# SYNTHESIS AND CHIRAL RECOGNITION PROPERTY OF MACROCYCLIC CHIRAL PEEKK OLIGOMER

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#### Introduction

Macrocyclic molecules exhibit unique properties that have been the focus of fundamental and applied research<sup>1</sup>. Cyclic structures with a rigid molecular backbone contain a cavity with a well-defined size. This makes them unique in the design of host molecules with the capability of binding substrates within their cavities. In our recent studies, we prepared a series of diameter controllable nanometer scale rigid macrocyclic oligomers (RCO for abbreviation)<sup>2</sup>. These diameter-controllable RCOs have steady nanometer scale cavities due to its rigid chain and amphiphilic properties that come from hydrophilic oxygen atom and hydrophobic groups. The macrocycles themselves can be ordered by LB technique though they are not classical LB molecules. The structures of their LB films were detected by AFM<sup>3</sup>. The properties of the rigid cavities also intrigued us because their chiral structure that may play an important role in molecular arrangement and assembly. That also plays an important role in optoelectronics supramolecular structure<sup>4</sup>.

This paper reports the synthesis of chiral PEEKK macrocyclic oligomers containing binaphthyl moieties. The chirality of binaphthyl compounds are derived from the restricted rotation along the carbon-carbon single bond of the two naphthalene rings, and the  $C_2$  asymmetric chiral configuration of binaphthyl is remarkably stable. The chiral recognition property was also explored after the chiral PEEKK macrocyclic oligomers were synthesized.

## Experiment

### Synthesis of chiral-RCO

To synthsize the RCO containing chiral functional group, we developed a novel way called two-steps synthesis. The first step is synthesis of the trimer (in this example, synthesis of 2R, 2S. *Scheme 1*). The second step is ring closure. In a typical procedure, (R)-(+)- or (S)-(-)-1,1'-bi-2-naphthol (1R or 1S, 2.86 g, 0.01 mol) was mixed with 4,4'- difluorobenzophenone (21.8 g, 0.1 mol) and K<sub>2</sub>CO<sub>3</sub> (1.42 g, 0.0103 mol) in N, N-

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dimethylacetamide (100 mL). After refluxing for 10 h under vigorous stirring, the solution was poured into crashed ice water containing hydrochloric acid (3%) with stirring. White precipitate was collected by filtration. Upon washing with ethanol and drying, R-(+)- or S-(-)- 1-(4-(1-(2-(4-(4-fluorobenzoyl)phenoxy)-1-naphthalenyl -2-naphthalenoxy)phenyl)-1-(4-fluorophenyl) -1-one (2R or 2S) was obtained in 90% yield. The ring closure was accomplished similarly by refluxing mixture of equimolar 2R/S (6.82g, 0.01mol) and bisphenol-A (2.28g, 0.01mol) in DMF (200ml) which was added dropwise (8 hours) into the flask to give cyclic oligomer R-(+) or S-(-)-BN-RCO (yield 50%). After removal of the solvent, the resulting residue was purified by a silica gel column using  $CH_2Cl_2$  as eluent. As controls, corresponding racemic compounds 2 and raceme BN-RCO were also prepared by the same procedures. All these compounds were characterized by means of FTIR, MALDI-TOF-MS, 1H- and 13C-NMR spectroscopy and results are consistent with the proposed structures<sup>5</sup>. Compared the FTIR of 2 and BN-RCO, different functional groups' absorption peaks have different red shift or blue shift caused by the ring tension.



Scheme 1

#### **Results and discussion**

Through above synthesis route, we have synthesized chiral BN-RCO successfully. The VCD (Vibrational Circular Dichroism) spectrum (*Figure 1*) indicates that introduction of binaphthyl results in the asymmetric cavity. BN-RCO has a chiral cavity and many interesting properties may come from it. The following experiment showed the chiral recognition property of BN-RCO.



Figure 1. Comparison of VCD and IR spectrum of BN-RCO. VCD spectrum of BN-RCO/Binaphthol self-assembly system.

The BN-RCO (0.01 mol) was mixed with S-Binaphthol (0.01 mol) and R-Binaphthol (0.01 mol), respectively. The mixture was dissolved by tiny amount  $CHCl_2$ and the solution added to KBr chip dropwise. After the  $CHCl_2$  was volatilized completely, the KBr chip was scanned by VCD (8 hours).

Figure 2 indicates that chiral recognition property of BN-RCO. The solid line is the VCD spectrum of S-BN-RCO/S-BN self-assembly system. The dot line is the VCD spectrum of S-BN-RCO/R-BN self-assembly system. Ether bond asorption (1243 cm<sup>-1</sup>) and phenyl asorption showed obviously difference. This means that the self-assembly mode is different among these two systems. That is, BN-RCO can recognize binaphthol.



Figure 2. VCD Spectrum of BN-RCO/BN self-assembly system. VCD spectrum of BN-RCO/Binaphthol solution system

The BN-RCO (0.01 mol) was mixed with R-Binaphthol (0.01 mol, 25% e.e.), R-Binaphthol (0.01 mol, 50% e.e.), R-Binaphthol (0.01 mol, 75% e.e.), R-Binaphthol (0.01 mol, 100% e.e.), respectively. The mixtures were dissolved in 10 ml chloroform. The solution was scanned by VCD (10 min).



Figure 3. VCD Spectrum of BN-RCO/BN solution system.



Figure 4.e.e. vs. Absorbance unit curve

Figure 3 shows the intensity of VCD spectrum decreased accompany with increasing e.e.. The relationship between absorbance intensity and e.e. showed as figure 4. The above results also indicate that the solution recognition mode is different with self-assembly recogniton mode because the ether bond absorbtion is different in these two recogniton systems.

# Conclusion

We have synthesized chiral rigid macrocylic oligomer containing binaphthyl moieties. The VCD spectrum showed the introduction of binaphthyl moiesties results in the asymmetric cavities. We also found the interesting chiral recognition property of chiral-RCO. The self-assembly system recognition and solution system recognition were explored respectively. The results showed that these two recognition modes are different

## References

<sup>1</sup> a) H. Y. Jiang, T. L. Chen, J. P. Xu, *Macromol. Rapid Commun.* 1997, 18, 401. b) K.Chen, Y. F. Wang, A. S. Hay, *Macromolecules*, 1995, 28, 6075

<sup>2</sup> J. Z. Wang, Ch. H. Chen, X. M Xun, Sh. Y. Wang, Zh. W. Wu, Journal of Polymer Science: Part A: Polymer Chemistry. 1999, 37, 1957

<sup>3</sup> T. Ben, C. H. Chen, H. Cao, X. Wang, X. C. Liu, C. Wang, Z. W. Wu, W. J. Zhang, Y. Wei, *Macromol. Rapid Commun.* 2002, 23 (3), 196

<sup>4</sup> (a) Nakano, T.; Okamoto, Y.; Hatada, K. J. Am. Chem. Soc. 1992, 114,1318. (b) Moore,
J. S.; Stupp, S. I. J. Am, Chem. Soc. 1992, 114, 3429. (c) Muller, M.; Zentel, R.
Macromolecules 1996, 29, 1609. (d) Okamoto, Y.; Nakano, T. Chem. Rev. 1994, 94, 349.
(e) Singfield, K. L.; Brown, G. R. Macromolecules 1995, 28, 1290.

<sup>5</sup> Analytical data on new compounds. 2, 2R, 2S: yellow powder, [α]<sub>589</sub><sup>20</sup>=+44,-44 (c 1.00, CHCl<sub>3</sub>) for 2R and 2S respectively. MS (EI<sup>+</sup>) 682, <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub> for 2): δ 7.96 (d, 2H), δ 7.92 (d, 2H), δ 7.68 (m, 4H), δ 7.54 (d, 4H), δ 7.45 (t, 2H), δ 7.28 (m, 6H), δ 7.10 (t, 4H), δ 6.81 (d, 4H). IR:  $\tilde{\nu}$ =854, 927, 952, 1153, 1238, 1502, 1596, 1654 cm<sup>-1</sup>. *R-(+)-BN-RCO, S-(-)-BN-RCO*, : white powder, [α]<sub>589</sub><sup>20</sup>= +17, -17(c 1.00, THF) for 3R and 3S respectively. MS (EI<sup>+</sup>) 870, <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub> for 3): δ 7.90 (t, 4H), δ 7.68 (m, 6H), δ 7.54 (d,2H), δ 7.44 (t,2H), δ 7.26 (m,10H), δ 6.99 (m,10H), δ 6.80 (t,2H), δ 1.70(s, 6H). <sup>13</sup>C NMR (300MHz, CDCl<sub>3</sub>): δ = 194.1, 161.5, 153.5, 151.8, 146.9, 134.1, 132.2, 132.1, 132.0, 131.7, 130.9, 130.7, 128.4, 128.2, 127.0, 125.9, 125.3, 122.7, 122.3, 119.9, 119.7, 119.6, 119.2, 118.6, 117.4, 117.3, 117.0, 115.6, 115.2, 42.4,  $\tilde{\nu}$ 

31.0. IR: v = 836, 927, 1240, 1496, 1592, 1652 cm<sup>-1</sup>