Organic & **Biomolecular Chemistry**

COMMUNICATION

Check for updates

Cite this: Org. Biomol. Chem., 2019, 17, 8822

Received 31st August 2019, Accepted 23rd September 2019 DOI: 10.1039/c9ob01907c rsc li/obc

Synthesis and chiroptical properties of stereogenic cyclic dimers based on 2,2'-biselenophene and [2.2]paracyclophane⁺

Masashi Hasegawa, 🕑 * Kosuke Kobayakawa, Yuki Nojima and Yasuhiro Mazaki

Stereogenic cyclic dimers based on 2,2'-biselenophene linked with [2.2]paracyclophane have been synthesized to investigate their chiroptical properties. Embedding selenophene led to the formation of intramolecular Se $\cdots\pi$ interactions between the two biselenophene strands. The resulting rigid cyclic system exhibits enhanced chiroptical properties when compared with its precursor. In addition, the electrochemical properties were also investigated.

Stereogenic compounds containing π -conjugated units have attracted much attention in organic materials chemistry because the π -conjugated system in a chiral environment exhibits remarkable chiroptical and optoelectronic properties.^{1,2} It has been reported that stereogenic oligo- and polythiophene derivatives exhibit novel properties such as circular dichroism (CD) in the short wave infrared (SWIR) region,³ circularly polarized luminescence (CPL),⁴ electroactive chirality,⁵ and magneto-optic properties.⁶ These properties are associated with the electronic structure derived from oligo(or poly)-thiophene in the chiral scaffold.

Selenophene is a heteroaromatic analogue of thiophene.⁷ Replacing sulfur with selenium alters the molecular structure and electronic properties. The large number of electrons in the selenium element results in high polarizability that may give rise to singular optoelectronic properties.8 Therefore, the introduction of selenophene into a stereogenic system is a fascinating approach to obtain novel chiroptical materials. In addition, the relatively large van der Waals radius of Se can lead to strong molecular interactions in the solid state, which is advantageous for charge-transportation in conducting materials.9 However, few studies have focused on chiroptical properties based on selenium-containing compounds, albeit a variety of their sulfur counterparts have been developed to

date. Thus, the exploration and development of functional materials containing a selenophene scaffold remain a worthwhile research topic.

In this study, we have designed stereogenic cyclic compounds based on 2,2'-biselenophene and pseudo-ortho[2.2] paracyclophane (PC) (1, Fig. 1). As a robust planar chiral scaffold, pseudo-ortho[2.2]PC has been widely employed as a catalyst in asymmetric synthesis and a chiroptical material.¹⁰⁻¹⁵ In particular, directly connecting aryl groups to the [2.2]PC scaffold can give rise to a helical geometry in the embedded π -conjugation structure, which can lead to pronounced chiroptical properties.^{3,6,14,15} The combination of chirality with selenophene may lead to emergent electroconductive materials based on a chiral organic semiconductor transistor.¹⁶⁻¹⁸ To investigate the intrinsic nature of selenophene in a stereogenic system, we herein report the synthesis, structure, and chiroptical properties of 1 using optical rotation and CD spectra. In addition, the electrochemical properties of 1 are also described.

The synthetic route used to prepare 1 is shown in Scheme 1. We chose racemic 4.12-diiode[2.2]paracyclophane (rac)-2 as a starting compound.¹⁹ A Suzuki coupling reaction of 2 with 3, which was derived from commercially available selenophene, in the presence of Pd(PPh₃)₄ gave (rac)-4 in 81% yield. The separation of (rac)-4 into (R_p) -4 and (S_p) -4 was accomplished using HPLC on a chiral stationary phase (Chiralpak IA). The absolute configuration was determined using X-ray analysis of (S_p) -4 (Fig. S6b[†]). Subsequently, the transformation of each enantiomer into 5 was carried out

 $(R_{\rm D}, R_{\rm D})$ -1 $(S_{\rm D}, S_{\rm D})$ -1

Fig. 1 Stereogenic biselenophene in pseudo-ortho[2.2]paracyclophane.

View Article Online



Department of Chemistry, Graduate School of Science, Kitasato University, 1-15-1 Kitasato, Minami-ku, Sagamihara, Kanagawa 252-0373, Japan.

E-mail: masasi.h@kitasato-u.ac.jp

[†] Electronic supplementary information (ESI) available. CCDC 1939516-1939518. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9ob01907c



Scheme 1 Synthesis of (R_p,R_p) -**1** and (S_p,S_p) -**1**. Reagents and conditions: (a) Cs_2CO_3 (aq), Pd(PPh₃)₄, toluene, 120 °C, 81%; (b) separation using HPLC on a chiral stationary phase (Chiralpak IA); (c) ICl, THF, 0 °C, >99% (for (R_p) -5) and >99% (for (S_p) -5); (d) Ni(cod)₂, 2,2'-bipyridyl, THF, 80 °C, 20% (for (R_p,R_p) -**1**) and 18% (for (S_p,S_p) -**1**).

upon treatment with iodomonochloride (ICl) followed by a Ni-catalysed coupling reaction to give the stereogenic homocoupling products (R_p,R_p) -1 and (S_p,S_p) -1 together with unidentified products. (R_p,R_p) -1 and (S_p,S_p) -1 were sufficiently stable under ambient conditions and characterized as D_2 symmetric structures using ¹H, ¹³C, and ⁷⁷Se NMR spectroscopy.

The solid state structure of (R_p, R_p) -1 was determined using X-ray crystallography (Fig. 2). The orientation of the biselenophene was restricted by the selenium atoms; compound 1 adopts a C_1 symmetric structure composed of a pair of biselenophene units in a cisoid and transoid arrangement. These two biselenophene moieties are arranged in an edge-to-face fashion with Se... π interactions; the distances between Se(2) and the least-squares plane of selenophene A, and Se(1) and selenophene B were found to be 3.373(2) and 3.382(3) Å, respectively (i and ii in Fig. 2b). Both biselenophene units are distorted from the benzene ring of the cyclophane in the range of 37.6-38.4°, leading to helical arrays between the two [2.2]PC units, whereas the dihedral angles within two selenophenes are relatively small. In the packing diagram there are intermolecular C-H··· π interactions (Fig. 2b). Overall, the biselenophene units arrange in an edge-to-face fashion along the *c*-axis in the crystal structure.

Compound 1 exhibits a relatively large optical specific rotation when compared with its acyclic precursor (4). The rotation value for $(R_{\rm p},R_{\rm p})$ -1 was $[\alpha]_{\rm D}^{25}$ = +563 (CH₂Cl₂, *c* = 0.8 × 10⁻³), while that of $(R_{\rm p})$ -4 was $[\alpha]_{\rm D}^{25}$ = +26 (CH₂Cl₂, *c* = 5.0 × 10⁻³). Embedding the selenophene moieties into the rigid stereogenic system may lead to an increase in the optical rotation properties.



Fig. 2 (a) The crystal structure of (R_p,R_p) -1 (thermal ellipsoids at 50% probability). Selected dihedral angles (°): C(18)–C(17)–C(1)–Se(1) = 38.3(7), C(30)–C(29)–C(8)–Se(2) = 38.4(7), C(23)–C(24)–C(9)–Se(3) = -37.7(7), C(35)–C(36)–C(16)–Se(4) = -37.6(7), Se(1)–C(4)–C(5)–Se(2) = 19.6(6), and C(11)–C(12)–C(13)–Se(4) = -12.1(9). (b) Intermolecular contacts between the stacks. Selected short contacts (Å) *i*: Se(2)--least squares plane (LSP) of Se(4)–C(13)–C(14)–C(15)–C(16) = 3.373(2), *ii*: Se(1)--LSP of Se(3)–C(9)–C(10)–C(11)–C(12) = 3.382(3), *iii*: C(12)--H(1) 2.878, *iv*: C(13)--H(6) 2.892, and *v*: C(13)--H(6) 2.642.

Subsequently, we measured the UV-vis and CD spectra of 1 and 4 in CH_2Cl_2 (Fig. 3). The UV-vis spectrum of (R_p, R_p) -1 revealed an absorption maximum at 380 nm together with a shoulder at ~436 nm. In contrast, 2,2'-biselenophene exhibits an absorption maximum at 320 nm (CHCl₃).^{20a} Furthermore, the UV-vis spectrum of (R_p) -4 exhibits maxima at 262 and 315 nm. The observed bathochromic shift in 1 was attributed to the extension of the π -conjugation in the selenophene moieties. As expected, embedding biselenophene into a stereogenic [2.2]PC scaffold remarkably enhanced the intensity of the CD spectra. We found mirror image CD spectra for both 1 and 4. The CD spectrum of (R_p, R_p) -1 exhibits a roughly bisignate shape with small splitting peaks in the range corresponding to the absorption band found in its UV-vis spectrum. Peaks or valleys were found at 432, 409, 375, and 360 nm. The maximum intensity of the Cotton effect was recorded as $\Delta \varepsilon = 57$ (at 432 nm) for $(R_{\rm p},R_{\rm p})$ -1. On the other hand, a very small first Cotton effect was found in the CD spectrum of (R_p) -4 at ~360 nm (Fig. 3b, inset). Fig. 3c shows $g_{\rm abs}$ plots, which are defined as $\Delta \varepsilon / \varepsilon$ obtained from CD and UV-vis spectra. The largest $|g_{abs}|$ values were found at 434 nm in 1. Thus, this indicates that the magnetic transition dipole moment in the corresponding transition band may be enhanced in the present rigid cyclic system. Unfortunately, compounds 1 and 4 were not fluorescent, which was attributed to the internal heavy atom effect.

We performed a TD-DFT calculation study to validate the experimental UV-vis and CD spectra. We initially optimised



Fig. 3 (a) The UV-vis spectra of (R_p,R_p) -1 (2.6 × 10⁻⁵ M) and (R_p) -4 (2.8 × 10⁻⁵ M) in CH₂Cl₂ together with the simulated spectrum of (R_p,R_p) -1 using TD-B3LYP/6-311+G(2d,p). (b) The CD spectra of (R_p,R_p) -1 and (S_p,S_p) -1 (1.4 × 10⁻⁵ M), (R_p) -4, and (S_p) -4 (4.1 × 10⁻⁵ M) together with the simulated spectrum of (R_p,R_p) -1 using TD-B3LYP/6-311+G(2d,p); the inset shows the enlarged spectra of (R_p) -4 and (S_p) -4. (c) The g_{abs} ($\Delta \varepsilon / \varepsilon$) plots obtained for (R_p,R_p) -1, (S_p,S_p) -1, (R_p) -4, and (S_p) -4.

the geometry of (R_p,R_p) -1 at the B3LYP/6-31G(d,p) level of theory. The most stable geometry was consistent with the molecular structure obtained during X-ray crystallography. The obtained structure adopts a C_1 symmetric geometry composed of cisoid and transoid 2,2'-biselenophene moieties. Both the highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital (LUMO) are spread over one side of the 2,2'-biselenophene and phenyl rings in the cyclophanes. The next HOMO and LUMO were also delocalized in a similar manner, but located on the other biselenophene (Fig. 4).

Time dependent (TD)-DFT calculations were performed at the B3LYP/6-311+G(2d,p) level of theory based on the optimized C_1 geometry. TD-DFT calculations for the R_p configuration revealed that the longest absorption band of 1 involved four transition bands associated with HOMO(H) \rightarrow LUMO(L) (S_1) , H-1 \rightarrow L (S_2) , H-1 \rightarrow L+1 (S_3) , and H \rightarrow L+1 (S_4) . These transitions gave a qualitatively reproducible absorption spectrum, as shown in Fig. 3a. The calculated CD spectrum also reproduced a qualitatively similar Cotton effect to that observed experimentally. From the analysis of the transition



state, the S_1 and S_2 excitation contributes to the positive sign, while S_3 and S_4 result in a negative Cotton effect in the R_p configuration. S_1 and S_3 are composed of transannular transitions, which are associated with the electronic transition from one biselenophene to the other. Although these are basically forbidden in the absorption spectra, these transitions have a strong influence on the Cotton effect in the CD spectra. Thus, this indicates that the magnetic transition dipole moment may be predominant in this transition. This is consistent with the larger g_{abs} values found in **1**, in particular that observed at 434 nm (Fig. 3c).

The electrochemical properties of **1** were investigated using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in CH₂Cl₂ containing ^{*n*}Bu₄PF₆. The CV curve obtained for (R_p , R_p)-**1** exhibited two sets of reversible and semi-reversible peaks (Fig. 5), although compound **4** did not exhibit any oxidation peak within the potential window. Similar oxidation waves were observed in the DPV curve ($E_1 = 0.52$ and $E_2 = 0.71$ V, *vs.* Fc/Fc⁺) together with a further oxidation peak at a higher potential ($E_3 = 0.99$ V). The multi-redox process corresponds to the redox reactions derived from the two biselenophene moieties. Since the redox potential of biselenophene was recorded as a much higher value (>1.20 V) in the literature,²⁰ the reduction in the first and second potentials suggests favourable interactions between the two biselenophenes, which are present in a face-to-face arrangement.



Fig. 5 CV (100 mV s⁻¹) and DPV curves recorded for (R_p, R_p) -1 (5.0 × 10⁻⁴ M) in CH₂Cl₂ containing ^{*n*}Bu₄NPF₆ (0.1 M) at 25 °C.

A similar tendency has been observed in an oligothiophene-containing cyclophane scaffold. $^{\rm 3}$

Conclusions

We have prepared rigid stereogenic cyclic dimers based on 2,2'-biselenophene linked with a [2.2]PC framework. X-ray crystallography revealed that (R_p,R_p) -1 adopted a C_1 symmetric geometry bearing cisoid and transoid biselenophene moieties. Embedding 2,2'-biselenophene into a robust chiral scaffold remarkably enhanced the chiroptical properties when compared to its acyclic chiral precursor. In addition, CV revealed stepwise redox properties, which suggest that interactions were formed between the two intramolecular biselenophene arrays. To the best of our knowledge, this is the first example of chiroptical properties based on a biselenophene scaffold. Our results provide a foundation for the synthesis of new selenophene-containing materials.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

This work was partially supported by the JSPS KAKENHI Grant Number 18K05092 and Kitasato Research Centre for Environment Science. All calculations were performed at the Research Centre for Computational Science, Okazaki (Japan).

Notes and references

- (a) J. R. Brandt, F. Salerno and M. J. Fuchter, *Nat. Rev. Chem.*, 2017, 1, 0045; (b) M. Rickhaus, M. Mayor and M. Jurícek, *Chem. Soc. Rev.*, 2016, 45, 1542.
- For selected recent examples: (a) K. Miki, T. Noda, M. Gon, K. Tanaka, Y. Chujo, Y. Mizuhata, N. Tokitoh and K. Ohe, *Chem. – Eur. J.*, 2019, 25, 9211; (b) Y. Nojima, M. Hasegawa, N. Hara, Y. Imai and Y. Mazaki, *Chem. Commun.*, 2019, 55, 2749; (c) X. Shang, I. Song, H. Ohtsu, Y. H. Lee, T. Zhao, T. Kojima, J. H. Jung, M. Kawano and J. H. Oh, *Adv. Mater.*, 2017, 29, 1605828; (d) Y. Nakakuki, T. Hirose, H. Sotome, H. Miyasaka and K. Matsuda, *J. Am. Chem. Soc.*, 2018, 140, 4317; (e) M. Hasegawa, D. Kurebayashi, H. Matsuzawa and Y. Mazaki, *Chem. Lett.*, 2018, 47, 989.
- 3 M. Hasegawa, K. Kobayakawa, H. Matsuzawa, T. Nishinaga, T. Hirose, K. Sako and Y. Mazaki, *Chem. – Eur. J.*, 2017, 23, 326.
- 4 (a) F. Sannicolò, P. R. Mussini, T. Benincori, R. Cirilli,
 S. Abbate, S. Arnaboldi, S. Casolo, E. Castiglioni,
 G. Longhi, R. Martinazzo, M. Panigati, M. Pappini,
 E. Q. Procopio and S. Rizzo, *Chem. Eur. J.*, 2014, 20,
 15298; (b) T. Ikai, K. Takayama, Y. Wada, S. Minami,
 C. Apiboon and K.-i. Shinohara, *Chem. Sci.*, 2019, 10, 4890;

(c) K. Takase, K. Noguchi and K. Nakano, J. Org. Chem., 2018, 83, 15057.

- 5 F. Sannicolò, S. Arnaboldi, T. Benincori, V. Bonometti, R. Cirilli, L. Dunsch, W. Kutner, G. Longhi, P. R. Mussini, M. Panigati, M. Pierini and S. Rizzo, *Angew. Chem., Int. Ed.*, 2014, 53, 2623.
- 6 P. Wang, I. Jeon, Z. Lin, M. D. Peeks, S. Savagatrup,
 S. E. Kooi, T. V. Voorhis and T. M. Swager, *J. Am. Chem. Soc.*, 2018, 140, 6501.
- 7 T. Otsubo and K. Takimiya, Selenophenes as Hetero-analogues of Thiophene-based Materials, in *Handbook of Thiophene-based Materials: Applications in Organic Electronics and Photonics*, ed. I. F. Perepichka and D. F. Perepichka, Wiley, Chichester, 2009, vol. 1, p. 321.
- 8 N.-H. You, N. Fukuzaki, Y. Nakamura, T. Higashihara, S. Ando and M. Ueda, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 4428.
- 9 (a) K. Takimiya, Y. Kunugi, Y. Konda, N. Niihara and T. Otsubo, *J. Am. Chem. Soc.*, 2004, **126**, 5084; (b) H.-W. Lin, W.-Y. Lee and W.-C. Chen, *J. Mater. Chem.*, 2012, 22, 2120.
- 10 (a) K. J. Weiland, A. Gallego and M. Mayor, *Eur. J. Org. Chem.*, 2019, 3073; (b) Z. Hassan, E. Spuling, D. M. Knoll, J. Lahann and S. Bräse, *Chem. Soc. Rev.*, 2018, 47, 6947; (c) A. Marrocchi, I. Tomasi and L. Vaccaro, *Isr. J. Chem.*, 2012, 52, 41.
- 11 (a) Y. Morisaki and Y. Chujo, Bull. Chem. Soc. Jpn., 2019,
 92, 265; (b) Y. Morisaki, M. Gon, T. Sasamori, N. Tokitoh and Y. Chujo, J. Am. Chem. Soc., 2014, 136, 3350;
 (c) M. Gon, Y. Morisaki and Y. Chujo, Chem. Eur. J., 2017, 23, 6323.
- 12 (a) L. G. Sarbu, L. G. Bahrin, P. G. Jones, L. M. Birsa and H. Hopf, *Beilstein J. Org. Chem.*, 2015, **11**, 1917;
 (b) C. Mézière, M. Allain, C. Oliveras-Gonzalez, T. Cauchy, N. Vanthuyne, L. G. Sarbu, L. M. Birsa, F. Pop and N. Avarvari, *Chirality*, 2018, **30**, 568; (c) K. Kobayakawa, M. Hasegawa, H. Sasaki, J. Endo, H. Matsuzawa, K. Sako, J. Yoshida and Y. Mazaki, *Chem. – Asian J.*, 2014, **9**, 2751.
- 13 (a) K. J. Weiland, T. Brandl, K. Atz, A. Prescimone, D. Häussinger, T. Šolomek and M. Moyor, J. Am. Chem. Soc., 2019, 141, 2104; (b) Y. Morisaki, R. Hifumi, L. Lin, K. Inoshita and Y. Chujo, Polym. Chem., 2012, 3, 2727; (c) L. Guyard, C. Dumas, F. Miomandre, R. Pansu, R. Renault-Méallet and P. Audebert, New J. Chem., 2003, 27, 1000.
- 14 S. Ishioka, M. Hasegawa, N. Hara, Y. Imai and Y. Mazaki, *Chem. Lett.*, 2019, **47**, 640.
- 15 X. Liu, Y. Ma, W. Duan, F. He, L. Zhao and C. Song, *J. Org. Chem.*, 2011, **76**, 1953.
- 16 Y. Yang, R. C. da Costa, M. J. Fuchter and A. J. Campbell, *Nat. Photonics*, 2013, 7, 634.
- 17 R. C. da Costa, G. J. Hedley, D.-M. Smilgies, J. M. Frost, I. D. W. Samuel, A. Otero-de-Roza, E. R. Johnson, K. E. Helfs, J. Nelson, A. J. Campbell and M. J. Fuchter, ACS Nano, 2017, 11, 8329.
- 18 X. Shang, I. Song, H. Ohtsu, Y. H. Lee, T. Zhao, T. Kojima, J. H. Jung, M. Kawano and J. H. Oh, *Adv. Mater.*, 2017, 29, 1605828.

Communication

- 19 G. Meyer-Eppler, E. Vogelsang, C. Benkhäuser, A. Schneider, G. Schnakenburg and A. Lützen, *Eur. J. Org. Chem.*, 2013, 4523.
- 20 (a) R. Shabana, A. Galal, H. B. Mark Jr., H. Zimmer, H. Gronowitz and A.-B. Hörnfeldt, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1990, 48, 239; (b) S. Inoue,

H. Nakanishi, K. Takimiya, Y. Aso and T. Otsubo, *Synth. Met.*, 1997, **84**, 341; (c) S. Das and S. S. Zade, *Chem. Commun.*, 2010, **46**, 1168; (d) B. Lu, S. Ming, K. Lin, S. Zhen, H. Liu, H. Gu, S. Chen, Y. Li, Z. Zhu and J. Xu, *New J. Chem.*, 2016, **40**, 8316.