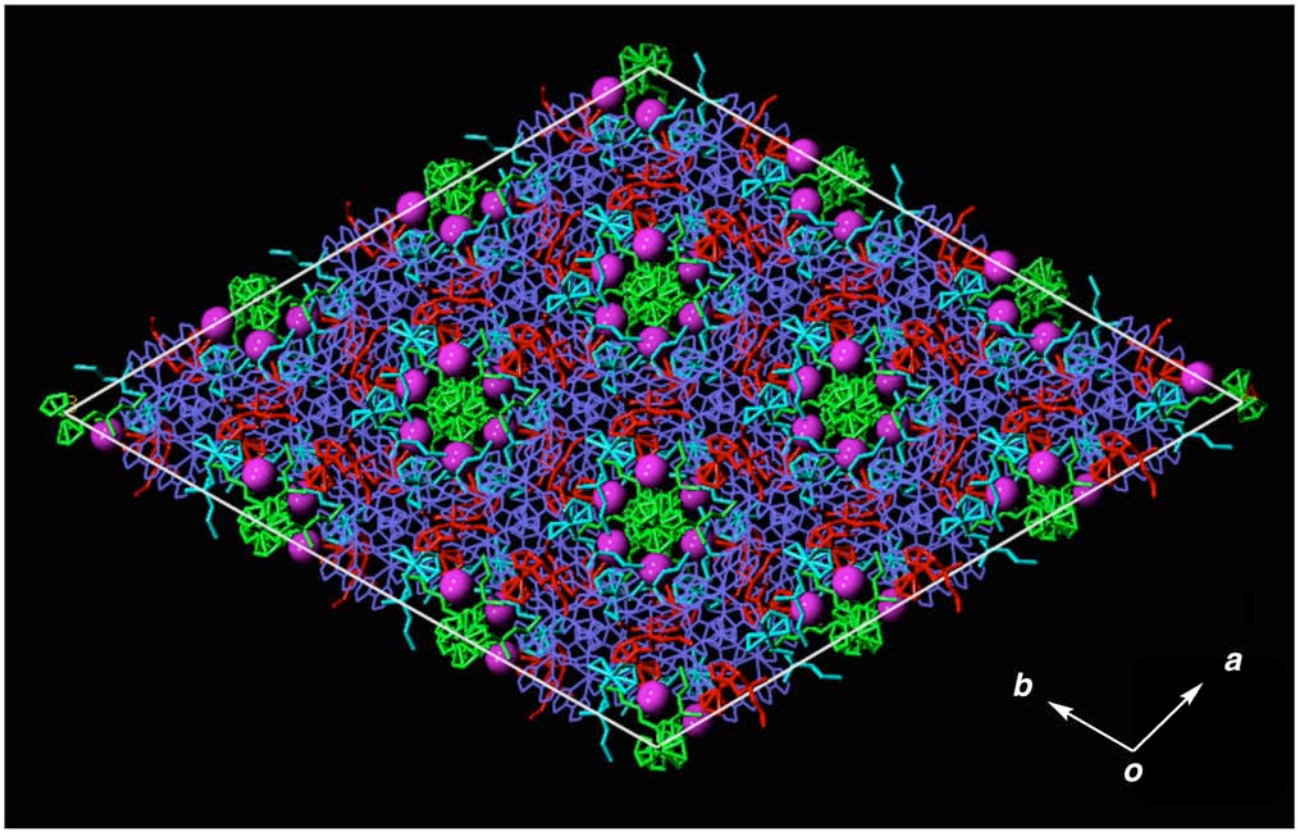

Fig. 8S

Down view of crystal sturcture of 1 along the c axis: the green, red and blue lines show three kinds of $[Pr(DMAF)]^{+}$, and the dark blue lines are $[Ni^{II}(Hbim)_3]^{-}$ fromed from the porous framework. The magenda sphere is I^{-} ions.

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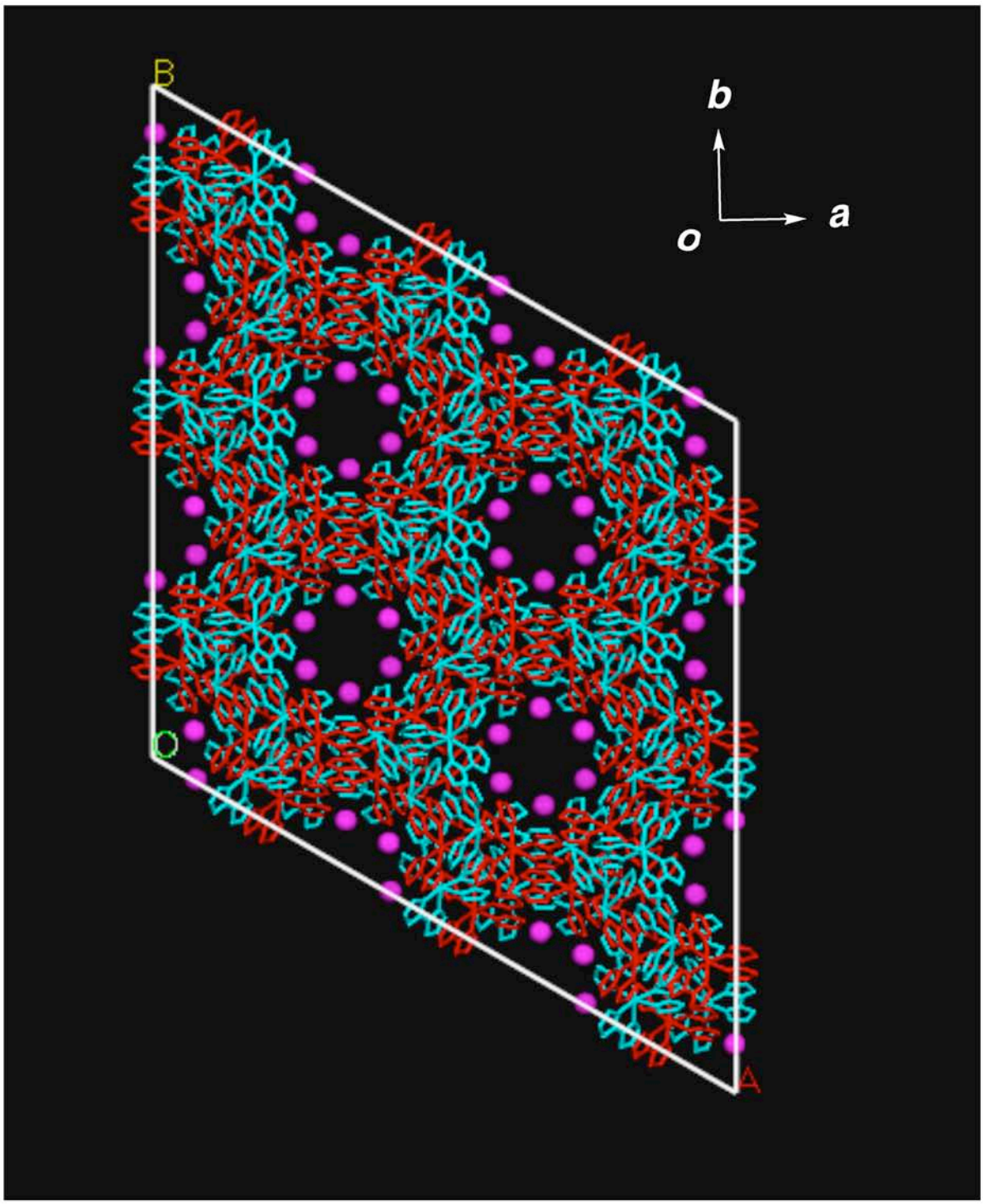

Fig. 9S

The down view along the c axis of crysta structure of chiral nanoporous framework with of 6^5 spiral channels is represented. The Δ and Λ optical isomers of $[Ni(Hbim)_3]^-$ are shown by the red and blue stick, respectively, and the magenda spheres are I^- ions. The images of tublar triple helices of $[Pr(DMAF)]^+$ are omitted.

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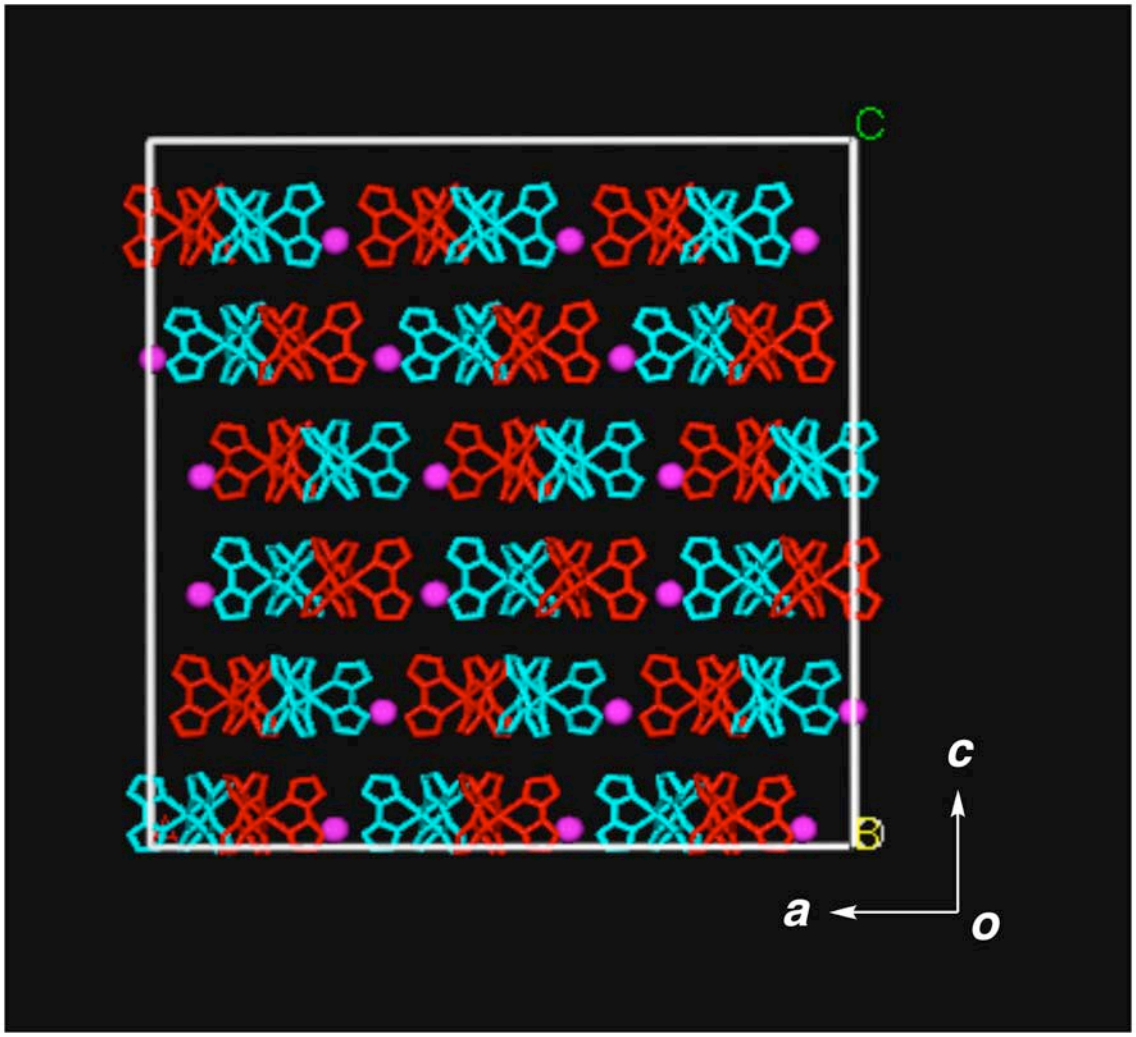

Fig. 10S

The down view along the b axis of crysta structure of chiral nanoporous framework with of 6^5 spiral channels is represented. The Δ and Λ optical isomers of $[Ni(Hbim)_3]^-$ are shown by the red and blue stick, respectively, and the magenda spheres are I^- ions. The images of tublar triple helices of $[Pr(DMAF)]^+$ are omitted.

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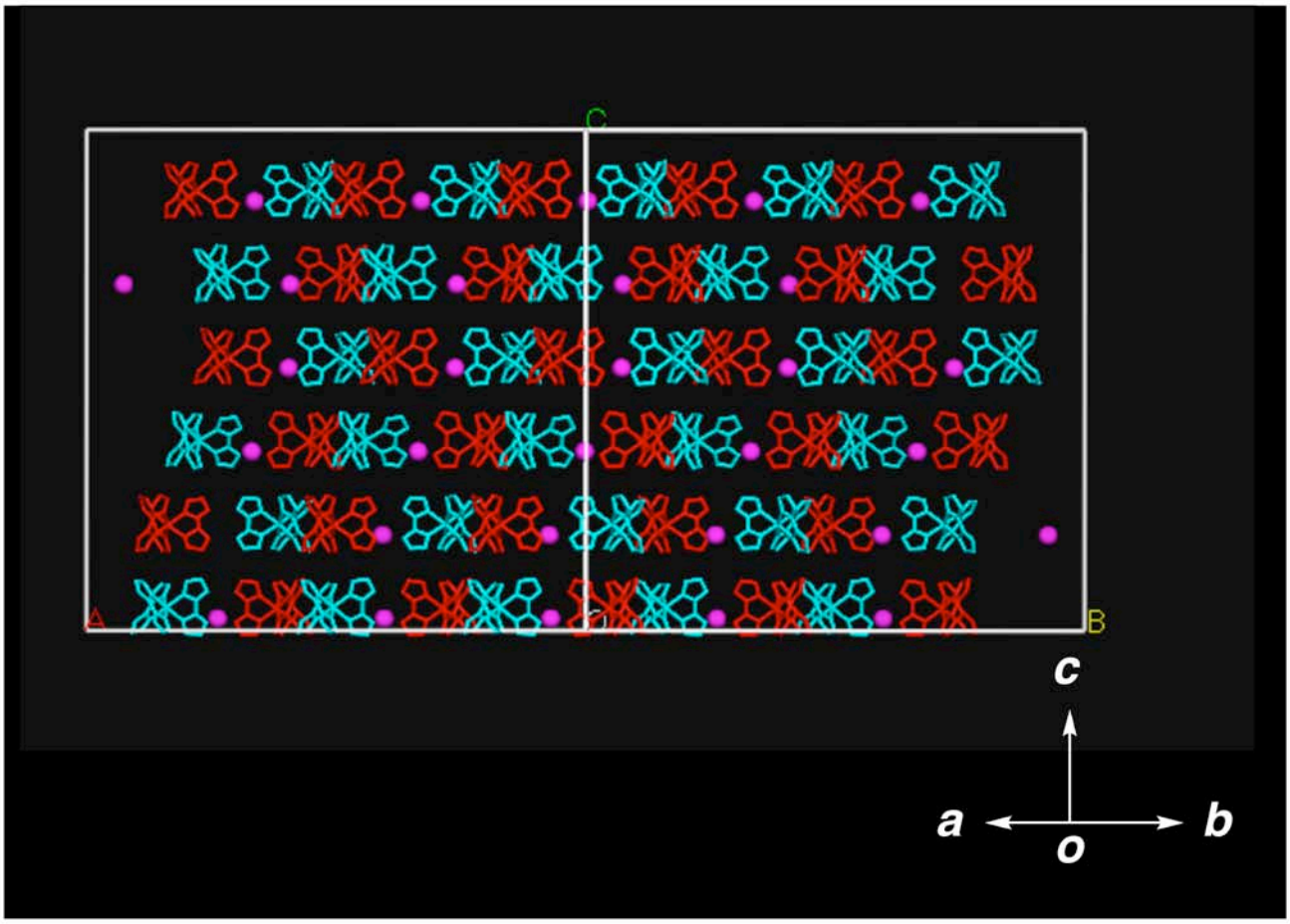

Fig. 11S

The down view along the ab diagonal direction of crysta structure of chiral nanoporous framework with of 6^5 spiral channels is represented. The Δ and Λ optical isomers of $[Ni(Hbim)_3]^-$ are shown by the red and blue stick, respectively, and the magenda spheres are I^- ions. The images of tublar triple helices of $[Pr(DMAF)]^+$ are omitted.

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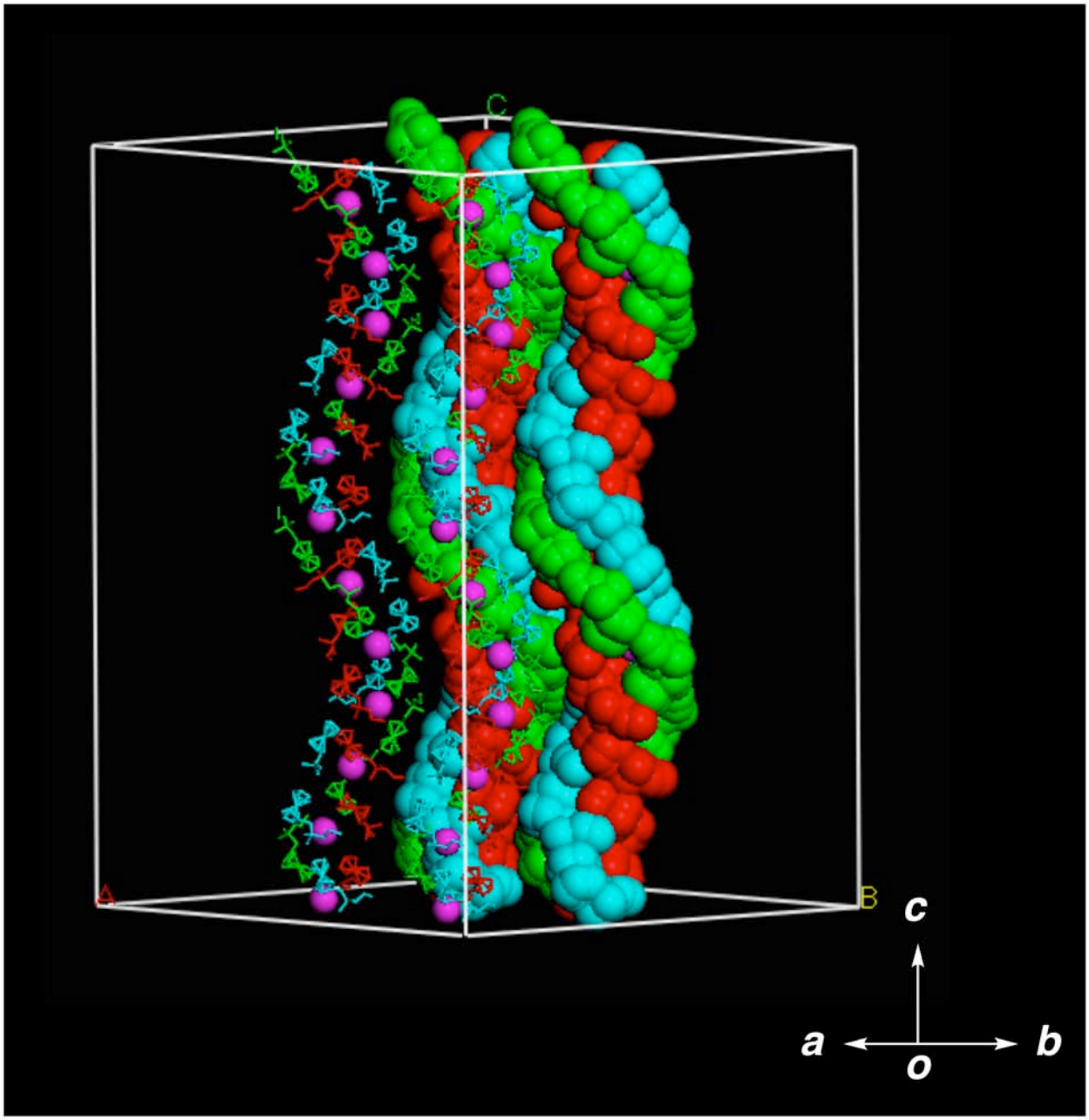

Fig. 12S

Four triple helices formed from red, green and blue $[Pr(DMAF)]^{+}$ including the magenda I^{-} ionic chains in crystal are represented by two images of Ball and Stick. The image of nanoporous framework is omitted.

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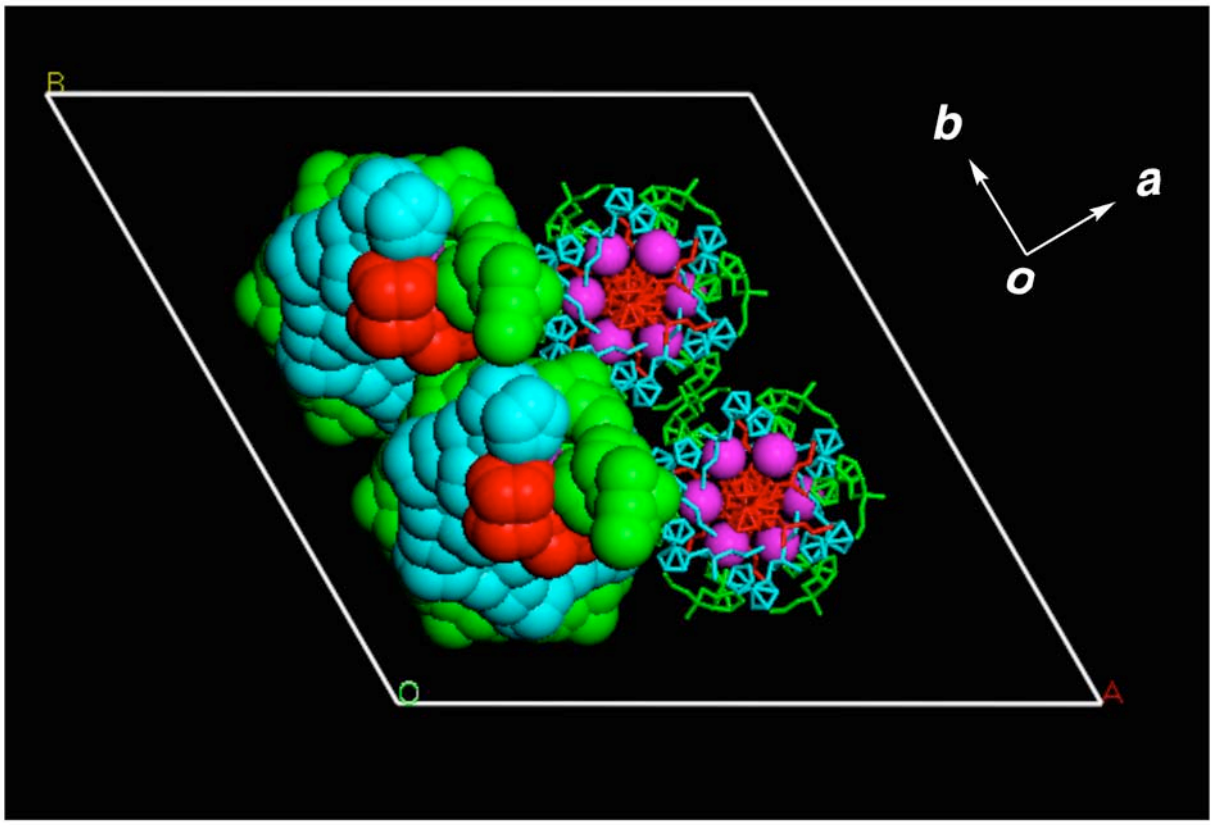

Fig. 13S

Down view along the c axis of four triple helices formed from red, green and blue $[Pr(DMAF)]^{+}$ including the magenda sphere I^{-} ionic chains in crystal are represented by Ball or Stick images. The image of nanoporous framework is omitted.

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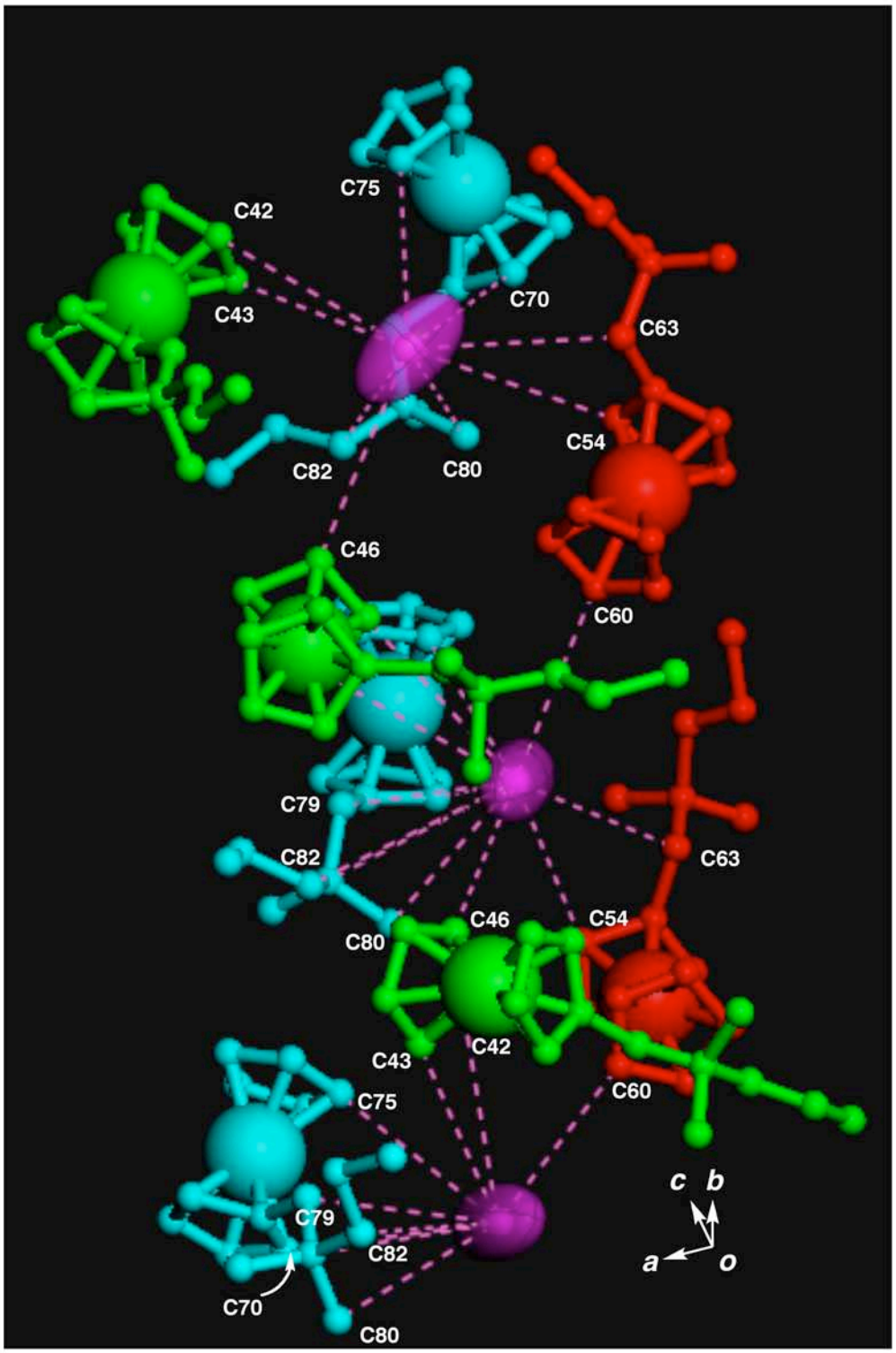

Fig. 14S

CH···I⁻ contact interactions surrounded three I⁻ ions into three kinds of green, red and blue [Pr(DMAF)]⁺ : (dot lines < 3.5 Å): The elliptic spheres of magenda show I⁻ ions.