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Enantioselective Brønsted base catalyzed [4+2] cycloaddition using novel amino-substituted tetraphenylene derivatives

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ABSTRACT

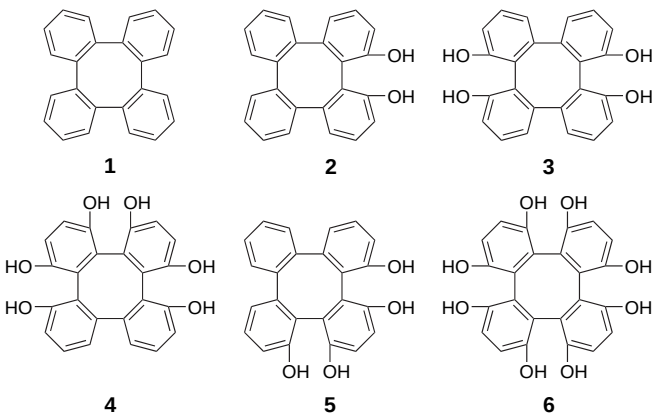
This paper is concerned with the syntheses of 1,8,9,16-tetrahydroxytetraphenylene derivatives and their applications as Brønsted base organocatalysts for [4+2] cycloaddition between anthrone and maleimides. The structural modifications of the catalysts and their related catalytic properties are described and discussed in details.

1. Introduction

Since its discovery in 1926, Diels–Alder reaction is regarded as one of the most important and fascinating transformations in organic synthesis.[1] It has been extensively used as one of the most versatile synthetic tools in the construction of a large number of important building blocks. Many past efforts have shown that chiral metal complexes are efficient catalysts in asymmetric Diels–Alder reaction. Years ago, Corey reviewed the art of enantioselective metal-catalyzed Diels–Alder reaction, which had been developed by his group.[1] In contrast, asymmetric Diels–Alder reaction catalyzed by organocatalysts has only a rather short history and has been neglected for quite a long time.

After the first example was reported by Kagan in 1989,[2] there was limited examples for Brønsted base-catalyzed Diels–Alder reactions.[3–5] More recently, Tan reported a highly enantioselective and diastereoselective Diels–Alder reaction between anthrones and maleimides using modified guanidines.[6] Deng also reported a highly enantioselective and diastereoselective Diels–Alder reaction with pyrones using modified cinchona alkaloids as an acid-base bifunctional catalyst.[7]

Tetraphenylene (tetrabenzo[*a*,*c*,*e*,*g*]cyclooctatetraene) (**1**) is a structurally exceptional molecule featuring a rigid conformation (Scheme 1).[8] It consists of four benzene rings, which are arranged alternatively above and below the mean plane of the molecule. The molecule then belongs to a D_{2d} symmetry point group.[9,10] Due to the high inversion barrier of the central cyclooctatetraene,[11] a chiral version of tetraphenylenes can be obtained by introducing substituents appropriately. A program has then been initiated in our laboratories in the syntheses of building blocks **2**,[12] **3**,[13] **4**,[14] **5**,[15] and



Scheme 1.

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6.[16] Noteworthy is that **2**–**4** are chiral, while **5** and **6** are achiral. Geometrically, **3** is a linear unit containing reactive sites, pointing toward opposite directions.

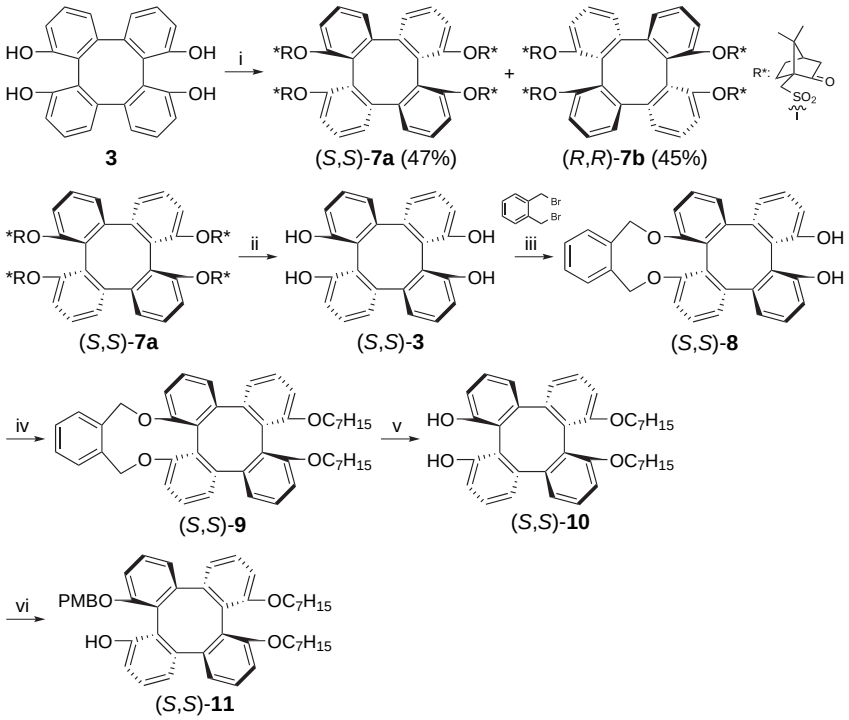
In this article, we would like to report the syntheses of thirteen amino-alcohols derived from tetraphenylenol **3** and their catalytic efficiencies by employing them as organocatalysts in [4+2] cycloaddition reactions.

2. Results and discussion

Scheme 2 shows that tetraphenylenol **3** can be resolved in its optically pure forms after sulfonylation to the two corresponding diastereomeric tetrakis-(*S*)-camphorsulfonates. The diastereomer **7a** was subjected to hydrolysis to give the (*S*,*S*)-tetraphenylenol **3**. Two of the hydroxy groups of (*S*,*S*)-**3** was then protected. The remaining hydroxy groups underwent Williamson ether synthesis to introduce the long lipophilic alkyl chains on the core structure, which significantly enhance the solubility in organic solvents. Diol (*S*,*S*)-**10** was obtained in good yields after hydrogenolysis. Controlled mono-protection of the hydroxy groups that led to the formation of the key intermediate (*S*,*S*)-**11**.

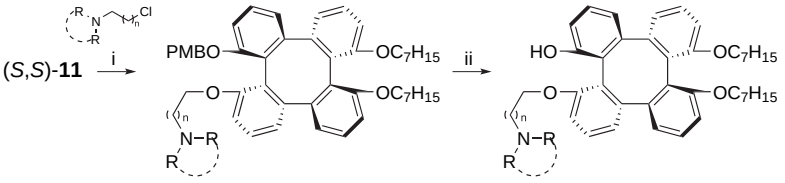
As can be seen in Scheme 3, (*S*,*S*)-**11** was allowed to react with different chloro-substituted amines through substitution reaction. Three different amino-alcohols were accordingly prepared followed by hydrogenolysis.

Alcohol (*S*,*S*)-**10** was also converted to the corresponding cyano-compound (*S*,*S*)-**18** through esterification and palladium-catalyzed cyanation. With (*S*,*S*)-**18** in hand, the hydroxy group was then protected and subsequent reduction by DIBAL-H to give the corresponding aldehyde. After preliminary purification, the resulting aldehyde was allowed to undergo reductive amination with pyrrolidine to give amine (*S*,*S*)-**20** in a moderate yield. Subsequent hydrogenolysis provided amino-alcohol (*S*,*S*)-**21**, in which there is only one carbon between the pyrrolidine and the core tetraphenylene (Scheme 4).



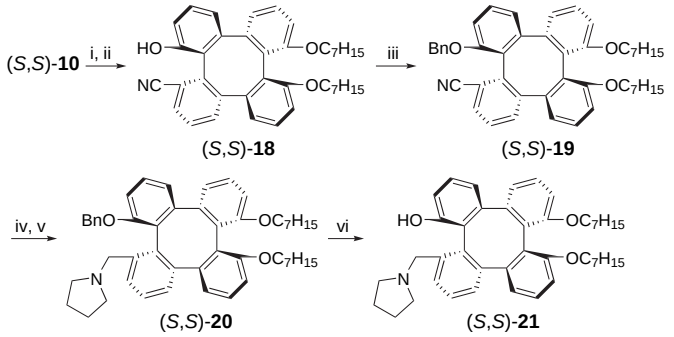
Scheme 2. Reagents and conditions: (i)R*Cl, Et_3N, THF, 0–23 °C. (ii) KOH (aq), MeOH, reflux, 97%. (iii) Cs_2CO_3, DMSO, 38%. (iv) C_7Hi_5Br, Cs_2CO_3, DMF, 80 °C, 88%. (v) H_2, Pd–C, THF, EtOH, 95%. (vi) PMBBr, K_2CO_3, DMF, 79%.

All the four synthesized amino-alcohols were able to catalyze the cycloaddition reactions. As shown in Table 1, (*S*,*S*)-**13** catalyzed the reaction to furnish the desired Diels–Alder adduct in 15.3% ee value (entry 2). The enantioselectivity provided by (*S*,*S*)-**15** was much lower (entry 3). The long distance between the active site (pyrrolidine) and the hydroxy group seems to reduce the influence of the hydroxy group in asymmetric reactions. Unfortunately, neither (*S*,*S*)-**17** nor (*S*,*S*)-**21** demonstrated a better catalytic activity than that of (*S*,*S*)-**13**. The product yields were low at 40% even though complete reactions were resulted. When the pyrrolidine was replaced by *N*,*N*-dimethylamine, only partial enantioselectivity was



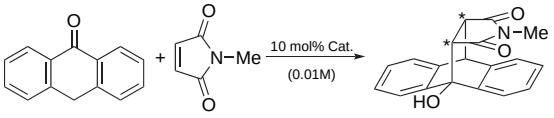
(*S*,*S*)-**12**, R = –$(CH_2CH_2)_2$–, n = 1 (75%) (*S*,*S*)-**13**, R = –$(CH_2CH_2)_2$–, n = 1 (67%)
(*S*,*S*)-**14**, R = –$(CH_2CH_2)_2$–, n = 2 (61%) (*S*,*S*)-**15**, R = –$(CH_2CH_2)_2$–, n = 2 (80%)
(*S*,*S*)-**16**, R = CH_3, n = 1 (72%) (*S*,*S*)-**17**, R = CH_3, n = 1 (75%)

Scheme 3. Reagents and conditions: (i) KI, Cs_2CO_3, DMF, reflux, (ii) H_2, Pd–C, THF, EtOH.



Scheme 4. Reagents and conditions: (i) $PhNTf_2$, collidine, DMAP, CH_2Cl_2, 93%. (ii) Zn $(CN)_2$, $Pd(PPh_3)_4$, DMF, reflux, 48 h, 99%. (iii) BnBr, K_2CO_3, DMF, 93%. (iv) DIBAL-H, CH_2Cl_2, −78 °C, 83%. (v) Pyrrolidine, $NaBH_3CN$, THF, MeOH, 68%. (vi) H_2, Pd–C, THF, EtOH, 70%.

Table 1
Summary of results of the [4+2] cycloaddition reaction in the catalysis of chiral amino-alcohols (*S*,*S*)-**13**, (*S*,*S*)-**15**, (*S*,*S*)-**17**, and (*S*,*S*)-**21**



Entry	Cat.	Solvent/Temp (°C)	Time (min)	Yield (%)	ee% (*S*,*S*)[a]
1	Et_3N	$CHCl_3$/18	15	92	—
2	(*S*,*S*)-**13**	$CHCl_3$/20	40	75	15.3
3	(*S*,*S*)-**15**	$CHCl_3$/16	40	83	4.1
4	(*S*,*S*)-**17**	$CHCl_3$/20	40	40	11.7
5	(*S*,*S*)-**21**	$CHCl_3$/20	40	40	1.3

[a] ee% was determined by HPLC with Chiralcel OD, absolute configuration of **22** was determined by comparison of the optical rotation value with literature value.[2–4]

observed, which implied that the cyclic amine structure showed some noticeable effects on the reactivity as well as the enantioselectivity of the catalyst (entry 4). However, when the distance between the core and the pyrrolidine was shortened to one carbon distance, the enantioselectivity dropped dramatically from 15.3 to 1.3% (entry 5).

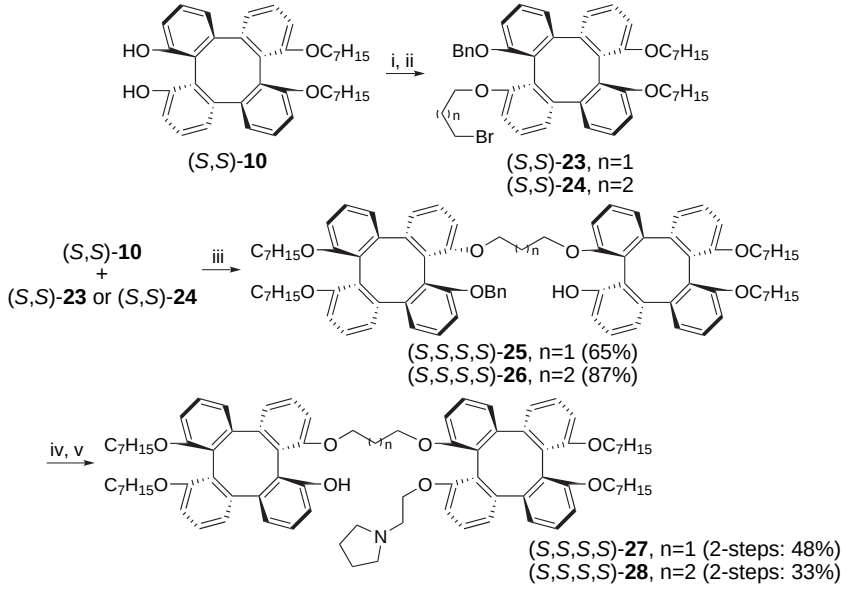
According to the aforementioned results, the spatial environment between the hydroxy group and the pyrrolidine was estimated to be less effective for providing a good enantioselectivity. To improve the spatial environment of the cavity, we designed to link two tetraphenylenes together. Scheme 5 describes the syntheses of two different dimeric forms of amino-alcohol based on the structural framework of the amino-alcohol (*S*,*S*)-**13**.

Thus, alcohol (*S*,*S*)-**10** was first mono-protected and was followed by reaction with 1,3-bromopropane to form bromo-containing compound (*S*,*S*)-**23**. Compound (*S*,*S*)-**24** was obtained in the same manner by changing 1,3-dibromopropane into 1,4-dibromobutane. Either (*S*,*S*)-**23** or (*S*,*S*)-**24** reacted with a slightly excess (*S*,*S*)-**10**, giving dimeric alcohols (*S*,*S*,*S*,*S*)-**25** and (*S*,*S*,*S*,*S*)-**26**, respectively. Each of the dimeric alcohols was allowed to undergo substitution reaction and hydrogenation to provide the dimeric amino-alcohols (*S*,*S*,*S*,*S*)-**27** and (*S*,*S*,*S*,*S*)-**28**.

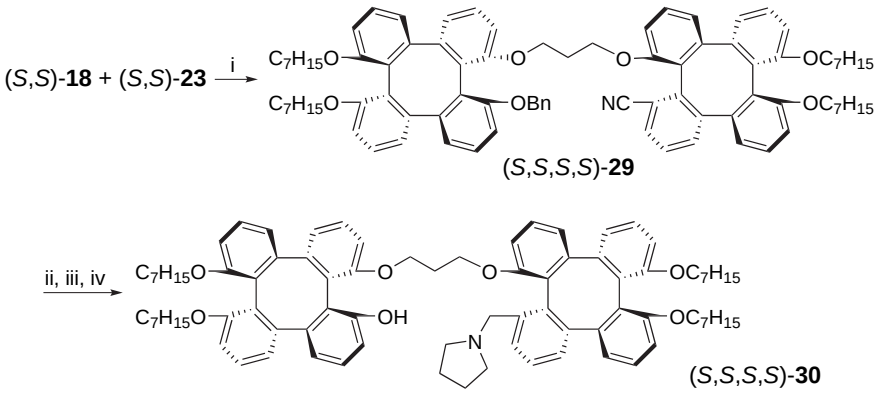
Further modifications were carried out based on the structural framework of (*S*,*S*,*S*,*S*)-**27**, as described in Scheme 6. Alcohol (*S*,*S*)-**18** was coupled with bromo-containing compound (*S*,*S*)-**23**, affording the dimeric cyano-compound (*S*,*S*,*S*,*S*)-**29**. Further reduction of the cyano group and reductive amination with pyrrolidine gave the corresponding amine. Subsequent hydrogenolysis gave the amino-alcohol (*S*,*S*,*S*,*S*)-**30** in an acceptable yield.

Furthermore, compound (*S*,*S*)-**31** was prepared from diol (*S*,*S*)-**10** using a similar method as that for the preparation of compound (*S*,*S*)-**23** (Scheme 7). Cross-coupling of (*S*,*S*)-**18** and (*S*,*S*)-**31** gave the cyano-compound (*S*,*S*,*S*,*S*)-**32**, in which a two-carbon linkage was placed in-between the two tetraphenylenes. Similar to the preparation of (*S*,*S*,*S*,*S*)-**30**, amino-alcohol (*S*,*S*,*S*,*S*)-**34** was obtained in an acceptable yield after a three-step reaction. The catalytic properties of each dimeric form of amino-alcohol in Diels–Alder reaction are summarized in Table 2.

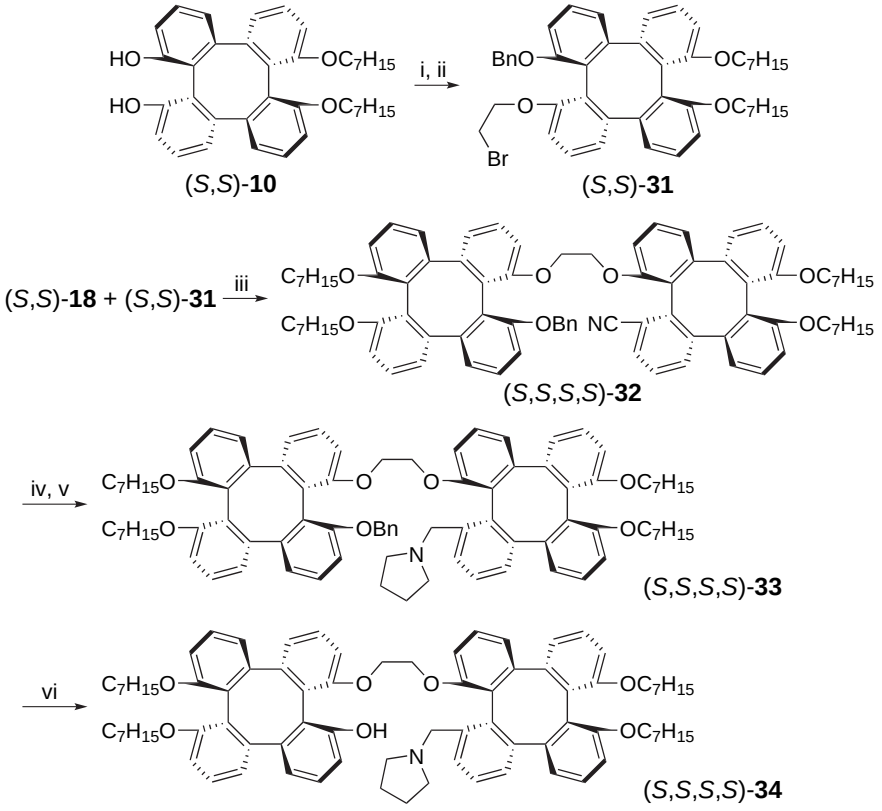
As expected, the dimeric form of the amino-alcohol (*S*,*S*,*S*,*S*)-**27** provided a better enantioselectivity than the monomeric form (*S*,*S*)-**13**, and up to 25.3% ee was obtained (entry 2). The product yield of **22** was also slightly increased and a lower loading of catalyst was needed. However, when the distance of the ether linkage between the two tetraphenylenes increased from three-carbon to four-carbon, the enantioselectivity dropped to only 10% (entry 3). This has led to an observation that the cavity size of (*S*,*S*,*S*,*S*)-**28** was



Scheme 5. Reagents and conditions: compound (*S*,*S*)-**23**: (i) BnBr, K_2CO_3, DMF, 89%. (ii) 1,3-Dibromopropane, Cs_2CO_3, DMF, 80 °C, 95%. Compound (*S*,*S*)-**24**: (i) BnBr, K_2CO_3, DMF, 89%. (ii) 1,4-Dibromobutane, Cs_2CO_3, DMF, 80 °C, 95%. (iii) Cs_2CO_3, DMF, 80 °C. (iv) 1-(2-Chloroethyl) pyrrolidine, KI, Cs_2CO_3, DMF, reflux, (v) H_2, Pd–C, THF, EtOH.

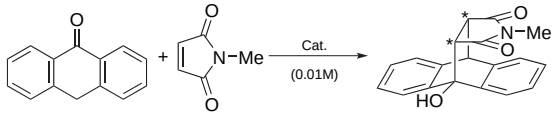


Scheme 6. Reagents and conditions: (i) Cs_2CO_3, DMF, 80 °C, 81%. (ii) DIBAL-H, CH_2Cl_2, −78 °C, 99%. (iii) Pyrrolidine, $NaBH_3CN$, MeOH, 54%. (iv) H_2, Pd−C, THF, 67%.



Scheme 7. Reagents and conditions: (i) BnBr, K_2CO_3, DMF, 89%. (ii) 1,2-Dibromopropane, CS_2CO_3, acetone, reflux, 74%. (iii) CS_2CO_3, acetone, reflux, 70%. (iv) DIBAL-H, CH_2Cl_2, −78 °C, 98%. (v) Pyrrolidine, $NaBH_3CN$, THF, 46%. (vi) H_2, Pd−C, THF, 68%.

Table 2
Summary of results of the [4+2] cycloaddition reaction in the catalysis of chiral amino-alcohols (*S*,*S*)-**13**, (*S*,*S*,*S*,*S*)-**27**, (*S*,*S*,*S*,*S*)-**28**, (*S*,*S*,*S*,*S*)-**30**, (*S*,*S*,*S*,*S*)-**33**, and (*S*,*S*,*S*,*S*)-**34**



Entry	Cat. (mol %)	Solvent/Temp (°C)	Time (min)	Yield (%)	ee% (*S*,*S*)[a]
1	(*S*,*S*)-**13** (10)	$CHCl_3$/20	40	75	15.3
2	(*S*,*S*,*S*,*S*)-**27** (5)	$CHCl_3$/20	60	85	25.3
3	(*S*,*S*,*S*,*S*)-**28** (5)	$CHCl_3$/20	60	85	10.0
4	(*S*,*S*,*S*,*S*)-**30** (5)	$CHCl_3$/20	100	81	35.9
5	(*S*,*S*,*S*,*S*)-**34** (5)	$CHCl_3$/21	120	91.3	41.8
6	(*S*,*S*,*S*,*S*)-**33** (5)	$CHCl_3$/0	120	89	11.5
7	(*S*,*S*,*S*,*S*)-**34** (5)	$CHCl_3$/0	120	88	31.5

[a] ee% was determined by HPLC with Chiralcel OD, absolute configuration of **22** was determined by comparison of the optical rotation value with literature value.[2–4]

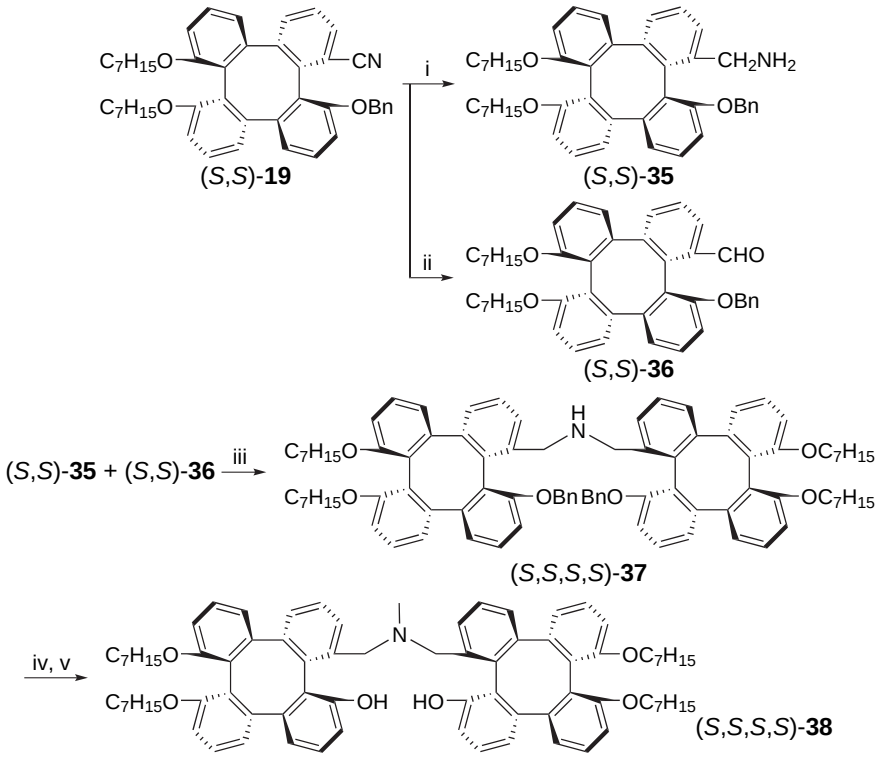
too large and the conformation of (*S*,*S*,*S*,*S*)-**28** was much flexible, which gave a low enantioselectivity of product.

At room temperature, (*S*,*S*,*S*,*S*)-**30** was found to have a similar reactivity as that of (*S*,*S*,*S*,*S*)-**27** based on TLC monitoring. Prolonged reaction time was used to ensure the completeness of the reaction. Gratifyingly, the enantioselectivity was found to be improved, which was upgraded to 35.9% ee (entry 4). Amino-alcohol (*S*,*S*,*S*,*S*)-**34** provided a better enantioselectivity than (*S*,*S*,*S*,*S*)-**30** at room temperature (entry 5). Unfortunately, amino-alcohol (*S*,*S*,*S*,*S*)-**34** did not show improvement in the ee value when the reaction was carried out at a lower temperature (entry 6). The conformation of the catalyst may change to a less favorable form, leading to a low ee value. The only difference between the chiral amine (*S*,*S*,*S*,*S*)-**33** and chiral amino-alcohol (*S*,*S*,*S*,*S*)-**34** is the protected hydroxy group. The absence of the hydroxy group did not affect the reactivity of the catalyst, but largely deteriorated the enantioselectivity of the catalyst (entries 6 and 7). This further demonstrated the importance of

the hydroxy group in the chiral catalytic induction, which might imply the involvement of hydrogen bonding between the catalyst and the substrate in the transition state of the catalysis.

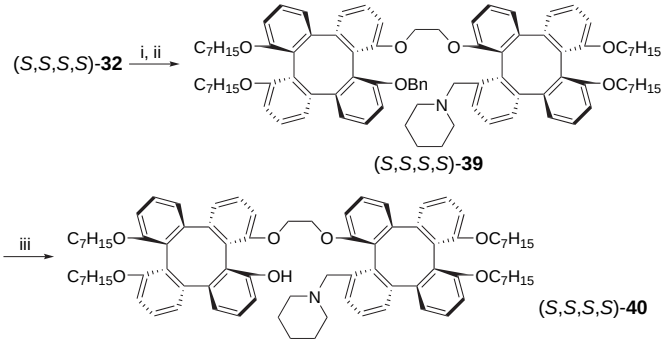
Based on the above line of thinking, four different amino-alcohols were synthesized.

Cyano-compound (*S*,*S*)-**19** was reduced to the corresponding primary amine (*S*,*S*)-**35** (Scheme 8). Aldehyde (*S*,*S*)-**36**, which was also generated from (*S*,*S*)-**19**, was allowed to undergo reductive amination with the amine (*S*,*S*)-**35** and the cross-coupled amine (*S*,*S*,*S*,*S*)-**37** was obtained in good yield. Subsequent reductive amination with formaldehyde and hydrogenolysis gave the amino-alcohol (*S*,*S*,*S*,*S*)-**38** in an acceptable yield.



Scheme 8. Reagents and conditions: (i) LAH, THF, reflux, 85%. (ii) DIBAL-H, CH_2Cl_2, −78 °C, 98%. (iii) $NaBH_3CN$, THF, MeOH, 80%. (iv) HCHO, $NaBH_4$, TFA, THF, 85%. (v) H_2, Pd–C, THF, 48%.

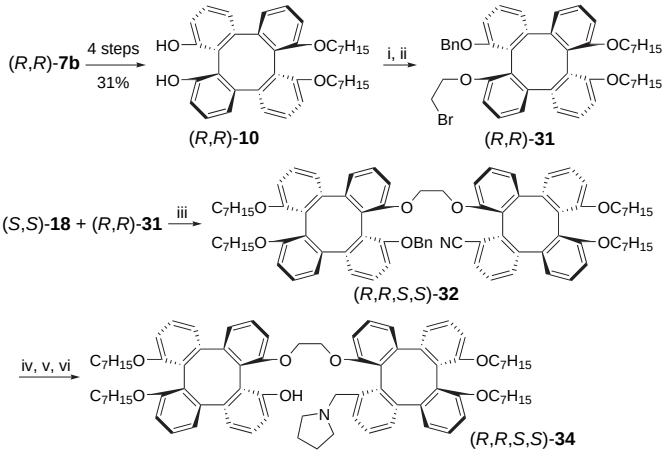
On the other hand, cyano-compound (*S*,*S*,*S*,*S*)-**32** underwent reduction and was then allowed to react with piperidine, giving chiral amine (*S*,*S*,*S*,*S*)-**39** (Scheme 9). Subsequent hydrogenation afforded amino-alcohol (*S*,*S*,*S*,*S*)-**40**.



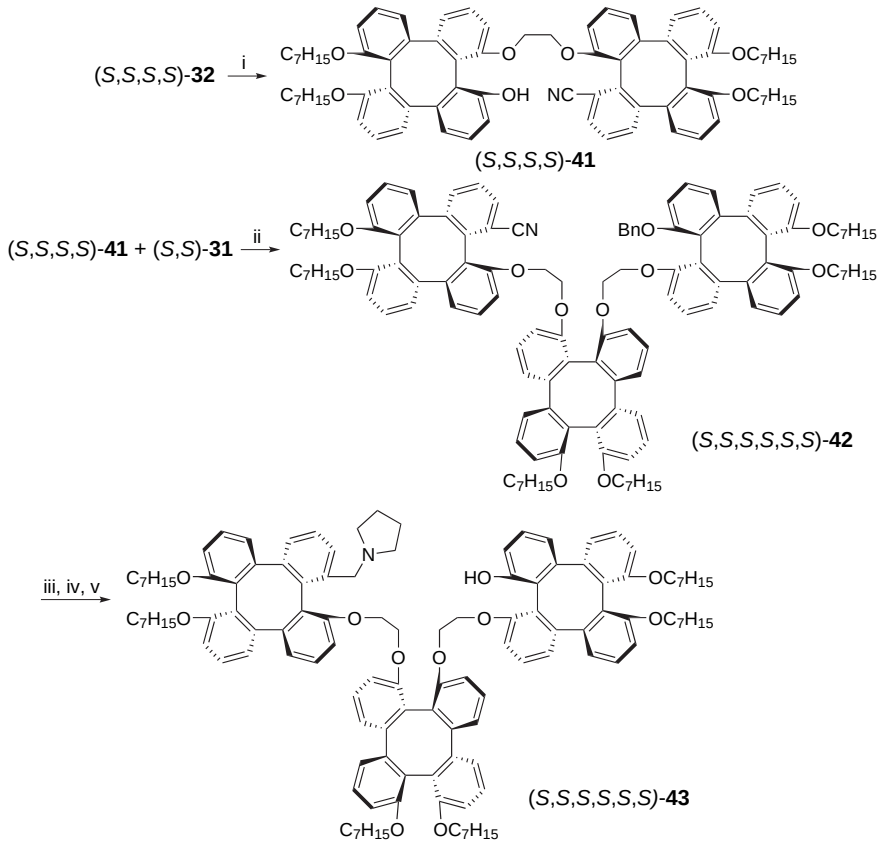
Scheme 9. Reagents and conditions: (i) DIBAL-H, CH_2Cl_2, −78 °C, 98%. (ii) Piperidine, $NaBH_3CN$, THF, MeOH, 65%. (iii) H_2, Pd–C, THF, 86%.

To investigate any possibilities of chirality mismatch during the catalysis, an amino-alcohol with mixed chiralities (*R*,*R*,*S*,*S*)-**34** was synthesized. Utilizing the same method for the preparation of (*S*,*S*,*S*,*S*)-**34**, the bromo-compound (*R*,*R*)-**31** was synthesized from tetrakis-(*S*)-camphorsulfonate (*R*,*R*)-**7b** through a six-step sequence. Cross-coupling between (*S*,*S*)-**18** and (*R*,*R*)-**31** gave the cyano-compound (*R*,*R*,*S*,*S*)-**32** in good yield. After reduction by DIBAL-H and reductive amination with pyrrolidine, the corresponding amine was obtained in good yield. Hydrogenolysis of the amine provided amino-alcohol (*R*,*R*,*S*,*S*)-**34**, in which the hydroxy group was orientated according to the *R* configuration of the tetraphenylene (Scheme 10).

In order to further increase the cavity size of the catalyst, we turned our effort to synthesize a trimeric form of tetraphenylenes. As revealed in Scheme 11, dimeric cyano-compound (*S*,*S*,*S*,*S*)-**32** was deprotected by hydrogenolysis to generate alcohol (*S*,*S*,*S*,*S*)-**41**. Compound (*S*,*S*,*S*,*S*)-**41** was coupled with (*S*,*S*)-**31** to furnish the trimeric cyano-compound (*S*,*S*,*S*,*S*,*S*,*S*)-**42** in a moderate yield.



Scheme 10. Reagents and conditions: (i) BnBr, K_2CO_3, DMF, 89%. (ii) 1,2-Dibromopropane, Cs_2CO_3, acetone, reflux, 74%. (iii) Cs_2CO_3, acetone, reflux, 83%. (iv) DIBAL-H, CH_2Cl_2, −78 °C, 98%. (v) Pyrrolidine, $NaBH_3CN$, THF, 75%. (vi) H_2, Pd–C, THF, 50%.

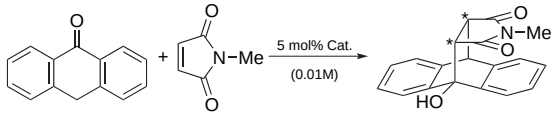


Scheme 11. Reagents and conditions: (i) H_2, Pd–C, THF, 70%. (ii) Cs_2CO_3, acetone, reflux, 43%. (iii) DIBAL-H, CH_2Cl_2, −78 °C. (iv) Pyrrolidine, $NaBH_3CN$, THF, two-step: 58%. (v) H_2, Pd–C, THF, 61%.

Compound (*S*,*S*,*S*,*S*,*S*,*S*)-**42** underwent aldehyde generation and reductive amination to give the corresponding amine. The trimeric form of amino-alcohol (*S*,*S*,*S*,*S*,*S*,*S*)-**43** was obtained in 61% after hydrogenolysis.

The catalytic properties of the four different amino-alcohols in Diels–Alder reaction are summarized in Table 3.

Table 3
Summary of results of the [4+2] cycloaddition reaction in the catalysis of chiral amino-alcohols (*S*,*S*,*S*,*S*)-**34**, (*S*,*S*,*S*,*S*)-**38**, (*S*,*S*,*S*,*S*)-**40**, (*R*,*R*,*S*,*S*)-**34**, and (*S*,*S*,*S*,*S*,*S*,*S*)-**43**



Entry	Cat. (mol %)	Solvent/Temp (°C)	Time (min)	Yield (%)	ee% (*S*,*S*)[a]
1	(*S*,*S*,*S*,*S*)-**34**	$CHCl_3$/21	120	91.3	41.8
2	(*S*,*S*,*S*,*S*)-**38**	$CHCl_3$/21	1260	58	2.5
3	(*S*,*S*,*S*,*S*)-**40**	$CHCl_3$/0	120	68.8	15.5
4	(*R*,*R*,*S*,*S*)-**34**	$CHCl_3$/0	120	84	10.9
5	(*S*,*S*,*S*,*S*,*S*,*S*)-**43**	$CHCl_3$/0	120	88	9.1

[a] ee% was determined by HPLC with Chiralcel OD, absolute configuration of **22** was determined by comparison of the optical rotation value with literature value.[2–4]

The change of the amine group from pyrrolidine into a bulky alkyl tertiary amine greatly retarded the reactivity of the catalyst, not only on the rate of reaction, but also on the yield of the Diels–Alder adduct. The amine group positioned at the centre of the linking chain was unfavorable for asymmetric Diels–Alder reactions (entry 2). For this reason, (*S*,*S*,*S*,*S*)-**38** provided almost no enantioselectivity for the reaction.

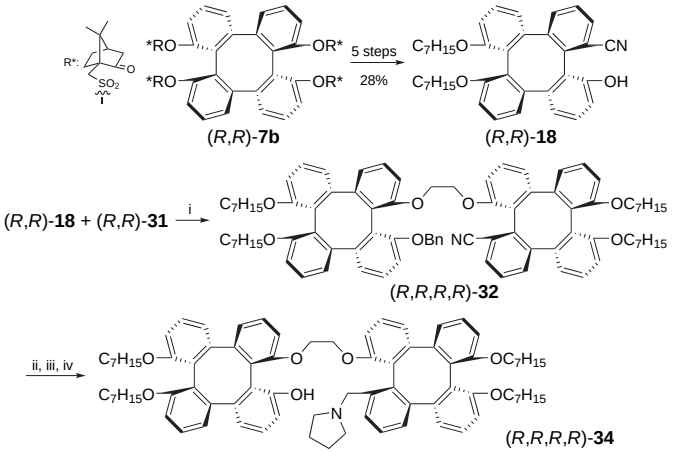
Increasing the ring size of the amine decreased the product yield of the Diels–Alder adduct, as well as the ee value of the Diels–Alder adduct (entry 3). The result of entry 4 proved that the hydroxy group orientation was crucial to the enantioselectivity of the catalyst. If the hydroxy group was orientated in an opposite direction, the enantioselectivity of (*R*,*R*,*S*,*S*)-**34** (entry 4) was comparable with that of protected amine (*S*,*S*,*S*,*S*)-**33** (entry 6 in Table 2). The conformation of the trimeric form (*S*,*S*,*S*,*S*,*S*,*S*)-**43** was found ineffective to improve the enantioselectivity (entry 5).

Finally, to prove that the chiral induction was completely based on the chirality of the tetraphenylene, the enantiomer of (*S*,*S*,*S*,*S*)-**34** was also synthesized. Thus, compound (*R*,*R*,*R*,*R*)-**34** was synthesized from tetrakis-(*S*)-camphorsulfonate (*R*,*R*)-**7b** in a way similar to the same synthetic route for amino-alcohol (*S*,*S*,*S*,*S*)-**34** (Scheme 12).

Amino-alcohol **34** was chosen as the best catalyst for the Diels–Alder cycloaddition reaction among all the aforementioned synthetic amino-alcohols. The corresponding enantiomers were tested with different solvent systems and different substituent on the maleimide.

Fig. 1 illustrates the plausible reaction mechanism of the catalytic Diels–Alder cycloaddition by (*S*,*S*,*S*,*S*)-**34**. As can be seen, the pyrrolidine moiety will first interact with anthrone to generate the corresponding enolate and the enolate will then position itself near the catalyst due to electrostatic interaction. It is suggested that the tetraphenylene, in its (*S*,*S*) configuration, will provide a chiral environment during the catalytic process. With the presence of the hydroxy group, the *N*-methylmaleimide will be directed toward the enolate from a more favorable direction by hydrogen bonding.

As revealed in Table 4, the result of entry 2 strongly substantiated that the enantioselectivity of the catalyst was chirality-dependent, because (*R*,*R*,*R*,*R*)-**34** provided the opposite enantioselectivity to that of (*S*,*S*,*S*,*S*)-**34**.



Scheme 12. Reagents and conditions: (i) Cs_2CO_3, acetone, reflux, 70%. (ii) DIBAL-H, CH_2Cl_2, −78 °C. (iii) Pyrrolidine, $NaBH_3CN$, THF, two-steps: 46%. (iv) H_2, Pd–C, THF, 68%.

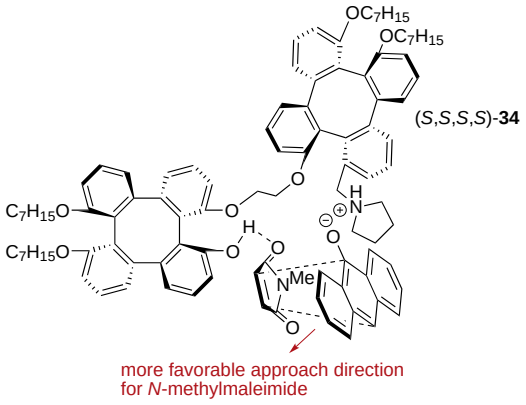
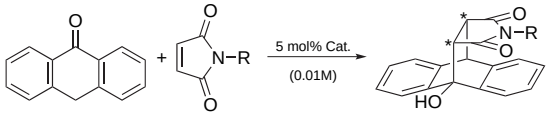


Fig. 1. The plausible reaction mechanism of the catalytic Diels–Alder cycloaddition by (*S*,*S*,*S*,*S*)-**34**.

Table 4
Summary of results of the [4+2] cycloaddition reaction in the catalysis of chiral amino-alcohols (*S*,*S*,*S*,*S*)-**34** and (*R*,*R*,*R*,*R*)-**34** at different conditions



Entry	Cat. (mol %)	Solvent/Temp(°C)	R	Yield (%)	ee% (*S*,*S*)[a]
1	(*S*,*S*,*S*,*S*)-**34**	$CHCl_3$/21	Me (**22**)	91.3	41.8
2	(*R*,*R*,*R*,*R*)-**34**	$CHCl_3$/24	Me (**22**)	92	−41.1 (*R*,*R*)
3	(*R*,*R*,*R*,*R*)-**34**	Toluene/23	Me (**22**)	82	−43.3 (*R*,*R*)
4	(*R*,*R*,*R*,*R*)-**34**	TBME/23	Me (**22**)	93	−5.7 (*R*,*R*)
5	(*S*,*S*,*S*,*S*)-**34**	$CHCl_3$/21	Ph (**44**)	89	31.9
6	(*S*,*S*,*S*,*S*)-**34**	$CHCl_3$/21	*i*-Bu (**45**)	76	0.9
7	(*S*,*S*,*S*,*S*)-**34**	$CHCl_3$/21	Cyclohexyl (**46**)	52	17.1
8	(*S*,*S*,*S*,*S*)-**34**	$CHCl_3$/21	*m*-NO_2Ph (**47**)	67	26.3

[a] ee% was determined by HPLC with Chiralcel OD, absolute configuration of each Diels–Alder adduct was determined by comparison of the optical rotation value or the retention time with literature value.[2–4]

Compound (*R*,*R*,*R*,*R*)-**34** performed similarly in toluene as well as in $CHCl_3$, except a lower product yield was obtained in the former solvent. When the reaction was carried out in *tert*-butyl methyl ether (TBME), a similar product yield was obtained but the ee value decreased dramatically. This may be due to the hydrogen bonding interaction between TBME and the hydroxy group of the catalyst. It is likely that more phenolic tautomer 9-anthracenol was formed in TBME that manifested an interference effect.

The increase in size of the substituent on the maleimide led to the decrease of the ee value of the Diels–Alder adduct. Notably, flexible alkyl chains like *iso*-butyl group caused severe effect to the enantioselectivity of the catalyst, while cyclic or aromatic substituent caused relatively less effect on the ee value of the Diels–Alder adduct. Such variation should be counted on the strength of the directing effect by the hydroxy group of the catalyst after the formation of the transition state with anthrone.

3. Conclusion

In summary, over 10 chiral amino-alcohols were synthesized and tested for the enantioselectivity of the Diels–Alder cycloaddition reaction between anthrone and maleimide. Amino-alcohol **34** was found to be the best performer among all, and up to 40% ee was achieved. The chirality of the Diels–Alder adduct was found to be dependent on the chirality of the tetraphenylenes in the catalyst, indicating that the chirality of tetraphenylene is the key chiral factor to affect the enantioselectivity of the cycloaddition. Moreover, up to 80% recovery of all the synthetic amino-alcohol catalysts were achieved after the Diels–Alder reaction without lost of catalytic properties. Further efforts will be put to introduce bulky alkyl substituents on the *ortho*-positions of the phenyl rings on the tetraphenylenes, which may magnify the chiral effect by the tetraphenylenes. On the other hand, changing the hydroxy group into a much stronger hydrogen bond donor will expectedly enhance the directing effect during the catalytic procedure. Based on mechanistic consideration, our catalysts may also be potential catalysts for asymmetric Michael addition reaction or asymmetric Morita–Baylis–Hillman reaction.

4. Experimental

4.1. General information

All reagents and solvents were reagent grade. Further purification and drying following the guidelines of Perrin and Armarego were used when necessary.[17] Organic solvents were concentrated under reduced pressure on a rotary evaporator. Chromatographic purification of products was performed on Macherey Nagel Kieselgel 60 M (230–400 mesh). Thin-layer chromatography (TLC) was performed on E. Merck silica gel 60 F_{254} (0.25 mm thickness) coated on aluminum plates. Visualization of the developed chromatogram was performed by a spray of 5% w/v dodecamolybdophosphoric acid in ethanol and subsequent heating. Melting points were measured with a Reichert apparatus in Celsius degrees and are uncorrected. Optical rotations were obtained with a Perkin–Elmer model 341 polarimeter, operating at 589 nm. Nuclear magnetic resonance (NMR) spectra were recorded with a Bruker DPX300 NMR spectrometer at 300 MHz (^{1}H) or at 75 MHz (^{13}C) or a Bruker ADVANCE-III NMR spectrometer at 400 MHz (^{1}H) or at 100 MHz (^{13}C). All NMR measurements were carried out at room temperature in deuterated solution and were internally referenced to residual proton solvent signals (note: $CDCl_3$ referenced at δ 7.26 in ^{1}H and δ 77.16 for central line of the triplet in ^{13}C; acetone-d_6 referenced at δ 2.05 in ^{1}H and δ 29.84 for central line of the septet in ^{13}C; DMSO-d_6 referenced at δ 2.50 in ^{1}H and δ 39.52 for central line of the quintet in ^{13}C; CD_2Cl_2 referenced at δ 5.32 in ^{1}H and δ 53.10 for central line of the quintet in ^{13}C). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, p=pentet, br s=broad singlet, dd=doublet of doublets, dt=doublet of triplets, td=triplet of doublets, m=multiplet), integration, coupling constant (Hz) and assignment. Data for ^{13}C NMR are reported in terms of chemical shift. Mass spectrometry (MS) and high resolution mass spectrometry (HRMS) were measured on a ThermoFinnigan MAT 95XL

and Bruker Autoflex MALDI-TOF MS. Elemental analyses were carried out by Shanghai Institute of Organic Chemistry, the Chinese Academy of Science, China. HPLC analysis was performed on a Hewlett Packard Series 1050 HPLC, or Hewlett Packard Series 1100 HPLC, or Agilent 1100 HPLC with a diode array UV detector (λ=214–258 nm), using Chiralcel OD (0.46 cm×25 cm), Chiracel OD Guard (0.46×5 cm), and Chiralpak AD-H (0.46 cm×25 cm) as noted for each compound.

4.2. General procedure for the catalytic Diels–Alder reaction

To a solution of amino-alcohol (*S*,*S*,*S*,*S*)-**34** (5 mol %, 0.01 M) in $CHCl_3$, anthrone (1.1 equiv) was added. After stirring for 10 min, maleimide (1 equiv) was added in one portion to the mixture. The stirring was continued for another 2 h. The mixture was directly purified by column chromatography on silica gel (EtOAc/*n*-hexanes) to yield the desired DA product.

Column chromatography on silica gel (MeOH/$CHCl_3$, 1:40) was used to recover the catalyst.

*4.2.1. 4-Hydroxy-2-methyl-3a,4,9,9a-tetrahydro-4,9[1′,2′]-benzeno-1H-benz[f]isoindole-1,3(2H)-dione (**22**).* Column chromatography on silica gel (3 g, EtOAc/hexanes, 1:5) gave pure **22** (27 mg, 93%) as colorless solids from *N*-methylmaleimide (11 mg, 0.09 mmol): R_f=0.29 (EtOAc/hexanes, 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.50 (s, 3H, CH_3), 3.11 (d, *J*=8.6 Hz, 1H, C*H*), 3.32 (dd, *J*=3.4, 8.5 Hz, 1H, C*H*), 4.50 (br s, 1H, O*H*), 4.73 (d, *J*=3.4 Hz, 1H, C*H*), 7.13–7.28 (m, 5H, Ar*H*), 7.37 (d, *J*=7.2 Hz, 1H, Ar*H*), 7.48 (d, *J*=7.4 Hz, 1H, Ar*H*), 7.69 (d, *J*=7.4 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.4, 44.6, 47.7, 50.9, 120.9, 120.9, 123.8, 124.6, 126.9, 126.9, 127.2, 127.3, 136.5, 139.1, 140.8, 142.5, 176.6, 178.0.

The ee values were determined by chiral HPLC; CHIRALCEL OD with guard column; hexanes/2-propanol 50:50; flow rate 0.75 mL/min; temp 25 °C; detection UV 214 nm; retention time: 11.1 min (*R*) and 13.5 min (*S*).

*4.2.2. 4-Hydroxy-2-phenyl-3a,4,9,9a-tetrahydro-4,9[1′,2′]-benzeno-1H-benz[f]isoindole-1,3(2H)-dione (**44**).* Column chromatography on silica gel (3 g, EtOAc/hexanes, 1:8) gave pure product (19.7 mg, 89%) as colorless solids from *N*-phenylmaleimide (10.5 mg, 0.06 mmol): R_f=0.29 (EtOAc/hexanes, 1:6); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.27 (d, *J*=8.7 Hz, 1H, C*H*), 3.48 (dd, *J*=3.3, 8.7 Hz, 1H, C*H*), 4.59 (br s, 1H, O*H*), 4.84 (d, *J*=3.3 Hz, 1H, C*H*), 6.48–6.51 (m, 2H, Ar*H*), 7.24–7.34 (m, 8H, Ar*H*), 7.42 (d, *J*=7.2 Hz, 1H, Ar*H*), 7.57 (d, *J*=7.5 Hz, 1H, Ar*H*), 7.75 (d, *J*=7.2 Hz, 1H, Ar*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ 44.9, 47.8, 50.9, 121.0, 121.2, 123.9, 124.8, 126.4, 127.0, 127.1, 127.4, 129.1, 129.3, 131.0, 136.7, 139.0, 141.0, 142.4, 175.8, 177.3.

The ee values were determined by chiral HPLC; CHIRALPAK AD-H; hexanes/2-propanol 80:20; flow rate 0.75 mL/min; temp 25 °C; detection UV 214 nm; retention time: 29.9 min (*S*) and 38.2 min (*R*).

*4.2.3. 4-Hydroxy-2-isobutyl-3a,4,9,9a-tetrahydro-4,9[1′,2′]-benzeno-1H-benz[f]isoindole-1,3(2H)-dione (**45**).* Column chromatography on silica gel (3 g, EtOAc/hexanes, 1:8) gave pure product (22.6 mg, 76%) as colorless solids from maleimide[18] (13 mg, 0.08 mmol): R_f=0.49 (EtOAc/hexanes, 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.43–0.47 (m, 6H, CH_3), 1.37–1.47 (m, 1H, C*H*), 2.89–2.98 (m, 2H, CH_2), 3.11 (d, *J*=8.9 Hz, 1H, C*H*), 3.30 (dd, *J*=3.4, 8.8 Hz, 1H, C*H*), 4.48 (br s, 1H, O*H*), 4.73 (d, *J*=3.2 Hz, 1H, C*H*), 7.12–7.28 (m, 5H, Ar*H*), 7.35 (d, *J*=7.2 Hz, 1H, Ar*H*), 7.51 (d, *J*=7.4 Hz, 1H, Ar*H*), 7.67 (d, *J*=7.4 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.0, 20.1, 27.2, 44.5, 46.4, 47.5, 50.6, 120.8, 121.2, 123.8, 124.7, 126.8, 126.9, 127.4, 127.5, 136.9, 139.5, 141.2, 142.9, 176.8, 178.3.

The ee values were determined by chiral HPLC; CHIRALCEL OD; hexanes/2-propanol 50:50; flow rate 0.75 mL/min; temp 25 °C; detection UV 214 nm; retention time: 10.4 min (*S*) and 15.7 min (*R*).

*4.2.4. 4-Hydroxy-2-cyclohexyl-3a,4,9,9a-tetrahydro-4,9[1′,2′]-benzeno-1H-benz[f]isoindole-1,3(2H)-dione (**46**).* Column chromatography on silica gel (3 g, EtOAc/hexanes, 1:12) gave pure product (15.9 mg, 52%) as colorless solids from maleimide[18] (14.8 mg, 0.08 mmol): R_f=0.28 (EtOAc/hexanes, 1:12); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.76–0.87 (m, 2H, CH_2), 0.98–1.13 (m, 3H, CH_2), 1.52–1.71 (m, 5H, CH_2), 3.01 (d, *J*=8.6 Hz, 1H, C*H*), 3.23 (dd, *J*=3.6, 8.6 Hz, 1H, C*H*), 3.46–3.54 (m, 1H, C*H*), 4.61 (br s, 1H, O*H*), 4.71 (d, *J*=3.5 Hz, 1H, C*H*), 7.13–7.28 (m, 5H, Ar*H*), 7.36 (d, *J*=7.2 Hz, 1H, Ar*H*), 7.49 (d, *J*=7.4 Hz, 1H, Ar*H*), 7.68 (d, *J*=7.4 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.0, 25.7, 27.9, 28.1, 44.8, 47.1, 50.1, 51.6, 120.8, 121.2, 123.8, 124.7, 126.8, 126.9, 127.1, 127.2, 136.7, 139.2, 141.1, 142.7, 176.7, 178.4.

The ee values were determined by chiral HPLC; CHIRALPAK AD-H; hexanes/2-propanol 60:40; flow rate 0.75 mL/min; temp 25 °C; detection UV 214 nm; retention time: 10.2 min (*S*) and 12.1 min (*R*).

*4.2.5. 4-Hydroxy-2-(3-nitrophenyl)-3a,4,9,9a-tetrahydro-4,9[1′,2′]-benzeno-1H-benz[f]isoindole-1,3(2H)-dione (**47**).* Column chromatography on silica gel (2 g, EtOAc/hexanes, 1:2) gave pure product (17.2 mg, 67%) as colorless solids from maleimide[19] (13.9 mg, 0.06 mmol): R_f=0.15 (EtOAc/hexanes, 1:4); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 3.34 (d, *J*=8.6 Hz, 1H, C*H*), 3.56 (dd, *J*=3.5, 8.6 Hz, 1H, C*H*), 4.68 (br s, 1H, O*H*), 4.85 (d, *J*=3.5 Hz, 1H, C*H*), 6.91–6.94 (m, 1H, Ar*H*), 7.23–7.38 (m, 6H, Ar*H*), 7.45–7.57 (m, 3H, Ar*H*), 7.71 (d, *J*=7.2 Hz, 1H, Ar*H*), 8.15–8.17 (m, 1H, Ar*H*); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 44.5, 47.5, 50.7, 77.0, 120.4, 120.6, 121.3, 123.3, 123.6, 124.4, 126.6, 127.1, 127.2, 129.7, 131.7, 132.0, 136.4, 138.4, 140.6, 141.8, 148.0, 174.5, 176.1.

The ee values were determined by chiral HPLC; CHIRALPAK AD-H; hexanes/2-propanol 60:40; flow rate 0.75 mL/min; temp 25 °C; detection UV 214 nm; retention time: 38.4 min (*S*) and 48.5 min (*R*).

4.3. Synthesis and characterization

*4.3.1. Resolution of 1,8,9,16-tetrahydroxytetraphenylene (**3**)[13].* Compound**3** (1 g, 2.7 mmol) was first dissolved in dry THF (30 mL) under nitrogen atmosphere, followed by the subsequent addition of Et_3N (3.7 mL, 27 mmol) and (1*S*)-camphor-10-sulfonyl chloride (3.2 g, 12.2 mmol) at 0 °C. The mixture was warmed to room temperature and stirred overnight. The mixture was diluted with water (100 mL) and extracted with CH_2Cl_2 (20 mL×3). The combined organic layer was washed with aqueous HCl solution (2 M, 30 mL×2) successively and was then dried over anhydrous Na_2SO_4. After concentration, the residue was purified by column chromatography on silica gel (150 g, EtOAc/toluene, 1:4) to give the two diastereomers. The less polar fraction isolated was diastereomer (*S*,*S*)-**7a** (1.55 g, 47%) as colorless solids: mp 167–168 °C (lit.:[13] 168–169 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.80 (s, 12H, 4×CH_3), 1.04 (s, 12H, 4×CH_3), 1.35–1.42 (m, 4H, 2×CH_2), 1.48–1.55 (m, 4H, 2×CH_2), 1.88 (s, 2H, CH_2), 1.93 (s, 2H, CH_2), 1.95–2.04 (m, 4H, 2×CH_2), 2.06–2.08 (m, 4H, 2×CH_2), 2.29–2.38 (m, 8H, 4×CH_2), 2.99 (d, *J*=15 Hz, 4H, 2×SCH_2), 3.15 (d, *J*=15 Hz, 4H, 2×SCH_2), 7.30–7.37 (m, 8H, Ar*H*), 7.38–7.40 (m, 4H, Ar*H*); MS (ESI) *m*/*z* 1247 $[M+Na]^+$.

The more polar fraction isolated was diastereomer (*R*,*R*)-**7b** (1.48 g, 45%) as colorless solids: mp 159–160 °C (lit.:[13] 160–161 °C); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.77 (s, 12H, 4×CH_3), 0.94 (s, 12H, 4×CH_3), 1.38–1.43 (m, 4H, 2×CH_2), 1.52–1.59 (m, 8H, 4×CH_2), 1.88 (s, 2H, CH_2), 1.89 (s, 2H, CH_2), 1.93–2.02 (m, 6H, 3×CH_2), 2.05–2.09 (m, 6H, 3×CH_2), 2.31–2.38 (m, 4H, 2×CH_2), 2.80 (d, *J*=15 Hz, 4H, 2×SCH_2), 3.53 (d, *J*=15 Hz, 4H, 2×SCH_2), 7.19–7.22 (m, 4H, Ar*H*), 7.36–7.41 (m, 8H, Ar*H*); MS (ESI) *m*/*z* 1247 $[M+Na]^+$.

To a suspension of the diastereomer (*S*,*S*)-**7a** or (*R*,*R*)-**7b** (2 g, 1.6 mmol) in methanol (150 mL) was added aqueous KOH solution (3 M, 30 mL). The mixture was heated to reflux overnight. After solvent was evaporated, the mixture was diluted with water (50 mL) and extracted with EtOAc (30 mL×3) successively. The

combined organic layer was dried over anhydrous Na_2SO_4 and concentrated. After column chromatography on silica gel (100 g, EtOAc/CH_2Cl_2, 1:8), pure (*S*,*S*)-**3** (590 mg, 97%) or (*R*,*R*)-**3** (571 mg, 94%) was isolated: mp >300 °C (lit.:[13] >300 °C); ^{1}H NMR (300 MHz, acetone-d_6): δ 6.72 (dd, *J*=0.9, 6.2 Hz, 4H, Ar*H*), 6.75 (dd, *J*=1.2, 6.8 Hz, 2H, Ar*H*), 7.06 (dd, *J*=7.8, 7.8 Hz, 2H, Ar*H*); MS (EI) *m*/*z* 368 $[M]^+$. Compound (*R*,*R*)-**3**: $[\alpha]_D^{20}$ +53.3 (*c* 0.83, MeOH) (lit.:[13] $[\alpha]_D^{20}$ +55.3 (*c* 1.07, MeOH)); (*S*,*S*)-**3**: $[\alpha]_D^{20}$ −54.8 (*c* 0.93, MeOH) (lit.:[13] $[\alpha]_D^{20}$ −55.8 (*c* 1.05, MeOH)).

*4.3.2. (S,S)- and (R,R)-5,22-Dihydrobenzo[h]tetraphenyleno[1,16-bcd][1,6]dioxecine-13,14-diol (**8**).* Compound (*S*,*S*)-**3** (667 mg, 1.65 mmol) was first added to a suspension of Cs_2CO_3 (805 mg, 2.47 mmol) in DMSO (33 mL). The mixture was then heated to 80 °C for 30 min with stirring. After heating, the mixture was cooled to 15 °C. A solution of 1,2-bis(bromomethyl)benzene[20] (480 mg, 1.82 mmol) in DMSO (33 mL) was added to the mixture dropwise by a dropping funnel. After the addition, the mixture was stirred for 30 min at room temperature. The mixture was then diluted with water (50 mL) and was extracted with CH_2Cl_2 (60 mL×3). The combined organic layer was washed with saturated brine solution (200 mL×2) successively. The organic layer was then dried over anhydrous Na_2SO_4 and concentrated. After column chromatography on silica gel (70 g, EtOAc/CH_2Cl_2, 1:90), pure **8** (295 mg, 38%) was collected as colorless sticky solids: R_f=0.15 (EtOAc/CH_2Cl_2, 1:90); ^{1}H NMR (300 MHz, DMSO-d_6): δ 5.08 (br s, 2H, OCH_2), 5.30 (d, *J*=11.4 Hz, 2H, OCH_2), 6.45 (d, *J*=7.4 Hz, 2H, Ar*H*), 6.66 (d, *J*=7.9 Hz, 2H, Ar*H*), 6.73 (d, *J*=5.3 Hz, 2H, Ar*H*), 6.96 (dd, *J*=7.7, 7.7 Hz, 2H, Ar*H*), 7.07 (d, *J*=7.7 Hz, 2H, Ar*H*), 7.13 (d, *J*=6.4 Hz, 2H, Ar*H*), 7.33 (dd, *J*=3.4, 5.3 Hz, 2H, Ar*H*), 7.49 (br s, 2H, Ar*H*), 8.97 (br s, 2H, O*H*); ^{13}C NMR (75 MHz, DMSO-d_6): δ 113.7, 119.3, 121.7, 124.2, 127.4, 127.8, 128.6, 131.5, 136.3, 143.0, 143.6, 154.4; HRMS (EI) *m*/*z* calcd for $C_{32}H_{22}O_4$ $[M]^+$ 470.1513, found 470.1508. Compounds (*S*,*S*)-**8** and (*R*,*R*)-**8**: $[\alpha]_D^{20}$ cannot be determined due to the poor solubility in organic solvents or water.

*4.3.3. (S,S)- and (R,R)-13,14-Bis(heptyloxy)-5,22-dihydrobenzo[h]tetraphenyleno[1,16-bcd][1,6]dioxecine (**9**).* To a stirring suspension of compound (*S*,*S*)-**8** (176 mg, 0.37 mmol) and Cs_2CO_3 (365 mg, 1.12 mmol) in DMF (3 mL), 1-bromoheptane (200 mg, 1.12 mmol) was added. The mixture was heated to 80 °C for 30 min. After that, the mixture was cooled and diluted with water (15 mL). The mixture was extracted with EtOAc (15 mL×3). The combined organic layer was then washed with saturated brine solution (30 mL×2). The organic layer was dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (15 g, EtOAc/hexanes, 1:6) to give pure (*S*,*S*)-**9** (217 mg, 88%) as colorless solids: mp 233–234 °C; R_f=0.35 (EtOAc/hexanes, 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, *J*=7.2 Hz, 6H, 2×CH_3), 1.14–1.19 (m, 12H, 6×CH_2), 1.22–1.26 (m, 4H, 2×CH_2), 1.44–1.49 (m, 4H, 2×CH_2), 3.68–3.77 (m, 4H, 2×OCH_2), 5.08 (d, *J*=1.2 Hz, 2H, OCH_2), 5.28 (d, *J*=1.2 Hz, 2H, OCH_2), 6.74 (dd, *J*=8.6, 8.6 Hz, 4H, Ar*H*), 6.84 (d, *J*=7.5 Hz, 2H, Ar*H*), 6.93 (d, *J*=8.0 Hz, 2H, Ar*H*), 7.09–7.15 (m, 4H, Ar*H*), 7.29–7.33 (m, 2H, Ar*H*), 7.34–7.37 (m, 2H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 22.7, 25.8, 29.1, 29.5, 32.0, 69.1, 111.7, 121.5, 122.4, 127.1, 127.7, 127.8, 128.4, 128.8, 131.5, 136.3, 143.1, 143.9, 156.4; HRMS (MALDI-TOF) *m*/*z* calcd for $C_{46}H_{50}O_4$ $[M+Na]^+$ 689.3601, found 689.3585; (*R*,*R*)-**9**: $[\alpha]_D^{20}$ +265.3 (*c* 0.95, $CHCl_3$); (*S*,*S*)-**9**: $[\alpha]_D^{20}$ −242.8 (*c* 0.75, $CHCl_3$).

*4.3.4. (S,S)- and (R,R)-8,9-Bis(heptyloxy)tetraphenylene-1,16-diol (**10**).* A mixed solution of compound (*S*,*S*)-**9** (217 mg, 0.33 mmol) in THF and EtOH (1:1, v/v ratio) was prepared, followed by the addition of palladium black catalyst (10 mol %). The mixture was stirred under H_2 for 2 h. The mixture was then filtered through Celite. The filtrate was concentrated and purified by column chromatography on silica gel (20 g, EtOAc/hexanes, 1:4) to yield pure (*S*,*S*)-**10** (174 mg, 95%) as colorless solids: mp 176–178 °C; R_f=0.25 (EtOAc/hexanes, 1:4); ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.87 (t, *J*=7.2 Hz, 6H, 2×CH_3), 1.16–1.26 (m, 16H, 8×CH_2), 1.43–1.48 (m, 4H, 2×CH_2), 3.69–3.74 (m, 4H, 2×OCH_2), 4.93 (br s, 2H, O*H*), 6.74 (dd, *J*=0.6, 8.1 Hz, 2H, Ar*H*), 6.81 (dd, *J*=0.9, 7.5 Hz, 2H, Ar*H*), 6.85 (dd, *J*=0.9, 8.1 Hz, 2H, Ar*H*), 6.88 (dd, *J*=1.2, 7.5 Hz, 2H, Ar*H*), 7.16 (dd, *J*=8.1, 8.1 Hz, 2H, Ar*H*), 7.20 (dd, *J*=7.8, 7.8 Hz, 2H, Ar*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.3, 22.7, 25.9, 29.1, 29.4, 32.0, 68.9, 111.7, 114.5, 120.2, 120.4, 121.5, 126.9, 128.1, 129.8, 142.4, 145.3, 152.3, 156.6; HRMS (EI) *m*/*z* calcd for $C_{38}H_{44}O_4$ $[M]^+$ 564.3234, found 564.3251; (*R*,*R*)-**10**: $[\alpha]_D^{20}$ −2.8 (*c* 1.07, $CHCl_3$); (*S*,*S*)-**10**: $[\alpha]_D^{20}$ +5.7 (*c* 0.83, $CHCl_3$).

*4.3.5. (S,S)-8,9-Bis(heptyloxy)-16-(4-methoxybenzyloxy)tetraphenylen-1-ol (**11**).* To a solution of compound (*S*,*S*)-**10** (112 mg, 0.20 mmol) in dried DMF (3 mL) under nitrogen atmosphere, K_2CO_3 (30 mg, 0.22 mmol) was added. The mixture was allowed to stir for 20 min at room temperature. *p*-Methoxybenzyl bromide (28 μL, 0.20 mmol) was injected to the mixture slowly. After stirring for another 1 h, the mixture was diluted with water and was extracted with EtOAc (15 mL×3). The combined organic layer was washed with saturated brine solution (20 mL×2) successively. The organic layer was dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (10 g, EtOAc/hexanes, 1:4) to yield pure (*S*,*S*)-**11** (107 mg, 79%) as colorless solids: mp 150–151 °C; R_f=0.25 (EtOAc/hexanes, 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J*=7.0 Hz, 3H, CH_3), 0.88 (t, *J*=7.3 Hz, 3H, CH_3), 1.13–1.28 (m, 16H, 8×CH_2), 1.46–1.51 (m, 4H, 2×CH_2), 3.71–3.76 (m, 4H, 2×OCH_2), 3.77 (s, 3H, OCH_3), 4.81 (dd, *J*=12.4, 14.0 Hz, 2H, OCH_2), 4.89 (br s, 1H, O*H*), 6.72–6.75 (m, 2H, Ar*H*), 6.76–6.85 (m, 7H, Ar*H*), 6.94 (dd, *J*=1.1, 7.6 Hz, 1H, Ar*H*), 7.00–7.04 (m, 2H, Ar*H*), 7.12–7.16 (m, 3H, Ar*H*), 7.18 (dd, *J*=5.5, 5.5 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 22.7, 25.9, 29.1, 29.4, 31.9, 55.1, 68.8, 68.8, 71.0, 111.2, 111.6, 113.7, 113.7, 114.2, 120.4, 120.6, 122.6, 123.6, 124.7, 126.9, 127.0, 127.7, 127.9, 128.4, 128.6, 129.0, 129.1, 142.5, 143.3, 143.6, 145.6, 152.5, 155.0, 156.4, 156.4, 159.1; HRMS (MALDI-TOF) *m*/*z* calcd for $C_{46}H_{52}O_5$ $[M+Na]^+$ 707.3706, found 707.3712; $[\alpha]_D^{20}$ −68.1 (*c* 1.29, $CHCl_3$).

*4.3.6. (S,S)-1-(2-(8,9-Bis(heptyloxy)-16-(4-methoxybenzyloxy)tetraphenylen-1-yloxy)ethyl)-py rrolidine (**12**).* To a solution of compound (*S*,*S*)-**11** (152 mg, 0.22 mmol) in DMF (2 mL) under nitrogen atmosphere, Cs_2CO_3 (188 mg, 0.58 mmol) and KI (17 mg, 0.11 mmol) were added. After the injection of 1-(2-chloroethyl) pyrrolidine[21] (59 mg, 0.44 mmol), the mixture was heated to reflux overnight. The mixture was then cooled and diluted with water. The biphasic mixture was extracted with CH_2Cl_2 (20 mL×3) successively. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated. After column chromatography on silica gel (15 g, MeOH/$CHCl_3$, 1:40), pure compound (*S*,*S*)-**12** (128 mg, 75%) was isolated as colorless sticky solids: R_f=0.15 (MeOH/$CHCl_3$, 1:20); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, *J*=7.2 Hz, 6H, 2×CH_3), 1.18–1.28 (m, 16H, 8×CH_2), 1.45–1.49 (m, 4H, 2×CH_2), 1.69 (m, 4H, 2×CH_2), 2.33–2.40 (m, 4H, 2×NCH_2), 2.53–2.59 (m, 1H, 0.5×NCH_2), 2.66–2.71 (m, 1H, 0.5×NCH_2), 3.68–3.77 (m, 4H, 2×OCH_2), 3.76 (s, 3H, OCH_3), 3.90–3.93 (m, 2H, OCH_2), 4.77 (s, 2H, OCH_2), 6.72–6.80 (m, 7H, Ar*H*), 6.84–6.89 (m, 4H, Ar*H*), 6.96 (d, *J*=8.6 Hz, 2H, Ar*H*), 7.11 (dd, *J*=7.9, 7.9 Hz, 1H, Ar*H*), 7.12–7.17 (m, 2H, Ar*H*), 7.19 (dd, *J*=7.9, 7.9 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 22.7, 23.5, 25.9, 29.1, 29.4, 31.9, 54.5, 54.6, 55.3, 67.9, 69.0, 70.8, 111.0, 111.5, 111.6, 112.9, 113.6, 120.6, 120.7, 121.1, 121.5, 126.8, 127.1, 127.2, 127.7, 127.8, 128.0, 128.2, 130.0, 143.2, 143.3, 143.8, 144.0, 155.9, 156.0, 156.5, 158.9; HRMS (ESI) *m*/*z* calcd for $C_{52}H_{63}O_5N$ $[M+H]^+$ 782.4779, found 782.4791; $[\alpha]_D^{20}$ −35.5 (*c* 1.28, $CHCl_3$).

*4.3.7. (S,S)-8,9-Bis(heptyloxy)-16-(2-(pyrrolidin-1-yl)ethoxy)tetraphenylen-1-ol (**13**).* A mixed solution of compound (*S*,*S*)-**12** (128 mg, 0.16 mmol) in THF and EtOH (1:1, v/v, 2 mL) was prepared,

followed by the addition of palladium black (10 mol %). The mixture was stirred under H_2 for 7 h. The mixture was then filtered through a Celite pad. The filtrate was diluted with CH_2Cl_2 (20 mL). The organic layer was then washed with aqueous HCl solution (2 M, 15 mL) and aqueous NaOH solution (3 M, 20 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated. After column chromatography on silica gel (13 g, MeOH/$CHCl_3$, 1:20), pure compound (*S*,*S*)-**13** (72 mg, 67%) was obtained as colorless sticky solids: R_f=0.23 (MeOH/$CHCl_3$, 1:20); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.89 (t, *J*=7.1 Hz, 6H, 2×CH_3), 1.21–1.27 (m, 16H, 8×CH_2), 1.49–1.52 (m, 4H, 2×CH_2), 1.91 (br s, 4H, 2×CH_2), 2.65–2.67 (m, 2H, NCH_2), 2.78–2.87 (m, 3H, 1.5×NCH_2), 2.99–3.02 (m, 1H, 0.5×NCH_2), 3.76–3.80 (m, 4H, 2×OCH_2), 4.12–4.16 (m, 1H, 0.5×OCH_2), 4.22–4.26 (m, 1H, 0.5×OCH_2), 6.76–6.82 (m, 6H, Ar*H*), 6.89 (dd, *J*=7.3, 7.3 Hz, 2H, Ar*H*), 7.11 (dd, *J*=7.8, 7.8 Hz, 1H, Ar*H*), 7.16–7.25 (m, 3H, Ar*H*); ^{13}C NMR (75 MHz, CD_2Cl_2): δ 13.6, 22.2, 22.8, 25.4, 28.6, 28.9, 31.4, 53.8, 54.1, 65.2, 68.3, 110.4, 110.5, 110.7, 118.4, 120.2, 120.9, 121.3, 126.1, 126.2, 126.7, 127.3, 127.5, 127.9, 142.5, 143.1, 143.2, 143.7, 153.8, 154.5, 155.9, 156.0; HRMS (MADLI-TOF) *m*/*z* calcd for $C_{44}H_{55}O_4N$ $[M+H]^+$ 662.4204, found 662.4235. Anal. Calcd for $C_{44}H_{55}O_4N\cdot{}^1/_2CH_3COOCH_2CH_3$: C, 78.26; H, 8.42; N, 1.98, found C, 77.94; H, 8.23; N, 1.84; $[\alpha]_D^{20}$ −120.2 (*c* 0.93, CH_2Cl_2).

*4.3.8. (S,S)-1-(3-(8,9-Bis(heptyloxy)-16-(4-methoxybenzyloxy)tetraphenylen-1-yloxy)propyl) pyrrolidine (**14**).* Compound (*S*,*S*)-**14** was prepared from compound (*S*,*S*)-**11** (103 mg, 0.15 mmol) by using the same preparative method as that for compound **12** from compound **11**, except 1-(3-chloropropyl)pyrrolidine[22] (44 mg, 0.30 mmol) was used.

Column chromatography on silica gel (10 g, MeOH/$CHCl_3$, 1:40) gave pure (*S*,*S*)-**14** (72 mg, 61%) as colorless sticky solids: R_f=0.35 (MeOH/$CHCl_3$, 1:20); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J*=7.2 Hz, 6H, 2×CH_3), 1.66–1.26 (m, 16H, 8×CH_2), 1.45–1.48 (m, 4H, 2×CH_2), 1.79 (br s, 6H, 3×CH_2), 2.26–2.33 (m, 1H, 0.5×NCH_2), 2.35–2,42 (m, 1H, 0.5×NCH_2), 2.51 (br s, 4H, 2×NCH_2), 3.66–3.81 (m, 6H, 3×OCH_2), 3.77 (s, 3H, OCH_3), 4.72 (s, 2H, OCH_2), 6.7–6.77 (m, 6H, Ar*H*), 6.79–6.84 (m, 2H, Ar*H*), 6.88 (dd, *J*=6.7, 6.7 Hz, 2H, Ar*H*), 6.94 (d, *J*=8.6 Hz, 2H, Ar*H*), 7.09–7.21 (m, 4H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 22.7, 23.5, 25.9, 28.0, 29.1, 29.4, 31.9, 53.0, 54.0, 55.3, 67.2, 69.0, 69.0, 70.0, 111.5, 111.6, 112.1, 113.2, 113.6, 120.6, 120.7, 121.4, 121.7, 127.1, 127.2, 127.7, 127.8, 127.9, 128.0, 128.4, 129.9, 143.2, 143.3, 143.8, 144.1, 156.0, 156.0, 156.5, 156.6, 159.0; HRMS (EI) *m*/*z* calcd for $C_{53}H_{65}O_5N$ $[M]^+$ 795.4857, found 795.4872; $[\alpha]_D^{20}$ −41.5 (*c* 1.03, $CHCl_3$).

*4.3.9. (S,S)-8,9-Bis(heptyloxy)-16-(3-(pyrrolidin-1-yl)propoxy)tetraphenylen-1-ol (**15**).* Compound (*S*,*S*)-**15** was prepared from compound (*S*,*S*)-**14** (58 mg, 0.07 mmol) by using the same preparative method as that for compound **13** from compound **12**.

Column chromatography on silica gel (6 g, MeOH/$CHCl_3$, 1:20) gave pure (*S*,*S*)-**15** (38 mg, 80%) as colorless sticky solids: R_f=0.23 (MeOH/$CHCl_3$, 1:20); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.90 (t, *J*=7.2 Hz, 6H, 2×CH_3), 1.18–1.31 (m, 16H, 8×CH_2), 1.50–1.55 (m, 4H, 2×CH_2), 1.76–1.82 (m, 6H, 3×CH_2), 2.22–2.28 (m, 1H, 0.5×NCH_2), 2.45–2.56 (m, 5H, 2.5×NCH_2), 3.77–3.81 (m, 4H, 2×OCH_2), 3.89–3.96 (m, 1H, 0.5×OCH_2), 3.97–4.00 (m, 1H, 0.5×OCH_2), 6.72–6.82 (m, 6H, Ar*H*), 6.88 (d, *J*=7.6 Hz, 2H, Ar*H*), 7.12 (dd, *J*=7.8, 7.8 Hz, 1H, Ar*H*), 7.16–7.22 (m, 2H, Ar*H*), 7.24 (dd, *J*=7.9, 7.9 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 13.6, 22.2, 22.9, 25.4, 27.7, 28.6, 28.9, 31.5, 52.0, 66.9, 68.4, 110.4, 110.6, 111.6, 115.0, 120.0, 120.1, 121.3, 124.9, 125.1, 126.2, 126.3, 127.4, 127.5, 127.6, 128.1, 142.5, 143.1, 143.2, 144.3, 153.1, 155.2, 155.9; HRMS (EI) *m*/*z* calcd for $C_{45}H_{57}O_4N$ $[M]^+$ 675.4282, found 675.4268; $[\alpha]_D^{20}$ −113.7 (*c* 0.98, CH_2Cl_2).

*4.3.10. (S,S)-2-(16-(Benzyloxy)-8,9-bis(heptyloxy)tetraphenylen-1-yloxy)-N,N-dimethyl ethanamine (**16**) and (S,S)-16-(2-(dimethylamino) ethoxy)-8,9-bis(heptyloxy) tetraphenylen-1-ol (**17**).* Compound (*S*,*S*)-**16** was prepared from (*S*,*S*)-**11** (36 mg, 0.06 mmol) by using the same preparative method as that for compound **12** from compound **11**, except 2-chloro-*N*,*N*-dimethylethanamine (16 mg, 0.11 mmol) was used.

Column chromatography on silica gel (5 g, MeOH/$CHCl_3$, 1:100) gave pure (*S*,*S*)-**16** (28 mg, 72%) as colorless waxy solids: R_f=0.45 (MeOH/$CHCl_3$, 1:40); ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.89 (t, *J*=7.2 Hz, 6H, 2×CH_3), 1.17–1.27 (m, 16H, 8×CH_2), 1.45–1.49 (m, 4H, 2×CH_2), 2.08 (s, 6H, 2×NCH_3), 2.41–2.45 (m, 2H, NCH_2), 3.70–3.79 (m, 4H, 2×OCH_2), 3.84–3.87 (m, 2H, OCH_2), 4.87 (s, 2H, OCH_2), 6.75 (dd, *J*=8.4, 8.4 Hz, 4H, Ar*H*), 6.80 (d, *J*=7.0 Hz, 1H, Ar*H*), 6.84–6.90 (m, 3H, Ar*H*), 7.05–7.09 (m, 2H, Ar*H*), 7.11–7.17 (m, 3H, Ar*H*), 7.19–7.24 (m, 3H, Ar*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.3, 22.7, 25.9, 29.1, 29.4, 32.0, 45.8, 58.0, 67.6, 69.1, 70.8, 111.3, 111.6, 112.4, 120.7, 120.8, 121.2, 121.5, 126.6, 127.0, 127.2, 127.4, 127.7, 127.8, 127.8, 128.0, 128.2, 138.0, 143.3, 143.4, 143.9, 144.0, 155.9, 156.0, 156.5; $[\alpha]_D^{20}$ −27.8 (*c* 0.96, $CHCl_3$).

Compound (*S*,*S*)-**17** was prepared from pure (*S*,*S*)-**16** (28 mg, 0.04 mmol) by using the same preparative method as that for compound **13** from compound **12**.

Column chromatography on silica gel (5 g, MeOH/$CHCl_3$, 1:20) gave pure compound (*S*,*S*)-**17** (19 mg, 75%) as colorless waxy solids: R_f=0.33 (MeOH/$CHCl_3$, 1:20); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J*=7.2 Hz, 6H, 2×CH_3), 1.17–1.29 (m, 16H, 8×CH_2), 1.42–1.49 (m, 4H, 2×CH_2), 2.29 (s, 6H, 2×NCH_3), 3.68–3.77 (m, 4H, 2×OCH_2), 4.01–4.10 (m, 2H, OCH_2), 6.72 (d, *J*=8.1 Hz, 3H, Ar*H*), 6.79–6.86 (m, 5H, Ar*H*), 7.06–7.17 (m, 4H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 22.7, 25.9, 29.1, 29.5, 32.0, 45.1, 57.8, 65.2, 69.1, 110.7, 111.5, 111.7, 119.4, 120.9, 121.0, 121.8, 121.9, 126.7, 127.1, 127.3, 127.6, 127.7, 127.9, 128.8, 143.1, 143.6, 143.7, 143.4, 153.8, 155.1, 156.3, 156.4; HRMS (EI) *m*/*z* calcd for $C_{42}H_{53}O_4N$ $[M]^+$ 635.3969, found 635.3945; $[\alpha]_D^{20}$ −76.3 (*c* 0.63, $CHCl_3$).

*4.3.11. (S,S)-and (R,R)-8,9-Bis(heptyloxy)-16-hydroxytetraphenylene-1-carbonitrile (**18**).* To a solution of compound (*S*,*S*)-**10** (21 mg, 0.04 mmol) in CH_2Cl_2 (0.5 mL) under nitrogen atmosphere, collidine (15 μL, 0.11 mmol) and DMAP (4.6 mg, 0.04 mmol) were added. The mixture was cooled to −78 °C with stirring. 1,1,1-Trifluoro-*N*-phenyl-*N*-(trifluoromethylsulfonyl)methanesulfonamide (15 mg, 0.04 mmol) was added to the mixture. After that, the mixture was warmed to room temperature. The stirring was continued for 2 h. The mixture was then diluted with water (10 mL) and extracted by CH_2Cl_2 (10 mL×2). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated. After column chromatography on silica gel (5 g, EtOAc/CH_2Cl_2/hexanes, 1:1:10), pure triflate compound (24 mg, 93%) was yielded as colorless sticky solids: R_f=0.35 (EtOAc/hexanes, 1:6).

A Schlenk bottle was charged with a mixture of compound (*S*,*S*)-triflate compound (103.3 mg, 0.15 mmol), $Pd(PPh_3)_4$ (135 mg, 0.12 mmol), and $Zn(CN)_2$ (91 mg, 0.78 mmol). The mixture was degassed and refilled with nitrogen three times. Dried DMF (2 mL) was injected to the mixture. The mixture was again degassed and refilled with nitrogen three times. After that, the mixture was heated to 150 °C for 18 h. The mixture was cooled and filtered through a Celite pad. The filtrate was diluted with EtOAc (30 mL) and washed with saturated brine solution (30 mL×2) successively. The organic layer was dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (10 g, EtOAc/CH_2Cl_2/hexanes, 1:1:10) to give compound (*S*,*S*)-**18** (85 mg, 99%) as colorless sticky solids: R_f=0.21 (EtOAc/hexanes, 1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J*=7.2 Hz, 6H, 2×CH_3), 1.14–1.28 (m, 16H, 8×CH_2), 1.44–1.51 (m, 4H, 2×CH_2), 3.70–3.76 (m, 4H, 2×OCH_2), 5.28 (br s, 1H, O*H*), 6.66 (dd, *J*=0.8, 8.0 Hz, 1H, Ar*H*), 6.73 (dd, *J*=0.6, 8.2 Hz, 1H, Ar*H*), 6.76–6.84 (m, 3H, Ar*H*), 6.88 (dd, *J*=0.9, 7.6 Hz, 1H, Ar*H*), 7.11–7.20 (m, 3H, Ar*H*), 7.30 (dd, *J*=7.7, 7.7 Hz, 1H, Ar*H*), 7.47 (dd, *J*=1.3, 7.8 Hz, 1H, Ar*H*), 7.54 (dd, *J*=1.3, 7.7 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 22.7, 25.9,

25.9, 29.1, 29.4, 31.9, 68.7, 68.9, 111.2, 112.1, 113.4, 114.8, 118.6, 120.2, 120.9, 121.0, 123.9, 126.1, 127.1, 127.9, 128.3, 128.3, 129.7, 131.6, 133.0, 140.1, 141.3, 142.3, 143.7, 144.5, 152.0, 156.4, 156.6; HRMS (EI) m/z calcd for $C_{39}H_{43}O_3N$ $[M]^+$ 573.3237, found 573.3234; (*S,S*)-**18**: $[\alpha]_D^{20}$ −65.3 (*c* 0.76, $CHCl_3$); (*R,R*)-**18**: $[\alpha]_D^{20}$ +59.3 (*c* 0.95, $CHCl_3$).

*4.3.12. (S,S)-16-(Benzyloxy)-8,9-bis(heptyloxy)tetraphenylene-1-carbaldehyde (**36**) and (S,S)-1-((16-(benzyloxy)-8,9-bis(heptyloxy)tetraphenylen-1-yl)methyl)pyrrolidine (**20**).* Compound (*S,S*)-**19** (34 mg, 0.05 mmol) was first dissolved in CH_2Cl_2 (2 mL) under nitrogen atmosphere with stirring. After cooling to −78 °C, DIBAL-H solution (1 M in cyclohexane, 61 μL, 0.06 mmol) was injected to the mixture slowly. The mixture was kept stirring at −78 °C for 1 h. After the addition of aqueous HCl solution (2 M, 1 mL), the mixture was warmed to room temperature. The mixture was stirred for 15 min and was diluted with water. The mixture was partitioned between water and CH_2Cl_2 (10 mL×2). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated. The residue was diluted with CH_2Cl_2 (10 mL) and filtered through a silica gel pad. The filtrate was concentrated to give crude (*S,S*)-**36** (28 mg, 83%) as a pale yellow oil: R_f=0.21 (EtOAc/hexanes, 1:10); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.90 (t, J=7.0 Hz, 6H, 2×CH_3), 1.22–1.31 (m, 16H, 8×CH_2), 1.53–1.56 (m, 4H, 2×CH_2), 3.81 (q, J=6.6 Hz, 4H, 2×OCH_2), 4.88 (dd, J=12.3, 23.6 Hz, 2H, OCH_2), 6.77–6.87 (m, 5H, Ar*H*), 6.93 (dd, J=0.8, 7.6 Hz, 1H, Ar*H*), 7.02–7.04 (m, 2H, Ar*H*), 7.17–7.29 (m, 6H, Ar*H*), 7.41 (dd, J=7.1, 7.1 Hz, 1H, Ar*H*), 7.51 (dd, J=1.4, 7.5 Hz, 1H, Ar*H*), 7.82 (dd, J=1.4, 7.6 Hz, 1H, Ar*H*), 9.64 (s, 1H, C*H*O); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 13.6, 22.2, 25.5, 28.6, 28.9, 28.9, 31.5, 68.2, 68.3, 69.9, 110.6, 110.8, 111.0, 120.0, 120.1, 121.1, 124.8, 124.9, 125.8, 126.4, 126.4, 127.1, 127.2, 127.7, 127.8, 127.9, 128.8, 133.5, 136.5, 139.4, 141.6, 142.1, 143.3, 143.8, 154.8, 156.0, 156.0, 192.1; HRMS (EI) m/z calcd for $C_{46}H_{50}O_4$ $[M]^+$ 666.3704, found 666.3732.

Without further purification, compound (*S,S*)-**36** (28 mg, 0.04 mmol) was dissolved in a mixed solution of THF and MeOH (v/v, 1:1, 2 mL) under nitrogen atmosphere. After cooling to 0 °C, pyrrolidine (21 μL, 0.25 mmol) was added. Sodium cyanoborohydride (1.0 M in THF, 51 μL, 0.05 mmol) was injected slowly to the mixture after 30 min. The mixture was stirred overnight at room temperature. Dilute HCl solution (2 M, 2 mL) was dropped to the mixture slowly. The mixture was then diluted with water and extracted with CH_2Cl_2 (10 mL×3). The combined organic layer was washed with aqueous HCl solution (2 M, 20 mL) and aqueous NaOH solution (3 M, 30 mL) successively and then was dried over anhydrous Na_2SO_4. The organic layer was concentrated and purified by column chromatography on silica gel (5 g, MeOH/$CHCl_3$, 1:60) to give pure (*S,S*)-**20** (20 mg, 68%) as colorless waxy solids: R_f=0.45 (MeOH/$CHCl_3$, 1:20); ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, J=7.2 Hz, 6H, 2×CH_3), 1.18–1.27 (m, 16H, 8×CH_2), 1.48 (br s, 4H, 2×CH_2), 1.72 (br s, 4H, 2×CH_2), 2.40 (br s, 4H, 2×NCH_2), 3.16 (d, J=13.8 Hz, 1H, 0.5×NCH_2), 3.67–3.76 (m, 4H, 2×OCH_2), 3.82 (d, J=14.1 Hz, 1H, 0.5×NCH_2), 4.76 (dd, J=12.3, 26.7 Hz, 2H, OCH_2), 6.71–6.74 (m, 3H, Ar*H*), 6.77–6.81 (m, 2H, Ar*H*), 6.89 (d, J=6.9 Hz, 1H, Ar*H*), 6.94–6.96 (m, 2H, Ar*H*), 7.09–7.24 (m, 8H, Ar*H*), 7.65 (d, J=7.2 Hz, 1H, Ar*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.3, 22.7, 23.4, 25.9, 29.1, 29.4, 32.0, 54.0, 57.1, 68.9, 71.3, 111.3, 111.6, 113.6, 120.0, 120.7, 122.1, 126.8, 127.1, 127.2, 127.6, 127.8, 128.4, 129.1, 135.7, 137.2, 142.7, 143.6, 144.0, 154.9, 156.4, 156.6; HRMS (MADLI-TOF) m/z calcd for $C_{50}H_{59}O_3N$ $[M+H]^+$ 722.4568, found 722.4549; $[\alpha]_D^{20}$ −39.2 (*c* 0.99, $CHCl_3$).

*4.3.13. (S,S)-8,9-Bis(heptyloxy)-16-(pyrrolidin-1-ylmethyl)tetraphenylen-1-ol (**21**).* Compound (*S,S*)-**21** was prepared from (*S,S*)-**20** (19 mg, 0.03 mmol) by using the same preparative method as that for compound **13** from compound **12**.

Column chromatography on silica gel (3 g, MeOH/$CHCl_3$, 1:20) gave pure (*S,S*)-**21** (11.6 mg, 70%) as colorless waxy solids: R_f=0.35 (MeOH/$CHCl_3$, 1:20); ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.87 (t, J=6.9 Hz, 6H, 2×CH_3), 1.24–1.32 (m, 16H, 8×CH_2), 1.49–1.51 (m, 4H, 2×CH_2), 1.76–1.90 (m, 4H, 2×CH_2), 2.50–2.53 (m, 2H, NCH_2), 2.65–2.68 (m, 2H, NCH_2), 3.07 (d, J=11.7 Hz, 1H, 0.5×NCH_2), 3.71–3.78 (m, 5H, 2×OCH_2, and 0.5×NCH_2), 6.67–6.72 (m, 4H, Ar*H*), 6.84 (dd, J=0.9, 7.5 Hz, 1H, Ar*H*), 6.88 (dd, J=1.2, 8.1 Hz, 1H, Ar*H*), 7.03–7.15 (m, 6H, Ar*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.3, 22.7, 23.3, 25.9, 29.1, 29.5, 32.0, 53.1, 59.3, 68.9, 111.2, 111.4, 119.7, 119.9, 120.5, 120.6, 126.6, 127.0, 127.2, 127.5, 127.8, 128.2, 128.8, 128.9, 130.2, 134.6, 137.7, 143.5, 143.5, 143.7, 143.8, 155.1, 156.0, 156.2; HRMS (MADLI-TOF) m/z calcd for $C_{43}H_{53}O_3N$ $[M+H]^+$ 632.4098, found 632.4117; $[\alpha]_D^{20}$ −155.0 (*c* 0.56, $CHCl_3$).

*4.3.14. 1-(Benzyloxy)-16-(3-bromopropoxy)-8,9-bis(heptyloxy)tetraphenylene (**23**).* To a stirring solution of compound **10** (86 mg, 0.15 mmol) in dried DMF (2 mL) under nitrogen atmosphere, K_2CO_3 (23 mg, 0.17 mmol) was added. After stirring for 20 min at room temperature, benzyl bromide (19 μL, 0.15 mmol) was injected to the mixture slowly. The stirring was continued for another 1 h. After that, the mixture was diluted with water (30 mL) and extracted with EtOAc (15 mL×3). The combined organic layer was washed with saturated brine solution (20 mL×2). The organic layer was dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (10 g, EtOAc/hexanes, 1:4) to yield pure protected alcohol (88 mg, 89%) as colorless solids: mp 131–132 °C; R_f=0.25 (EtOAc/hexanes, 1:4).

The isolated alcohol (87 mg, 0.13 mmol) was the dissolved in DMF (2 mL), followed by the addition of Cs_2CO_3 (66 mg, 0.20 mmol). After the injection of 1,3-dibromopropane (54 μL, 0.53 mmol), the mixture was heated to 80 °C with stirring. After 1 h, the mixture was cooled and diluted with water (15 mL). The mixture was extracted with EtOAc (10 mL×3). The combined organic layer was washed with saturated brine solution (20 mL×2) successively and was dried over anhydrous Na_2SO_4. After filtration and concentration, the residue was purified by column chromatography on silica gel (10 g, EtOAc/CH_2Cl_2/hexanes, 1:1:25) to give pure **23** (96 mg, 95%) as colorless waxy solids: R_f=0.53 (EtOAc/hexanes, 1:20); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, J=7.2 Hz, 6H, 2×CH_3), 1.18–1.27 (m, 16H, 8×CH_2), 1.47–1.50 (m, 4H, 2×CH_2), 1.96–2.01 (m, 2H, CH_2), 3.13–3.22 (m, 2H, CH_2Br), 3.68–3.88 (m, 6H, 3×OCH_2), 4.85 (dd, J=12.6, 21.2 Hz, 2H, OCH_2), 6.72–6.79 (m, 4H, Ar*H*), 6.84–6.91 (m, 4H, Ar*H*), 7.04 (dd, J=1.3, 7.5 Hz, 2H, Ar*H*), 7.11–7.25 (m, 7H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 22.7, 25.9, 29.1, 29.5, 30.4, 32.0, 32.8, 66.5, 69.0, 69.0, 70.9, 111.6, 111.9, 112.5, 120.7, 121.5, 121.6, 126.7, 127.2, 127.2, 127.3, 127.3, 127.7, 127.8, 127.9, 128.0, 128.2, 137.9, 143.2, 143.3, 143.9, 144.0, 155.8, 155.9, 156.6; HRMS (EI) m/z calcd for $C_{48}H_{55}O_4Br$ $[M+H]^+$ 775.3356, found 775.3352.

*4.3.15. (S,S)-1-(Benzyloxy)-16-(4-bromobutoxy)-8,9-bis(heptyloxy)tetraphenylene (**24**).* Compound (*S,S*)-**24** was prepared from (*S,S*)-**10** (106 mg, 0.16 mmol) by using the same preparative method as that for compound **23** from compound **10**, except using 1,4-dibromobutane (105 mg, 0.48 mmol).

Column chromatography on silica gel (10 g, EtOAc/CH_2Cl_2/hexanes, 1:1:25) gave pure compound (*S,S*)-**24** (120 mg, 95%) as colorless waxy solids: R_f=0.53 (EtOAc/hexanes, 1:20); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, J=7.1 Hz, 6H, 2×CH_3), 1.18–1.30 (m, 16H, 8×CH_2), 1.45–1.51 (m, 4H, 2×CH_2), 1.55–1.64 (m, 2H, CH_2), 1.66–1.77 (m, 2H, CH_2), 3.08–3.18 (m, 2H, CH_2Br), 3.68–3.79 (m, 6H, 3×OCH_2), 4.86 (dd, J=12.6, 15.5 Hz, 2H, OCH_2), 6.73–6.77 (m, 4H, Ar*H*), 6.86 (d, J=7.2 Hz, 2H, Ar*H*), 6.88–6.91 (m, 2H, Ar*H*), 7.04–7.07 (m, 2H, Ar*H*), 7.12–7.24 (m, 7H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 22.7, 25.9, 27.9, 29.1, 29.5, 29.8, 32.0, 33.9, 68.0, 69.1, 69.1, 70.8, 111.5, 111.6, 112.6, 120.7, 120.8, 121.3, 121.6, 126.6, 127.1, 127.2, 127.3, 127.3, 127.4, 127.7, 127.8, 127.9, 128.0, 128.2, 138.0, 143.4, 143.9, 155.8, 156.1, 156.6, 156.6;

HRMS (ESI) *m/z* calcd for $C_{49}H_{57}O_4Br$ $[M+Na]^+$ 811.3332, found 811.3323; $[\alpha]_D^{20}$ −40.9 (*c* 1.11, $CHCl_3$).

*4.3.16. 16-(3-(16-(Benzyloxy)-8,9-bis(heptyloxy)tetraphenylen-1-yloxy)propoxy)-8,9-bis (heptyloxy)tetraphenylen-1-ol (**25**).* To a solution of compounds **10** (124 mg, 0.22 mmol) and **23** (108 mg, 0.14 mmol) in DMF (2 mL), Cs_2CO_3 (79 mg, 0.24 mmol) was added. The mixture was heated to 80 °C with stirring overnight. After cooling, the mixture was diluted with water (15 mL). The mixture was extracted with EtOAc (15 mL×3) subsequently. The combined organic layer was washed with saturated brine solution (30 mL×2) and was dried over anhydrous Na_2SO_4. After concentration and column chromatography on silica gel (10 g, EtOAc/CH_2Cl_2/hexanes, 1:1:10), pure **25** (114 mg, 65%) was collected as colorless waxy solids: R_f=0.25 (EtOAc/hexanes, 1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J*=7.2 Hz, 6H, 2×C*H*$_3$), 0.88 (t, *J*=7.2 Hz, 6H, 2×C*H*$_3$), 1.18–1.26 (m, 32H, 16×C*H*$_2$), 1.47–1.52 (m, 8H, 4×C*H*$_2$), 1.65–1.69 (m, 2H, C*H*$_2$), 3.65–3.78 (m, 12H, 6×OC*H*$_2$), 4.70 (s, 2H, OC*H*$_2$), 4.85 (br s, 1H, O*H*), 6.57 (d, *J*=8.2 Hz, 1H, Ar*H*), 6.64 (dd, *J*=7.7, 7.7 Hz, 2H, Ar*H*), 6.70–6.75 (m, 8H, Ar*H*), 6.79 (d, *J*=7.4 Hz, 1H, Ar*H*), 6.83–6.89 (m, 4H, Ar*H*), 6.92–6.94 (m, 2H, Ar*H*), 7.05–7.18 (m, 11H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 22.7, 25.9, 29.0, 29.1, 29.5, 32.0, 64.9, 65.5, 69.0, 69.1, 71.0, 111.3, 111.4, 111.5, 111.6, 111.7, 112.0, 113.4, 114.1, 120.5, 120.6, 120.7, 120.9, 121.7, 121.9, 123.7, 124.1, 126.7, 126.8, 127.0, 127.1, 127.2, 127.3, 127.7, 127.7, 127.8, 127.9, 128.0, 128.2, 128.9, 137.9, 142.7, 143.3, 143.4, 143.6, 143.6, 144.0, 145.4, 152.6, 155.1, 155.7, 155.9, 156.4, 156.4, 156.5; HRMS (ESI) *m/z* calcd for $C_{86}H_{98}O_8$ $[M+Na]^+$ 1281.7154, found 1281.7180.

Column chromatography on silica gel (EtOAc/CH_2Cl_2/hexanes, 1:1:2) was used to recover un-reacted compound **10**.

*4.3.17. (S,S,S,S)-16-(4-(16-(Benzyloxy)-8,9-bis(heptyloxy)tetraphenylen-1-yloxy)butoxy)-8,9-bis(heptyloxy)tetraphenylen-1-ol (**26**).* Compound (*S*,*S*,*S*,*S*)-**26** was prepared from (*S*,*S*)-**10** (134 mg, 0.24 mmol) and (*S*,*S*)-**24** (112 mg, 0.14 mmol) by using the same preparative method as that for compound **25** from compounds **10** and **23**.

Column chromatography on silica gel (10 g, EtOAc/CH_2Cl_2/hexanes, 1:1:10) gave pure (*S*,*S*,*S*,*S*)-**26** (155 mg, 87%) as colorless waxy solids: R_f=0.25 (EtOAc/hexanes, 1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, *J*=7.2 Hz, 12H, 4×C*H*$_3$), 1.18–1.30 (m, 32H, 16×C*H*$_2$), 1.37–1.38 (m, 4H, 2×C*H*$_2$), 1.46–1.49 (m, 8H, 4×C*H*$_2$), 3.52–3.56 (m, 1H, 0.5×OC*H*$_2$), 3.60–3.63 (m, 3H, 1.5×OC*H*$_2$), 3.67–3.75 (m, 8H, 4×OC*H*$_2$), 4.77 (s, 2H, OC*H*$_2$), 4.87 (br s, 1H, O*H*), 6.63 (dd, *J*=0.8, 8.4 Hz, 1H, Ar*H*), 6.69–6.75 (m, 8H, Ar*H*), 6.76–6.79 (m, 3H, Ar*H*), 6.83–6.90 (m, 4H, Ar*H*), 6.95–6.98 (m, 2H, Ar*H*), 7.06–7.22 (m, 11H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 22.7, 25.3, 25.4, 25.9, 29.1, 29.5, 29.5, 32.0, 68.1, 68.6, 69.0, 69.0, 69.1, 69.1, 70.6, 111.4, 111.5, 111.6, 111.7, 111.8, 112.1, 112.4, 114.1, 120.5, 120.7, 120.8, 120.8, 121.0, 121.5, 122.1, 123.7, 123.8, 124.0, 126.6, 127.0, 127.0, 127.1, 127.3, 127.3, 127.5, 127.7, 127.7, 127.8, 127.8, 127.9, 128.2, 129.0, 138.0, 142.7, 143.4, 143.4, 143.5, 143.6, 143.8, 143.9, 145.5, 152.5, 152.5, 155.2, 155.8, 156.2, 156.4, 156.5, 156.5; HRMS (MADLI-TOF) *m/z* calcd for $C_{87}H_{100}O_8$ $[M+Na]^+$ 1295.7310, found 1295.7355; $[\alpha]_D^{20}$ −75.8 (*c* 0.99, $CHCl_3$).

*4.3.18. (S,S,S,S)-16-(3-(8,9-Bis(heptyloxy)-16-(2-(pyrrolidin-1-yl)ethoxy)tetraphenylen-1-yloxy)propoxy)-8,9-bis(heptyloxy)tetraphenylen-1-ol (**27**).* Compound (*S*,*S*,*S*,*S*)-**27** was prepared from (*S*,*S*,*S*,*S*)-**25** (78 mg, 0.06 mmol) by using the same preparative method as that for compound (*S*,*S*)-**13** from compounds (*S*,*S*)-**11**.

Column chromatography on silica gel (10 g, MeOH/CH_2Cl_3, 1:40) gave pure (*S*,*S*,*S*,*S*)-**27** (36 mg, two-step overall yield: 48%) as colorless waxy solids: R_f=0.31 (MeOH/CH_2Cl_3, 1:20); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, *J*=7.2 Hz, 12H, 4×C*H*$_3$), 1.18–1.27 (m, 32H, 16×C*H*$_2$), 1.46–1.48 (m, 8H, 4×C*H*$_2$), 1.65–1.72 (m, 6H, 3×C*H*$_2$), 2.43 (br s, 4H, 2×NC*H*$_2$), 2.61 (br s, 2H, NC*H*$_2$), 3.62–3.74 (m, 12H, 6×OC*H*$_2$), 3.86–3.87 (m, 2H, OC*H*$_2$), 6.63 (dd, *J*=8.6, 8.6 Hz, 2H, Ar*H*), 6.68–6.82 (m, 12H, Ar*H*), 6.86 (dd, *J*=7.3, 7.3 Hz, 2H, Ar*H*), 7.05–7.17 (m, 8H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 22.7, 23.4, 25.9, 29.1, 29.3, 29.4, 32.0, 54.3, 54.4, 64.7, 65.6, 67.2, 69.0, 69.1, 111.0, 111.1, 111.4, 111.6, 111.7, 112.2, 114.0, 120.2, 120.5, 120.6, 120.6, 120.7, 120.7, 121.3, 121.8, 124.3, 125.5, 126.8, 127.0, 127.1, 127.2, 127.2, 127.7, 127.7, 127.8, 128.0, 128.5, 143.0, 143.3, 143.5, 143.7, 143.9, 144.8, 153.4, 155.6, 155.7, 156.0, 156.4, 156.5, 156.5, 156.6; HRMS (ESI) *m/z* calcd for $C_{85}H_{103}O_8N$ $[M+H]^+$ 1266.7756, found 1266.7758; $[\alpha]_D^{20}$ −84.9 (*c* 1.05, $CHCl_3$).

*4.3.19. (S,S,S,S)-16-(4-(8,9-Bis(heptyloxy)-16-(2-(pyrrolidin-1-yl)ethoxy)tetraphenylen-1-yloxy)butoxy)-8,9-bis(heptyloxy)tetraphenylen-1-ol (**28**).* Compound (*S*,*S*,*S*,*S*)-**28** was prepared from (*S*,*S*,*S*,*S*)-**26** (65 mg, 0.05 mmol) by using the same preparative method as that for compound (*S*,*S*)-**13** from compounds (*S*,*S*)-**11**.

Column chromatography on silica gel (8 g, MeOH/CH_2Cl_3, 1:40) gave pure (*S*,*S*,*S*,*S*)-**28** (21 mg, two-steps overall yield: 33%) as colorless waxy solids: R_f=0.31 (MeOH/CH_2Cl_3, 1:20); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, *J*=7.2 Hz, 12H, 4×C*H*$_3$), 1.18–1.27 (m, 32H, 16×C*H*$_2$), 1.40–1.48 (m, 12H, 6×C*H*$_2$), 1.72 (br s, 4H, 2×C*H*$_2$), 2.45 (br s, 4H, 2×NC*H*$_2$), 2.59–2.62 (m, 1H, 0.5×NC*H*$_2$), 2.69–2.72 (m, 1H, 0.5×NC*H*$_2$), 3.57–3.61 (m, 2H, OC*H*$_2$), 3.66–3.77 (m, 10H, 5×OC*H*$_2$), 3.84–3.94 (m, 2H, OC*H*$_2$), 6.64–6.83 (m, 15H, Ar*H*), 6.89 (d, *J*=7.5 Hz, 1H, Ar*H*), 7.04–7.15 (m, 7H, Ar*H*), 7.19 (dd, *J*=8.0, 8.0 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 22.7, 23.4, 25.5, 25.8, 25.9, 29.1, 29.5, 32.0, 54.4, 54.6, 68.6, 68.9, 69.0, 69.1, 69.1, 110.7, 111.4, 111.5, 111.6, 111.7, 111.8, 112.2, 113.9, 120.2, 120.6, 120.6, 120.7, 120.7, 121.0, 121.1, 121.9, 124.1, 125.0, 126.7, 127.1, 127.1, 127.2, 127.7, 127.7, 127.7, 127.9, 128.1, 128.7, 142.9, 143.3, 143.4, 143.5, 143.7, 143.8, 145.1, 153.1, 155.5, 155.7, 156.2, 156.4, 156.5, 156.5, 156.6; HRMS (MADLI-TOF) *m/z* calcd for $C_{86}H_{105}O_8N$ $[M+H]^+$ 1280.7913, found 1280.7945; $[\alpha]_D^{20}$ −62.3 (*c* 1.35, $CHCl_3$).

*4.3.20. (S,S,S,S)-16-(3-(16-(Benzyloxy)-8,9-bis(heptyloxy)tetraphenylen-1-yloxy)prop-oxy)-8,9-bis(heptyloxy)tetraphenylene-1-carbonitrile (**29**).* To a solution of compounds (*S*,*S*)-**18** (23 mg, 0.04 mmol) and (*S*,*S*)-**23** (26 mg, 0.03 mmol) in DMF (2 mL), Cs_2CO_3 (20 mg, 0.06 mmol) was added. The mixture was heated to 80 °C with stirring overnight. After cooling, the mixture was diluted with water (15 mL). The mixture was extracted with EtOAc (15 mL×3) successively. The combined organic layer was washed with saturated brine solution (20 mL×2) and was dried over anhydrous Na_2SO_4. After removal of solvent, the residue was purified by column chromatography on silica gel (5 g, EtOAc/CH_2Cl_2/hexanes, 1:1:10) to give pure (*S*,*S*,*S*,*S*)-**29** (33 mg, 81%) as colorless waxy solids: R_f=0.28 (EtOAc/hexanes, 1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, *J*=7.2 Hz, 6H, 2×C*H*$_3$), 0.90 (t, *J*=7.2 Hz, 6H, 2×C*H*$_3$), 1.19–1.29 (m, 32H, 16×C*H*$_2$), 1.49–1.50 (m, 8H, 4×C*H*$_2$), 1.67–1.78 (m, 2H, C*H*$_2$), 3.67–3.76 (m, 12H, 6×OC*H*$_2$), 4.85 (s, 2H, OC*H*$_2$), 6.55 (d, *J*=8.0 Hz, 1H, Ar*H*), 6.62 (d, *J*=7.6 Hz, 1H, Ar*H*), 6.71–6.79 (m, 8H, Ar*H*), 6.82–6.87 (m, 5H, Ar*H*), 7.04–7.23 (m, 12H, Ar*H*), 7.40 (dd, *J*=1.2, 7.7 Hz, 1H, Ar*H*), 7.45 (dd, *J*=1.2, 7.6 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 22.7, 25.9, 29.1, 29.1, 29.4, 29.5, 32.0, 65.6, 65.8, 68.7, 69.0, 69.0, 69.1, 70.8, 111.2, 111.3, 111.6, 111.7, 111.9, 112.5, 113.8, 118.8, 120.4, 120.8, 120.8, 120.9, 120.9, 121.1, 121.5, 126.0, 126.2, 126.7, 127.1, 127.1, 127.2, 127.3, 127.4, 127.7, 127.7, 127.9, 127.9, 128.1, 128.2, 128.2, 129.5, 131.1, 132.5, 138.0, 140.9, 141.6, 142.4, 143.4, 143.4, 143.8, 143.9, 155.1, 155.8, 156.0, 156.3, 156.5, 156.6; HRMS (MADLI-TOF) *m/z* calcd for $C_{87}H_{97}O_7N$ $[M+Na]^+$ 1290.7157, found 1290.7112; $[\alpha]_D^{20}$ −75.1 (*c* 1.06, $CHCl_3$).

Column chromatography on silica gel (EtOAc/CH_2Cl_2/hexanes, 1:1:2) was used to recover un-reacted compound (*S*,*S*)-**18**.

*4.3.21. (S,S,S,S)-16-(3-(8,9-Bis(heptyloxy)-16-(pyrrolidin-1-ylmethyl)tetraphenylen-1-yloxy)propoxy)-8,9-bis(heptyloxy)tetraphenylen-1-ol (**30**).* Compound (*S*,*S*,*S*,*S*)-**30** was prepared from (*S*,*S*,*S*,*S*)-**29**

(17.5 mg, 0.01 mmol) by using the same preparative method as that for compound (*S*,*S*)-**21** from compound (*S*,*S*)-**19**.

Column chromatography on silica gel (5 g, MeOH/CH_2Cl_2, 1:40) gave pure (*S*,*S*,*S*,*S*)-**30** (4.3 mg, three-step overall yield: 35%) as colorless waxy solids: R_f=0.31 (MeOH/CH_2Cl_2, 1:20); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.88 (t, J=7.1 Hz, 12H, 4×CH_3), 1.20–1.30 (m, 32H, 16×CH_2), 1.50–1.51 (m, 8H, 4×CH_2), 1.67–1.73 (m, 6H, 3×CH_2), 2.45 (br s, 4H, 2×NCH_2), 3.61–3.72 (m, 5H, 0.5×NCH_2, and 2×OCH_2), 3.76–3,80 (m, 9H, 0.5×NCH_2, and 4×OCH_2), 6.70–6.79 (m, 12H, Ar*H*), 6.85–6.90 (m, 2H, Ar*H*), 7.09–7.21 (m, 6H, Ar*H*), 7.23–7.30 (m, 3H, Ar*H*); ^{13}C NMR (75 MHz, CD_2Cl_2): δ 13.5, 22.2, 22.6, 25.4, 28.4, 28.6, 28.9, 31.5, 55.1, 64.0, 64.6, 68.3, 68.3, 110.4, 110.6, 111.2, 119.7, 119.9, 120.0, 120.8, 121.2, 123.3, 124.5, 126.2, 126.6, 127.3, 127.4, 127.5, 127.8, 128.1, 128.4, 136.1, 142.3, 142.4, 142.6, 143.0, 143.1, 143.2, 144.5, 152.9, 154.4, 155.0, 155.8, 155.9, 156.1; HRMS (MADLI-TOF) m/z calcd for $C_{84}H_{101}O_7N$ [M+H]$^+$ 1236.7650, found 1236.7663; $[\alpha]_D^{20}$ −75.3 (*c* 0.57, $CHCl_3$).

*4.3.22. (S,S)- and (R,R)-1-(Benzyloxy)-16-(2-bromoethoxy)-8,9-bis (heptyloxy)tetraphenylene (**31**).* Compound (*S*,*S*)-**31** was prepared from (*S*,*S*)-**10** (184 mg, 0.28 mmol) by using the same preparative method as that for compound **23** from compound **10**, except using 1,2-dibromoethane (263 mg, 1.4 mmol) and acetone as solvent.

Column chromatography on silica gel (15 g, EtOAc/CH_2Cl_2/hexanes, 1:1:25) gave pure (*S*,*S*)-**31** (145 mg, two-step overall yield: 66%) as colorless waxy solids: R_f=0.53 (EtOAc/hexanes, 1:20); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91 (t, J=7.1 Hz, 6H, 2×CH_3), 1.20–1.30 (m, 16H, 8×CH_2), 1.45–1.50 (m, 4H, 2×CH_2), 3.14–3.23 (m, 2H, CH_2Br), 3.70–3.80 (m, 4H, OCH_2), 3.91–4.00 (m, 2H, OCH_2), 4.88 (dd, J=12.6, 20.9 Hz, 2H, OCH_2), 6.74–6.77 (m, 3H, Ar*H*), 6.81–6.90 (m, 4H, Ar*H*), 6.97 (dd, J=0.7, 7.6 Hz, 1H, Ar*H*), 7.07–7.09 (m, 2H, Ar*H*), 7.13–7.25 (m, 7H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 22.7, 25.9, 29.1, 29.3, 29.4, 32.0, 69.0, 69.7, 70.9, 111.6, 111.6, 112.6, 113.8, 120.6, 120.7, 121.5, 122.5, 126.7, 127.0, 127.1, 127.2, 127.3, 127.8, 127.8, 128.0, 128.1, 128.1, 128.3, 137.9, 143.1, 143.2, 143.9, 144.3, 155.5, 155.7, 156.5, 156.6; HRMS (MADLI-TOF) m/z calcd for $C_{47}H_{53}O_4Br$ [M+Na]$^+$ 785.3010, found 785.3021. Anal. Calcd for $C_{47}H_{53}O_4Br$: C, 74.10; H, 7.01, found C, 74.18; H, 7.08; (*S*,*S*)-**31**: $[\alpha]_D^{20}$ −31.4 (*c* 1.10, $CHCl_3$); (*R*,*R*)-**31**: $[\alpha]_D^{20}$ +30.1 (*c* 1.00, $CHCl_3$).

*4.3.23. (S,S,S,S)-, (R,R,R,R)-, and (R,R,S,S)-16-(2-(16-(Benzyloxy)-8,9-bis(heptyloxy)tetraphenylen-1-yloxy)ethoxy)-8,9-bis(heptyloxy)tetraphenylene-1-carbonitrile (**32**).* Compound (*S*,*S*,*S*,*S*)-**32** was prepared from (*S*,*S*)-**18** (65 mg, 0.11 mmol) and (*S*,*S*)-**31** (97 mg, 0.13 mmol) by using the same preparative method as that for compound (*S*,*S*,*S*,*S*)-**29**, but using acetone as solvent.

Column chromatography on silica gel (5 g, EtOAc/CH_2Cl_2/hexanes, 1:1:10) gave pure (*S*,*S*,*S*,*S*)-**32** (96 mg, 70%) as colorless waxy solids: R_f=0.26 (EtOAc/hexanes, 1:10); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88–0.93 (m, 12H, 4×CH_3), 1.22–1.29 (m, 32H, 16×CH_2), 1.48–1.53 (m, 8H, 4×CH_2), 3.49 (br s, 2H, OCH_2), 3.72–3.81 (m, 10H, 5×OCH_2), 4.87 (dd, J=13.0, 18.3 Hz, 2H, OCH_2), 5.73 (br s, 1H, Ar*H*), 5.87 (br s, 1H, Ar*H*), 6.38–6.39 (m, 2H, Ar*H*), 6.62 (m, 2H, Ar*H*), 6.69–6.77 (m, 7H, Ar*H*), 6.82–6.84 (m, 3H, Ar*H*), 6.95–7.01 (m, 2H, Ar*H*), 7.06–7.17 (m, 5H, Ar*H*), 7.22–7.29 (m, 4H, Ar*H*), 7.41 (d, J=7.1 Hz, 1H, Ar*H*), 7.49 (d, J=7.5 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 22.7, 25.9, 25.9, 29.1, 29.1, 29.4, 29.5, 31.9, 32.0, 66.9, 67.0, 68.7, 68.7, 69.0, 70.5, 111.0, 111.3, 111.5, 112.0, 113.6, 118.7, 120.4, 120.7, 120.8, 120.9, 121.1, 121.2, 121.5, 125.4, 126.2, 126.6, 126.8, 126.9, 127.1, 127.2, 127.3, 127.4, 127.7, 127.9, 128.0, 128.1, 128.3, 128.4, 130.0, 131.1, 132.7, 138.0, 140.7, 140.9, 141.8, 142.4, 142.9, 143.4, 143.4, 143.5, 143.8, 154.6, 155.4, 155.6, 156.3, 156.5, 156.5.

For (*R*,*R*,*S*,*S*)-**32**, ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88–0.91 (m, 12H, 4×CH_3), 1.19–1.27 (m, 32H, 16×CH_2), 1.48–1.50 (m, 8H, 4×CH_2), 3.67–3.85 (m, 10H, 5×OCH_2), 3.88–3.97 (m, 2H, OCH_2), 4.71 (s, 2H, OCH_2), 6.56 (d, J=8.1 Hz, 3H, Ar*H*), 6.71–6.76 (m, 5H, Ar*H*), 6.82–6.88 (m, 6H, Ar*H*), 6.94–6.96 (m, 2H, Ar*H*), 7.00–7.05 (m, 2H, Ar*H*), 7.16–7.20 (m, 10H, Ar*H*), 7.39–7.41 (m, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 27.7, 25.9, 29.1, 29.1, 29.4, 29.4, 29.5, 32.0, 68.3, 68.5, 68.7, 69.0, 69.1, 70.8, 111.2, 111.6, 111.9, 112.3, 112.5, 113.1, 118.7, 120.5, 120.9, 120.9, 121.0, 121.4, 121.5, 121.6, 126.2, 126.3, 126.7, 127.2, 127.2, 127.3, 127.4, 127.7, 127.9, 128.0, 128.0, 128.2, 129.7, 131.1, 132.4, 137.9, 140.7, 141.7, 142.3, 143.3, 143.4, 143.7, 143.8, 143.8, 155.5, 155.6, 156.3, 156.5, 156.5, 156.5, 156.6; HRMS (ESI) m/z calcd for $C_{86}H_{95}O_7N$ [M+Na]$^+$ 1276.7001, found 1276.6997; (*S*,*S*,*S*,*S*)-**32**: $[\alpha]_D^{20}$ −71.7 (*c* 0.86, $CHCl_3$); (*R*,*R*,*R*,*R*)-**32**: $[\alpha]_D^{20}$ +64.4 (*c* 0.98, $CHCl_3$); (*R*,*R*,*S*,*S*)-**32**: $[\alpha]_D^{20}$ −15.1 (*c* 1.00, $CHCl_3$).

*4.3.24. (S,S,S,S)-, (R,R,R,R)-, and (R,R,S,S)-1-((16-(2-(16-(Benzyloxy)-8,9-bis(heptyloxy)tetraphenylen-1-yloxy)ethoxy)-8,9-bis(heptyloxy) tetraphenylen-1-yl)methyl)pyrrolidine (**33**).* Compound (*S*,*S*,*S*,*S*)-**33** was prepared from (*S*,*S*,*S*,*S*)-**32** (68 mg, 0.05 mmol) by using the same preparative method as that for compound (*S*,*S*)-**20**.

Column chromatography on silica gel (8 g, MeOH/$CHCl_3$, 1:70) gave pure (*S*,*S*,*S*,*S*)-**33** (32 mg, two-step overall yield: 45%) as colorless waxy solids: R_f=0.34 (MeOH/$CHCl_3$, 1:20); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, J=7.2 Hz, 12H, 4×CH_3), 1.17–1.25 (m, 16H, 8×CH_2), 1.46 (br s, 8H, 4×CH_2), 1.64 (m, 8H, 2×CH_2, and 2×NCH_2), 3.53–3.73 (m, 14H, NCH_2, and 6×OCH_2), 4.80 (s, 2H, OCH_2), 6.44–6.52 (m, 2H, Ar*H*), 6.61 (d, J=7.4 Hz, 1H, Ar*H*), 6.66–6.76 (m, 8H, Ar*H*), 6.80–6.88 (m, 4H, Ar*H*), 7.00–7.21 (m, 14H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 22.7, 23.3, 25.9, 25.9, 29.1, 29.4, 29.4, 31.9, 67.6, 67.9, 68.8, 68.9, 69.0, 71.0, 111.1, 111.4, 111.5, 112.8, 113.0, 120.1, 120.6, 120.7, 120.8, 121.7, 126.7, 126.8, 127.1, 127.1, 127.2, 127.4, 127.5, 127.7, 127.9, 128.0, 128.3, 128.6, 135.7, 137.9, 142.6, 142.9, 143.2, 143.3, 143.6, 143.8, 144.0, 154.7, 155.7, 155.8, 156.3, 156.5, 156.5.

For (*R*,*R*,*S*,*S*)-**33**, ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.85–0.90 (m, 12H, 4×CH_3), 1.17–1.26 (m, 16H, 8×CH_2), 1.45–1.48 (m, 8H, 4×CH_2), 1.64 (m, 8H, 2×CH_2, and 2×NCH_2), 3.60–3.80 (m, 14H, NCH_2, and 6×OCH_2), 4.73 (s, 2H, OCH_2), 6.38 (d, J=8.1 Hz, 1H, Ar*H*), 6.60–6.73 (m, 9H, Ar*H*), 6.80–6.83 (m, 2H, Ar*H*), 6.86–6.90 (m, 2H, Ar*H*), 6.96–7.16 (m, 15H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 22.7, 23.3, 25.9, 29.1, 29.5, 32.0, 67.7, 68.3, 68.9, 69.0, 69.0, 69.1, 71.0, 111.4, 111.6, 112.6, 112.8, 120.2, 120.6, 120.7, 120.9, 121.6, 121.8, 121.8, 126.7, 127.1, 127.2, 127.2, 127.3, 127.5, 127.8, 127.8, 127.9, 128.2, 128.3, 128.5, 135.7, 137.8, 142.6, 142.9, 143.2, 143.4, 143.7, 143.7, 143.9, 155.3, 155.7, 156.1, 156.3, 156.5, 156.6; HRMS (ESI) m/z calcd for $C_{90}H_{105}O_7N$ [M+H]$^+$ 1312.7964, found 1312.7947; (*S*,*S*,*S*,*S*)-**33**: $[\alpha]_D^{20}$ −46.2 (*c* 0.67, $CHCl_3$); (*R*,*R*,*S*,*S*)-**33**: $[\alpha]_D^{20}$ −6.6 (*c* 0.90, $CHCl_3$); (*R*,*R*,*R*,*R*)-**33**: $[\alpha]_D^{20}$ +41.1 (*c* 0.80, $CHCl_3$).

*4.3.25. (S,S,S,S)-, (R,R,R,R)-, and (R,R,S,S)-16-(2-(8,9-Bis(heptyloxy)-16-(pyrrolidin-1-ylmethyl)tetraphenylen-1-yloxy)ethoxy)-8,9-bis(heptyloxy)tetraphenylen-1-ol (**34**).* Compound (*S*,*S*,*S*,*S*)-**34** was prepared from (*S*,*S*,*S*,*S*)-**33** (20 mg, 0.02 mmol) by using the same preparative method as that for compound (*S*,*S*)-**21** from compound (*S*,*S*)-**20**.

Column chromatography on silica gel (3 g, MeOH/CH_2Cl_2, 1:40) gave pure (*S*,*S*,*S*,*S*)-**34** (13 mg, 68%) as colorless waxy solids: R_f=0.32 (MeOH/CH_2Cl_2, 1:20); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, 12H, J=7.1 Hz, 4×CH_3), 1.18–1.25 (m, 32H, 16×CH_2), 1.45 (br s, 8H, 4×CH_2), 1.73 (br s, 4H, 2×CH_2), 3.52–3.75 (m, 14H, NCH_2, and 6×OCH_2), 6.42 (d, J=8.1 Hz, 1H, Ar*H*), 6.48 (d, J=8.1 Hz, 1H, Ar*H*), 6.62–6.84 (m, 12H, Ar*H*), 6.90 (d, J=7.4 Hz, 1H, Ar*H*), 7.02–7.18 (m, 8H, Ar*H*), 7.26–7.31 (m, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 22.7, 23.2, 25.9, 29.1, 29.4, 32.0, 67.9, 68.8, 68.9, 68.9, 69.0, 111.2, 111.3, 111.5, 111.7, 112.7, 114.3, 120.1, 120.5, 120.6, 122.1, 123.1, 123.7, 126.9, 127.0, 127.1, 127.2, 127.6, 127.8, 127.9, 128.2, 128.4, 129.0, 142.6, 143.4, 143.6, 143.7, 145.3, 153.0, 154.8, 155.5, 156.3, 156.4, 156.6, 156.7.

For (*R*,*R*,*S*,*S*)-**34**, ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85–0.90 (m, 12H, 4×CH_3), 1.17–1.27 (m, 16H, 8×CH_2), 1.46–1.48 (m, 10H, 5×CH_2), 1.71 (m, 6H, CH_2, and 2×NCH_2), 3.68–3.90 (m, 14H, NCH_2, and 6×OCH_2), 6.55–6.93 (m, 15H, Ar*H*), 7.05–7.16 (m, 9H, Ar*H*); ^{13}C NMR (75 MHz,

$CDCl_3$): δ 14.3, 22.7, 23.3, 25.9, 29.1, 29.4, 32.0, 67.9, 68.9, 69.0, 111.3, 111.5, 111.8, 113.8, 114.2, 119.9, 120.4, 120.7, 121.7, 122.9, 123.5, 127.0, 127.2, 127.5, 127.7, 127.9, 128.4, 128.7, 129.0, 135.6, 142.6, 142.7, 143.5, 143.8, 145.4, 152.8, 154.9, 155.8, 156.3, 156.4, 156.6; HRMS (ESI) *m*/*z* calcd for $C_{83}H_{99}O_7N$ $[M+H]^+$ 1222.7494, found 1222.7486; (*S*,*S*,*S*,*S*)-**34**: $[\alpha]_D^{20}$ −89.7 (*c* 0.63, $CHCl_3$); (*R*,*R*,*R*,*R*)-**34**: $[\alpha]_D^{20}$ +80.0 (*c* 0.66, $CHCl_3$); (*R*,*R*,*S*,*S*)-**34**: $[\alpha]_D^{20}$ −7.2 (*c* 0.69, $CHCl_3$).

*4.3.26. (S,S)-(16-(Benzyloxy)-8,9-bis(heptyloxy)tetraphenylen-1-yl) methanamine (**35**).* To a stirring solution of compound (*S*,*S*)-**19** (25 mg, 0.037 mmol) in dried THF (1 mL) under nitrogen atmosphere, lithium aluminum hydride (14 mg, 0.38 mmol) was added slowly at 0 °C. The mixture was then heated to reflux for 30 min. After cooling to 0 °C, the mixture was diluted with THF and water (1 mL) was dropped slowly to it. After the formation of white precipitates, the mixture was filtered under vacuum and the residue was washed with EtOAc (5 mL×2). The filtrate was dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (EtOAc/CH_2Cl_2/hexanes, 1:1:3) to give pure (*S*,*S*)-**35** (21 mg, 85%) as colorless waxy solids: R_f=0.31 (EtOAc/hexanes, 1:2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J*=7.2 Hz, 3H, C*H*$_3$), 0.88 (t, *J*=7.2 Hz, 3H, C*H*$_3$), 1.17–1.26 (m, 16H, 8×C*H*$_2$), 1.45–1.49 (m, 4H, 2×C*H*$_2$), 3.49 (dd, *J*=14.2, 38.3 Hz, 2H, C*H*$_2$), 3.67–3.77 (m, 4H, 2×OC*H*$_2$), 4.81 (dd, *J*=12.4, 26.2 Hz, 2H, OC*H*$_2$), 6.72 (d, *J*=8.2 Hz, 2H, Ar*H*), 6.77–6.81 (m, 2H, Ar*H*), 6.84 (d, *J*=6.9 Hz, 1H, Ar*H*), 6.89 (d, *J*=0.7, 7.5 Hz, 1H, Ar*H*), 6.96–6.98 (m, 2H, Ar*H*), 7.12–7.19 (m, 4H, Ar*H*), 7.21–7.24 (m, 5H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 22.7, 25.9, 29.1, 29.4, 32.0, 45.3, 68.9, 71.1, 111.4, 111.7, 113.8, 119.9, 120.6, 122.0, 126.5, 126.8, 127.0, 127.1, 127.3, 127.5, 127.8, 128.0, 128.4, 129.2, 135.1, 137.4, 142.9, 143.0, 143.7, 144.1, 154.8, 156.5, 156.6; HRMS (ESI) *m*/*z* calcd for $C_{46}H_{53}O_3N$ $[M+H]^+$ 668.4098, found 668.4094. Anal. Calcd for $C_{46}H_{53}O_3N$: C, 82.72; H, 8.00; N, 2.10, found C, 82.27; H, 7.92; N, 1.81; $[\alpha]_D^{20}$ −28.1 (*c* 0.70, $CHCl_3$).

*4.3.27. (S,S,S,S)-Bis((16-(benzyloxy)-8,9-bis(heptyloxy)tetraphenylen-1-yl)methyl)amine (**37**).* Compounds (*S*,*S*)-**36** (20 mg, 0.03 mmol) and (*S*,*S*)-**35** (21 mg, 0.03 mmol) were dissolved in a mixed solution of THF and MeOH (v/v, 1:1, 0.6 mL) under nitrogen atmosphere. The mixture was cooled to 0 °C with stirring. After stirring for 2 h, $NaBH_3CN$ solution (1.0 M in THF, 45 μL, 0.045 mmol) was injected slowly to the mixture. The stirring was continued overnight at room temperature. The mixture was then treated with aqueous HCl solution (2 M, 2 mL). After dilution with water, the mixture was extracted with CH_2Cl_2 (10 mL×3). The combined organic layer was washed with aqueous HCl solution (2 M, 20 mL) and aqueous NaOH solution (3 M, 30 mL) successively. The organic layer was dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (3 g, EtOAc/CH_2Cl_2/hexanes, 1:1:4) to give pure (*S*,*S*,*S*,*S*)-**37** (31 mg, 80%) as colorless waxy solids: R_f=0.35 (EtOAc/hexanes, 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, *J*=7.0 Hz, 12H, 4×C*H*$_3$), 1.14–1.25 (m, 32H, 16×C*H*$_2$), 1.44–1.53 (m, 8H, 4×C*H*$_2$), 3.14 (d, *J*=13.8 Hz, 2H, NC*H*$_2$), 3.29 (d, *J*=13.8 Hz, 2H, NC*H*$_2$), 3.65–3.75 (m, 8H, 4×OC*H*$_2$), 4.68 (dd, *J*=16.3, 19.6 Hz, 4H, 2×OC*H*$_2$), 6.67–6.72 (m, 7H, Ar*H*), 6.81 (d, *J*=7.1 Hz, 4H, Ar*H*), 6.85–6.89 (m, 4H, Ar*H*), 6.99–7.13 (m, 12H, Ar*H*), 7.15–7.18 (m, 7H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 22.7, 25.9, 29.1, 29.4, 32.0, 51.5, 69.0, 69.1, 70.8, 111.4, 111.8, 113.3, 120.1, 120.7, 121.8, 126.5, 126.6, 127.1, 127.3, 127.3, 127.7, 127.9, 128.0, 128.3, 129.3, 135.4, 137.5, 138.9, 142.3, 143.1, 143.9, 144.0, 154.9, 156.4, 156.5; HRMS (FAB) *m*/*z* calcd for $C_{92}H_{103}O_6N$ $[M+H]^+$ 1318.7858, found 1318.7848; $[\alpha]_D^{20}$ −46.2 (*c* 0.67, $CHCl_3$).

*4.3.28. (S,S,S,S)-16,16′-(Methylazanediyl)bis(methylene)bis(8,9-bis (heptyloxy)tetrapheny len-1-ol) (**38**).* Compound (*S*,*S*,*S*,*S*)-**37** (20 mg, 0.015 mmol) was dissolved in a mixed solution of THF (2 mL) and 37% HCHO solution (37 μL, 0.45 mmol) with stirring. After the addition of TFA (5 μL, 0.06×10^{-3} mmol), the mixture was stirred for 2 h at room temperature. The mixture was then cooled to 0 °C. Sodium borohydride (6 mg, 0.15 mmol) was added slowly to the mixture and warmed to room temperature. After stirring for 30 min, the mixture was diluted with water (5 mL) and extracted with CH_2Cl_2 (5 mL×3) successively. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (3 g, EtOAc/CH_2Cl_2/hexanes, 1:1:8) to give pure protected amine (17 mg, 85%) as colorless waxy solids: R_f=0.75 (EtOAc/hexanes, 1:4).

A mixed solution of protected amine (17 mg, 0.01 mmol) in THF and EtOH (1:1, v/v, 2 mL) was prepared, followed by the addition of palladium black (10 mol %). The mixture was stirred under H_2 for 7 h. The mixture was then filtered through a Celite pad. The filtrate was diluted with CH_2Cl_2 (20 mL). The organic layer was then washed with aqueous HCl solution (2 M, 15 mL) and aqueous NaOH solution (3 M, 20 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated. After column chromatography on silica gel (3 g, EtOAc/CH_2Cl_2/hexanes, 1:1:4), pure (*S*,*S*,*S*,*S*)-**38** (7 mg, 48%) was obtained as colorless waxy solids: R_f=0.35 (EtOAc/hexanes, 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, *J*=7.1 Hz, 12H, 4×C*H*$_3$), 1.14–1.26 (m, 32H, 16×C*H*$_2$), 1.46–1.48 (m, 8H, 4×C*H*$_2$), 1.69 (s, 3H, NC*H*$_3$), 2.81 (d, *J*=12.6 Hz, 2H, NC*H*$_2$), 3.66 (d, *J*=12.6 Hz, 2H, NC*H*$_2$), 3.69–3.75 (m, 8H, 4×OC*H*$_2$), 6.66–6.75 (m, 8H, Ar*H*), 6.79–6.81 (m, 4H, Ar*H*), 7.03–7.12 (m, 6H, Ar*H*), 7.14–7.23 (m, 6H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 22.7, 25.9, 29.1, 29.4, 32.0, 42.2, 58.9, 68.9, 111.3, 111.5, 116.5, 120.1, 120.5, 120.9, 127.0, 127.0, 127.4, 127.6, 127.7, 127.9, 128.6, 129.3, 134.9, 135.7, 143.1, 143.2, 143.4, 144.2, 153.2, 156.2, 156.4; HRMS (ESI) *m*/*z* calcd for $C_{79}H_{93}O_6N$ $[M+H]^+$ 1152.7076, found 1152.7055; $[\alpha]_D^{20}$ −307.8 (*c* 0.20, $CHCl_3$).

*4.3.29. (S,S,S,S)-1-((16-(2-(16-(Benzyloxy)-8,9-bis(heptyloxy)tetraphenylen-1-yloxy)ethoxy)-8,9-bis(heptyloxy)tetraphenylen-1-yl) methyl)piperidine (**39**).* Compound (*S*,*S*,*S*,*S*)-**39** was prepared from (*S*,*S*,*S*,*S*)-**32** (40 mg, 0.03 mmol) by using the same preparative method as that for compound (*S*,*S*,*S*,*S*)-**33**, but using piperidine (19 μL, 0.19 mmol) instead.

Column chromatography on silica gel (5 g, MeOH/$CHCl_3$, 1:70) gave pure (*S*,*S*,*S*,*S*)-**39** (26 mg, 64%) as colorless waxy solids: R_f=0.34 (MeOH/$CHCl_3$, 1:20); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J*=7.3 Hz, 6H, 2×C*H*$_3$), 0.89 (t, *J*=7.2 Hz, 6H, 2×C*H*$_3$), 1.18–1.26 (m, 32H, 16×C*H*$_2$), 1.47 (br s, 12H, 6×C*H*$_2$), 1.61 (br s, 2H, C*H*$_2$), 1.99 (br s, 4H, 2×NC*H*$_2$), 3.50–3.54 (m, 2H, OC*H*$_2$), 3.59–3.63 (m, 2H, OC*H*$_2$), 3.67–3.79 (m, 8H, 4×OC*H*$_2$), 4.81 (s, 2H, OC*H*$_2$), 6.31 (m, 1H, Ar*H*), 6.36 (d, *J*=8.0 Hz, 1H, Ar*H*), 6.56 (d, *J*=7.5 Hz, 1H, Ar*H*), 6.64 (d, *J*=7.5 Hz, 1H, Ar*H*), 6.63–6.87 (m, 10H, Ar*H*), 6.91–7.16 (m, 11H, Ar*H*), 7.19–7.24 (m, 4H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 22.5, 22.7, 25.1, 25.9, 29.1, 29.5, 29.8, 32.0, 52.4, 67.7, 68.9, 69.0, 70.9, 111.2, 111.6, 120.4, 120.6, 120.7, 120.8, 121.6, 121.9, 126.7, 127.1, 127.2, 127.3, 127.3, 127.4, 127.7, 127.9, 128.0, 128.2, 128.3, 137.9, 143.2, 143.7, 144.0, 155.7, 156.1, 156.3, 156.5; HRMS (MADLI-TOF) *m*/*z* calcd for $C_{91}H_{107}O_7N$ $[M+H]^+$ 1327.8154, found 1327.8208; $[\alpha]_D^{20}$ −43.8 (*c* 0.88, $CHCl_3$).

*4.3.30. (S,S,S,S)-16-(2-(8,9-Bis(heptyloxy)-16-(piperidin-1-ylmethyl) tetraphenylen-1-yloxy)ethoxy)-8,9-bis(heptyloxy)tetraphenylen-1-ol (**40**).* Compound (*S*,*S*,*S*,*S*)-**40** was prepared from (*S*,*S*,*S*,*S*)-**39** (26 mg, 0.02 mmol) by using the same preparative method as that for compound (*S*,*S*)-**21** from compound (*S*,*S*)-**20**.

Column chromatography on silica gel (5 g, MeOH/$CHCl_3$, 1:40) gave pure (*S*,*S*,*S*,*S*)-**40** (21 mg, 86%) as colorless waxy solids: R_f=0.32 (MeOH/$CHCl_3$, 1:20); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, *J*=7.2 Hz, 12H, 4×C*H*$_3$), 1.17–1.25 (m, 32H, 16×C*H*$_2$), 1.46 (br s, 12H, 6×C*H*$_2$), 3.60–3.72 (m, 14H, NC*H*$_2$, and 6×OC*H*$_2$), 6.47 (d, *J*=8.1 Hz, 1H, Ar*H*), 6.52–6.54 (m, 1H, Ar*H*), 6.64–6.76 (m, 8H, Ar*H*), 6.78–6.84 (m, 4H, Ar*H*), 6.91 (d, *J*=7.4 Hz, 1H, Ar*H*), 7.04–7.15 (m, 8H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 22.7, 25.9, 25.9, 29.1, 29.4, 32.0, 67.8, 68.9, 68.9, 68.9, 69.0, 111.2, 111.3, 111.5, 111.8, 112.6, 114.3, 120.4, 120.6,

120.7, 120.8, 122.0, 123.0, 123.7, 127.1, 127.1, 127.2, 127.4, 127.8, 127.9, 128.4, 128.9, 142.7, 143.5, 143.6, 143.6, 154.8, 156.3, 156.4, 156.5; HRMS (ESI) *m/z* calcd for $C_{84}H_{101}O_7N$ $[M+H]^+$ 1236.7651, found 1236.7612; $[\alpha]_D^{20}$ −70.9 (*c* 0.80, $CHCl_3$).

*4.3.31. (S,S,S,S)-16-(2-(8,9-Bis(heptyloxy)-16-hydroxytetraphenylen-1-yloxy)ethoxy)-8,9-bis(heptyloxy)tetraphenylene-1-carbonitrile (**41**).* To a solution of compound (*S*,*S*,*S*,*S*)-**32** (47 mg, 0.037 mmol) in THF (2 mL), palladium black (10 mol %) was added. The mixture was stirred under H_2 for 3 h. The mixture was then filtered through a Celite pad. The filtrate was dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (5 g, EtOAc/CH_2Cl_2/hexanes, 1:1:6) to give pure (*S*,*S*,*S*,*S*)-**41** (31 mg, 70%) as colorless waxy solids: R_f=0.3 (EtOAc/hexanes, 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87–0.92 (m, 12H, 4×C*H*$_3$), 1.20–1.30 (m, 32H, 16×C*H*$_2$), 1.49–1.54 (m, 8H, 4×C*H*$_2$), 3.52 (br s, 2H, OC*H*$_2$), 3.68–3.80 (m, 10H, 5×OC*H*$_2$), 4.86 (s, 1H, O*H*), 5.81–5.82 (m, 2H, Ar*H*), 6.35–6.41 (m, 2H, Ar*H*), 6.56–6.64 (m, 2H, Ar*H*), 6.69–6.81 (m, 10H, Ar*H*), 7.06–7.17 (m, 5H, Ar*H*), 7.24–7.28 (m, 1H, Ar*H*), 7.42 (d, *J*=7.3 Hz, 1H, Ar*H*), 7.51 (d, *J*=7.6 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 14.3, 22.7, 22.7, 25.9, 25.9, 29.1, 29.1, 29.1, 29.1, 29.4, 29.4, 29.4, 31.9, 32.0, 66.7, 67.2, 68.7, 68.9, 110.9, 111.0, 111.2, 111.5, 111.6, 112.0, 113.5, 114.0, 118.8, 120.4, 120.6, 120.7, 120.7, 120.9, 121.3, 122.3, 123.5, 123.6, 125.3, 126.2, 126.7, 126.8, 127.1, 127.4, 127.9, 127.9, 128.2, 128.4, 128.5, 129.3, 130.0, 131.2, 132.8, 140.9, 141.8, 142.3, 143.1, 143.5, 143.6, 143.9, 145.1, 152.4, 152.5, 154.4, 154.5, 156.3, 156.4, 156.5, 156.6; HRMS (MADLI-TOF) *m/z* calcd for $C_{79}H_{89}O_7N$ $[M+Na]^+$ 1186.6531, found 1186.6581; $[\alpha]_D^{20}$ −84.9 (*c* 0.93, $CHCl_3$).

*4.3.32. (S,S,S,S,S,S)-16-(2-(16-(2-(16-(Benzyloxy)-8,9-bis(heptyloxy) tetraphenylen-1-yloxy)ethoxy)-8,9-bis(heptyloxy)tetraphenylen-1-yloxy)ethoxy)-8,9-bis(heptyloxy)tetraphenylene-1-carbonitrile (**42**).* Compound (*S*,*S*,*S*,*S*,*S*,*S*)-**42** was prepared from (*S*,*S*,*S*,*S*)-**41** (37 mg, 0.03 mmol) and (*S*,*S*)-**31** (79 mg, 0.10 mmol) by using the same preparative method as that for compound (*S*,*S*,*S*,*S*)-**32**.

Column chromatography on silica gel (5 g, EtOAc/CH_2Cl_2/hexanes, 1:1:10) gave pure (*S*,*S*,*S*,*S*,*S*,*S*)-**42** (24 mg, 43%) as colorless waxy solids: R_f=0.51 (EtOAc/hexanes, 1:4); ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.88 (t, *J*=7.1 Hz, 18H, 6×C*H*$_3$), 1.20–1.29 (m, 48H, 24×C*H*$_2$), 1.50 (br s, 12H, 6×C*H*$_2$), 3.74–3.83 (m, 20H, 10×OC*H*$_2$), 4.82 (s, 2H, OC*H*$_2$), 6.51–6.60 (m, 4H, Ar*H*), 6.61–6.71 (m, 4H, Ar*H*), 6.74–6.88 (m, 14H, Ar*H*), 6.99–7.01 (m, 2H, Ar*H*), 7.07–7.22 (m, 14H, Ar*H*), 7.31 (dd, *J*=7.7, 7.7 Hz, 1H, Ar*H*), 7.44 (dd, *J*=1.2, 7.7 Hz, 1H, Ar*H*), 7.50 (dd, *J*=1.2, 7.6 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 13.6, 22.2, 25.4, 28.6, 28.9, 28.9, 31.5, 68.0, 68.2, 68.4, 70.1, 110.5, 111.0, 111.5, 112.0, 112.3, 112.7, 113.1, 118.0, 119.8, 120.1, 120.2, 120.9, 121.1, 121.2, 125.5, 126.0, 126.2, 126.4, 126.6, 126.7, 127.0, 127.0, 127.4, 127.5, 127.6, 127.7, 127.9, 129.3, 130.8, 132.1, 137.3, 140.1, 141.1, 141.7, 142.7, 142.8, 143.0, 143.2, 143.4, 143.5, 154.9, 155.2, 155.5, 155.8, 155.9; HRMS (ESI) *m/z* calcd for $C_{126}H_{141}O_{11}N$ $[M+Na]^+$ 1868.0430, found 1868.0408; $[\alpha]_D^{20}$ −53.1 (*c* 0.79, $CHCl_3$).

*4.3.33. (S,S,S,S,S,S)-16-(2-(16-(2-(8,9-Bis(heptyloxy)-16-(pyrrolidin-1-ylmethyl)tetraphenylen-1-yloxy)ethoxy)-8,9-bis(heptyloxy)tetraphenylen-1-yloxy)ethoxy)-8,9-bis(heptyloxy)tetraphenylen-1-ol (**43**).* Compound (*S*,*S*,*S*,*S*,*S*,*S*)-**43** was prepared from (*S*,*S*,*S*,*S*,*S*,*S*)-**42** (28 mg, 0.015 mmol) by using the same preparative method as that for compound (*S*,*S*,*S*,*S*)-**34** from compounds (*S*,*S*,*S*,*S*)-**32**.

Column chromatography on silica gel (2 g, MeOH/$CHCl_3$, 1:40) gave pure (*S*,*S*,*S*,*S*,*S*,*S*)-**43** (9.5 mg, three-step: 35%) as colorless waxy solids: R_f=0.33 (MeOH/$CHCl_3$, 1:20); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J*=7.2 Hz, 18H, 6×C*H*$_3$), 1.17–1.25 (m, 48H, 24×C*H*$_2$), 1.46 (br s, 14H, 7×C*H*$_2$), 1.62 (br s, 6H, 3×C*H*$_2$), 3.53–3.74 (m, 22H, 10×OC*H*$_2$, and NC*H*$_2$), 6.46–6.48 (m, 3H, Ar*H*), 6.56–6.78 (m, 16H, Ar*H*), 6.83–6.88 (m, 4H, Ar*H*), 7.00–7.15 (m, 13H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 22.7, 25.9, 29.1, 29.4, 32.0, 69.0, 70.7, 111.3, 111.4, 111.6, 111.8, 113.9, 114.6, 116.8, 120.7, 120.8, 122.1, 122.6, 124.2, 125.7, 127.0, 127.1, 127.2, 127.5, 127.9, 128.2, 128.9, 140.4, 142.8, 143.1, 143.4, 143.8, 143.9, 144.9, 153.0, 155.0, 156.0, 156.3, 156.4, 156.5; HRMS (ESI) *m/z* calcd for $C_{123}H_{145}O_{11}N$ $[M+H]^+$ 1814.0924, found 1814.0942; $[\alpha]_D^{20}$ −48.6 (*c* 0.4, $CHCl_3$).

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Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2010.10.064.

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22. Prepared following the steps (Page, P.C.B.; Buckley, B.R.; Blacker, A.J. *Org. Lett.* **2004**, *6*, 1543–1546 and Chattopadhyay, S.K.; Biswas, T.; Maity, S. *Synlett* **2006**, 2211–2214). 1-(3-Chloropropyl)pyrrolidine: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.74–1.78 (m, 4H, C*H*$_2$), 1.92–2.01 (m, 2H, C*H*$_2$), 2.48–2.59 (m, 6H, NC *H*$_2$), 3.59 (t, *J*=6.6 Hz, 2H, C*H*$_2$Cl); ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.6, 32.1, 43.5, 53.7, 54.4.