



Contents lists available at ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/ccl

Communication

Thiophene and naphthalene-based double helix: Synthesis, structures and chirality

Chunmei Zhao^{a,b}, Zhiying Ma^a, Chunli Li^a, Li Xu^{c,*}, Hua Wang^{a,*}^a Engineering Research Center for Nanomaterials, Henan University, Kaifeng 475004, China^b School of Chemical Engineering and Food Science, Zhengzhou Institute of Technology, Zhengzhou 450044, China^c College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, China

ARTICLE INFO

Article history:

Received 27 February 2020

Received in revised form 20 May 2020

Accepted 28 May 2020

Available online 1 June 2020

Keywords:

Binaphthylcyclooctatertiophene

Dinaphthylcyclooctatertiophene

Double helix

Crystal structure

Chirality

ABSTRACT

Both racemate and enantiomer of a novel double helix, binaphthylcyclooctatertiophene (**BN-COTh**), which is a DNA-like molecule constructed by two single helices intertwined with each other *via* covalent bonds, have been synthesized with two building blocks, cycloocta-tetrathiophene (**COTh**) and cyclooctadinaphthylidithiophene (**CONT**) fused together *via* Negishi coupling reaction. Another homologue, dinaphthylcyclooctatertiophene (**DN-COTh**) has been employed together as a model compound. Besides the synthetic work, **BN-COTh** and **DN-COTh** have been investigated by studying their crystal structures, spectroscopic behaviors, chiral resolution and chiral characteristics, including circular dichroism (CD) spectra and optical rotations. In addition, the novel crystal of enantiomer of (*R,R*)-**BN-COTh** has been explored. The enantiomer molecules packing along *b*-axis to form a larger and extended assembly packing due to intermolecular interactions between the enantiomer molecules and chloroform molecules in crystal.

© 2020 Chinese Chemical Society and Institute of Materia Medica, Chinese Academy of Medical Sciences.

Published by Elsevier B.V. All rights reserved.

Being composed of four thiophene rings fused to cyclooctatetraene (**COT**), **COTh** possesses special saddle-shaped molecular structure, which is usually employed as an important building block in organic functional materials. As early as in 1974 [1], the first isomer of **COTh** was reported by Kauffmann. Over the past four decades, many work about the derivatives based on **COTh** units in both organic synthesis and applications have been carried out [2]. Among them, all thiophene-based double helix has a novel helical structure, in which two single helices are intertwined with each other *via* the C–C single bonds [3–6]. Such DNA-like double helical motifs connected by covalent bonds show extraordinary aesthetically pleasing structures, which are very rare to be presented in the literature. In our previous work, we have focused on synthesis and property research of **COThs** and their derivatives, including double helicenes [4–7]. Our recent double helices constructed with **COTh** units [8] (Fig. 1) show the same molecular frameworks of double helices constructed by cyclooctatraphene (**COPh**) units, reported by Rajca [9] (Fig. 1) and Wong [10]. These derivatives have not only novel helical structures but also potential applications in supramolecular polymer [11,12], molecular muscle

[13,14] and self-assembly [15], and therefore have attracted continuous attention.

In these pioneering work, the structures of double helices are constructed of **COTh** [3,8,16] and **COPh** [9,10] composed of thiophene and benzene ring, respectively. In this work, both **COTh** (marked by a pink circle, Fig. 1) and cycloocta-dinaphthylidithiophene (**CONT**, marked by a green circle, Fig. 1) are employed as building blocks for construction of a new double helix, binaphthylcyclooctatertiophene (**BN-COTh**). As model compound, dinaphthylcyclooctatertiophene (**DN-COTh**) has been investigated together with **BN-COTh** to enrich the study of such novel double helix. The introduction of an aromatic photoluminescence (PL) group, naphthylene to the molecular framework is to functionalize molecule in material science, such as photoluminescence and circularly polarized luminescence (CPL), *etc.* Besides the synthetic work, herein, we have obtained their racemic crystal structures, done their chiral resolutions, studied on their chiral properties. In addition, the novel crystal of enantiomer of (*R,R*)-**BN-COTh** has been explored.

The synthetic route to **BN-COTh** and **DN-COTh** constructed with **CONT** and **COTh** is shown in Scheme 1. As revealed in our previous work, the deprotonation of **COTh-TMS₄** in the presence of *n*-BuLi exhibited high ipsilateral selectivity [8]. On the basis of this deprotonation selectivity, **COTh-TMS₄** is treated with 2.0 equiv. of *n*-BuLi, the formed bicarbonate anions are transferred to Negishi

* Corresponding authors.

E-mail addresses: xuli@henu.edu.cn (L. Xu), hwang@henu.edu.cn (H. Wang).

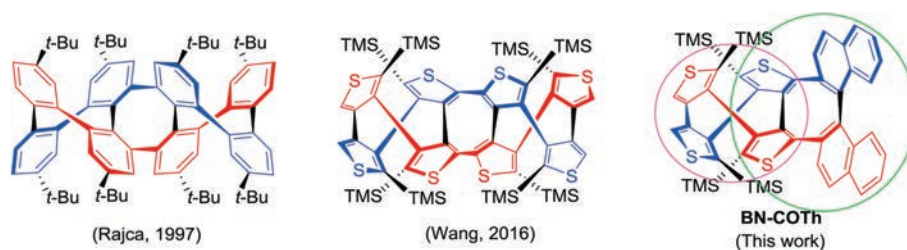
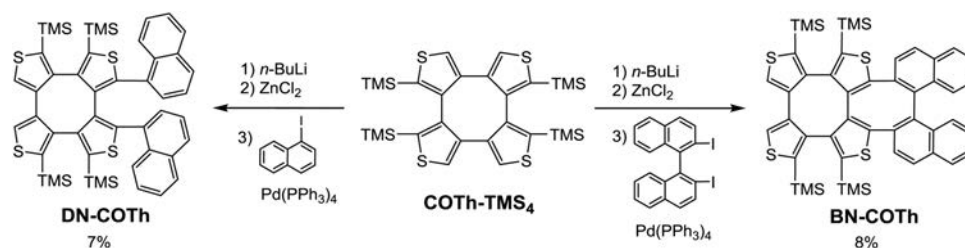


Fig. 1. The molecular structures of covalent bonds linked double helices based on phenyl and thienylunits.



Scheme 1. The synthetic route to **DN-COTh** and **BN-COTh**.

regents by quenching with 2.2 equiv. of ZnCl_2 , and subsequent Negishi couplings with 1-iodonaphthalene and 2,2'-diiodo-1,1'-binaphthalene are occurred to obtained racemic **DN-COTh** and **BN-COTh** in 7% and 8% yields, respectively. The characterization data of chemical structures for **DN-COTh** and **BN-COTh** are shown in Figs. S1-S8 (Supporting information). The low synthetic yields mainly depend on two factors. One is the rigid molecular structure of **COTh-TMS₄** formed by the repulsion of steric hindrance between its TMS groups. Molecular rigidity makes **Ar-I** molecule hard to fit the fixed spatial orientation of Negishi reagent from **COTh-TMS₄** for the coupling procedure. Another one is the intramolecular tension of **DN-COTh** and **BN-COTh**, which is higher than that of **COTh-TMS₄**. Normally, it is hard to make target

molecule with high intramolecular tension from its precursor bearing low intramolecular tension.

The molecular structures of **BN-COTh** and **DN-COTh** are confirmed by X-ray single crystal analyses. Their specific single crystal data are listed in Tables S1 and S2 (Supporting information). The single crystal structure of **BN-COTh** is shown in Fig. 2A, which belongs to monoclinic system, space group $P121/n1$. **BN-COTh** possesses double helical molecular structure, in which there are two eight-membered rings composed with **COTh** and **COPhTh** units fused together in the molecular center to form the new double helix, different from the reported cases contained **COTh** [3,8,16] or **COPh** [9,10] only. In the crystal of **BN-COTh**, the two naphthyl groups in the molecule are approximately vertical with

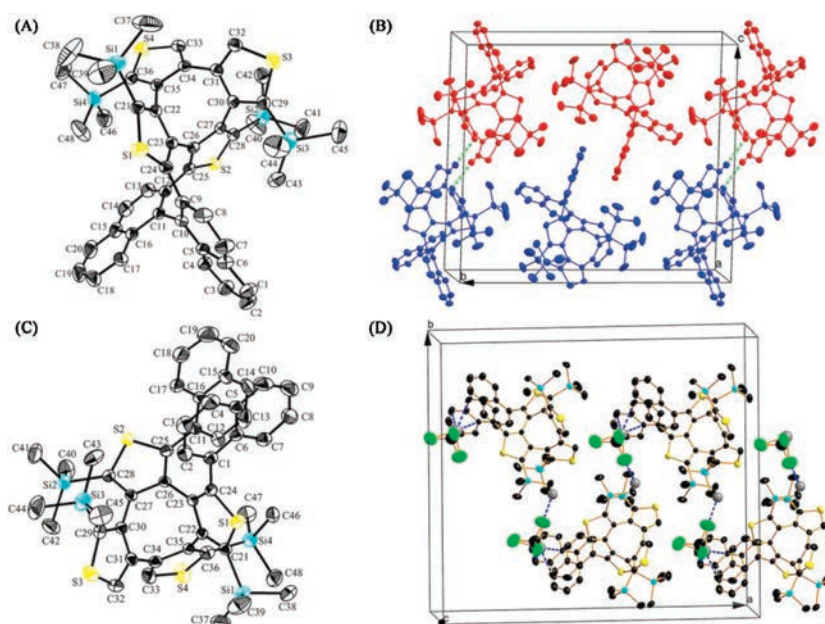


Fig. 2. The crystal structures and packings of **BN-COTh** (A, B) and **DN-COTh** (C, D). Carbon, silicon, sulfur and chlorine atoms are depicted with thermal ellipsoids set at 30% probability level. Hydrogen atoms are omitted for clarity.

dihedral angle of 81.6° (Fig. 2A), the average dihedral angle between naphthyl moiety and the linked thiophene ring is 51.5° . Fig. 2B shows the packing of **BN-COTh**, in which two pairs of enantiomers are stacked in a unit cell. The two enantiomers, (*S,S*)-**BN-COTh** (red) and (*R,R,R*)-**BN-COTh** (blue) are stacked closely via two intermolecular interactions of C33...H32 (2.824 Å), and each enantiomer is stacked via an intermolecular interaction of H42A...H44B (2.343 Å) along *a*-axis.

DN-COTh belongs to the orthorhombic system, space group Fdd2. The two naphthyl groups are parallel and ipsilateral with a small dihedral angle of 7.5° in **DN-COTh** (Fig. 2C). However, the average dihedral angle between naphthyl moiety and the linked thiophene ring is 74.6° , which is bigger than the dihedral angle of 51.5° in **BN-COTh**. Such dihedral angle difference is the key role to explain the distinction between their spectroscopic behaviors. In packing of **DN-COTh**, the molecule of chloroform is observed with 1:1 ratio to molecule **DN-COTh**. The multiple intermolecular interactions exist between **DN-COTh** and chloroform, such as Cl...H (Cl2...H42B: 2.947 Å) and H...C (H49...C14: 2.812 Å, H49...C16: 2.812 Å, H49...C20: 2.895 Å). The three H...C interactions are observed between chloroform and one enantiomer (such as (*R,R*)-**DN-COTh**), while the Cl...H interaction is found between chloroform and another enantiomer (such as (*S,S*)-**DN-COTh**) to form the zigzag packing in the crystal (Fig. 2D).

BN-COTh shows a short wavelength peak at 225 nm and shoulder peak at 285 nm, while **DN-COTh** has a peak at 231 nm and a shoulder peak at 306 nm (Fig. 3). The shoulder peak intensity of **BN-COTh** is much higher than that in the case of **DN-COTh**. Compared to **DN-COTh**, **BN-COTh** has better intramolecular conjugation due to its smaller average dihedral angle between naphthyl moiety and the linked thiophene ring (Fig. 2). Such conjugation difference is also presented in their emission behaviors. **BN-COTh** shows single emission peaked at 420 nm, while **DN-COTh** exhibits shorter emission peak at 406 nm (Fig. 3).

The chiral resolutions of *rac*-**DN-COTh** and *rac*-**BN-COTh** were done by chiral HPLC with hexane as eluent for *rac*-**DN-COTh** and hexane/isopropanol (99.7:0.3, v/v) as eluent for *rac*-**BN-COTh**, respectively. The enantiomers of both **DN-COTh** and **BN-COTh** were obtained successfully with high *ee* value ($\geq 97\%$) as shown in Fig. S11 (Supporting information).

All enantiomers of **DN-COTh** and **BN-COTh** possess moderate optical rotations as shown in Table 1. The CD spectra of the enantiomers were given in Fig. 4. We can see that all enantiomers exhibit characteristic mirror positive and negative CD spectra images in dichloromethane with remarkable cotton effect.

Fortunately, the single crystal of enantiomer **BN-COTh** was obtained via solvent evaporation method and characterized as shown in Fig. 5. The absolute configuration of (*R,R,R*)-**BN-COTh** is confirmed by an X-ray crystallographic analysis. (*R,R,R*)-**BN-COTh** belongs to monoclinic system, space group P1211 (the single

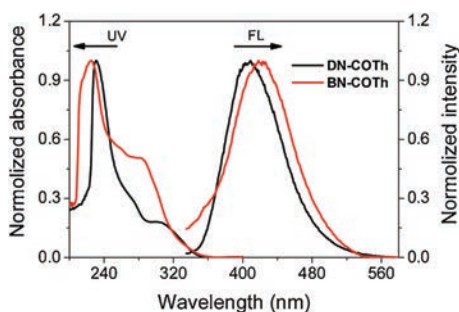


Fig. 3. The normalized UV-vis and fluorescence spectra of **DN-COTh** and **BN-COTh** in THF ($[C] = 1.0 \times 10^{-5}$ mol/L, $\lambda_{\text{ex}} = 300$ nm).

Table 1

The specific optical rotation data of enantiomers in CH_2Cl_2 .

Compd.	(+)- BN-COTh	(-)- BN-COTh	(-)- DN-COTh	(+)- DN-COTh
<i>c</i> (mg/mL) ^a	0.17	0.18	0.30	0.53
$[\alpha]_{\text{D}}^{20}$	247°	-233°	-193°	224°

^a Concentrations of samples were determined by using molar extinction coefficient, obtained from the linear Lambert-Beer plots for racemic samples in CH_2Cl_2 (Figs. S9 and S10 in Supporting information).

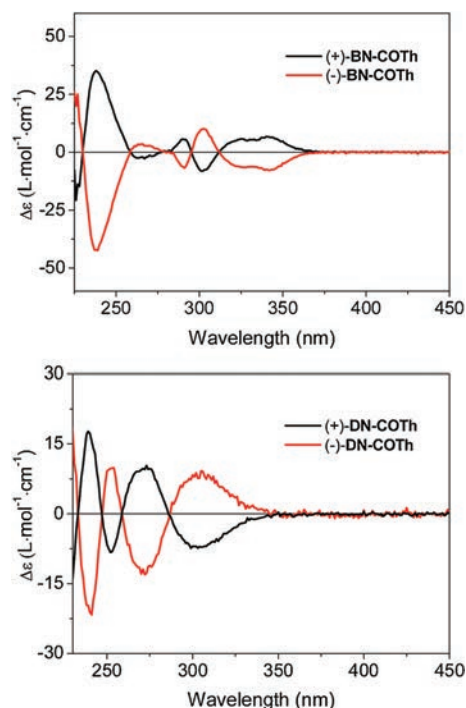


Fig. 4. CD spectra of **BN-COTh** and **DN-COTh** in CH_2Cl_2 at 20°C .

crystal data is exhibited in Table S3 in Supporting information). The two naphthalene rings in molecule are almost vertical with dihedral angle of 74.1° , close to its racemate as shown as 81.6° . The average dihedral angle between naphthalene ring and thiophene ring is 52.5° , which is very close to its racemate as shown as 51.5° . The torsion angle of **COT** in **COTh** of molecule (*R,R,R*)-**BN-COTh** is about 58.5° (C6-C7-C10-C11), and another torsion angle of 62.3° (C1-C2-C15-C16) is observed from the **COT** in **CONT** of the molecule. Both two torsion angles are much smaller than that as shown as 77.8° [8] in **COTh** itself due to introduction of binaphthyl moiety with high intramolecular steric tension in (*R,R,R*)-**BN-COTh**.

In packing of (*R,R,R*)-**BN-COTh**, two (*R,R,R*)-**BN-COTh** molecules and two chloroform molecules per unit cell are shown along *b*-axis (Fig. 5B). The intermolecular interactions between (*R,R,R*)-**BN-COTh** and chloroform molecule are observed with short distances of Cl3...C44 (3.369 Å), Cl3...H44B (2.866 Å) and H49...S4 (2.970 Å). Such intermolecular interactions make molecules packing along *b*-axis to form a larger and extended assembly packing in crystal.

Up to now, only two types of chiral double helices constructed of **COTh** [8] and **COPh** [10], respectively. Each double helical scaffold has two single helices intertwined with each other via the C–C single bonds to form a special type of DNA-like molecular structure, which is important part in artificial simulation of DNA. Different from those pioneering work constructed with **COTh** or **COPh** only, (*R,R,R*)-**BN-COTh** is a novel one composed with two building blocks, **COTh** and **CONT** fused together in its molecular

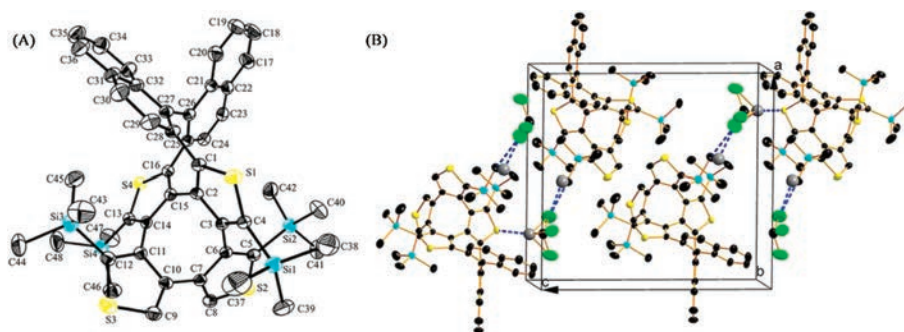


Fig. 5. Single crystal (A) and crystal packing structure (B) of *(R,R,R)*-BN-COTh. Carbon, silicon, sulfur, and chlorine atoms are depicted with thermal ellipsoids set at 30% probability level. Part of hydrogen atoms are omitted for clarity.

framework. The construction of **BN-COTh** provides a new route to design new double helices based on two or more building blocks, such as **COTh** and **COPh**.

In summary, two naphthyl-substituted **COThs**, **BN-COTh** and **DN-COTh** were synthesized and their crystal structures, photo-physical behaviors and chiral properties were classically characterized. **BN-COTh** is a new double helical molecule constructed with two building blocks, **COTh** and **CONT** fused together to form its molecular framework. The molecular design strategy of **BN-COTh** provides a feasible route to functionalize the novel double helices in high level based on two or more building blocks, such as **COTh**, **COPh** and **CONT**. The studies on the longer chain double helices and their chiroptical properties, such as circularly polarized luminescence based on the aromatic photoluminescence groups such as naphthylene are in progress in our group.

Declaration of competing interest

The authors declare that they have not any financial interests/personal relationships which may be considered as potential competing interests.

Acknowledgments

This research was supported by the National Natural Science Foundation of China (Nos. 21672053 and 21672054), Innovation Scientists and Technicians Troop Construction Projects of Henan Province (C20150011).

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.ccl.2020.05.040>.

References

- [1] B. Greviigi, A. Woltermann, T. Kaufmann, *Angew. Chem. Int. Ed.* 13 (1974) 467–468.
- [2] (a) C.M. Zhao, L. Xu, Y. Wang, et al., *Chin. J. Chem.* 33 (2015) 71–78; (b) L. Li, C.M. Zhao, H. Wang, *Chem. Rec.* 6 (2016) 797–809; (c) Z. Zhao, X.Y. Zheng, L.L. Du, et al., *Nat. Commun.* 10 (2019) 2952–2961; (d) Y. Tian, G.X. Wang, Z.Y. Ma, L. Xu, H. Wang, *Chem. -Eur. J.* 24 (2018) 15993–15997; (e) J. Urieta-Mora, I. García-Benito, I. Zimmermann, et al., *J. Mater. Chem. C* 7 (2019) 6656–6663; (f) L.Y. Zhao, L.L. Qiu, D.B. Xia, et al., *ACS Appl. Energy Mater.* 2 (2019) 8173–8180.
- [3] J.M. Marsella, I.T. Kim, F. Tham, *J. Am. Chem. Soc.* 122 (2000) 974–975.
- [4] C.L. Li, J.W. Shi, L. Xu, et al., *J. Org. Chem.* 74 (2009) 408–411.
- [5] Z.H. Wang, J.W. Shi, J.G. Wang, et al., *Org. Lett.* 12 (2010) 456–459.
- [6] X.M. Liu, P.P. Yu, L. Xu, et al., *J. Org. Chem.* 78 (2013) 6316–6321.
- [7] X.M. Liu, H.L. Sun, W. Xu, et al., *Org. Chem. Front.* 5 (2018) 1257–1261.
- [8] S. Zhang, X.M. Liu, C.L. Li, et al., *J. Am. Chem. Soc.* 138 (2016) 10002–10010.
- [9] A. Rajca, A. Safronov, S. Rajca, et al., *Angew. Chem. Int. Ed.* 36 (1997) 488–491.
- [10] J.X. Chen, J.W. Han, H.N.C. Wong, *Org. Lett.* 17 (2015) 4296–4299.
- [11] M.J. Marsella, R.J. Reid, *Macromolecules* 32 (1999) 5982–5984.
- [12] C.J. Sun, P.F. Wang, H. Wang, et al., *Polym. Chem.* 7 (2016) 5031–5038.
- [13] M.J. Marsella, R.J. Reid, S. Estassi, et al., *J. Am. Chem. Soc.* 124 (2002) 12507–12510.
- [14] M.J. Marsella, *Acc. Chem. Res.* 35 (2002) 944–951.
- [15] P. Li, Y.Q. Lai, Y. Wang, et al., *Sci. China Chem.* 61 (2018) 844–849.
- [16] B.B. Li, S. Zhang, L. Li, et al., *ACS Omega* 3 (2018) 16014–16020.