Pergamon

Tetrahedron Letters 42 (2001) 7083–7086

TETRAHEDRON
LETTERS

Synthesis and properties of optically active 6,6′-didodecyl-1,1′-binaphthyl-phthalocyanine linked through crown ether units

Hongwei Liu, Yaohu Liu, Minghua Liu, Chuanfu Chen and Fu Xi*

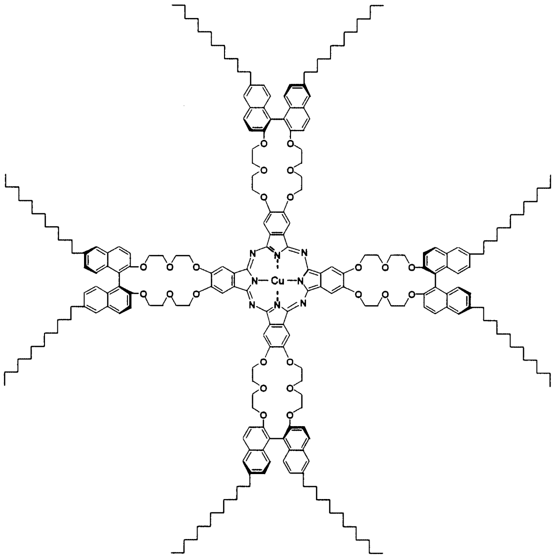
Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, PR China

Received 30 April 2001; revised 2 August 2001; accepted 7 August 2001

Abstract—A novel optically active 6,6′-didodecyl-1,1′-binaphthyl-metallophthalocyanine linked through crown ether units ((*S*)-**Pc**) has been synthesized. A stable monolayer of (*S*)-**Pc** that is able to bind metal ions can be formed at the air–water interface. Nonlinear absorption and optical limiting behavior of (*S*)-**Pc** have also been observed. © 2001 Elsevier Science Ltd. All rights reserved.

Phthalocyanines have been extensively studied for their remarkable optical and electrical behavior.[1] In the last decade, optically active phthalocyanines have attracted much attention.[2–4] Recently, we have been dealing with the design and synthesis of a series of optically active phthalocyanines, whose performance in constructing highly ordered thin films and exhibiting excellent optical limiting have been investigated. Herein, we wish to report the synthesis and properties of a novel optically active copper phthalocyanine.

The structure of optically active copper phthalocyanine (*S*)-**Pc** is shown in Scheme 1. It can be considered as consisting of a phthalocyanine core, four 20-crown-6 rings, and eight dodecyl chains linked through binaphthyl units to the crown ether rings. The synthesis of (*S*)-**Pc** is shown in Scheme 2. The optically active crown ether (*S*)-**10** was constructed from two building blocks of compound **9**[5] and (*S*)-**4**.[6] The starting material for the preparation of (*S*)-**4** was optically active (*S*)-**1**, which was brominated to give (*S*)-**2** and subsequently converted to (*S*)-**3**[7] by treatment with chloromethyl ether. (*S*)-**4** was obtained by in situ deprotection after the reaction of (*S*)-**3** with dodecylmagnesium bromide in dry ether using (dppp)NiCl$_2$ as the catalyst. The building block **9** was synthesized from catechol **5** as a starting material. Catechol **5** was brominated and then alkylated with diethyleneglycol monotosylate **7** to produce compound **8**, which was converted into **9** by tosylation with *p*-tosyl chloride. Then (*S*)-**10**[6] was prepared by the reaction of (*S*)-**4** and **9** in boiling *n*-BuOH in the presence of NaOH. Finally, (*S*)-**Pc**[6] was obtained directly by heating (*S*)-**10** in DMF with a large excess of copper cyanide at 130°C for 24 h. ^{1}H NMR, UV–vis, CD spectra and MALDI-TOF MS support the structure of (*S*)-**Pc** as proposed. According to the literature, the chiral configuration of 1,1′-binaphthyl molecules is relatively stable at higher temperatures over extended periods of time.[8] The design of the synthetic procedure shown in Scheme 2 was based on extensively employed literature reaction

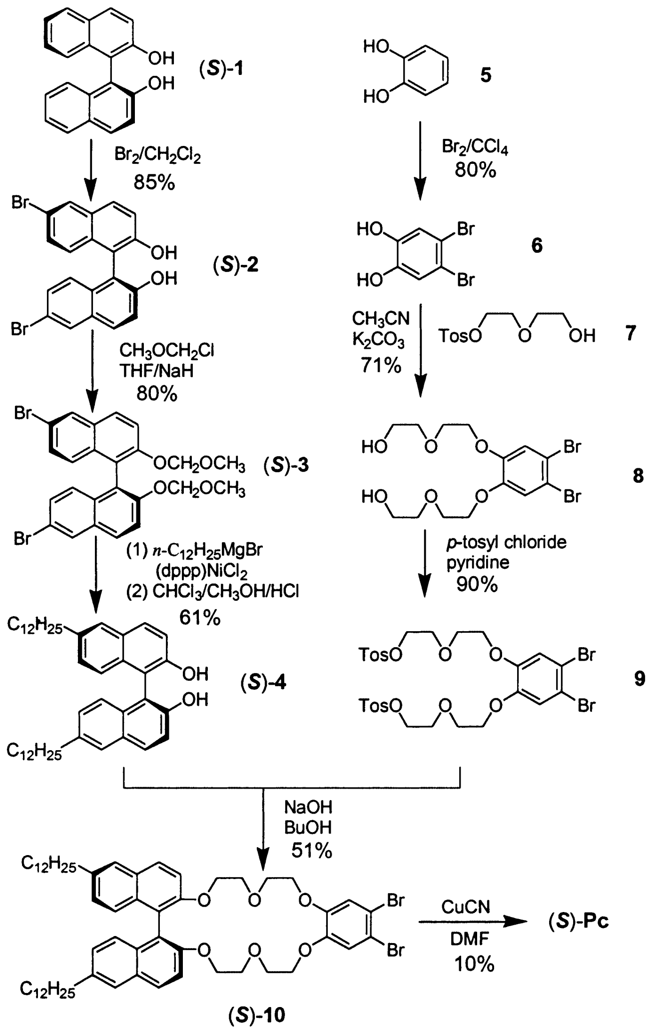


Scheme 1. The structure of the optically active (*S*)-**Pc**.

---

* Corresponding author. Tel.: ++86-010-62557907; fax: ++86-010-62559373; e-mail: xifu@infoc3.icas.ac.cn

PII: S0040-4039(01)01477-0



Scheme 2. The synthesis of the optically active (*S*)-**Pc**.

conditions.[2,5] It was confirmed that there was very little or no rotational loss of optically activity.[9]

The CD and UV–vis spectra of (*S*)-**Pc** in THF are displayed in Fig. 1. The UV–vis spectrum shows the two characteristic intense bands of metal phthalocyanine, the Q and the B band, both correlated to π–π* transitions. The CD spectrum of (*S*)-**Pc** in THF (1×10^{-4} M) exhibits strong absorptions in the region of 220–250 nm owing to the ^1B_b transition of the naphthalene moiety. In addition, the Soret band and Q band are observed, which are due to the introduction of the optically active binaphthyl moieties onto the periphery of the phthalocyanine.[2c] It can also be seen that (*S*)-**Pc** exhibits a mainly negative CD envelope resulting from the main Soret and Q bands. Furthermore, the binaphthyl moiety of (*S*)-**Pc** is right-handed, which is demonstrated by the Cotton effect in the 220–250 nm region.[10]

In Fig. 2, curves A–E show the surface pressure–area isotherm of the spreading monolayers of (*S*)-**Pc** fabricated from a chloroform solution (1×10^{-4} M) with water as the subphase in the absence and presence of potassium chloride (KCl). The (*S*)-**Pc** was observed to form stable films up to 40 mN/m whether in the absence or presence of K^+. From Fig. 2, it was also found that the crown ether rings of (*S*)-**Pc** have the ability to bind metal ions that can be demonstrated by the limiting molecular areas. The limiting molecular areas obtained by extrapolating the linear part of the isotherm to zero pressure are 340, 345, 425, 450, and 800 Å^2/molecule for curve A, B, C, D, and E, respectively. It is clear that the limiting molecular areas increase as the concentration of K^+ increases. When pure water is the subphase, the Pc core of (*S*)-**Pc** has a diameter of 20.8 Å, which was deduced from the large molecular area of 340 Å^2/molecule. This result means that the molecules of (*S*)-**Pc** in monolayers are stacked

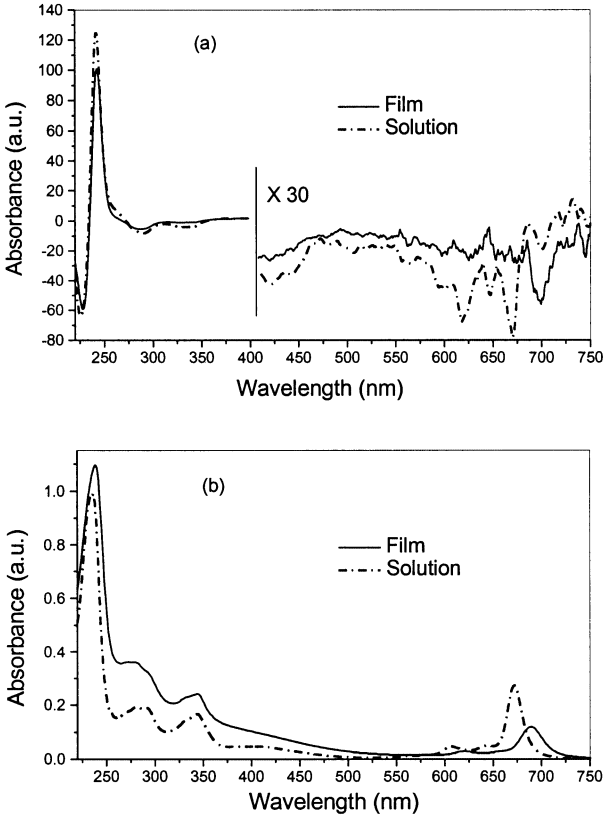


Figure 1. (a) CD and (b) UV–vis spectra of (*S*)-**Pc** in THF and thin film.

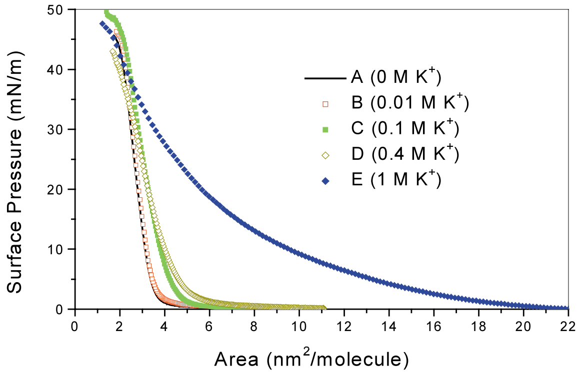


Figure 2. Surface pressure–area isotherms of the monolayers of (*S*)-**Pc** at the air–water interface in the absence and presence of K^+ at 20°C.

in a side-on arrangement with the substituents oriented away from the water surface, which is in line with the conformation of the CPK model. Furthermore, when potassium chloride is used as the subphase, the limiting molecular area is larger than that observed when water is used as the subphase. The reason may be that, when binding metal ions, the crown ether rings are dragged back to the water surface resulting in the molecular area increase.

The CD and UV–vis spectra of transferred LB films of (*S*)-**Pc** are shown in Fig. 1. In the UV–vis spectrum, the Q band is red shifted to 690 nm in comparison with that in THF. In the CD spectrum, the intense Q band is observed at 698 nm, and is obviously different from that in THF, though the sign of the Cotton effect is identical. These large changes in the CD and UV–vis spectra in comparison with those in THF may be attributed to the packed arrangement of (*S*)-**Pc** molecules in the side-on orientation.

The optical limiting (OL) properties of (*S*)-**Pc** with different linear transmittance in chloroform are shown in Fig. 3. It can be seen that at very low laser energy, the solutions have linear transmission. While at high input fluence, the nonlinear transmission is observed between the output and input fluence indicating that optical limiting performance occurs. The optical limiting thresholds of (*S*)-**Pc** in chloroform are 800, 490, 350 and 160 mJ/cm^2, at the linear transmittance of 73, 64, 47 and 31%, respectively. The thresholds decrease as the concentration of (*S*)-**Pc** increases which may be ascribed to reverse saturable absorption (RSA). The nonlinear absorption of (*S*)-**Pc** was investigated by open aperture Z-scan measurements as shown in Fig. 4. The large transmission decreases about 80% at the focus point indicating an RSA behavior. Moreover, the Z-scan data can be fitted well by the equation[11] of the RSA model. The solid curve in Fig. 4 shows the best fit of the unapertured data, which also demonstrates the OL is the result of RSA.

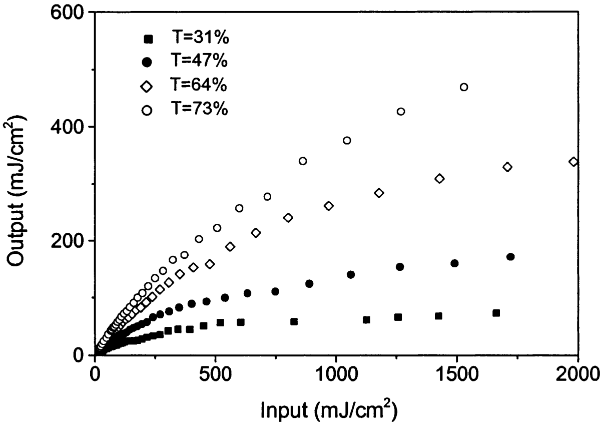


Figure 3. Optical limiting properties of (*S*)-**Pc** at different linear transmittance for 10 ns, 532 nm laser pulses in a 1 mm quartz cell.

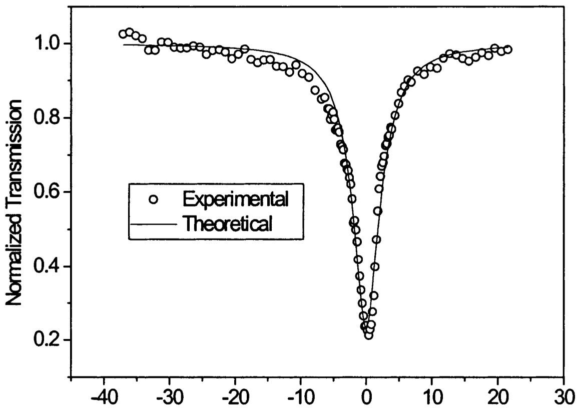


Figure 4. Open aperture Z-scan for (*S*)-**Pc** in chloroform at the transmittance of 64%.

Acknowledgements

We greatly appreciate the help from Professor C. Ye, Professor P. J. Wu, Dr. P. Wang, and Dr. S. Zhang for the detection of nonlinear absorption and optical limiting behavior in the samples. This project is supported by the National Science Foundation of China.

References

1. For reviews, see: (a) van Nostrum, C. F.; Nolte, R. J. M. *J. Chem. Soc., Chem. Commun.* **1996**, 2385; (b) da la Torre, G.; Vázquez, P.; Agulló-López, F.; Torres, T. *J. Mater. Chem.* **1998**, *8*, 1671; (c) da la Torre, G.; Claessens, C. G.; Torres, T. *Eur. J. Org. Chem.* **2000**, 2812 and references cited therein.
2. (a) Kobayashi, N.; Kobayashi, Y.; Osa, T. *J. Am. Chem. Soc.* **1993**, *115*, 10994; (b) Kobayashi, N. *Chem. Commun.* **1998**, 487; (c) Kobayashi, N.; Higashi, R.; Titeca, B. C.; Lamote, F.; Ceulemans, A. *J. Am. Chem. Soc.* **1999**, *121*, 12018.
3. Engelkamp, H.; Middelbeek, S.; Nolte, R. J. M. *Science* **1999**, *284*, 785.
4. Fox, J. M.; Katz, T. J.; Elshocht, S. V.; Verbiest, T.; Kauranen, M.; Persoons, A.; Thongpanchang, T.; Krauss, T.; Brus, L. *J. Am. Chem. Soc.* **1999**, *121*, 3453.
5. Liu, H. W.; Chen, C. F.; Ai, M.; Gong, A. J.; Jiang, J.; Xi, F. *Tetrahedron: Asymmetry* **2000**, *11*, 4915.
6. For (*S*)-**4**: mp 73–74°C; $[\alpha]_D = +58.4$ (c 0.514, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz): δ 0.87 (t, $J=6.6$ Hz, 6H, CH_3), 1.24–1.72 (m, 40H, CH_2), 2.71 (t, $J=7.6$ Hz, 4H, CH_2), 4.97 (s, 2H, OH), 7.06 (d, $J_{7,8}=8.6$ Hz, 2H, ArH_8), 7.14 (dd, $J_{7,8}=8.6$ Hz, $J_{5,7}=1.2$ Hz, 2H, ArH_7), 7.32 (d, $J_{3,4}=8.9$ Hz, 2H, ArH_3), 7.65 (s, 2H, ArH_5), 7.88 (d, $J_{3,4}=8.9$ Hz, 2H, ArH_4). Anal. calcd for $C_{44}H_{62}O_2$: C, 84.89; H, 9.97. Found: C, 84.67; H, 10.16%.

   For (*S*)-**10**: $[\alpha]_D = -82.7°$ (c 1.46, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz): δ 0.87 (t, $J=6.5$ Hz, 6H, CH_3), 1.25–1.78 (m, 40H, CH_2), 2.69 (t, $J=7.6$ Hz, 4H, CH_2), 3.48–4.18 (m, 16H, OCH_2), 7.03–7.06 (m, 6H, ArH), 7.37 (d, $J_{3,4}=9$ Hz, 2H, ArH_3), 7.58 (s, 2H, ArH_5), 7.75 (d, $J_{3,4}=9$ Hz, 2H, ArH_4). Anal. calcd for $C_{58}H_{78}Br_2O_6$: C, 67.57; H, 7.63. Found: C, 67.32; H, 7.90%. *m*/*z* (MALDI-TOF) 1028.45 (M^+).

For (*S*)-**Pc**: decomp. 324°C; ^1H NMR ($CDCl_3$, 300 MHz): δ 0.87 (br, s, 24H, CH_3), 1.25–1.78 (br, m, 160H, CH_2), 2.65 (br, s, 16H, CH_2), 3.2–4.2 (br, m, 64H, OCH_2), 7.0–7.8 (br, m, 48H, ArH); *m*/*z* calcd for $C_{240}H_{312}CuN_8O_{24}$: M, 3753.27. Found: (MALDI-TOF) 3753.29 (M^+).

7. Hu, Q. S.; Zheng, X. F.; Pu, L. *J. Org. Chem.* **1996**, *61*, 5200.
8. Kyba, E. P.; Gokel, G. W.; Jong, F. D.; Koga, K.; Sousa, L. R.; Siegel, M. G.; Kaplan, L.; Sogah, G. D. Y.; Cram, D. J. *J. Org. Chem.* **1977**, *42*, 4173.
9. In order to demonstrate the target optically active phthalocyanine has not undergone partial racemization during the reaction, the optical stability of compound (*S*)-**10** was measured by subjecting the (*S*)-**10** to the same reaction conditions which were used in the preparation of the optically active (*S*)-**Pc** as follows: a solution of (*S*)-**10** in DMF was heated with stirring under nitrogen at 130°C for 24 h, then DMF was removed at the reduced pressure. It is found that the specific rotation of the recovered (*S*)-**10** is $[\alpha]_D = -82.5°$. Comparing with the original specific rotation of (*S*)-**10** ($[\alpha]_D = -82.7°$), it is clear that no obvious rotational loss is occurred.
10. Harada, N.; Nakanishi, K. *Circular Dichromic Spectroscopy*, *Exciton Coupling in Organic Stereochemistry*; University Science Books: New York, 1983.
11. Wood, G. L.; Miller, M. J.; Mott, A. G. *Opt. Lett.* **1995**, *20*, 973.