

SYNTHESIS AND CHARACTERIZATION OF NOVEL RIGID MACROCYCLIC OLIGOMER (RCO) CONTAINING CARBOXYL GROUPS

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Abstract

Rigid macrocyclic oligomers (RCO), as a member of organic nanostructure, have received much interest due to their perfect properties. Cyclic oligomer containing carboxyl groups was obtained via hydroxylation of the corresponding ester, which was prepared via aromatic nucleophilic substitution according to the pseudo-high-dilution technology. Two carboxyl groups were introduced into the cyclic structure, this not only expanding the synthetic scope of cyclic oligomers, but also indicating the potential application. The structure of the novel macrocyclic oligomer was confirmed by a combination of IR, MS and ¹H-NMR analysis.

Keywords: rigid macrocyclic oligomer; nanostructure; carboxyl groups

Introduction

Nanometer-scale macrocyclic molecules are regarded as a kind of promising organic nanostructure for functional and applied research¹. Rigid macrocyclic oligomers (RCO), as a member of organic nanostructure, have received much interest due to their perfect properties², such as: (I) the RCO have high thermal stability while the nanoscale cavity is constantly, (II) the RCO itself can make steady LB film, (III) the functional groups can be introduced into the cyclic structure, which attract us to obtain new nanostructures with different quantum dot. Since the RCO molecules are able to be assembled into two-dimensional ordered films by LB technique³, we can forecast that the oligomers owing special cavity and functional groups can be applied in many fields.

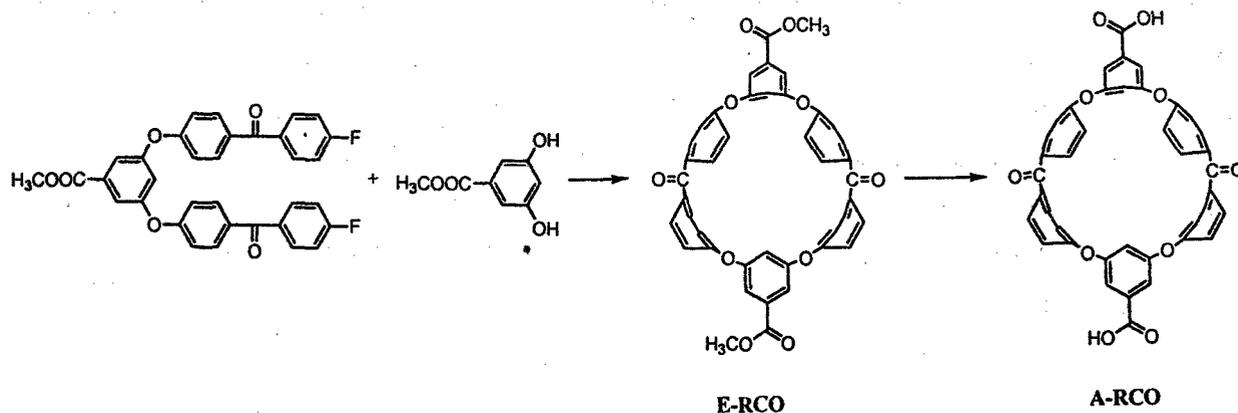
With the development of RCO, much attention has been paid to the preparation of new type of macrocyclic molecules⁴. In recent study, we have obtained a series of RCO containing different groups, such as the strong hydrophobic trifluoromethyl group, the normal hydrophobic methyl group⁵ and the 1,1'-Bi-2-naphthol moieties⁶ et al. Here, we introduced two carboxyl groups into the cyclic structure. The cavity properties could be influenced by the two carboxyl groups. This could make the macrocycle unique in the host-guest system and make such macrocycle special as a novel nano-fabric material with potential application.

In this paper, we have designed and synthesized the RCO containing two carboxyl groups. The structure of the novel macrocyclic oligomer was confirmed by a combination of IR, MS and ¹H-NMR analysis.

Experimental

The synthesis (Scheme 1) of the cyclic carboxyl ate (E-RCO) was prepared via aromatic nucleophilic substitution according to the pseudo-high-dilution. 3,5-dihydroxy-benzoic acid methyl ester was prepared by chemical synthesis, it was purified by recrystallization. The trimmer containing one 3,5-dihydroxy-benzoic acid

methyl ester moiety and two 4,4'-difluorobenzophenone moieties was prepared by chemical synthesis also, it was purified by silica gel column. The method has gone into particulars in my passed works³. Then, we obtained the macrocyclic oligomer containing two carboxyl groups (A-RCO) via hydroxylation.



Scheme 1. Synthesis of the RCO containing two carboxyl groups

Results and Discussion

The rigid macrocyclic oligomer was characterized by IR, MS and ¹H-NMR. IR Spectrum of KBr powder-pressed pellet was recorded on Bruker VECTOR 22 FT-IR spectrometer. MALDI-TOF-MS was performed on LDI-1700 laser desorbed ionization flying time spectrometer (Bio-molecular Co. US). ¹H-NMR spectrum was obtained on a Bruker AVANCE-500 spectrometer using 5 mm o.d. tubes. The sample was dissolved in DMSO containing 0.03% TMS as an internal reference.

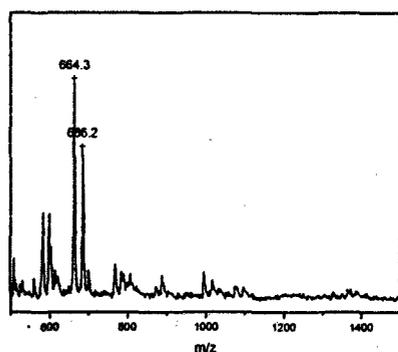


Figure 1. MALDI-TOF spectrum of the A-RCO

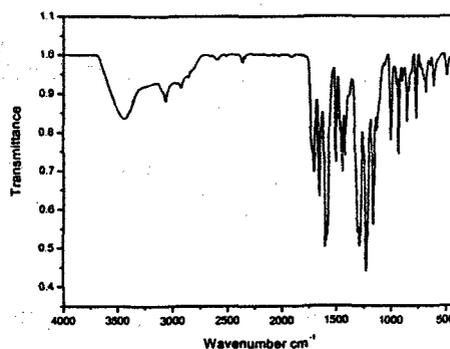


Figure 2. IR spectrum of the A-RCO

The A-RCO was confirmed by MALDI-TOF mass spectrometry. It is a so-called soft ionization technique affording pseudo molecular ions in the form of (M) R⁺ (R=H⁺, Na⁺ or K⁺) with little or no fragmentation. Figure 1 show MALDI-TOF spectrum of the A-RCO. It can be easily seen that there are two large peaks corresponding to molecular ions of the A-RCO, detected as MH⁺ and MNa⁺, at m/z=664.3 and m/z=686.2.

Figure 2 shows the FT-IR spectrum over the range 400-4000 cm^{-1} for the A-RCO, respectively. ν/cm^{-1} : 3441(-OH,STR,Very Broad),3064(Ar-H,STR), 2924(PhCOO-H,STR,Very Broad), 1703 and 1653(C=O,STR), 1596, 1584, 1499, 1463 and 1442(Ar-Ring,STR), 1417, 948, 929 and 897(PhCOO-H,DEF), the doublets 1302 and 1284(PhCOOH,STR), 1223(Ph-O-Ph,ASY-STR), 836(Ph-O-Ph,SYM-STR), 1163 and 997(1,3,5-trisubst. Ar-H, BEND), 948, 929, 853 and 836(1,3,5-trisubst. Ar-H,DEF), 853 and 836(p-disubst. Ar-H,DEF).

Figure 3 gives the $^1\text{H-NMR}$ (AVANCE-500MHz, DMSO) spectrum of macrocyclic oligomer. There are two doublets downfield, which correspond to the protons Ha ortho to the carbonyl groups and Hc ortho to the carboxyl groups. The other one doublet upfield is due to protons Hb ortho to the ether linkage. The proton Hd appears as a treble and moves to low field for the reason of the strain of cyclic structure, we think so. In addition, the carboxyl proton He appears as a singlet at $\delta=13.31$ ppm.

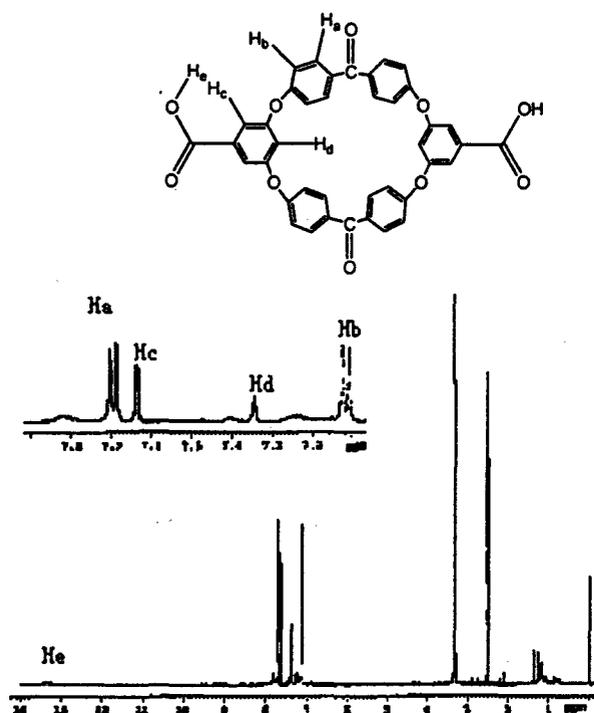


Figure 3. $^1\text{H-NMR}$ spectrum of the A-RCO

Conclusions

We have synthesized target rigid macrocyclic oligomer successfully. The product was characterized by IR, MS and $^1\text{H-NMR}$. Our ongoing works will focus on the applied research.

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