Synthesis and Chiral Molecular Recognition of Phenylene-Bridged Bispyrrole Derivatives Having *N*-Substituted Imino Groups

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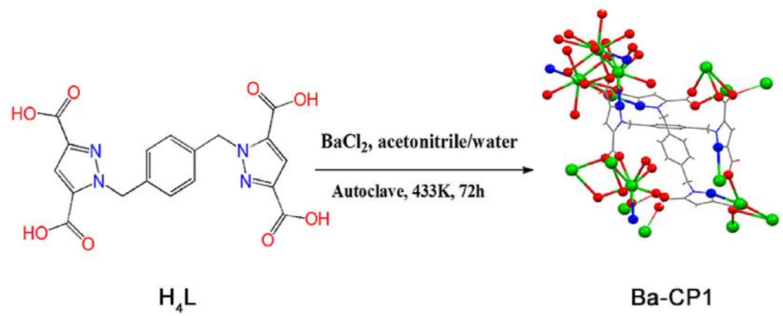
Introduction

Why is it important to detect dicarboxylic acids?

- Excessive intake, production, or inadequate clearance of oxalic acid, the simplest dicarboxylic acid, may cause health problems including nephropathy, recurrent kidney stone, and liver disease.

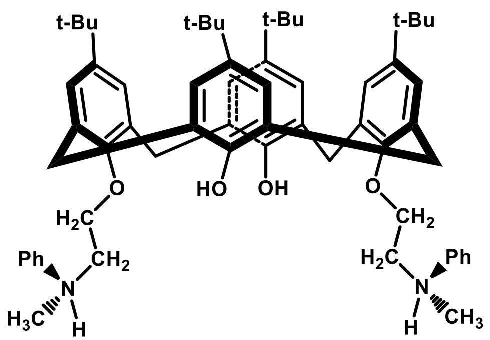
- The dicarboxylic acids are abundant in natural plants, and also produced and consumed in large amounts in the industrial productions of the polymers such as polyamides and polyesters.



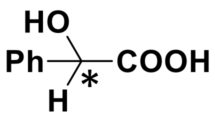
- Hence, the chemosensor that allows convenient detection and visualization of the dicarboxylic acids to output visible color change and/or spectral changes is valuable in terms of the health and environmental managements.

Introduction

Zheng et al. found that the chiral calix[4]arenes bearing amino alcohol groups were a class of excellent receptors for chiral recognition of carboxylic acids. They reported that a nitrogen containing calix[4]arene 1, which was more easily synthesized in excellent yield, has good ability to recognize the enantiomers of mandelic acid and 2,3-dibenzoyltartaric acid.



1



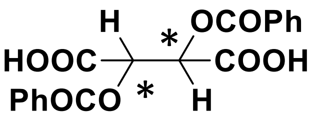


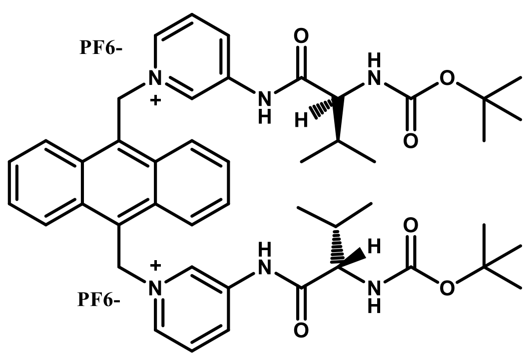
Figure 1. Molecular structure of compound **1**, L/D-mandelic acid, and L/D-2,3-dibenzoyl tartaric acid

Zheng, Y. S.; Xiao, Q. *Chin. J. Chem.*, **2005**, *23*, 1289-1291.

Introduction

Ghosh et al. designed and synthesized a new type of anthracene-based chiral fluorescent chemical sensor 2. It has significant enantioselectivity to L-tartrate. When L-tartrate is present, the sensor exhibits a significant increase in emission intensity in DMSO, while the isomer tartrate brings a relatively small change.

(a)



2

(b)

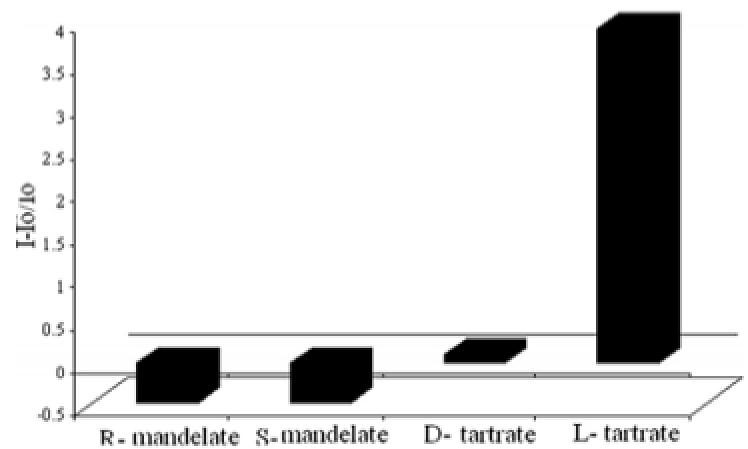
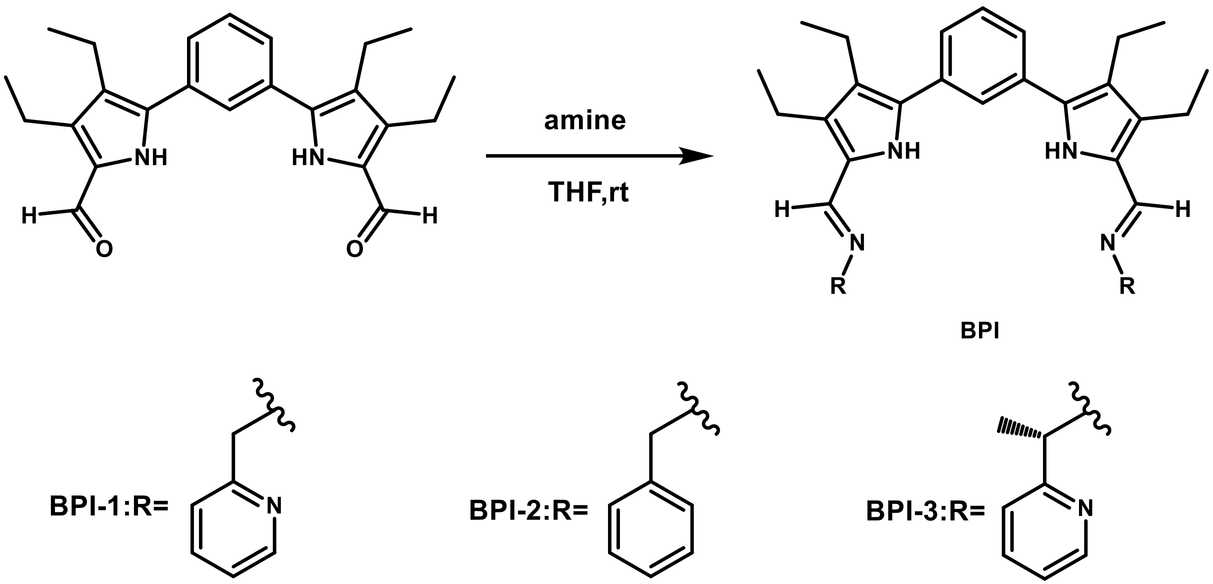


Figure 2. (a) the structure of compound 2; (b) Change in fluorescence ratio of 2 (c = 1.12×10^{-4} M) at 432 nm upon addition of 20 equiv amounts of anions.

Ghosh, K.; Sarkar, T. *Tetrahedron Lett.*, **2014**, *55*, 1342-1346.

Synthesis of Phenylene-bridged Bipyrrole Bearing *N*-Substituted Imino Groups(BPI)



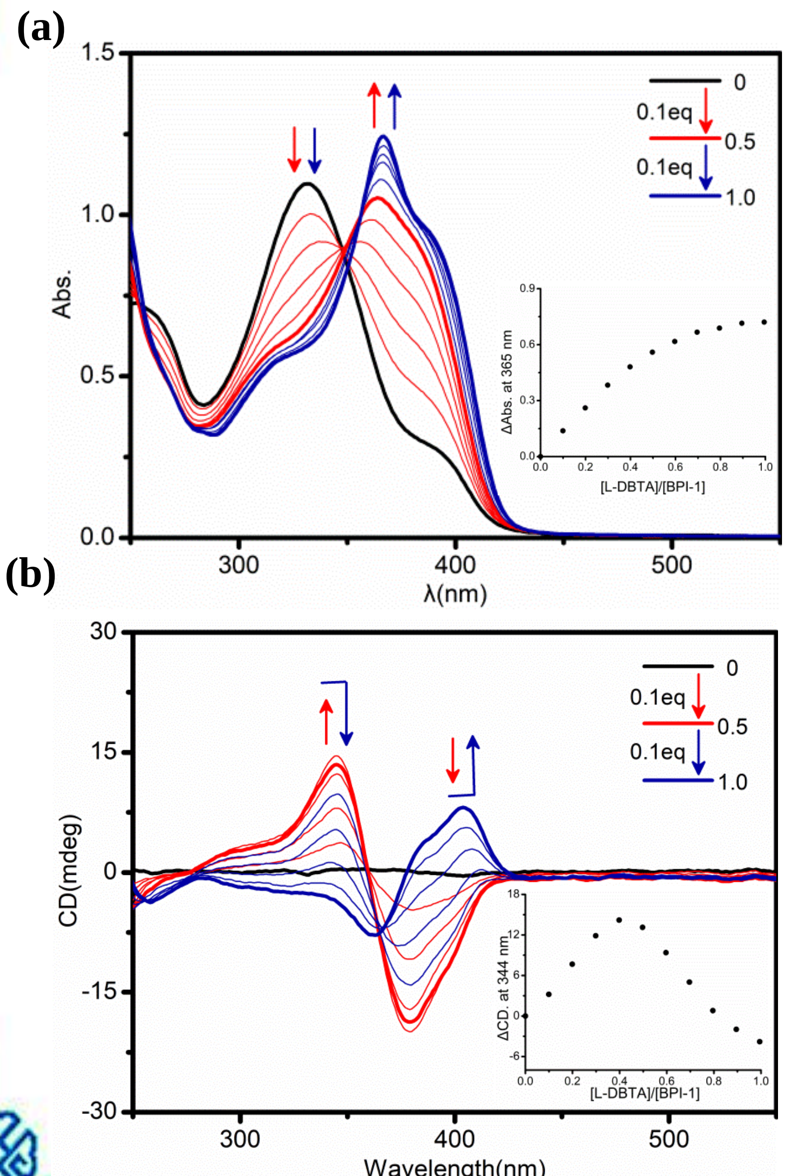
69.1% yield

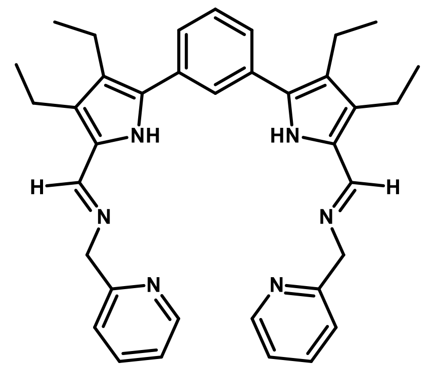
43.2% yield

72.1% yield

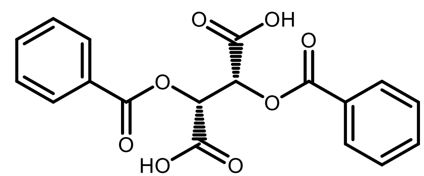
Figure 3. Synthesis of a series of BPI

Chiroptical Sensing of Chiral Guests with Achiral BPI-1





BPI-1

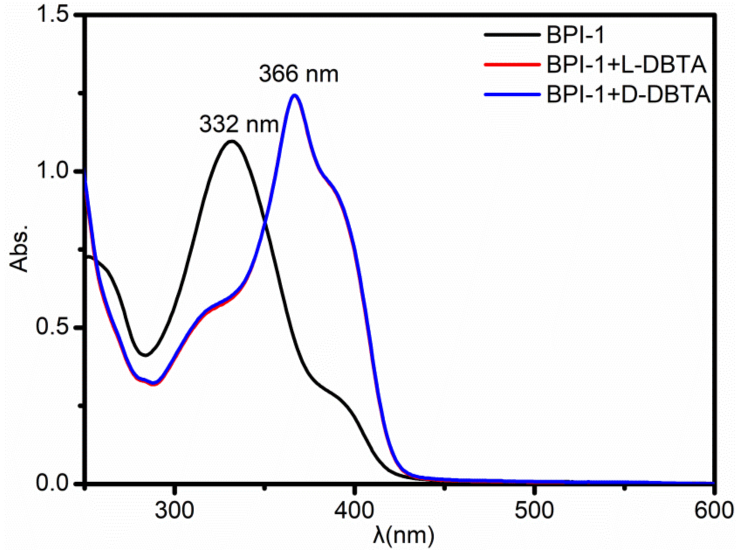


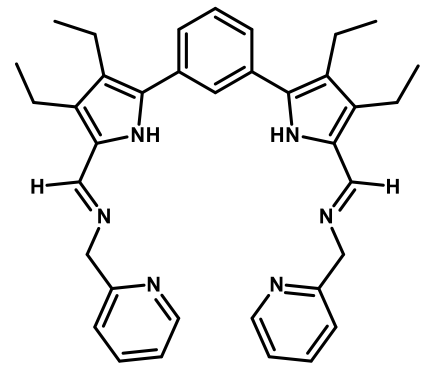
L-DBTA

Figure 4. (a) UV-vis absorption and (b) CD spectral titrations of BPI-1 (3.5×10^{-5} mol/L) with L-DBTA in CH_2Cl_2 at 298 K.

Chiroptical Sensing of Chiral Guests with Achiral BPI-1

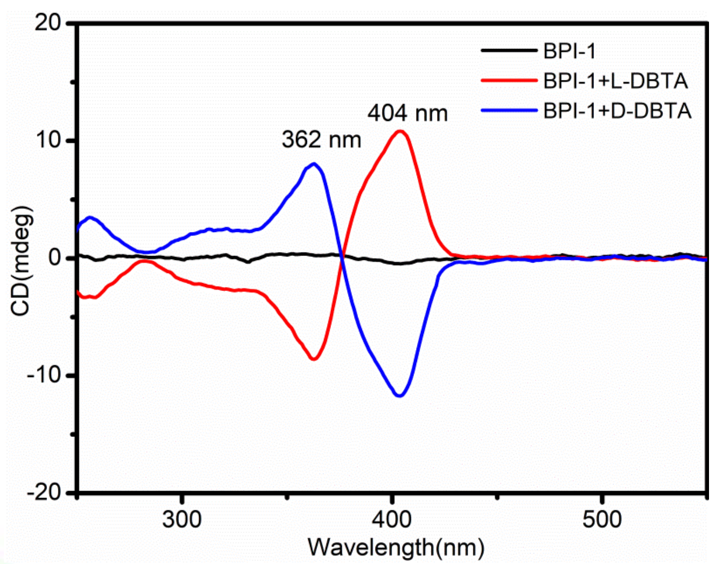
(a)

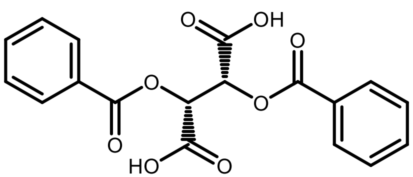




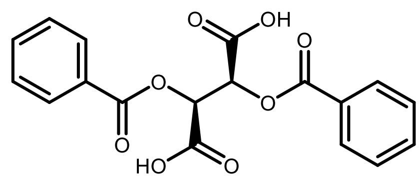
BPI-1

(b)





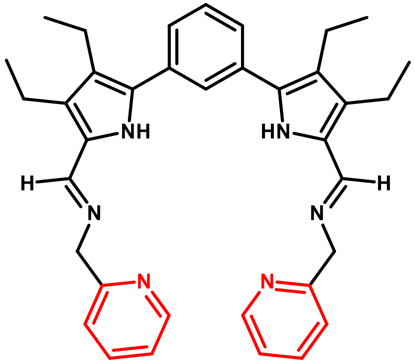
L-DBTA



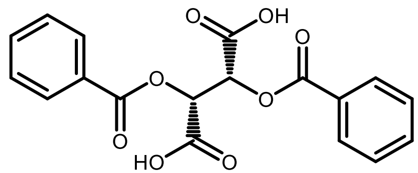
D-DBTA

Figure 5. (a) UV-vis absorption and (b) CD spectra of BPI-1 (3.5×10^{-5} mol/L), and mixtures of BPI-1 and L-DBTA or D-DBTA in CH_2Cl_2 at 298 K.

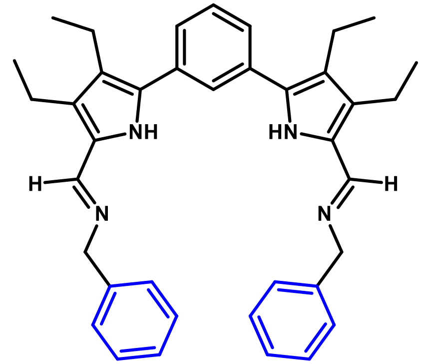
Chiroptical Sensing of Chiral Guests with Achiral BPI-1/ BPI-2



BPI-1



L-DBTA



BPI-2

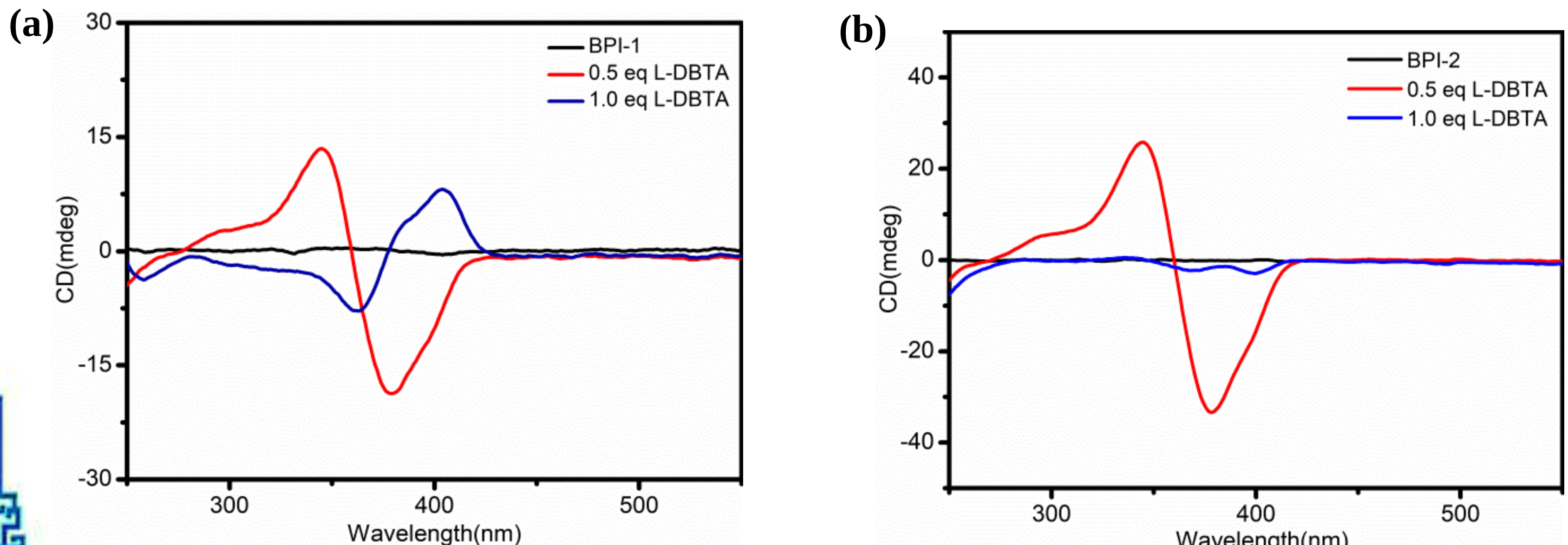
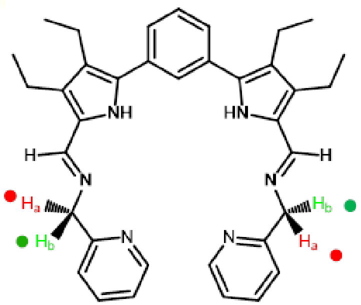
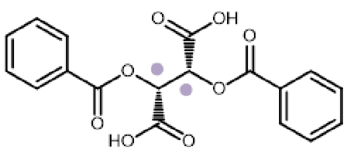


Figure 6. CD spectral changes of (a) BPI-1 (3.5×10^{-5} mol/L) and (b) BPI-2 (2.8×10^{-5} mol/L) upon mixing with L-DBTA in CH_2Cl_2 at 298 K.

^{1}H NMR Titration of L-DBTA and BPI-1



BPI-1



L-DBTA

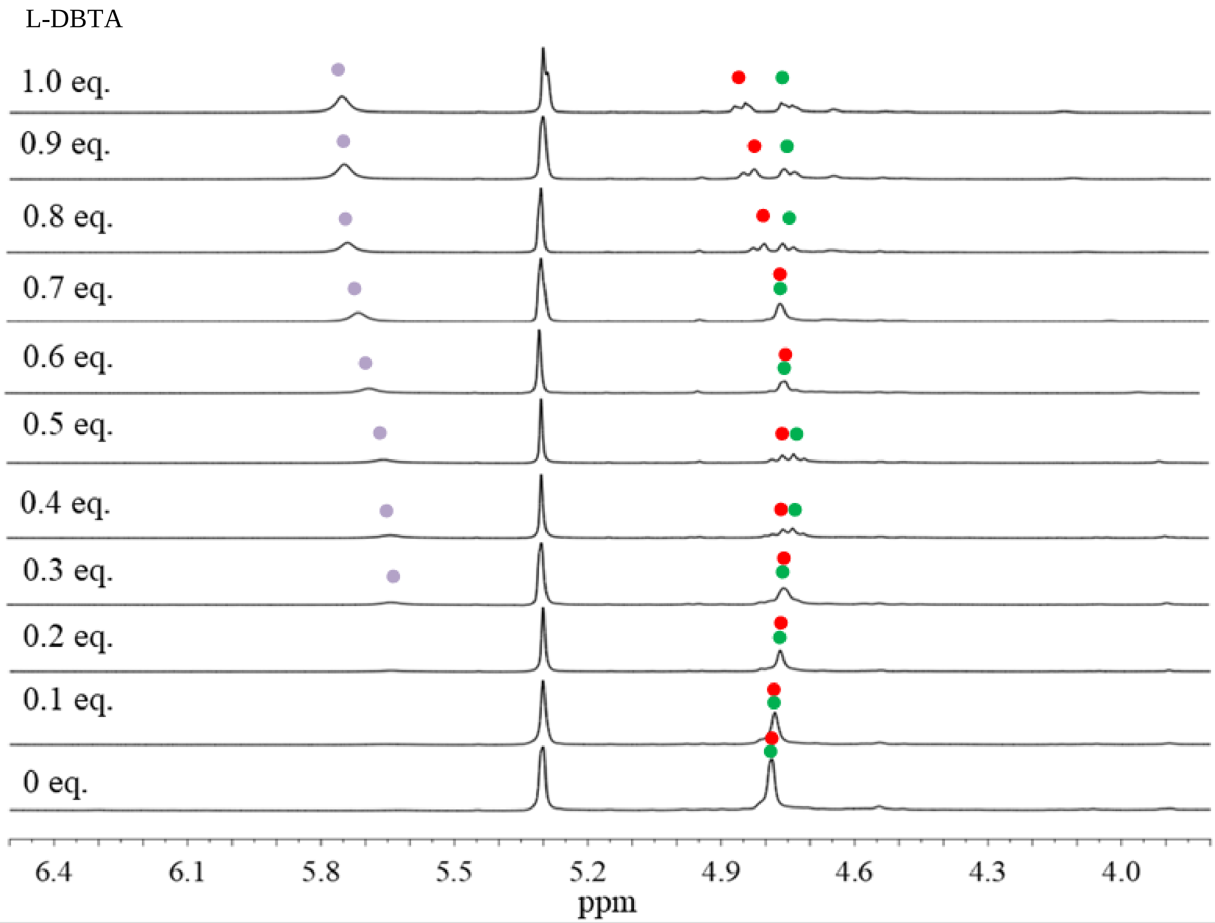


Figure 7. ^{1}H NMR spectral titration (600 MHz) of BPI-1 (1.1×10^{-2} mol/L) with L-DBTA in CD_2Cl_2 at 293 K.

Chiroptical Sensing of Chiral Guests with Achiral BPI-1

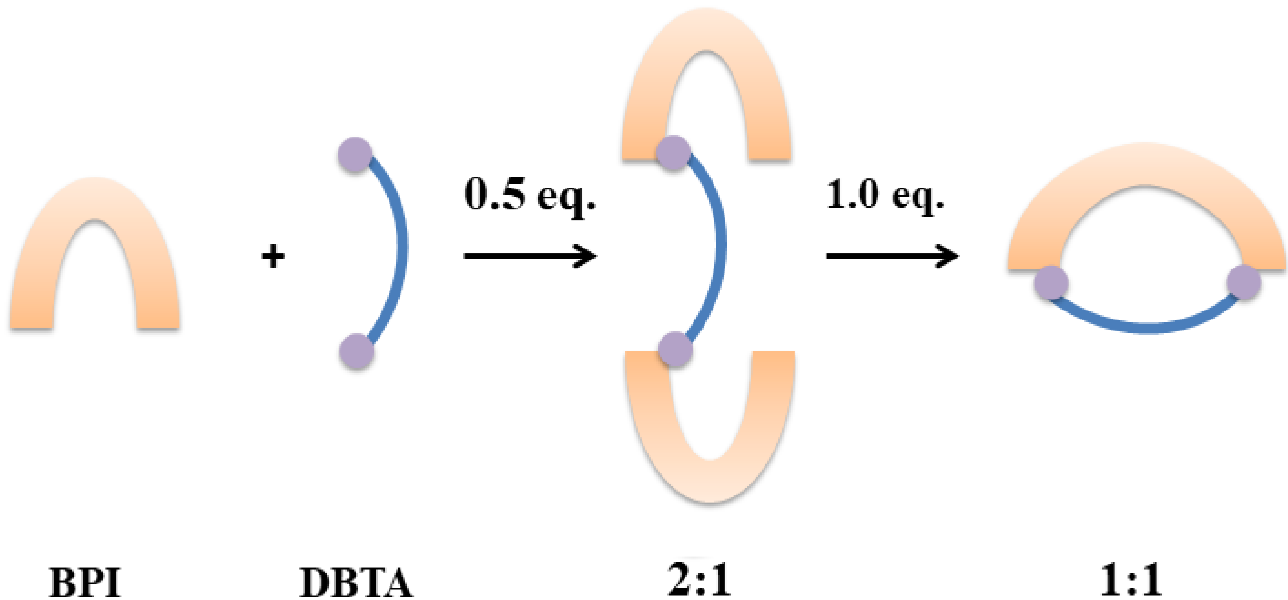
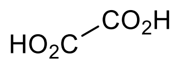
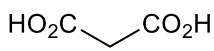
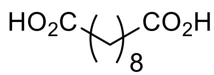
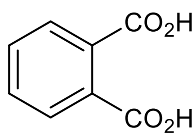
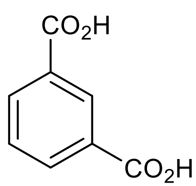
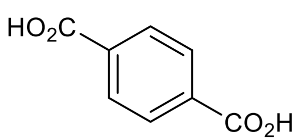


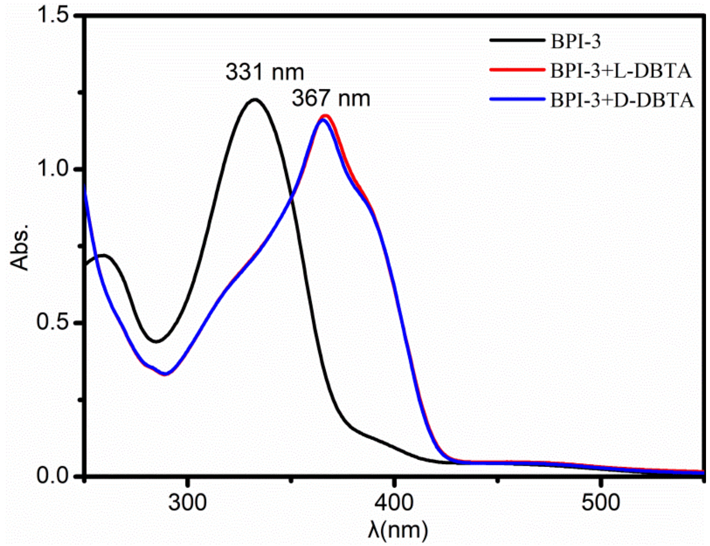
Figure 8. Schematic illustration for a possible complexation of BPI with L-DBTA

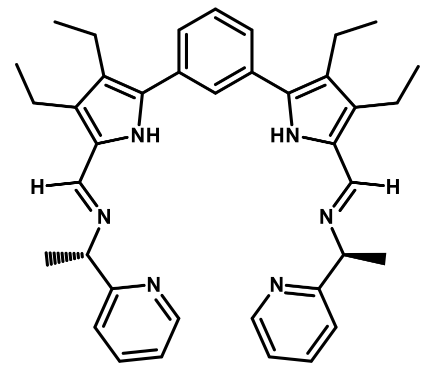
Chiroptical Sensing of Achiral Guests with Chiral BPI-3

Ligand Acid	Structure	CD data		UV-vis data	
		λ_{max}(nm) of the lowestest energy CD band	Relative CD intensity	λ_{max}/nm	$\Delta\varepsilon$($L \cdot moL^{-1}cm^{-1}$)
Oxalic acid		+(395)	14	363	1.66×10^4
Malonic acid		+(401)	17	369	1.91×10^4
Sebacic acid		+(395)	12	360	1.11×10^4
Phthalic acid		+(397)	17	368	1.86×10^4
Isophthalic acid		+(388)	12	365	1.62×10^4
Terephthalic acid		+(388)	11	365	1.24×10^4

Chiroptical Sensing of Chiral Guests with Chiral BPI-3

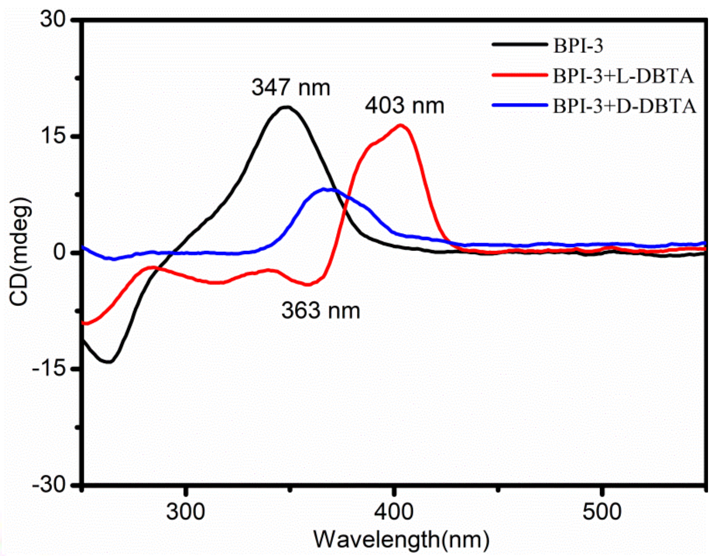
(a)

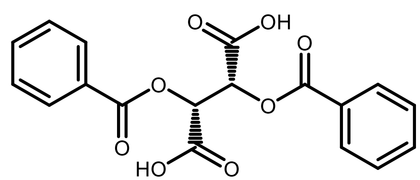




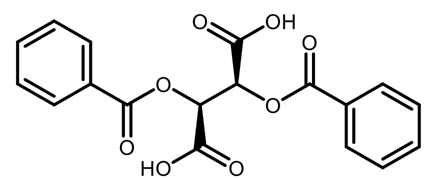
BPI-3

(b)





L-DBTA



D-DBTA

Figure 9. (a) UV-vis absorption and (b) CD spectra of BPI-3 (3.5×10^{-5} mol/L), and mixtures of BPI-3 and L-DBTA or D-DBTA in CH_2Cl_2 at 298 K.

Summary

- There is a 1:1 chemical binding ratio between BPI-1 and DBTA. When DBTA is identified, the configuration flipping phenomenon will occur, but BPI-2 does not have a flipping phenomenon, which may be caused by pyridine.

- BPI-3 does not show the mirror symmetry phenomenon that occurs when BPI-1 and BPI-2 interact with DBTA. BPI-3 can effectively distinguish between L-DBTA and D-DBTA.

- BPI-3 can effectively distinguish long-chain dicarboxylic acids from short-chain dicarboxylic acids, and oxalic acid exhibits specific selectivity in UV-visible absorption spectra and circular dichroism.

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Thank you for your attention

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