Organic & Biomolecular Chemistry

Dynamic Article Links

Cite this: *Org. Biomol. Chem.*, 2012, **10**, 1359

www.rsc.org/obc

PAPER

Synthesis, structure, fullerene-binding and resolution of C_3-symmetric cavitands with rigid and deep cavities†

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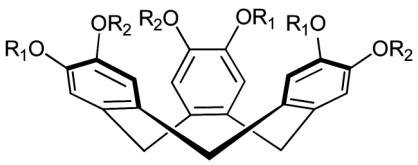
Received 26th August 2011, Accepted 8th November 2011
DOI: 10.1039/c1ob06465g

An efficient palladium-catalyzed Suzuki–Miyaura coupling method involving the reaction between CTV-Br_3 and a variety of aryl and heteroaryl boronic acids in the presence of indolyl phosphane ligands has been developed. This reaction procedure provided a series of C_3-symmetric aryl-extended rigid cavitands for the first time. X-ray crystal structure analysis revealed that the phenyl substituted cavitand **5a** has much larger rim edges and cavity height. This macrocyclic host adopts a linear head-to-tail "hand-shake" self-inclusion arrangement in the crystalline state. The fluorescence of **5a** was considerably quenched upon the addition of C_{60}, with a binding constant of 78 700 ± 2300 dm^3 mol^{-1} and a 1 : 1 stoichiometry according to the Job's plot. The interaction of C_{60} with **5a** in the excited state is stronger than that with CTV, which could be attributed to more binding sites in the extended arms of **5a**. Moreover, optically active C_3-symmetric cavitands (+)- and (−)-**6** were easily obtained with high efficiency through chemical resolution.

Introduction

Cyclotriveratrylene (CTV, **1**, Scheme 1) is a versatile macrocyclic molecule formed by the condensation of veratrole and formaldehyde, and the crown conformation gives it a bowl-shaped and electron-rich cavity.[1] The saddle conformation of CTV is very rare, and can only be isolated from quenching the melt[2] or be observed in the "imploded" cryptophane.[3] If the substituents of the upper rim are different, such CTV analogues are chiral. On the other hand, the enantiomers undergo slow interconversion through the twist-saddle conformations, giving rise to racemisation in solution.[4] Because of the convergent binding modes of CTV-type ligands, they are capable of constructing organic[5] or metallo-supramolecular[6] assemblies. CTV analogues can also be easily functionalized to form various host molecules, such as extended-CTVs, speleands and cryptophanes, as well as hemicryptophanes.[1,7] These CTV-based artificial receptors could be utilized to bind neutral molecules, cations, or anions in solution as well as in the solid state.[8–14] Recent progress in the study of CTV-hosts includes C_{60}/C_{70} binding and separations,[8] ion sensing,[9–11] chiral inclusion,[12] and cryptophane-type hyperpolarized ^{129}Xe biosensing.[13]



1 $R_1 = R_2 = Me$ CTV
2 $R_1 = R_2 = H$ CTC
3 $R_1 = H$, $R_2 = Me$ CTG

Scheme 1 Chemical structures of CTV analogues.

The bowl-shaped cavity of CTV is quite shallow. So in most cases, guest molecules cannot be included in its cavity but can only occupy the channels of the lattice in the crystalline state.[14] Extended-CTVs can be obtained by appending side-arms to the upper rims of hexameric CTC (**2**) or C_3-symmetric CTG (**3**) by etherification/esterification. Amino derived CTV analogues have also been developed in recent years.[15] Compared with the nonchiral C_{3v}-symmetric CTV (**1**) and CTC (**2**), inherently chiral macrocycles (CTG analogues) are more attractive. Their recognition and assembly properties could be applied in supramolecular asymmetric catalysis or utilized as chiral materials. To achieve these goals, we firstly need to enlarge the cavity of CTV. However, because of the free rotation of the "extended arms" around oxygen atoms, the substituents can bend outward or downward of the bowl, which is unfavourable for further recognition and assembly, according to the *preorganization* principles. Thus, we would like to attach rigid substituents (*e.g.* aryls) to the phenyl motifs of the CTV-core directly. CTV analogues with rigid arms do have unique advantages in the construction of functional materials.

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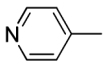
† Electronic supplementary information (ESI) available: Characterization of all new compounds. Copies of ^1H and ^{13}C NMR spectra. UV-vis spectra, HPLC data. CCDC reference numbers 841556. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1ob06465g

Table 1 Palladium-catalyzed Suzuki–Miyaura coupling of **4** and aryl boronic acids[a,b]

Entry	Ar	Pd-cat, ligand, base	(±)-**5**	Yield [%][c]
1	Ph	$Pd(PPh_3)_4$, K_2CO_3	**5a**	58
2	Ph	$Pd(OAc)_2$, **L**, K_3PO_4	**5a**	76
3	4-MeC_6H_4	$Pd(PPh_3)_4$, K_2CO_3	**5b**	35
4	4-MeC_6H_4	$Pd(OAc)_2$, **L**, K_3PO_4	**5b**	67
5	4-$Bu^tC_6H_4$	$Pd(OAc)_2$, **L**, K_3PO_4	**5c**	46
6	4-PhC_6H_4	$Pd(OAc)_2$, **L**, K_3PO_4	**5d**	45
7	3-$MeOC_6H_4$	$Pd(OAc)_2$, **L**, K_3PO_4	**5e**	67
8	4-$MeOC_6H_4$	$Pd(OAc)_2$, **L**, K_3PO_4	**5f**	65
9	4-FC_6H_4	$Pd(OAc)_2$, **L**, K_3PO_4	**5g**	73
10	4-ClC_6H_4	$Pd(OAc)_2$, **L**, K_3PO_4	**5h**	5
11	4-$MeCOC_6H_4$	$Pd(OAc)_2$, **L**, K_3PO_4	**5i**	68
12	4-$EtOCOC_6H_4$	$Pd(PPh_3)_4$, K_2CO_3	**5j**	28
13	4-$EtOCOC_6H_4$	$Pd(OAc)_2$, **L**, K_3PO_4	**5j**	42
14		$Pd(OAc)_2$, **L**, K_3PO_4	**5k**	23
15		$Pd(OAc)_2$, **L**, K_3PO_4	**5l**	21

[a] Reaction conditions for entry 1, 3, 12: **4** (0.16 mmol), boronic acid (4.5 eq, 0.72 mmol), anhydrous K_2CO_3 (6 eq, 0.96 mmol), $Pd(PPh_3)_4$ (10 mol%), DMF (6 mL), H_2O (0.5 mL), 95 °C, 48 h. [b] Reaction conditions for other entries: **4** (0.16 mmol), boronic acid (6 eq, 0.96 mmol), anhydrous K_3PO_4 (9 eq, 1.44 mmol), $Pd(OAc)_2$/**L** (10 mol%), Bu^tOH (15 mL), 130 °C, 44 h. [c] Yields of isolated products.

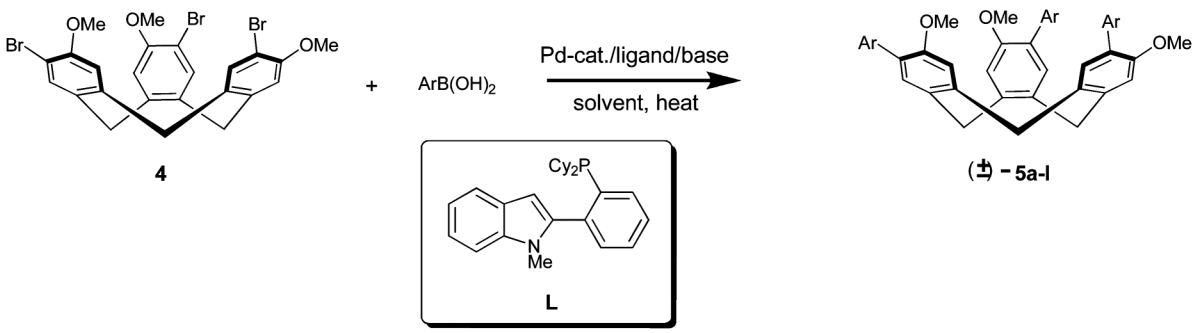
For example, aryl decorated CTV-type ligands can coordinate with metal ions or metal clusters to form chiral cryptophanes or robust metal–organic nanotubes by self-assembly.[16] While the study of the preparation of CTV analogues with "flexible" arms has been fruitful, when it comes to synthetic methods for rigid substituents, only very few examples are reported, but without experimental details included.[16] Here, for the first time, we systematically investigate a facile way to deepen the CTV's cavity with rigid aryl arms using palladium-catalyzed Suzuki–Miyaura coupling (Scheme 2). A variety of easily obtained aryl/heteroaryl boronic acids were chosen for coupling with CTV-Br_3 (**4**)[17] (Table 1). Moreover, we also measured the recognition property between compound **5a** and fullerene molecules, which gave stronger interactions in the excited state than that of CTV (**1**). The resolution of enantiomer (+)- and (−)-**6** is also investigated preliminarily.

Results and discussion

Synthesis

The classic conditions for Suzuki–Miyaura coupling were initially examined: in the presence of $Pd(PPh_3)_4$ and anhydrous K_2CO_3, the reactions of phenyl, 4-tolyl or 4-(ethoxycarbonyl)-phenyl boronic acid with **4** did give rise to the desired products. However, the yields were far from satisfactory (Table 1, entries 1, 3 and 12). According to Miyaura and Suzuki's point of view, in this coupling reaction, the oxidative addition is often the rate determining step, and aryl halides with electron-donating groups are less reactive to the oxidative addition than those with electron-withdrawing groups.[18] Thus the low efficiency could be attributed to the strong electron-donation from the *o*-methoxy as well as the steric hindrance in the upper rim of the CTV.[19] In addition, the introduction of three aryl groups into one substrate molecule at the same time gives a lower overall yield.[20] Hence, we need to find a catalytic system with much higher activity. The indolyl phosphane ligand **L** (Scheme 2) has been determined to be very efficient in the catalytic Suzuki–Miyaura coupling reaction.[21] By using this $Pd(OAc)_2$/**L** catalytic system, we have succeeded in the construction of $C(sp^2)$-$C(sp^2)$ linkage between CTV with phenyl and aryl/heteroaryl groups. After careful optimization of the reaction conditions, we finally chose anhydrous K_3PO_4 as a base, and the reaction was conducted at 130 °C in dry *t*-BuOH for about 44 h, and the corresponding products were obtained in good to moderate yields (Table 1, entries 2, 4–11, 13–15).

In general, using this $Pd(OAc)_2$/**L** catalytic system, we could get better yields than under classic conditions. Aryl boronic acids with electron-donating and electron-withdrawing substituents both worked well. For each CTV-Br_3 molecule, three aromatic substituents were introduced by coupling reaction at the same time. Therefore, in most cases, the transformation of each bromide group was very efficient, although the overall yield was moderate. However, the yield of **5h** that was obtained by coupling between *p*-chlorophenyl boronic acid and **4** was only 5% (Table 1, entry 10), which could be due to the high reactivity of the catalyst system: aryl chloride was activated, thus the homo-coupling product (biphenyl) was predominant for this boronic acid substrate. As we all know, the reactivity of aryl bromide is much higher than aryl chloride in coupling reactions,[18] thus such a low yield of **5h** further confirmed the difficulty of coupling on the upper rim of CTV-Br_3. For the two heteroaryl boronic acids, the yields of



Scheme 2 Palladium-catalyzed Suzuki-Miyaura coupling of CTV-Br_3 with aryl/heteroaryl boronic acids.

coupling were also unsatisfactory (Table 1, entries 14 and 15). The pyridin-4-ylboronic acid is naturally inert in Suzuki–Miyaura coupling.[22] The yield of this reaction could not be improved much even under optimized conditions and with much longer time. The nature of thiophen-2-ylboronic acid is that it is of lower stability and it is easily decomposed at higher temperatures. In addition, the product of **5l** was not very stable in air, which could change its colour from colourless to grey–green within 24 h in the solution of dichloromethane.

Crystal structure of 5a

CTV can form solid-state inclusion compounds with many small potential guest molecules such as benzene, toluene, water, acetone, *etc.*[14] CTV alone does not usually form intra-cavity host–guest complexes, except for spherical guests such as C_{60} and carborane.[8,23] However, the host cavity is easily occupied by another CTV molecule, as for α- and β-phase CTV,[14,24] where CTV molecules stack into misaligned columns and guest molecules are packed in the crystal channels. For CTV derivatives with stretched functional arms on the upper rims, they tend to form self-inclusion associations: the arm of one host is included in the hydrophobic cavity of itself or an adjacent host molecule.[25] A single crystal of **5a** was obtained by slow evaporation in the solution of acetone and methanol. The X-ray structure analysis shows that it has a rigid and deeper cavity[26] (Fig. 1a). The edge of the upper triangle rim and height of the cavity in the original CTV (**1**) was 6.7 and 2.2 Å on average, which increased to 12.8 and 4.6 Å in **5a**, respectively. Similar to other reported crystal structures of the C_3-symmetric CTG-derived macrocycles, we also found self-inclusion phenomenon in the crystal structure of **5a** (Fig. 1b, 1c). A linear chain of **5a** is formed through host–guest inclusion: one extended phenyl group was oriented into the bowl cavity of the adjacent cavitand, whose one extended phenyl arm was oriented into the cavity of the third cavitand, and so on. Note that, only one of the three phenyl arms is involved in this interaction, which is similar to linear head-to-tail associations of functionalised calixarenes.[27] Here, T-shaped π–π interaction (or C_{ph}–H···π interaction) between the phenyl and the cavity became the main driving force for the self-inclusion. The shortest distance of C_{ph}–H···π was 2.744 Å. Each two adjacent molecules in this 1D polymeric self-inclusion chain were a pair of enantiomers. Therefore, the whole crystal of **5a** is racemic.

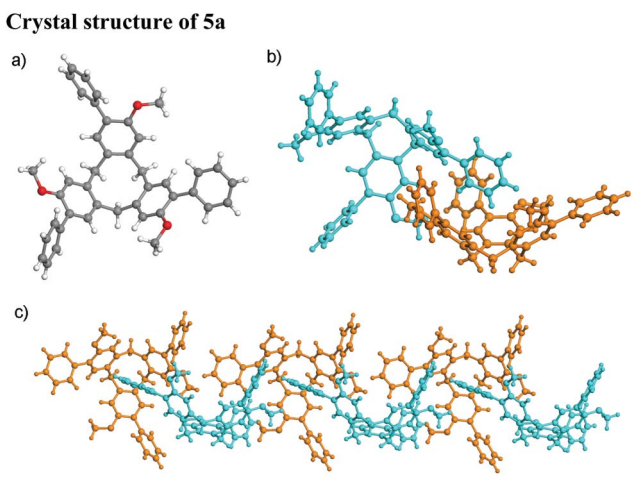


Fig. 1 (a) Ball-and-stick view of molecular structure of **5a**. (b) Asymmetric unit cell of **5a**. (c) The 1D chain of racemic **5a** connected by C_{ph}–H···π interactions. Two adjacent cavitands are shown as light blue and light brown, respectively.

Fullerene binding studies of 5a

Because of the concave skeleton structure and the electron-rich nature of CTV, it can complementally bind molecules with convex electron-poor surfaces such as fullerene C_{60}, to form "ball and socket" structures.[23a] Since C_{60} is much bigger than CTV, great efforts have been made to design CTV-type receptors to increase the binding affinity for fullerenes. Among them, CTV-based tweezer hosts,[8b,8d] hydrogen bonding-driven dimers[8e] and three-dimensional capsular receptors[8h] are found to be effective hosts for fullerene binding and separation. They tend to enclose fullerene molecules tightly in their relatively closed cavities. We speculate that these extended rigid hosts that we have obtained may be another choice for binding normal fullerene guests. Here we made a preliminary study of **5a** for its binding property with fullerenes. By UV-vis spectra titration, neither very obvious shifts nor isosbestic points were observed in the absorption curves of C_{60}, upon addition of compound **5a** in toluene solution. (see ESI†, Fig. S1) It indicates that there is no strong interaction between **5a** and C_{60} in the ground state. To further study the recognition of C_{60} by **5a**, a fluorescence titration was conducted (Fig. 2). The fluorescence intensity of **5a** at about λ_{em} = 346 nm decreased constantly with increasing concentration of C_{60}. To eliminate the competitive adsorption of C_{60} at excitation and emission wavelengths, the fluorescence intensity F_{exp} of **5a** was calibrated to F_{cal} according to a literature method.[28] The quenching was found to follow the Stern–Volmer equation, and the dependence of the calibrated F_0/F_{cal} on the concentration of C_{60} is illustrated

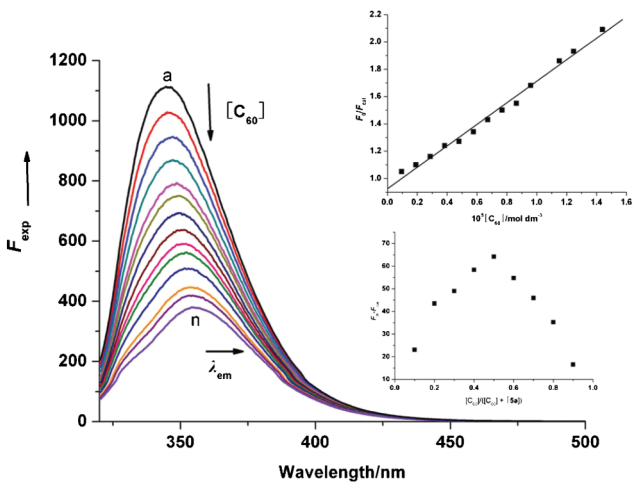
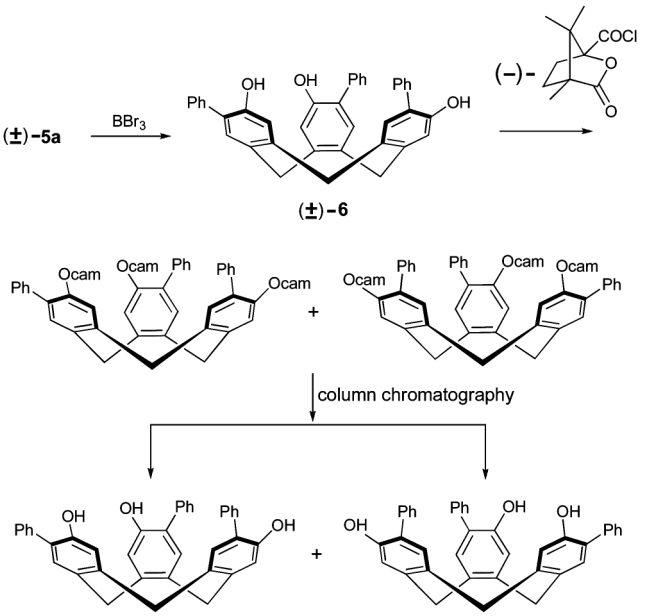


Fig. 2 Emission spectra (λ_{ex} = 305 nm, λ_{em} = 346 nm.) of **5a** (3.2×10^{-6} mol dm^{-3}) in the presence of C_{60} in toluene at 25 °C. The concentrations of C_{60} for curves a–n (from top to bottom) were 0, 0.096, 0.192, 0.288, 0.384, 0.480, 0.576, 0.672, 0.768, 0.864, 0.960, 1.152, 1.248, 1.44 ($\times 10^{-5}$ mol dm^{-3}). Insets: The top inset is the variation of fluorescence intensity F_0/F_{cal} of **5a** with increasing C_{60} concentration. The bottom inset is the Job's plot for the **5a**–C_{60} complex in toluene solution ([**5a**] + [C_{60}] = 6.4×10^{-6} mol dm^{-3}).

in the top inset to Fig. 2. The stability constant K_s calculated from the plot of F_0/F_{cal} *versus* C_{60} concentration is 78 700 ± 2300 $dm^3\ mol^{-1}$.[29] There is a shift from 344.8 nm to 354.2 nm in the emission maximum of the quenching curves upon increasing the C_{60} concentration, which indicates the formation of the charge–transfer complex. The excited state of **5a** is more stabilized by C_{60} molecules than the ground state, and this kind of interaction leads to the red-shift of the emission spectra.[30] The Job's plot indicates 1 : 1 complexation between **5a** and C_{60} in toluene (Fig. 2, bottom inset). This kind of binding could be due to photo induced charge transfer interactions between the electron-rich cavitand **5a** and the relatively electron-poor fullerene at the excited state. This value is a little bigger than the binding constant between **1** and C_{60} (51 900 ± 1100 $dm^3\ mol^{-1}$) measured under the same conditions in our laboratory, which indicates that the rigid extended CTV is a better C_{60} host. The fluorescence quenching phenomenon also occurred between **5a** and gradual addition of C_{70}, with a binding constant of 69 200 ± 1800 $dm^3\ mol^{-1}$, (see ESI†) a little smaller than that of C_{60}, and with less red shifts. Which means that, due to the relatively small cavity of **5a** and the oval shape of C_{70}, the charge transfer complex is not so stable. Another driving force for fullerene recognition between fullerenes and **5a** may be the van der Walls force between sterically fitted concave and convex π faces, which has been confirmed by the crystalline structure of the CTV-C_{60} complexes.[23a] Although we can't obtain the same evidence for the **5a**–C_{60} complex, the primary theoretical calculations indicate that there are weak interactions between the extended arms and C_{60}. (see ESI, Fig. S4†)

Chemical resolution of 6

C_3-symmetric molecules have been widely applied in the area of asymmetric catalysis, molecular recognition and chiral nanomaterials in recent years.[31] The conformational inversion of the 9-membered ring of CTV is quite slow at room temperature,[4b] so the C_3-symmetric CTV analogues can be resolved to obtain optical active isomers. Traditional method involve the introduction of appropriate chiral auxiliary groups to form diastereoisomers, which were then separated by chromatographic separation or recrystallization, followed by cleavage of the chiral groups.[32] Warmuth developed a new method of asymmetric synthesis through dynamic thermodynamic resolution.[5a] Here, in order to prepare the optically active CTVs, the chemical resolution method has been investigated. Firstly, **5a** was demethylated with BBr_3 in anhydrous dichloromethane to prepare (±)-**6**, which then reacted with (–)-ω-camphanic acid chloride to give a diastereoisomer mixture. By column chromatography, this diastereoisomer mixture could be separated easily. After reductive cleavage, (+)- and (–)-**6** were obtained with 93 and 96% ee. The $[\alpha]_D^{20}$ ($CHCl_3$, c = 0.12) values were +500.8° and –498.3°, respectively. (Scheme 3, see ESI for HPLC details†) The CD spectra of (+)- and (–)-**6** were measured and they were mirror images of each other, indicating their enantiomeric nature and the successfulness of the separation process (Fig. 3). Actually, optically pure (+)- and (–)-**3** has been obtained by this method before in our laboratory, but it required the preparative TLC technique with more than one operation according to our experimental experiences. But with the introduction of rigidly linked phenyl groups, we could prepare



Scheme 3 The chemical resolution of **6**.

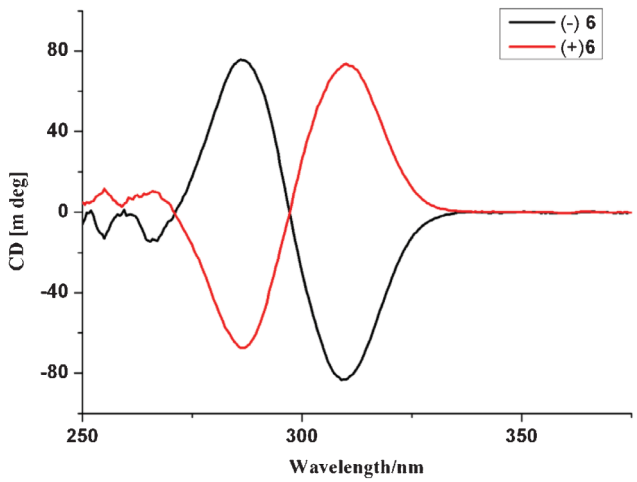


Fig. 3 CD spectra of (–)-**6** and (+)-**6** (1.0×10^{-4} M) in MeOH at 25 °C.

the optically pure C_3-symmetrical cavitands more conveniently, which is important for optical resolution on a larger scale.

Conclusions

In summary, in the presence of an active indolyl phosphane ligand, efficient palladium-catalyzed Suzuki–Miyaura coupling of CTV-Br_3 with a variety of aryl boronic acids has been developed. A series of novel C_3-symmetric cavitands with rigid and deep cavities have been prepared, and enriched the family of CTV-type hosts. X-ray crystal structure analysis showed that the phenyl substituted cavitand **5a** adopted a linear head-to-tail self-inclusion arrangement in the crystalline state. Its deeper cavity is a better C_{60} host than simple CTV (**1**), and can form a photoinduced charge transfer complex at the excited states. Optically active C_3-symmetric cavitands (+)- and (–)-**6** have been obtained through chemical resolution. Further investigation of chiral recognition and assembly of these new macrocycles is ongoing.

Experimental section

General

Melting points were taken on an electrothermal melting point apparatus and without correction. IR spectra were recorded on a FT-IR-480 spectrometer using KBr discs. The UV-vis and fluorescence titration experiments were performed on Shimadzu UV-1601PC and Hitachi F-4500 FL spectrophotometers, respectively. CD spectra were conducted on JASCO J-810 spectropolarimeter. HPLC chromatography was conducted on a VARIAN Prostar 335 spectrometer. Elemental analyses were performed by a Flash EA 1112 elemental analyzer. Mass spectra were recorded on a Thermal Finnigan Surveyor MSQ Plus Mass Detector. ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature on a Bruker (400 MHz) NMR spectrometer. X-ray diffraction data on single crystals were collected on a Rigaku RAXISRAPID diffractometer with graphite monochromated Mo-Kα radiation ($\lambda_{Mo\text{-}K\alpha}$ = 0.71073 Å) at 173 K. CTV (**1**)[33] and CTV-Br_3 (**4**)[17] were synthesized according to the literature method. Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification.

General procedures for $Pd(PPh_3)_4$ catalyzed Suzuki–Miyaura couplings

A two-neck round-bottom flask was charged with **4** (100 mg, 0.16 mmol), boronic acid (4.5 eq, 0.72 mmol), anhydrous K_2CO_3 (6 eq, 0.96 mmol) and $Pd(PPh_3)_4$ (18 mg, 10 mol%), evacuated and flashed with argon for three times. Then, degassed DMF (6 mL), H_2O (0.5 mL) was added. The mixture was allowed to heat at 95 °C for 48 h, and then cooled to room temperature, extracted with CH_2Cl_2 (3 × 15 ml). The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The desired product was then isolated by chromatography on silica gel (200–300 mesh).

General procedures for $Pd(OAc)_2$/L catalyzed Suzuki–Miyaura couplings

$Pd(OAc)_2$ (3.8 mg, 0.016 mmol, 10 mol%) and **L** (26 mg, Pd: **L** = 1: 4) were loaded into a Schlenk tube equipped with a Teflon-coated magnetic stirring bar. Precomplexation was applied by adding freshly distilled dichloromethane (0.5 mL) and Et_3N (50μL) into the tube. The solution was stirred and quickly heated until the solvent started boiling and then evaporated under high vacuum. **4** (100 mg, 0.16 mmol), arylboronic acid (6 eq, 9.6 mmol) and K_3PO_4 (9 eq, 1.44 mmol) were loaded into the tube under argon, degassed *tert*-butanol (15 mL) was then added. The tube was stirred at room temperature for 5 min and then placed into an oil bath and allowed to reach 130 °C rapidly. After about 44 h, the reaction tube was cooled to room temperature and quenched with water, extracted with CH_2Cl_2 (3 × 15 ml). The desired product was then isolated by chromatography on silica gel (200–300 mesh).

Chiral separation of compound (±)-6

Synthesis of racemic (±)-6. 0.3 mL (2.1 mmol) of BBr_3 was added dropwise to a solution of (±)-**5a** (300 mg, 0.51 mmol) in 10 mL of freshly distilled CH_2Cl_2 in ice bath. The mixture was allowed to warm to room temperature and stirred under argon for 5 h, poured into 10 g of ice, stirred, the precipitate was filtrated, dried under vacuum and an off-white powder of (±)-**6** was obtained, 255 mg, 91% yield.

Optical Resolution. To a solution of ((±)-**6** (200 mg, 0.44 mmol) in 10 mL anhydrous pyridine was added 380 mg of (–)-ω-camphanic acid chloride (1.74 mmol), and the reaction mixture was stirred under room temperature for 12 h, then 20 mL of cold water was added, a precipitation of the solid diastereomers were collected by suction filtration, washed with water, and dried. This crude 1 :1 mixture was separated by chromatography.

Cleavage of the diastereomers. To a solution of 150 mg of one pure diastereomer (0.14 mmol) in 5 mL of freshly distilled THF was added 25 mg of $LiAlH_4$, and it was stirred at 0 °C for 2 h. The reaction was quenched by dropwise addition of ethyl acetate, and 10% aqueous H_2SO_4 (ice bath), extracted with ethyl acetate followed by evaporation of the solvent under vacuum without heating. The desired triphenol was isolated by column chromatography, and about 70 mg (98% yield) of **(–)-6** was obtained, ($[\alpha]_D^{20}$ −498.3 ($CHCl_3$, c = 0.12) 96.3 ee% (HPLC)) (or **(+)-6** ($[\alpha]_D^{20}$ = +500.8 ($CHCl_3$, c = 0.12) 99.3% ee (HPLC))).

Acknowledgements

This work was supported by the National Natural Science Foundation of China (20932004), the Major State Basic Research Development Program of China (2011CB932501), and the Chinese Academy of Sciences.

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Where $\varepsilon_1 c_1 l$ is the absorption of **5a** at the excitation wavelength, $\varepsilon_2 c_2 l$ is the absorption of the guest at the excitation wavelength, and $\varepsilon_3 c_3 l$ is the absorption of the guest at the emission wavelength.

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