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COMMUNICATION

Synthesis and spectroscopic properties of chiral binaphthyl-linked subphthalocyanines

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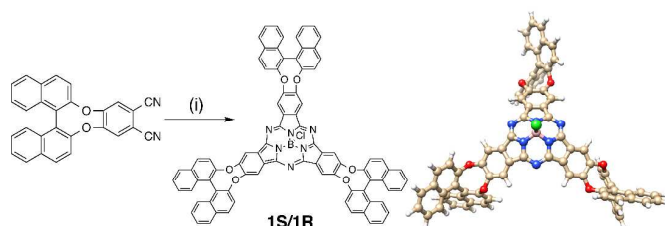
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Chiral binaphthyl-linked subphthalocyanines (SubPcs) (1**) have been prepared by cyclotrimerization reaction of a phthalonitrile linked with (*R*)- and (*S*)-2,2'-binaphthyl in the presence of BCl₃, and characterized by various spectroscopies including NMR, electronic absorption, CD, and MCD, as well as electrochemistry.**

Following two early reports in 1972¹ and 1974,² the existence of SubPc remained unnoticed until 1990, when one of the authors reported its ring-expansion leading to mono-substituted type Pcs.³ Because of its characteristic concave structure, many researchers were attracted to study this compound, so that the chemistry of SubPc has become popular over the past two decades.⁴ However, on the other hand, reports on chiral SubPcs are still limited because of the difficulties of preparation and understanding some of their properties. Torres was the first researcher to prepare this type of SubPc, but no circular dichroism (CD) data was reported which represents the chirality of chromophore molecules.⁵ Two years later, we succeeded in separating two enantiomers of a SubPc with C₃ symmetry, and demonstrated a mirror-image relationship in their CD spectra.⁶ However, even at this stage, the relationship between the CD signal and conformation was not elucidated. 10 years later, in 2012, the first report appeared on this relationship using chiral 1,2-subnaphthalocyanine.⁷ Thus, there are only two papers published so far with respect to “CD-signal active” chiral SubPc and its analogues. In this paper, we report the synthesis and some properties of (*R*)/(*S*)-2,2'-binaphthoxy-linked optically active SubPcs, **1S** and **1R** (Scheme 1). (*R*)/(*S*)-2,2'-binaphthyl-linked Pcs which show intense CD were already reported in 1999 and, in particular, their CD generation mechanism was completely rationalized quantitatively including their sign and magnitude.⁸

The synthesis of **1S** and **1R** is straightforward (Scheme 1). A mixture of BCl₃ and (*S*)/(*R*)-benzo[*b*]dinaphtho[2,1-*e*:1',2'-*g*][1,4]-dioxocine-5,6-dicarbonitrile (which can be prepared in one step from commercially available 4,5-dichlorophthalonitrile and (*S*)- or

(*R*)-1,1'-binaphthyl-2,2'-diol⁹) was refluxed in trichlorobenzene for 4 h, to yield **1S/1R** in good yields. The HR-MALDI-FT-ICR-MS spectra of **1S** and **1R** clearly showed intense signals for the molecular ion [M]⁺. The isotopic pattern closely resembled the simulated patterns given in Fig. S1 for **1S**.



Scheme 1 Synthesis of **1S** and **1R**. Reagents and conditions: (i) BCl₃ (1 eq), 1,2,4-trichlorobenzene, reflux, 4 h, 33%. Inset: optimized structure of **1S**.

Fig. 1 shows the ¹H NMR spectrum of SubPc **1S** recorded in CDCl₃ and the proposed assignments. With the help of a ¹H-¹H COSY analysis (Fig. S2), all of the signals are reasonably assigned. As can be seen, two singlet signals at δ = 8.80 and 8.73, attributed to the α proton, were observed due to the C₃ symmetric cone-shaped SubPc core structure plus the ring-current effect due to naphthalene rings positioned at the *endo* and *exo* sides of the SubPc macrocycle. The protons of peripherally-linked binaphthyl substituents were also observed as two sets of six group signals, each attributed to one proton, since binaphthyl rings are located inside (*endo*) or outside (*exo*) the bowl-shaped SubPc ring, outside of the rim. According to the NMR data of a cyclopentadienylruthenium π complex of SubPc,¹⁰ it is known that the ring current of the SubPc ring is stronger inside the bowl than outside it. Indeed, when methyl groups were linked to the beta positions of the saturated pyrrole ring of dibenzosubtriazachlorin, methyl signals appeared at two different positions (δ = 2.03 and 1.16 ppm), although the distance of these methyl groups from the central boron atom is approximately the

same whether it is positioned at the *endo* or *exo* side of the bowl.¹¹ As shown in Fig. 1, the two doublets at $\delta = 8.10$ and 8.01 ppm are attributed to two (*a,b*) of the four protons (*a,b,c,d*) in the binaphthyl substituent close to the SubPc ring. The difference between (*a,b*) and (*c,d*) is very large, since (*a,b*) are on the *endo* side while (*c,d*) are on the *exo* side, outside the SubPc ring. For the same reason, the difference in the positions of proton *e* and *k* is also large. Protons *f* are on the border of *endo* and *exo* so that the two *f* protons appear at almost the same field. Protons *g,h,i,j* appear at around 7.29–7.56 ppm. The elucidation of the NMR spectra of this kind of three dimensionally fixed complex system is very rare in porphyrinoid systems.

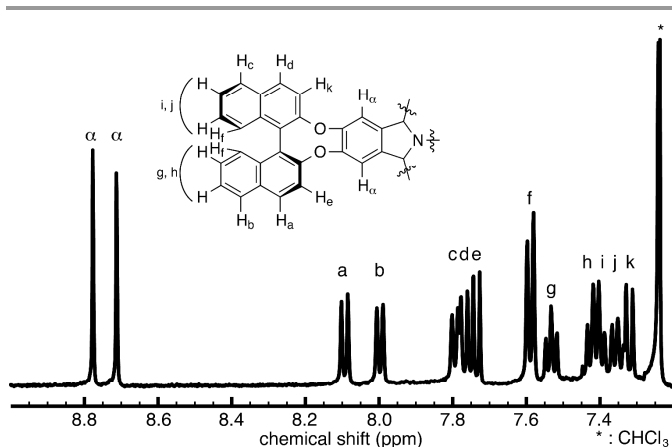


Fig. 1 ^1H NMR spectrum of **1S** in CDCl_3 , and its assignment (for the ^1H - ^1H COSY spectrum, see Fig. S2 in ESI).

Fig. 2 shows electronic absorption, MCD and CD spectra of **1** in CHCl_3 and calculated absorption and CD spectra for **1S**. Similarly to other reported SubPc absorption spectra,^{4c} the Q and Soret bands appeared in the close vicinity of 570 and 280 nm, respectively, in addition to a shoulder at ca. 340 nm that is not observed for normal SubPcs. The MCD signals in the Q and Soret band regions were mainly a contribution of Faraday *A* terms stemming from degeneracy in the excited states. Since an *A*-term-like band was observed corresponding to the absorption peak at 341 nm, this peak also may be a transition to the degenerate excited state. In the CD spectra, **1S** and **1R** showed, signals of minus and plus, respectively, in the 260–600 nm region, and the signals were mirror images with respect to the zero-intensity line. Since CD spectra of optically active binaphthyls appear at wavelengths shorter than ca. 260 nm,⁸ the CD in this region is an induced CD (ICD) generated by the binaphthyl moiety. Its generation mechanism is the same as that reported for binaphthyl-linked phthalocyanines⁸ and the ICD sign is also similarly explained, since the average angle α of the binaphthyl substituent is less than 90 degrees¹² (i.e. around 66 degrees^{9b}). Although the apparent intensities of the Q and Soret bands in the absorption spectra are approximately the same ($\epsilon = \text{ca. } 1.0 \times 10^5$), the Soret band CD intensity is much larger than the Q band CD intensity, which is due to the energy difference of the binaphthyl absorption (ca. 220–250 nm) and the Soret (ca. 280 nm) or Q band (ca. 570 nm). Here, since the induced CD intensity is proportional to $1/(v_N^2 - v_{\text{SubPc}}^2)$, where v_N and v_{SubPc} are the frequencies of the absorption of naphthalene and SubPc, respectively, the Soret band CD becomes stronger than the Q band CD.^{8,12} Compound **1** also shows fluorescence at 585 nm with a Stokes shift of 360 cm^{-1} , and the fluorescence quantum yield (Φ_F) of 0.25 is comparable with that of the general SubPcs.^{4a}

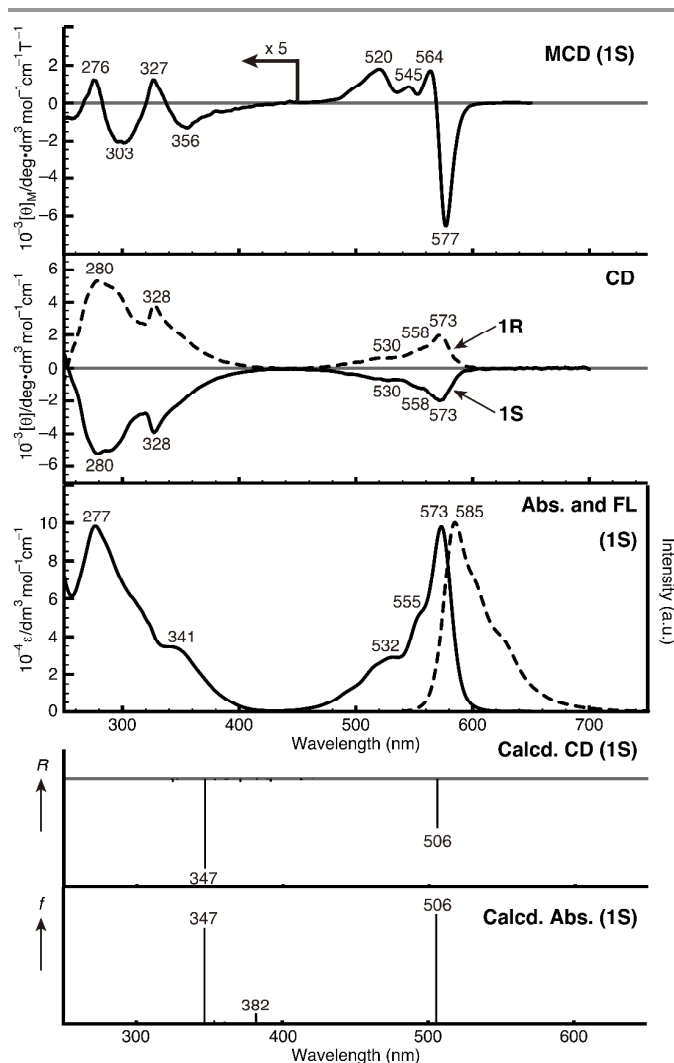


Fig. 2 MCD, CD, and electronic absorption spectra of **1** in CHCl_3 , and calculated CD and absorption spectra for **1S**.

In order to enhance the interpretation of the absorption and CD spectra, TD-DFT molecular orbital calculations have been performed using B3LYP optimized geometries.¹³ A partial MO energy diagram of **1S** is shown in Fig. 3, while the calculated absorption and CD spectra are shown at the bottom of Fig. 2, with the calculated transition energies, oscillator strengths (*f*), and configurations summarized in Table 1. The Q, Soret, and the band which may correspond to the experimental 341 nm peak were estimated at 506, 347, and 382 nm, respectively. Although the Q band is composed mostly of HOMO-LUMO transitions, the 382 nm transition appears to be a mixture of several CT transitions. As seen in Fig. 3, the HOMO-4-HOMO-6 are binaphthyl-centered orbitals and as shown in Table 1, the 382 nm band corresponds to transitions from these orbitals to the doubly degenerate LUMOs of the SubPc ligand. In the calculated CD spectrum using the optimized **1S** structure, negative CD was produced, associated with both the Q and Soret bands, and the latter band was more intense, in agreement with the experimental results. Thus, as explained conceptually for optically active binaphthyl-linked Pcs, (*S*)-binaphthyl-linked SubPc also appears to produce negative induced CD signals in both the Soret and Q band regions.

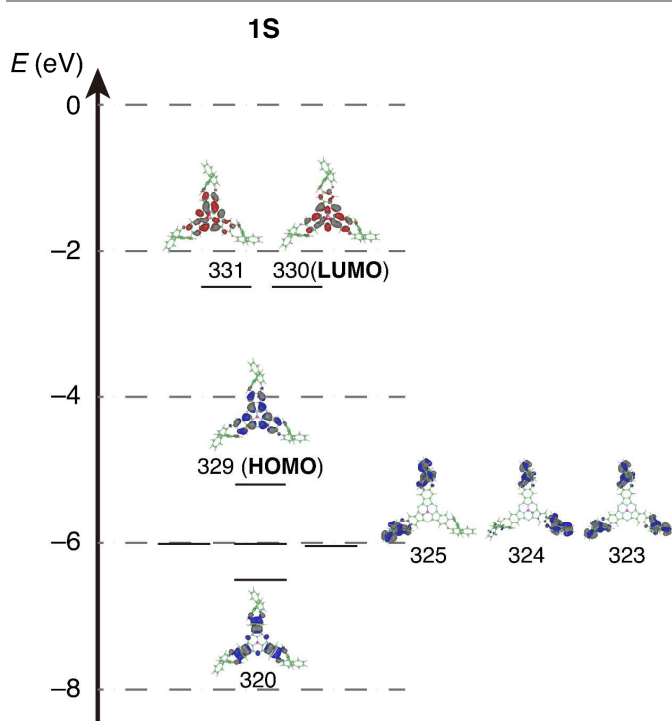


Fig. 3 Partial molecular energy diagram and orbitals of **1S**. Blue and red plots indicate occupied and unoccupied MOs, respectively. Calculations were performed at the B3LYP/6-31G* level (for details, see the ESI).

Table 1 Calculated excited wavelength (λ) and oscillator strengths (f) for components of selected transition energies.

λ (nm)	f	Composition (%) ^a
505.6	0.48	H \rightarrow L (94%), H-9 \rightarrow L+1 (3%)
505.6	0.48	H \rightarrow L+1 (94%), H-9 \rightarrow L (3%)
382.1	0.05	H-6 \rightarrow L (59%), H-4 \rightarrow L+1 (13%), H-5 \rightarrow L (13%), H-6 \rightarrow L+1 (12%)
382.1	0.05	H-6 \rightarrow L+1 (59%), H-4 \rightarrow L (13%), H-5 \rightarrow L+1 (13%), H-6 \rightarrow L (12%)
346.7	0.43	H-9 \rightarrow L (73%), H-9 \rightarrow L+1 (13%)
346.7	0.43	H-9 \rightarrow L (73%), H-9 \rightarrow L+1 (13%)

^aH-m, H, L, and L+n denote HOMO-m, HOMO, LUMO, and LUMO+n, respectively. (H-1 ~ H-6) are binaphthyl-centered orbitals, (H-7 ~ H-9) are SubPc-centered orbitals, and transitions from (H-1 ~ H-3) and (H-7 ~ H-8) have no intensity.

The redox behavior of the enantiomers was studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in CH₂Cl₂ containing 0.1 M [Bu₄N][ClO₄]. As shown in Fig. S3, the subphthalocyanine **1** exhibited one quasi-reversible one-electron oxidation (1.12 V vs. SCE) and one quasi-reversible one-electron reduction (-0.86 V), which are both shifted in the anodic direction relative to unsubstituted SubPc.^{4b} The potential difference between the first oxidation and the first reduction, which reflects the HOMO-LUMO gap, was found to be 1.98 V for **1**, a little smaller in comparison to that of unsubstituted SubPc. This result is in agreement with the red-shift of the lowest energy absorption band from 565 nm for unsubstituted SubPc^{4b} to 573 nm for **1**.

In conclusion, subphthalocyanines bearing optically active (*S*)- or (*R*)-binaphthyl were prepared and characterized using NMR, CD, MCD and electronic absorption spectroscopies, together with electrochemistry using cyclic voltammograms and differential pulse voltammetry. Their ¹H NMR spectra were unique, in that the bowl-shaped SubPc moiety and flat naphthalene rings constituting the

binaphthyl moiety are obliquely arranged. The spectra were interpreted using the previously accumulated knowledge that the ring current of SubPc is weaker on the *exo* side than the *endo* side. SubPcs containing (*S*)- and (*R*)-binaphthyl exhibited induced CD of opposite sign (minus and plus, respectively) in the 260-600 nm region. Faraday *A* MCD terms were detected corresponding to the Q and Soret absorption peaks, but at the red tail of the Soret band, another *A* term-like curve which suggests a degenerate excited state appeared. Molecular orbital calculations using the TD-DFT method succeeded in reproducing the absorption spectral characteristics and negative CD envelopes associated with the Q and Soret bands of the (*S*)-SubPc derivative.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Additional spectroscopic data and full details of experimental and calculation procedures. See DOI: 10.1039/c000000x/

- 1 A. Meller and A. Ossko, *Monatsh. Chem.*, 1972, **103**, 150-155.
- 2 H. Kietaihl, *Monatsh. Chem.*, 1974, **105**, 405-418.
- 3 N. Kobayashi, R. Kondo, S. Nakajima and T. Osa, *J. Am. Chem. Soc.*, 1990, **112**, 9640-9641.
- 4 (a) C. G. Claessens, D. González-Rodríguez, M. S. Rodríguez-Morgade, A. Medina and T. Torres, *Chem. Rev.*, 2014, **114**, 2192-2277; (b) C. G. Claessens, D. González-Rodríguez and T. Torres, *Chem. Rev.*, 2002, **102**, 835-853 and references therein; (c) N. Kobayashi, *The Porphyrin Handbook*; K. M. Kadish, K. M. Smith and R. Guilard, Eds.; Academic Press: San Diego, United States, 2003, **Vol. 15.**, 161-262.
- 5 C. G. Claessens and T. Torres, *Tetrahedron Lett.*, 2000, **41**, 6361-6365.
- 6 N. Kobayashi and T. Nonomura, *Tetrahedron Lett.*, 2002, **43**, 4253-4255.
- 7 S. Shimizu, A. Miura, S. Khene, T. Nyokong and N. Kobayashi, *J. Am. Chem. Soc.*, 2011, **133**, 17322-17328.
- 8 N. Kobayashi, R. Higashi, B. C. Titeca, F. Lamote and A. Ceulemans, *J. Am. Chem. Soc.*, 1999, **121**, 12018-12028.
- 9 (a) K. Wang, D. Qi, H. Wang, W. Cao, W. Li and J. Jiang, *Chem. – Eur. J.*, 2012, **18**, 15948-15952; (b) K. Wang, H. Wang, J. Mack, W. Li, N. Kobayashi and J. Jiang, *Acta. Chim. Sinica*, 2012, **70**, 1791-1797.

- 10 E. Caballero, J. Fernández-Ariza, V. M. Lynch, C. Romero-Nieto, M. S. Rodríguez-Morgade, J. L. Sessler, D. M. Guldi and T. Torres, *Angew. Chem. Int. Ed.*, 2012, **51**, 11337-11342.
- 11 S. Shimizu, T. Otaki, Y. Yamazaki and N. Kobayashi, *Chem. Commun.*, 2012, **48**, 4100-4102.
- 12 *Circular Dichroism and Magnetic Circular Dichroism Spectroscopy for Organic Chemists*, N. Kobayashi, A. Muranaka and J. Mack, Royal Society of Chemistry, UK, 2012.
- 13 M. J. Frisch *et al.*, *Gaussian 09, Revision C.01*, Gaussian, Inc., Wallingford, CT, 2009. See the ESI for the full list of authors.