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Optically active cyclic and linear poly(aryl esters) based on chiral 1,1′-bi-2-naphthol

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Abstract

Three optically active poly(aryl esters) — poly(terephthalyl esters) (PTEs), poly(isophthalyl esters) (PIEs) and *o*-phthaloyl ester (OPE) — were prepared from chiral 1,1-bi-2-naphthol reacted with terephthaloyl chloride (TPC), isophthaloyl chloride (IPC) and *o*-phthaloyl chloride (OPC), respectively, by condensation reactions. The ring-forming properties of 1,1′-bi-2-naphthol with the three biacid chlorides have been studied. It is found that the products formed by the optically active binaphthol and TPC are mainly linear poly(terephthalyl esters) (PTEs), while the polycondensates of the chiral binaphthol and IPC consist of both cyclic and linear PIEs, and the product formed by optically active binaphthol and OPC is a wholly monocyclic *o*-phthaloyl ester (OPE), i.e. 1,1-bi-2-naphthyl *o*-phthalate. The pure optically active cyclic dimer, trimer and tetramer of PIEs were successfully separated from their product mixture by preparative TLC. The specific rotations $[\alpha]_D^{25}$ were +210 and −214.8 for the cyclic (*R*)- and (*S*)-dimer of PIEs, +177.2 and −179.1 for the cyclic (*R*)- and (*S*)-trimer of PIEs and +80.3 and −80.8 for the (*R*)- and (*S*)-tetramer of PIEs, respectively. Their characterizations were carried out by MALDI-TOF MS, GPC, CD, etc. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

1,1′-Bi-2-naphthol or its derivatives have attracted much attention in various fields as attractive candidates in asymmetric synthesis, such as chiral catalysts and auxiliaries,[1] molecular recognition,[2] enantioselective chromatographic seperations[3] and host–guest complexes.[4] Most of the above compounds were linear and only relatively little literature has been reported about cyclic binaphthyl compounds.[5]

The compounds aforementioned have mostly been synthesized by ordinary organic synthetic methods. Recently, Takata[6] reported optically active poly(arylcarbonates) composed of the chiral 1,1′-bi-2-naphthyl moiety which adopt stable helical structures in solution synthesized by the polymerization

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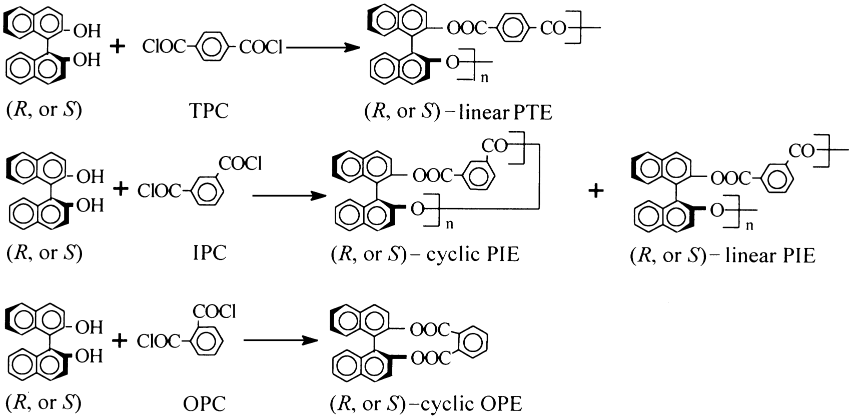
method, and found that if the chiral 1,1′-bi-2-naphthyl moiety was changed to a racemic binaphthyl group, according to earlier studies,[7] no helical structure was formed. Our laboratory[8] also reported the polymerization synthesis of optically active poly(ether sulfones) based on chiral 1,1′-bi-2-naphthol which can form rings of various sizes.

In the present work, we report the synthesis of poly(aryl esters) by the condensation reaction of homochiral 1,1′-bi-2-naphthol with the *p*-, *m*- and *o*-benzenedicarbonyl dichlorides. Clearly, different results of the condensation reactions and ring-forming properties were found.

2. Results and discussion

Optically active poly(aryl esters) have been synthesized by the condensation reaction of chiral 1,1′-bi-2-naphthol with an aromatic diacid chloride, such as terephthaloyl chloride (TPC), isophthaloyl chloride (IPC) and *o*-phthaloyl chloride (OPC) (Scheme 1). It was found that the products formed by (*R*)- or (*S*)-1,1′-bi-2-naphthol and TPC were only linear poly(terephthalyl esters) (PTEs), while the polycondensates of the chiral binaphthol and IPC consisted of both cyclic and linear poly(isophthalyl esters) (PIEs), and in contrast to the above two species, the product formed by optically active binaphthol and OPC was wholly monocyclic *o*-phthaloyl ester, i.e. 1,1′-bi-2-naphthyl *o*-phthalate.



Scheme 1.

GPC spectra showed that the average molecular weights were 0.9×10^4 and 1.0×10^4 for (*R*)-PTE and (*S*)-PTE, respectively, which were slightly lower than the M_w (6.1×10^4) of the condensation polymer of racemic 1,1-bi-2-naphthol with TPC using the interfacial polymerization reported by Liou et al.[9] The MALDI-TOF MS analysis of (*R*)-PTE and (*S*)-PTE showed that the condensation products were the linear polymers with three different types of end groups, i.e. both end groups were 1,1′-bi-2-naphthyl residues, both end groups were terephthaloyl chloride residues, and both end groups were 1,1′-bi-2-naphthyl and terephthaloyl chloride residues, respectively.

In the cases of (*R*)-PIE (M_w 4.9×10^3 by GPC) and (*S*)-PIE (M_w 5.9×10^3 by GPC), it was found from MALDI-TOF MS spectra that they clearly consisted of the cyclic and linear oligomers with the cyclic and linear molecular ionic peaks appearing alternately in the spectra. The lowest molecular weight shown in the MS spectrum was 644.01 ($+Na^+$), which coincided with the linear monomeric PIE which contained one 1,1′-bi-2-naphthol with two isophthaloyl chloride end groups. By calculation from the MS results, it was found that the end groups of all the linear oligomers of PIEs were isophthaloyl chloride residues. This means that in the condensation reaction of 1,1′-bi-2-naphthol with *m*-benzenedicarbonyl dichloride, the oligomers with a binaphthol end group and a chloride end group had a strong ring-forming tendency, which was the same as for poly(ether sulfones) which we reported previously.[8] While the (*R*)- or (*S*)-binaphthol condensed with OPC, only the molecular peak of monocyclic *o*-phthaloyl ester was found at 417.28.

In an attempt to obtain the pure cyclic PIE from the product mixture, separation was carried out by preparative thin layer chromatography (PTLC). It was rather difficult to separate every cyclic PIE from the mixture because of the very similar dissolution properties. Fortunately, the optically active cyclic dimers, trimers and tetramers of PIEs were successfully separated in almost pure form by PTLC. The results of their mass spectra, the specific rotation and the melting-point measurements are shown in Table 1.

Table 1
Characterization of optically active cyclic PIEs and OPEs

Sample (cyclic)			$[\alpha]_D^{25a)}$	Molecular Weight		m.p.(°C)
				Found$^{b)}$	Calculated	
PIE	dimer	(*R*)-	+210	833.22	832.85	325-327
		(*S*)-	-214.8	833.19	832.85	326-327
	trimer	(*R*)-	+177.2	1249.49	1249.2	215-218
		(*S*)-	-179.1	1249.43	1249.2	217-219
	tetramer	(*R*)-	+80.3	1665.71	1665.7	227-230
		(*S*)-	-80.8	1665.78	1665.7	231-233
OPE	monomer	(*R*)-	-470	417.28	416.42	273-275
		(*S*)-	+470	417.28	416.42	272-274

a) Specific optical rotation measured in THF, 25°C (C=0.05 g/dl for dimer, trimer, tetramer of (*S*)-PIE, and tetramer of (*R*)-PIE; C=0.10g/dl for dimer, trimer of (*R*)-PIE, and (*R*)-and (*S*)-monomer of OPE).

b) Measured by MALDI-TOF MS, matrix : CCA.

It was found that the magnitude of the specific rotation of optically active cyclic PIEs decreases with an increase in ring size, and the sign of the specific rotation was in agreement with that of their original binaphthol enantiomers. The characterization results of the monocyclic *o*-phthaloyl ester are also shown in Table 1. The enantiomers of OPE exhibited the highest values of specific rotation among these cyclic polymers, but the sign of the specific rotation was opposite to that of the original binaphthol. The MALDI-TOF MS spectra of the cyclic dimer, trimer and tetramer of (*R*)-PIEs and monomeric cyclic (*R*)-OPE are shown in Fig. 1.

The structures of the cyclic dimer, trimer and tetramer of PIEs, and the computer simulation (by Alchemy 2000) of their molecular static structures are shown in Fig. 2.

The UV spectra of both the cyclic dimer of (*R*)-PIE (Fig. 3, curve 1) and monocyclic (*R*)-OPE (Fig. 3, curve 2) exhibited strong absorption bands around 239 nm, together with a relatively weak transition at 279 nm for the dimer of (*R*)-PIE and three weak peaks appeared at 282 nm, 310 nm and 327 nm for monocyclic (*R*)-OPE, respectively.

The circular dichroism (CD) measurements were carried out in THF and the CD spectra of the chiral cyclic dimers of PIE and the monocyclic enantiomers of OPE are shown in Fig. 4. All the detected samples had their absorption in the range of 200–250 nm, and as expected from their rotations, the Cotton curves were complete mirror images. The CD spectrum from the (*R*)-cyclic dimer of PIE with positive chirality exhibited two broad positive absorption peaks at 215 nm and 223 nm and one negative absorption at 225 nm. The CD spectrum of monocyclic OPE was simpler than that of the cyclic dimers of PIE. The Cotton curve of (*R*)-monocyclic OPE with negative chirality showed a negative absorption at 215 nm and a positive absorption at 227 nm. These absorption peaks are attributable to the n → π*

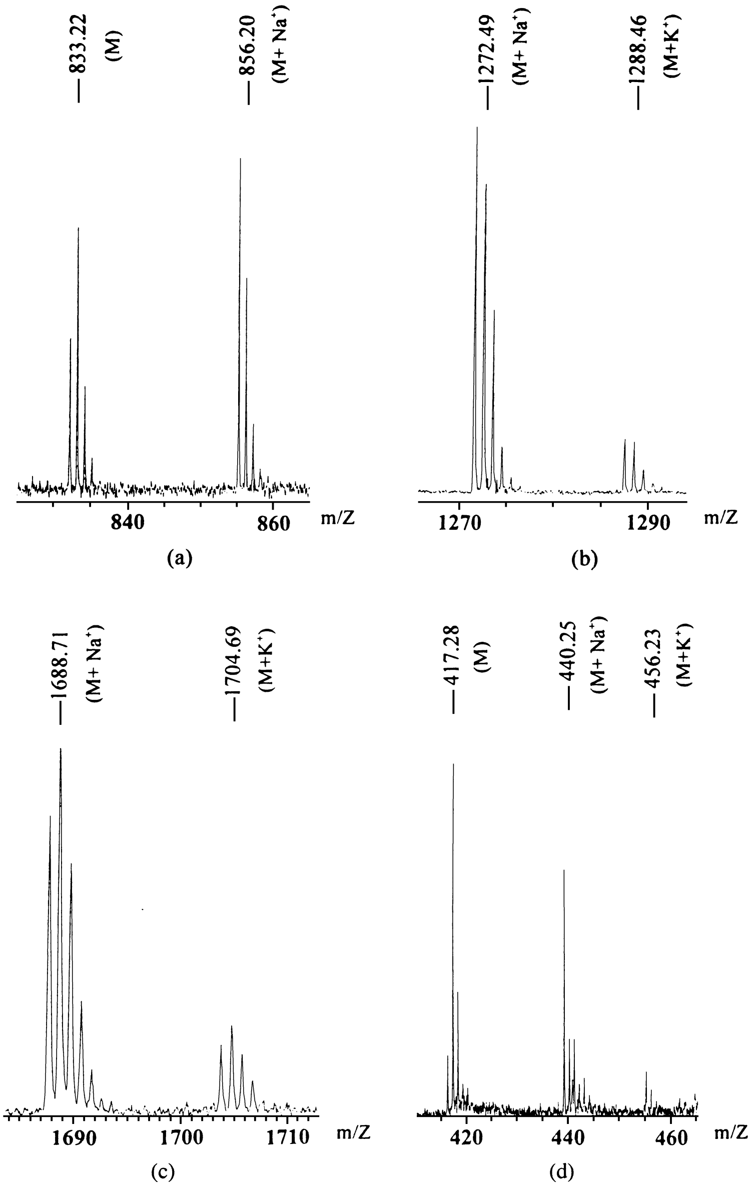


Figure 1. The MALDI-TOF MS spectra of cyclic dimer (a) (molecular peaks: M, $M+Na^+$), trimer (b) (molecular peaks: $M+Na^+$, $M+K^+$) and tetramer (c) (molecular peaks: $M+Na^+$, $M+K^+$) of (*S*)-PIEs, and monomer cyclic (*S*)-OPE (d) (molecular peaks: M, $M+Na^+$, $M+K^+$)

transition of the carbonyl groups and the $\pi \rightarrow \pi^*$ transition of the aromatic groups in the chiral cyclic compounds.

From the above analysis, it can be clearly seen that the lowest tendency for cyclization was between the chiral binaphthol and TPC whose two acid chlorides were in the 1,4-positions; its products were mainly linear PTEs. On the contrary, the OPC with its two acid chlorides in the 1,2-positions was prone to form cyclic OPEs with the chiral binaphthol; their condensation products were all monocyclic OPEs. When the two acid chlorides were in the 1,3-positions, the most interesting phenomenon appeared, i.e.

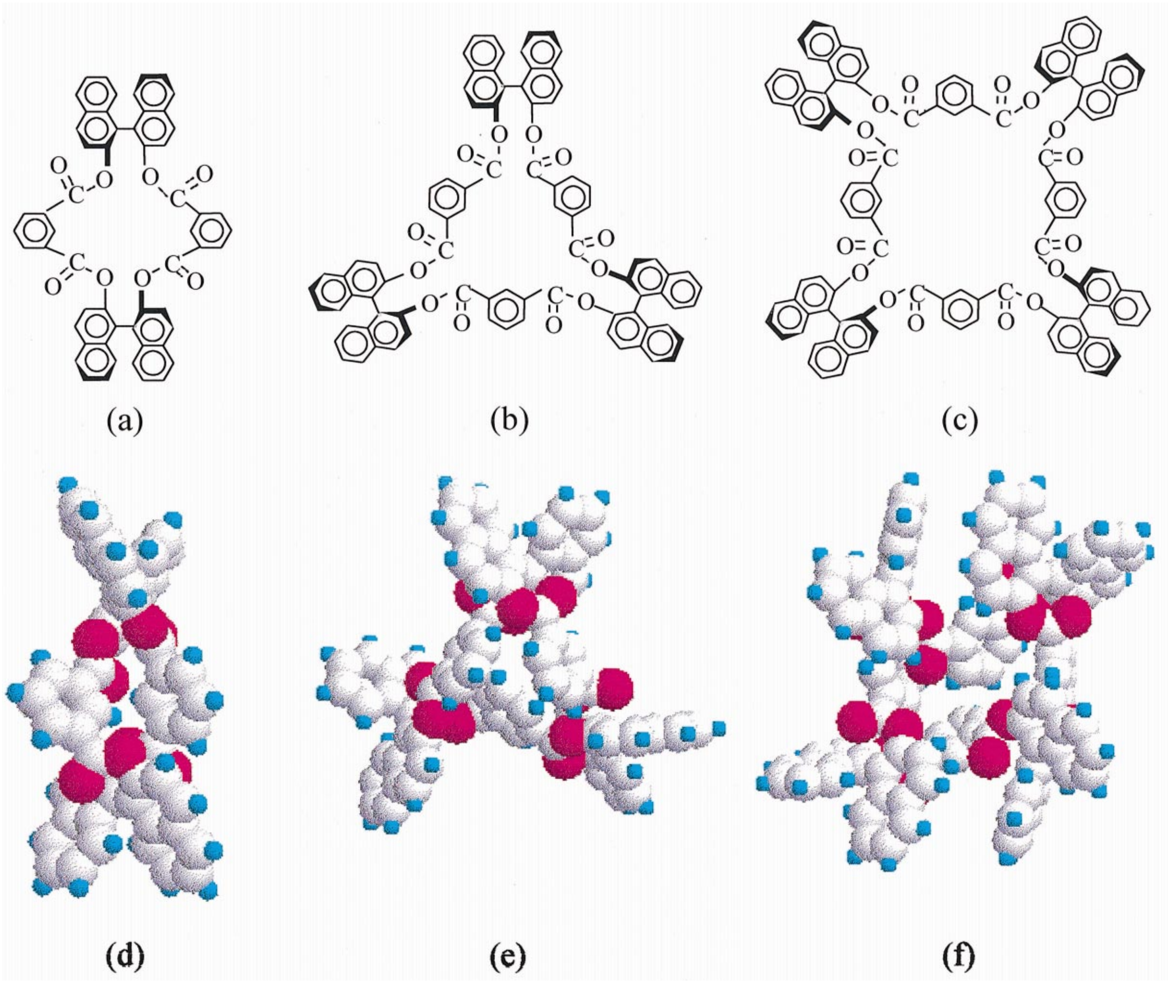


Figure 2. The chemical scheme of chiral cyclic PIEs, dimer (a), trimer (b), and tetramer (c). The computer simulation of molecular structure of chiral cyclic PIEs, dimer (d), trimer (e), and tetramer (f)

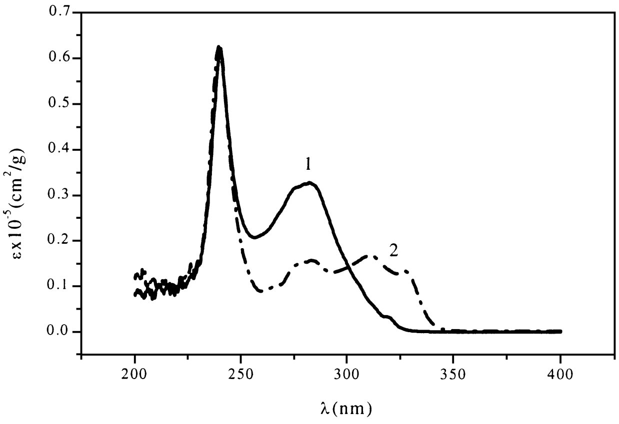
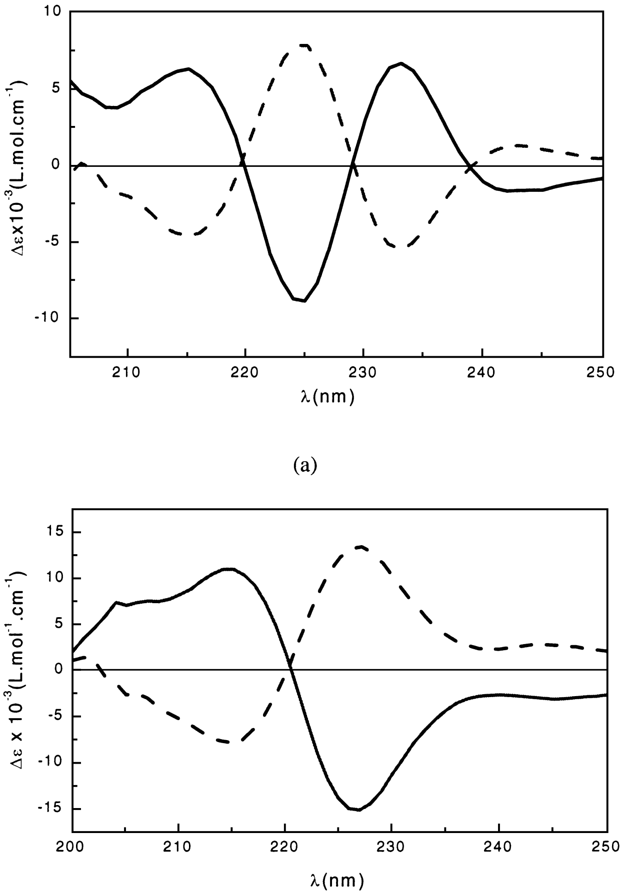


Figure 3. The UV spectra of cyclic dimeric (*R*)-PIE (1: solid line) and monocyclic (*R*)-OPE (2: dashed dot line)



(a)

(b)

Figure 4. The CD spectra of cyclic dimeric PIE (a) and monocyclic OPE (b) (*R*): solid line, (*S*): dashed line

both a series of linear PIEs and a series of cyclic PIEs were found. As a result, a series of novel cyclic compounds with axial chirality could be synthesized.

3. Experimental

3.1. Materials

Terephthaloyl chloride was purified by recrystallization from petroleum ether (90–120°C). Isophthaloyl chloride and *o*-phthaloyl chloride were purified by distillation under reduced pressure. (±)-1,1′-Bi-2-naphthol was resolved according to the method reported by Cai and co-workers.[10] (*S*)-1,1′-Bi-2-naphthol ($[\alpha]_D$=−34.1 deg dm^{-1} g^{-1} cm^3, *c* 1, THF) and (*R*)-1,1′-bi-2-naphthol ($[\alpha]_D$=+34.4 deg dm^{-1} g^{-1} cm^3, *c* 1, THF) were obtained.

3.2. Measurements

^{1}H NMR spectra were measured with an Instrum DMx300 spectrometer in $CDCl_3$ at room temperature. MALDI-TOF MS were detected on an Instrum Biflex III spectrometer with α-cyano-4-hydroxycinnamic acid (CCA) as a matrix. Optical rotations were measured on a Perkin–Elmer 241 MC polarimeter using the 589 nm wavelength of a sodium lamp at 25°C in THF. Circular dichroism (CD) spectra were measured in a 0.01 cm cell at room temperature on a JASCO-720 spectropolarimeter. UV spectra were measured on a UV-2101PC, UV–vis scanning spectrophotometer in the range of 200–400 nm in THF at room temperature.

3.3. Condensation

A typical example of the polymerization is described below.

To a solution of (*R*)- or (*S*)-1,1′-bi-2-naphthol (2 mmol), terephthaloyl chloride (2 mmol) in THF in a 25 ml flask with a magnetic stirrer, 0.72 ml (5 mmol) of triethylamine was added under nitrogen. After the reaction mixture had been heated at the refluxing temperature for 12 h, the product was precipitated with methanol. The resulting solid was filtered and washed with water and methanol, and was obtained as a white powder which was purified by reprecipitation from THF–methanol, the solvent-precipitation system. The yields of (*R*)-PTE and (*S*)-PTE were both 98 wt%. The other polyesters were obtained in yields of 93 wt% for (*R*)-PIE, 91 wt% for (*S*)-PIE, 60 wt% for (*R*)-POE and 57 wt% for (*S*)-POE.

3.4. Separation

Separation was performed by PTLC. The thin layer plate was coated with silica gel H(60) and the eluent was a solution of petroleum ether (60–90°C):chloroform, the ratio changing gradually from 100:15 to 100:20 (v/v) in the separation process. The bands which separated were collected and eluted with THF. After evaporation, the chiral cyclic dimer, trimer and tetramer of PIE, and cyclic monomer of POE, respectively, were obtained. Characterizations are as follows: (*R*)-dimeric cyclic PIE (yield 6.4%): mp 325–327°C; $[\alpha]_D^{25}$ +210; ^{1}H NMR in $CDCl_3$ δ 7.22–7.25 (m, 4H, ArH), 7.26–7.35 (m, 8H, ArH), 7.44–7.47 (m, 4H, ArH), 7.47–7.48 (m, 2H, PhH), 7.87–7.90 (m, 4H, PhH), 7.93–7.98 (m, 8H, ArH), 9.18 (s, 2H, PhH). (*S*)-Dimeric cyclic PIE (yield 6.1%): mp 326–327°C; $[\alpha]_D^{25}$ −214.8; ^{1}H NMR in $CDCl_3$ δ 7.26–7.32 (m, 12H, ArH), 7.44–7.47 (m, 4H, ArH; 2H, PhH), 7.87–7.90 (m, 4H, PhH), 7.92–8.00 (m, 8H, ArH), 9.17 (s, 2H, PhH). (*R*)-Trimeric cyclic PIE (yield 5.4%): mp 215–218°C; $[\alpha]_D^{25}$ +177.2; ^{1}H NMR in $CDCl_3$ δ 6.93–6.98 (m, 6H, ArH), 7.31–7.33 (m, 6H, ArH), 7.37–7.39 (m, 6H, ArH), 7.42–7.45 (m, 6H, ArH), 7.47–7.50 (m, 3H, PhH), 7.85–7.87 (m, 6H, PhH), 7.90–7.93 (m, 12H, ArH), 8.23 (s, 3H, PhH). (*S*)-Trimeric cyclic PIE (yield 5.2%): mp 217–219°C; $[\alpha]_D^{25}$ −179.1; ^{1}H NMR in $CDCl_3$ δ 6.91–6.98 (m, 6H, ArH), 7.26–7.44 (m, 18H, ArH), 7.46–7.49 (m, 3H, PhH), 7.60–7.85 (m, 6H, PhH), 7.87–7.93 (m, 12H, ArH), 8.29 (s, 3H, PhH). (*R*)-Tetrameric cyclic PIE (yield 2.5%): mp 227–230°C; $[\alpha]_D^{25}$ +80.3; ^{1}H NMR in $CDCl_3$ δ 6.98–7.06 (m, 8H, ArH), 7.41–7.44 (m, 16H, ArH), 7.70–7.73 (m, 8H, ArH; 4H, PhH), 7.83–7.92 (m, 24H, ArH), 8.21 (s, 4H, PhH). (*S*)-Tetrameric cyclic PIE (yield 2.1%): mp 231–233°C; $[\alpha]_D^{25}$ −80.8; ^{1}H NMR in $CDCl_3$ δ 6.98–7.06 (m, 8H, ArH), 7.39–7.43 (m, 16H, ArH), 7.70–7.73 (m, 8H, ArH; 4H, PhH), 7.83–7.92 (m, 24H, ArH), 8.21 (s, 4H, PhH). (*R*)-Monomeric cyclic OPE (yield 60%): mp 273–275°C; $[\alpha]_D^{25}$ −470; ^{1}H NMR in $CDCl_3$ δ 7.00–7.03 (m, 2H, ArH), 7.21–7.24 (m, 2H, ArH), 7.34–7.43 (m, 4H, ArH), 7.48–7.68 (m, 2H, PhH), 7.97–8.00 (m, 2H, PhH), 8.01–8.06 (m, 4H, ArH). (*S*)-Monomeric cyclic OPE (yield 57%): mp 272–274°C; $[\alpha]_D^{25}$ +470; ^{1}H NMR in $CDCl_3$

δ 7.00–7.03 (m, 2H, ArH), 7.21–7.24 (m, 2H, ArH), 7.34–7.43 (m, 4H, ArH), 7.48–7.68 (m, 2H, PhH), 7.98–8.00 (m, 2H, PhH), 8.01–8.06 (m, 4H, ArH).

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