

Synthesis and Characterization of Polycyclic (Aryl Ether Ketone)s

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Abstract

In order to make the oligomer of macrocyclic (aryl ether ketone)s functionalized, we designed and synthesized a new monomer 4'-chloro-biphenyl-2,5-diol as a precursor. Utilizing this monomer we synthesized a new aromatic macrocyclic oligomer containing a p-chlorophenyl substituent, then via a nickel-catalyzed coupling reaction a covalent bond was made between two single macrocycles, then we got a polycyclic (aryl ether ketone)s with a manacle-like structure. All the structures are supported by MALDI-TOF MASS spectrum, and ¹H NMR spectrum analysis.

Introduction

A series of macrocyclic aromatic etherketones oligomers have been explored and studied both theoretically and experimentally. These oligomers have been successfully converted to high molecular weight polymer utilizing a series of catalyst, owing to their lower molecular weight and inherently lower viscosity. But few attentions were paid to the nanoscale-structure of those macrocyclic oligomers. Until these two years, with the emergence of a new field of macromolecular nanotechnology, called molecular architecture, that utilizing programmed self-assembly combined with sequential methods of covalent chemical synthesis to achieve ordered structure. The cyclic oligomers have gained more and more attention because of their inherent advantages: a rigid structure, a hole with a diameter about 3-4 nanometer, and the size of the hole is controllable, good stability in high temperature, a simple synthesis method with high yield of final product, the final product can be purified easily. We are interested in producing some new macrocycles with novel nanoscale structure and novel optical or magnetic applications (data storage, nonlinear optics, electrichromism, and optical limiting). Herein, we disclose our preliminary results in this endeavor.

Experimental

Materials: 4'-chloro-biphenyl-2,5-diol () was synthesized by our lab. 4,4'-difluorobenzophenone () was purchased from Yanji Chemical Plant (purified by vacuum distillation). A linear aromatic difluoro ketone trimer () was prepared by the reaction of with a large excess of . Anhydrous potassium carbonate (K₂CO₃, A.R.), Methylene chloride (A.R.) and DMF (A.R.) were received from Tiantai Chemical Reagent Plant.

Instrumentation. The MALDI-TOF MS spectrum of the single macrocycle was performed on a Bruker ReflexIII MALDI-TOF Mass Spectrometer using dithranol as a matrix, CF₃COOAg as a cationic reagent. And the MS spectrum of the manacle-like structure was performed on a Bruker BiflexIII MALDI-TOF Mass Spectrometer.

The elementary analysis was performed on Flash EAIII2 with analysis temperature at 1800 . ¹H NMR spectra of the oligomers were obtained on a Bruker DR-500 spectrometer using 5 mm

o.d. tubes. Sample concentrations were about 25% (w/v) in CDCl₃ containing 1% TMS as an internal reference.

Synthesis of single macrocycle

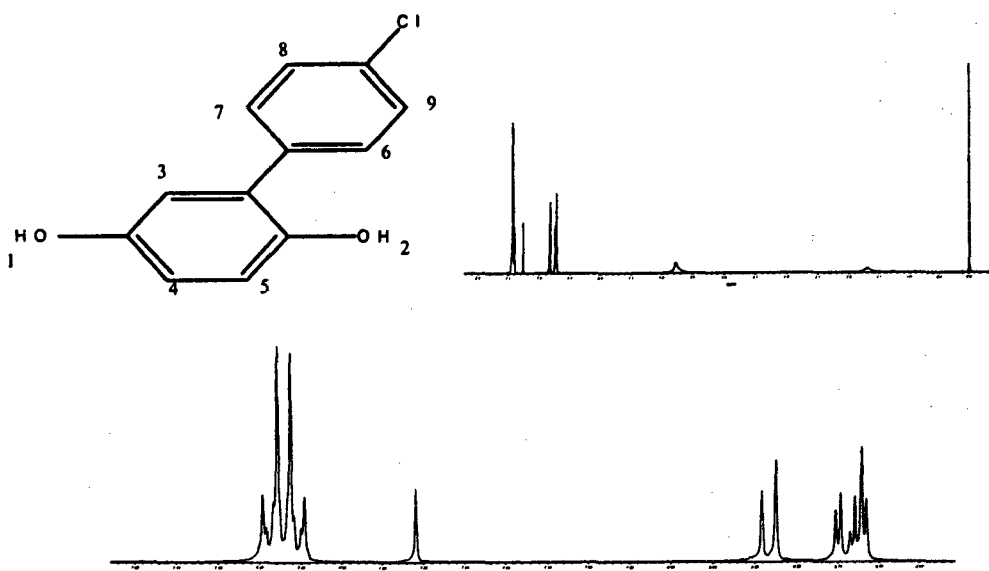
To a 1L three-neck round-bottomed flask were added 500mL DMF, 80mL toluene and K₂CO₃(1.3821g,10mmol). The system was under mechanical stirring and nitrogen protection. Azeotropic distillation (to move water) took about 3h. Then the system was cooled down to room temperature and 30mL solvent was taken from the flask to dissolve equimolar (III) (3.085g, 5.00mmol) and bisphenol-A (1.140g, 5.00mmol). The solution was transferred to a 50mL constant pressure and dripped into the flask at a rate of 0.8mL/h after the temperature in the flask was adjusted to 130 by distilling some toluene. The total reaction time including drop time was 48h. When the reaction completed, cooled the reaction system to room temperature and had a filtration to remove the salt. Then most solvent was removed by vacuum distillation, and the residual solution was poured into 1000mL water with 10mL hydrochloric acid to precipitate the product. The precipitate was filtered, and washed with hot water, then dried in a vacuum oven at 70 for 24 h. The solid was extracted with methylene chloride. The extracted solution was loaded onto a silica gel chromatographic column and eluted with methylene chloride. Yield of (a) is 62%

Synthesis of the manacle-like dimer.

A 100mL, three-neck, dried round-bottomed flask equipped with a mechanical stirrer, thermometer, and 100mL addition funnel, was charged with 0.215g(1mmol) of NiBr₂, 2.0g(7.6mmol) of triphenylphosphine, and 2.0g(30.6mmol) of zinc dust. The reaction flask was evacuated and filled with nitrogen several times. Nitrogen was then swept through the system by opening the stopcock to the addition funnel for 15 min. Nitrogen-purged, dry DMAC(60mL) was added through the additional funnel and the mixture was heated by an electric mantle. The solution quickly became red-brown. Then add the power of single macrocycle (2g) to the reaction flask. When the catalyst mixture reached 60 the heating mantle was adjusted to keep the reaction temperature at 90 for 3 h. At last, the solution was blood-red again, indicating complete reaction. The reaction mixture was filtered to remove excess Zn and the filtrate diluted with 50mL DMAC. The organic phase was dried over Na₂SO₄ for 1h, and filtrate to remove the excess Zn, and flash evaporated. The residual solid was dried in vacuum oven at 100°C for 24 h, then extracted with methylene chloride. The methylene chloride solution was loaded onto a silica gel chromatographic column and eluted with 300/1(v/v) methylene chloride/tetrahydrofuran. Yield of (b) is 83%

Results and Discussion

Structure of monomer. In order to lead a chlorophenyl substituent to an aromatic macrocyclic structure, we designed and synthesized a novel diphenol, that was the 4'-chloro-biphenyl-2,5-diol. The results of FTIR and ¹H NMR were agreed with the structure of monomer () FTIR showed that 3288cm⁻¹(-OH), 784 cm⁻¹(C-Cl).¹H NMR(Figure 1) shows δ(CDCl₃): 4.77ppm (2H, H1+H2), 6.72ppm (1H, H3), 6.74ppm (1H, H4), 6.83ppm (1H, H5), 7.44ppm (2H, H6+H7), 7.41ppm (2H, H8+H9).



Single macrocycle. The synthesis of single macrocycle (a) was depicted in Figure 1. A two-step method was adopted for the synthesis, in the first step a large excess of 4,4'-difluorobenzophenone reacted with 4'-chloro-biphenyl-2,5-diol to get a linear aromatic difluoro ketone trimer. The purification of was simple, just remove the excessive 4,4'-difluorobenzophenone by vacuum distillation, and then extract the residual solid with ethanol for 20 h and then remove the solvent to get pure in a yield of 80%. The cyclization reaction between compound and equimolar of bisphenol-A was carried out under a pseudo-high dilution condition. The solution of the two compounds dripped slowly into the reactor containing refluxing mixture of DMF and toluene and a 200% excess of K_2CO_3 . The temperature of the reaction was controlled by the fraction of toluene. The total reaction time was 48 h. Anal. Calcd for $C_{53}H_{37}ClO_6$: C, 79.05; H, 4.63. Found: C, 79.14; H, 4.69.

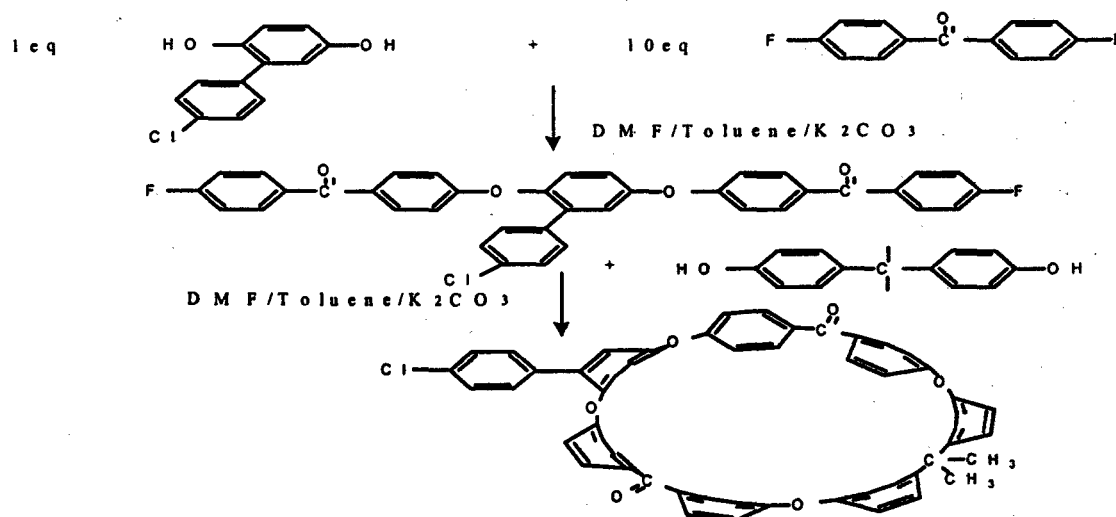


Figure 2. Synthesis of single macrocycle (a) containing a p-chlorophenyl substituent

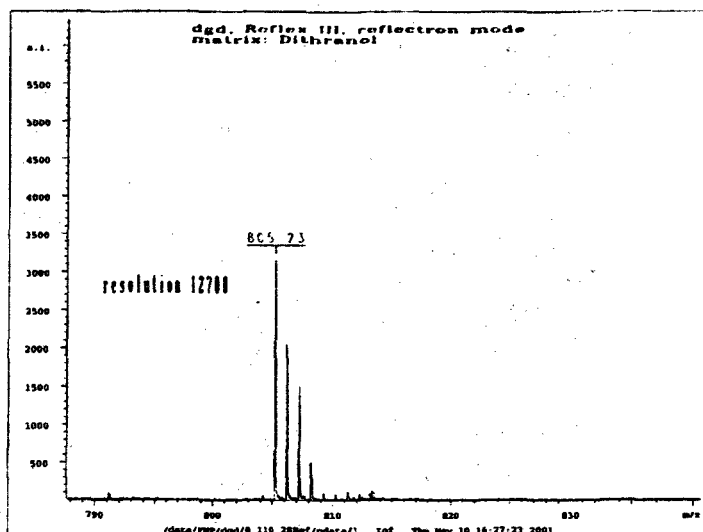


Figure3 MALDI-TOF spectra of oligomer (a). The spectra show the exact mass number of the macrocycle (a) with four isotopic peaks, the highest one shows the MS 805.235 [Ma+H]⁺; caculated:804.23.

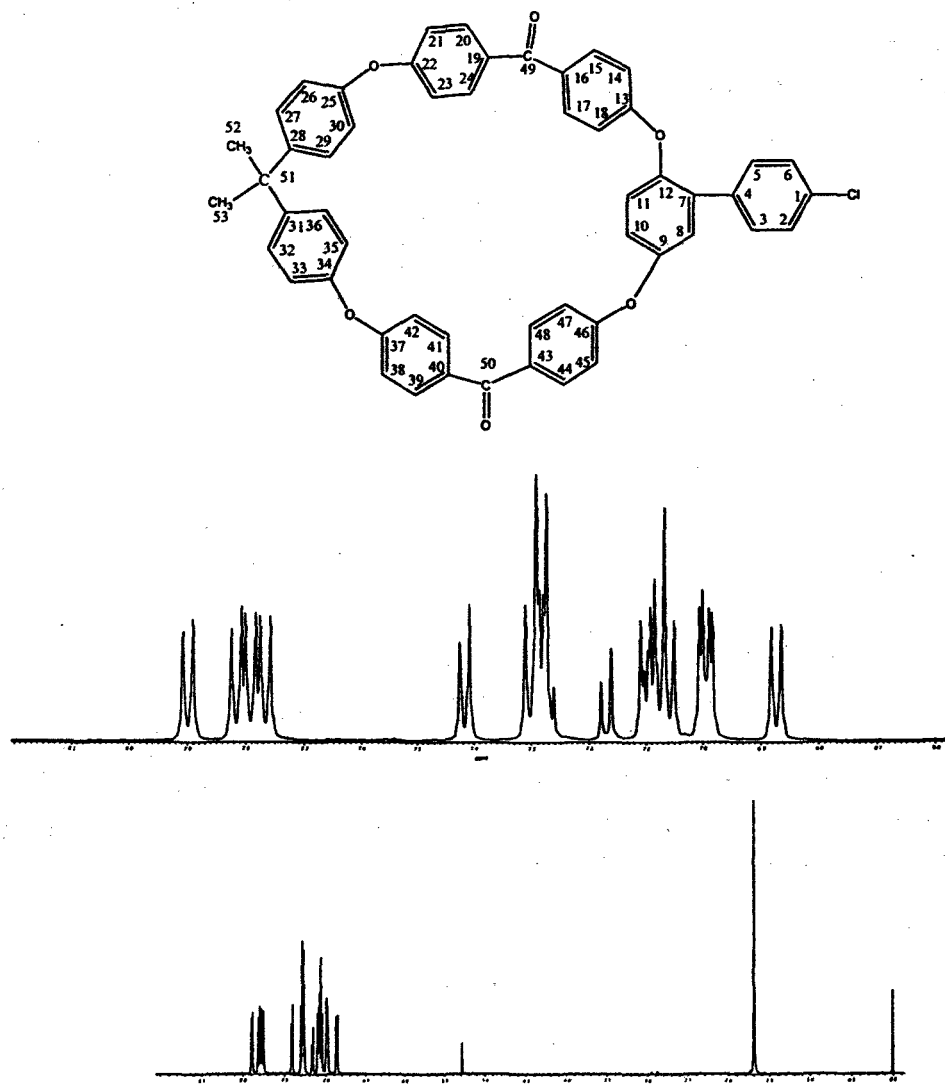


Figure 4. ¹H NMR spectrum and structural assignments of macrocycle (a)

Table 1. The ¹H NMR spectrum assignments of the single macrocycle(a) δ(CDCl₃)

Nuclear no.	δ(ppm)	Nuclear no.	δ(ppm)
H2,H6	7.288	H26,H30	6.984
H3,H5	7.409	H27,H29	7.276
H8	7.275	H32,H36	7.276
H10	7.086	H33,H35	6.989
H11	7.162	H38,H42	7.093
H14,H18	6.865	H39,H41	7.808
H15,H17	7.784	H44,H48	7.891
H20,H24	7.759	H45,H47	7.051
H21,H23	7.068	H52,H53	1.683

The manacle-like dimer (b). The synthesis of (b) is depicted in Figure 4. The coupling reaction of aryl chlorides by nickel and reducing metals has been efficiently developed and investigated.⁴ This kind of reaction was carried out in a mild condition at a temperature no more than 90°C and in a yield of 80%. Anal. Calcd for C₁₀₆H₇₄O₁₂: C, 82.69; H, 4.84. Found: C, 82.43; H, 4.98.

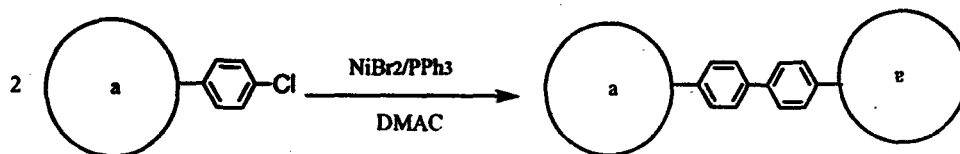


Figure 5. The Synthesis of the manacle-like dimer

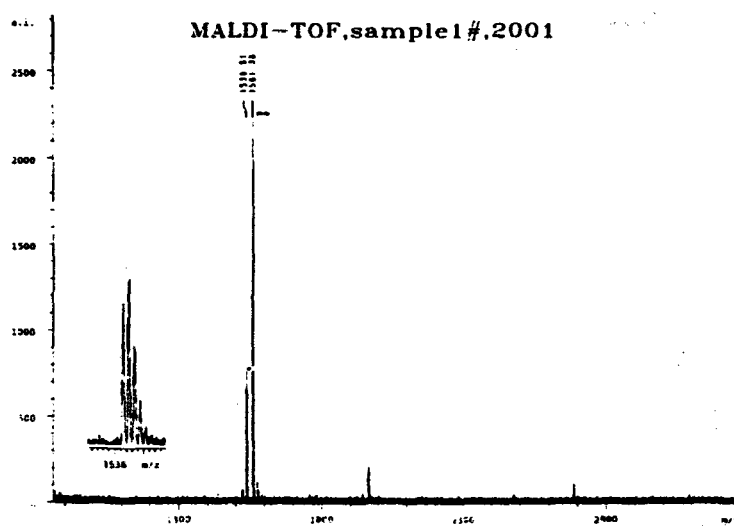


Figure 6 MALDI-TOF spectrum of the manacle-like dimer (b), the signal (m/e) 1539.51 is [M_b+H]⁺, and the signal (m/e) 1561.58 is [M_b+Na]⁺, the calculated m/e is 1538.52. The small figure on the left shows the isotopic peaks of (b).

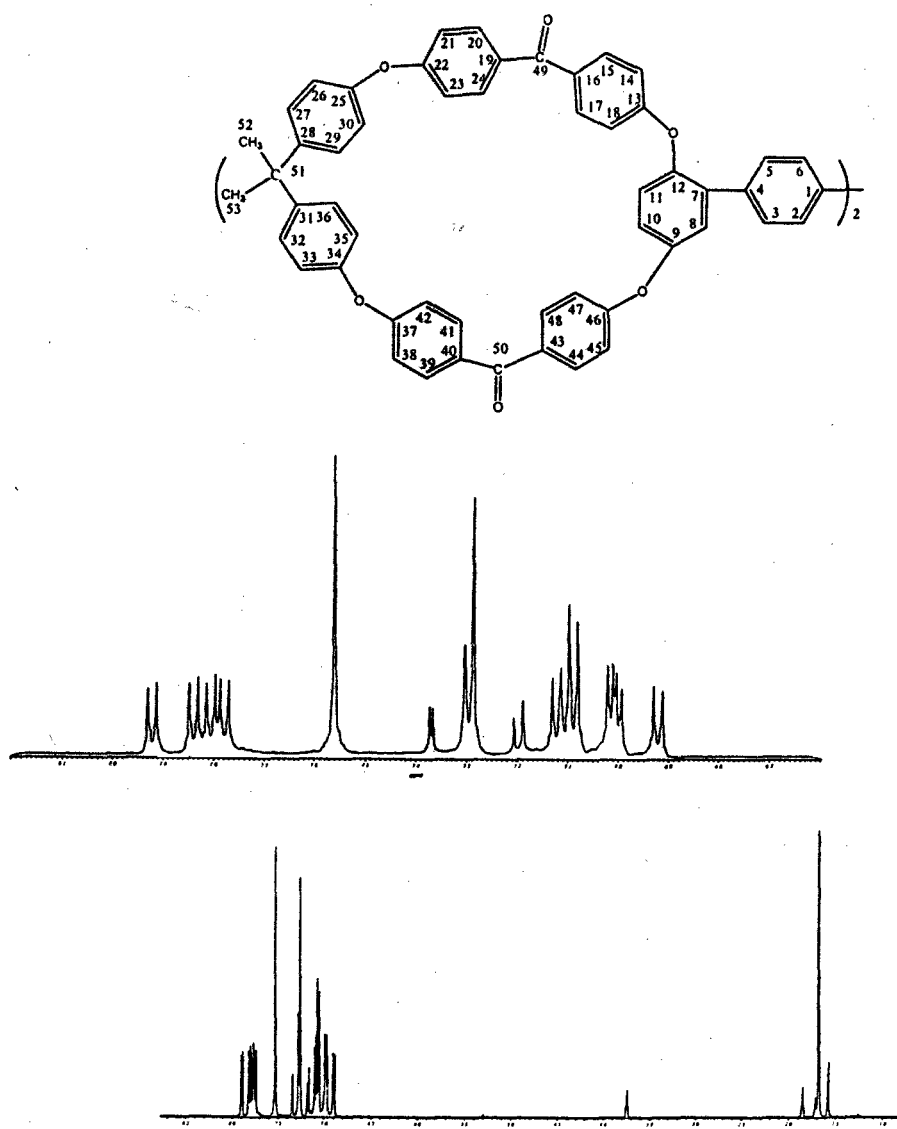


Figure 7. ^1H NMR spectrum and structure assignments of the manacle-like dimer.

Table 2. The ^1H NMR spectrum assignments of the dimer (b) $\delta(\text{CDCl}_3)$

Nuclear no.	$\delta(\text{ppm})$	Nuclear no.	$\delta(\text{ppm})$
H2,H6	7.534	H26,H30	6.976
H3,H5	7.534	H27,H29	7.270
H8	7.334	H32,H36	7.270
H10	7.074	H33,H35	6.986
H11	7.168	H38,H42	7.090
H14,H18	6.893	H39,H41	7.808
H15,H17	7.779	H44,H48	7.891
H20,H24	7.749	H45,H47	7.058
H21,H23	7.058	H52,H53	1.679

Conclusions

With a great molecular design, we lead a p-chlorophenyl substituent to a macrocyclic aryl (ether ketone) oligomer. Then by simple nickel-catalyzed coupling reaction, two macrocycles were connected with each other via covalent bonding to get a manacle-like dimer. This novel structure may have some unthinkable functions in optical or magnetic applications.

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摘要

为使聚芳醚酮大环功能化, 我们设计合成了一种新的单体, 氯代苯基对苯二酚, 通过经典的两步合成法, 得到一种全新的含氯代苯基的聚芳醚酮类大环。再通过镍催化偶联反应, 在两个大环分子间引入了共建键, 从而得到一种手铐形状的环的二聚体。所有涉及化合物的结构都用核磁和飞行时间质谱做了表征