

Fabrication of Chiral Self-Sorted Multifunctional Supramolecular Biocoordination Polymers

Joon Hak Oh (✉ joonhoh@postech.ac.kr)

POSTECH

Sang Kyu Kwak (✉ skkwak@unist.ac.kr)

UNIST

Xiaobo Shang

POSTECH

Inho Song

POSTECH

Gwan Yeong Jung

UNIST

Wanuk Choi

POSTECH

Hiroyoshi Ohtsu

Tokyo Institute of Technology

Jeong Hyeon Lee

UNIST

Jin Young Koo

POSTECH

Bo Liu

Zhejiang University

Jaeyong Ahn

POSTECH

Masaki Kawano

Tokyo Institute of Technology

Method Article

Keywords: coordination polymers, self-sorting, chirality, sensor, metal organic framework

Posted Date: October 2nd, 2018

DOI: <https://doi.org/10.1038/protex.2018.099>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

Chiral supramolecules have great potential for use in chiral recognition, sensing, and catalysis. Particularly, chiral supramolecular biocoordination polymers (SBCPs) provide a versatile platform for characterizing biorelated processes such as chirality transcription. Here, we selectively synthesize homochiral and heterochiral SBCPs, composed of a naphthalene diimide ligands and Zn ions, from enantiomeric and mixed R- and S-ligands, respectively. Notably, we find that the chiral self-sorted SBCPs exhibit multifunctional properties including photochromic, photoluminescent, photoconductive, and chemiresistive characteristics, thus can be used for various sensors. Specifically, these materials can be used for detecting a hazardous amine materials due to the electron transfer from hydrazine to the SBCP surface and for enantioselectively sensing the chiral species naproxen due to the different binding energies with regard to their chirality. These results provide guidelines for the synthesis of chiral SBCPs and demonstrate their versatility and feasibility for use in various sensors covering photoactive, chemiresistive, and chiral sensors.

Procedure

****Synthesis of the homochiral H₂AlaNDI ligands****

1. Reflux 1,4,5,8-naphthalenetetracarboxylic dianhydride (1.34 g; 0.005 mol) and L- or D-alanine (0.89 g; 0.01 mol) in pyridine (600 mL) for 12 h.
2. Add aq HCl (300 mL water and 100 mL concd HCl), as the volume of the mixture was reduced to 10 mL.
3. Filtrate the solid precipitate formed in solution

****Synthesis of the (R)-AlaNDI-Zn and (S)-AlaNDI-Zn SBCPs****

1. Dissolve ZnI₂ (0.1 mmol) and chiral H₂AlaNDI (0.1 mmol) in 3 mL DMF
2. Seal the solution in a stainless-steel tube with a Teflon liner.
3. Heat at 120 °C for 72 h.
4. Filtrate the crude product and wash with DMF to give the final single crystals.

****Synthesis of the (Rac)-AlaNDI-Zn SBCP****

1. Dissolve ZnI₂ (0.1 mmol), (R)-H₂AlaNDI (0.05 mmol) and (S)-H₂AlaNDI (0.05 mmol) homogenized in 3 mL DMF
2. Seal the solution in a stainless-steel tube with a Teflon liner.
3. Heat at 120 °C for 72 h.
4. Filtrate the crude product and wash with DMF to give the final single crystals.

Figures

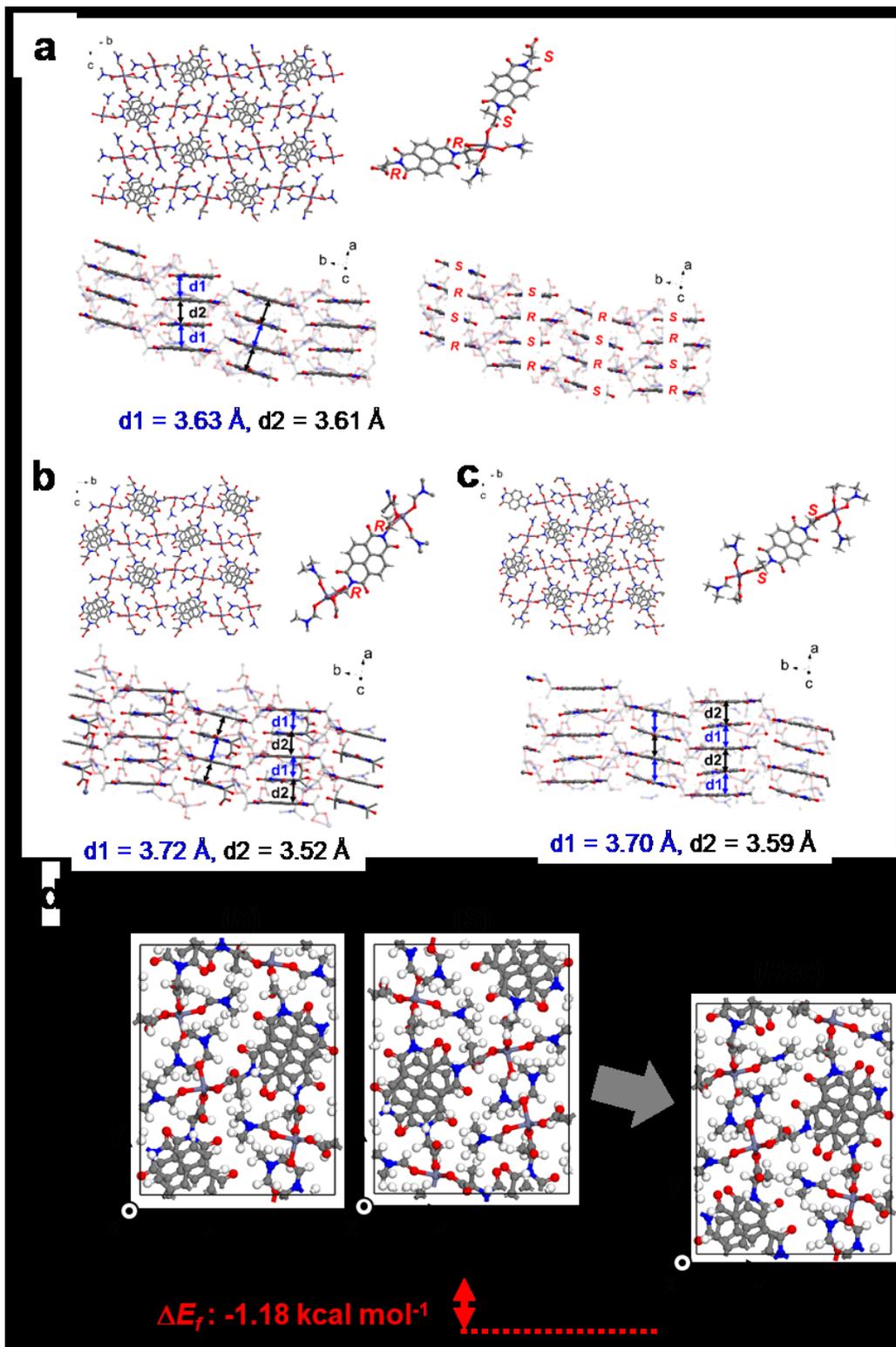


Figure 1

Chiral self-sorted supramolecular biocoordination polymers a-c, Crystal structures of (a) heterochiral (Rac)-AlaNDI-Zn SBCP (top-left shows the a-axis projection, top-right shows a unit description containing two AlaNDI units in a 1D chain with the chirality description, bottom-left shows a pi-pi stacking scheme with centroid-centroid distances, and the bottom-right shows the chiral configuration in this SBCP), (b) homochiral (S)-AlaNDI-Zn SBCP (top-left shows the a-axis projection, top-right shows a unit description

containing one AlaNDI unit in a 1D chain with the chirality description, and bottom shows a pi-pi stacking scheme with centroid-centroid distances) and (c) (R)-AlaNDI-Zn SBCP (top-left shows the a-axis projection, top-right shows a unit description containing one AlaNDI unit in a 1D chain with the chirality description, and bottom shows a pi-pi stacking scheme with centroid-centroid distances. Atom coloring: Zn, thin-purple, C, gray, N, blue, O, red and H, white. Except for the top right figure in each, hydrogen atoms were omitted for clarity. d, Formation energy calculation results for chiral discrimination phenomena in heterochiral SBCPs. The carbon, hydrogen, oxygen, nitrogen and zinc atoms of AlaNDI-Zn SBCPs are colored gray, white, red, blue and navy blue, respectively.