Organic & Biomolecular Chemistry

Dynamic Article Links

Cite this: *Org. Biomol. Chem.*, 2011, **9**, 7007

www.rsc.org/obc

PAPER

Efficient synthesis of copillar[5]arenes and their host–guest properties with dibromoalkanes†

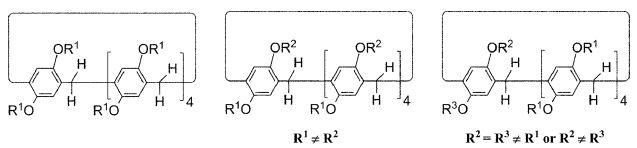
Luzhi Liu,[a] Derong Cao,*[a,b] Yi Jin,[a] Hongqi Tao,[a] Yuhui Kou[a] and Herbert Meier*[c]

Received 1st June 2011, Accepted 12th July 2011
DOI: 10.1039/c1ob05871a

An efficient method for the synthesis of copillar[5]arenes was developed with $FeCl_3$ as catalyst and different 1,4-dialkoxybenzenes and paraformaldehyde as reactants (yields: 50–85%). The host–guest property of (co)pillar[5]arenes and terminal dibromoalkanes was investigated by ^{1}H NMR measurements and an X-ray study. The complexation behavior of the copillar[5]arenes can be tuned by changing the substituents on the host. A complete complexation selectivity was found between pillar[5]- and pillar[6]arenes, which is an interesting aspect for sensor techniques.

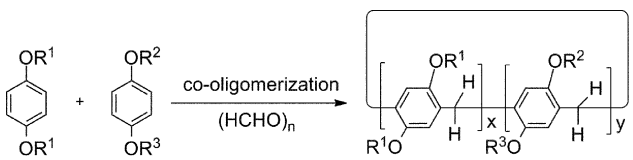
Introduction

Pillar[n]arenes,[1–18] a new class of macrocyclic hosts, are attracting considerable attention because of their applications in host-guest chemistry,[1,5–7] self-assembly chemistry[8,11,12] and fluorescence chemistry. As electron donors with the character of hydroquinone derivatives, pillararenes have shown very interesting host-guest binding properties and three types of structures (Scheme 1) were reported. In contrast to the fully symmetrical pillar[5]arenes (structure type I) and the unsymmetrical pillar[5]arenes (structure type II), copillar[5]arenes (structure type III) have some advantages. Firstly, they can easier be selectively functionalized to synthesize various other copillar[5]arenes. Secondly, they can bear substituents, which are suitable for self-complexation. Thus, the copillar[5]arenes obtained considerable attention.



Scheme 1 Three types of pillar[5]arenes.

Huang and coworkers prepared copillar[5]arenes by the co-oligomerization of two different monomers with [BF_3·$O(C_2H_5)_2$] as catalyst in a yield of 9%–27%.[9] Stoddart *et al.*[13] synthesized a monofunctionalized copillar[5]arene containing a bromoalkyl chain by condensation of 1-(2-bromoethoxy)-4-methoxybenzene and 1,4-dimethoxybenzene in the presence of BF_3·$O(C_2H_5)_2$. Recently, Huang *et al.*[12] synthesized a copillar[5]arene bearing an octyl group by the same way in a yield of 9% and studied the formation of linear supramolecular polymers. However, syntheses of copillar[5]arenes meet two problems: low yields and separation difficulties. In fact, many different types of copillar[5]arenes can be expected as reaction products of two different hydroquinone derivatives (Scheme 2). Therefore, it is very important to develop a new method for the synthesis of copillar[5]arenes with high selectivity and high yield.



	$R^2 = R^3 \neq R^1$ isomers	$R^2 \neq R^3$ isomers
a: x = 5, y = o	1	1
b: x = 4, y = 1	1	1
c: x = 3, y = 2	2	6
d: x = 2, y = 3	2	8
e: x = 1, y = 4	1	10
f: x = 0, y = 5	1	4

Scheme 2 Formation of pillar[5]arenes and copillar[5]arenes by the reaction of two different hydroquinone derivatives.

Pillararenes serve as an important class of hosts for a variety of guest molecules including electron accepting molecules such as viologen, pyridinium salts, acetonitrile, amines and alkanes.[4,7,9,13] Among the various guest molecules, alkanes have been employed as model molecules to study the influence of host-guest self-assembled structures.[19] However, until now, the host-guest binding

[a]*School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, 510640, China. E-mail: drcao@scut.edu.cn; Fax: +86-20-87110245; Tel: +86-20-87110245*
[b]*State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou, 510640, China*
[c]*Institute für Organishche Chemie, Johannes Gutenberg-Universität Mainz, Duesbergweg 10-14, 55099, Mainz, Germany. E-mail: hmeier@uni-mainz.de*
† Electronic supplementary information (ESI) available: Fundamental characteristics (^{1}H NMR and ^{13}C NMR spectra) of the compounds (**3b–i**). CCDC reference number 821446. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1ob05871a

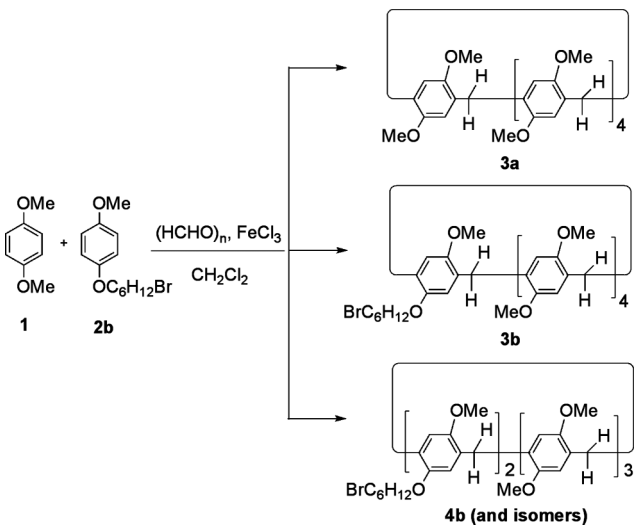
properties between pillararenes and bromoalkyl chains or dibromoalkanes have not been studied.

In this paper, we develop a new method for the synthesis of copillar[5]arenes in high yields by using $FeCl_3$ as catalyst and study their host-guest properties with terminal dibromoalkanes and bromoalkyl pendants.

Results and discussion

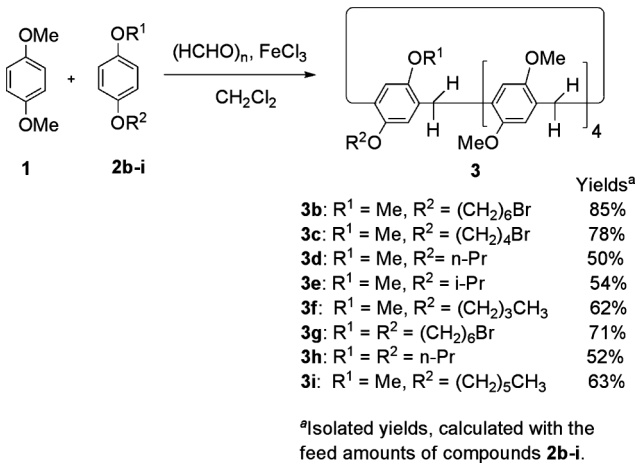
Synthesis

Generally, there are two major ways to make fully symmetrical pillar[5]arenes with $BF_3{\cdot}O(C_2H_5)_2$ or *p*-toluenesulfonic acid as catalyst. However, the yields of copillar[5]arenes are too low by applying these methods (9–27%).[9,12,13] We tried to synthesize copillar[5]arenes by direct co-oligomerization of different 1,4-dialkoxybenzenes. After screening a variety of catalysts, solvents and mixture ratios of the related 1,4-dialkoxybenzenes, we found that $FeCl_3$ in CH_2Cl_2 as solvent is an excellent catalyst. Scheme 3 shows the product formation of the reaction of paraformaldehyde,1,4-dimethoxybenzene (**1**) and 1-(6-bromohexyloxy)-4-methoxybenzene (**2b**). A 4/1 mixture of equally reactive compounds **1** and **2b** should give the product distribution **3a**:**3b**:**4b** = 4^5:5 × 4^4:10 × 4^3 (Bernoulli chain) and a small amount of products which contain 3, 4 or 5 components **2b**. This corresponds for example to a distribution: 24% **3a**, 30% **3b**, 15% **4b**. The obtained absolute yields are very close to this ratio (Table 1). A 16/1 ratio of **1** and **2b** enhanced the yield of **3b** to 85%.



Scheme 3 Optimization of reaction conditions by varying the mixture ratio of **1** and **2b**.

Under these reaction conditions, a series of new copillar[5]arenes **3c–i** were synthesized in isolated yields of 50–78% (Scheme 4).



Scheme 4 Preparation of copillar[5]arenes by oligomerization of different 1,4-dialkoxybenzenes.

Host-guest properties

In the ^{1}H NMR spectrum of **3b** in $CDCl_3$, the protons signals (–2.0–2.5 ppm) of the bromoalkyl group are shifted significantly to high field (accompanied with line broadening) in comparison to 6-bromohexanol. This phenomenon indicates that alkyl bromides could complex with pillar[5]arenes. To confirm this hypothesis, we studied the ^{1}H NMR spectra of the mixtures of **3a** with different terminal dibromoalkanes and found that protons of the alkyl chains showed analogous up-field shifts. For example, in the complex of **3a** with 1,6-dibromohexane (DBH), the protons of DBH showed strong up-field shifts (Δδ = 0.93, 1.41 and 2.65 ppm for peak H_1, H_2 and H_3, respectively) (Fig. 1). The Δδ values are much larger than those of the complexes with viologen

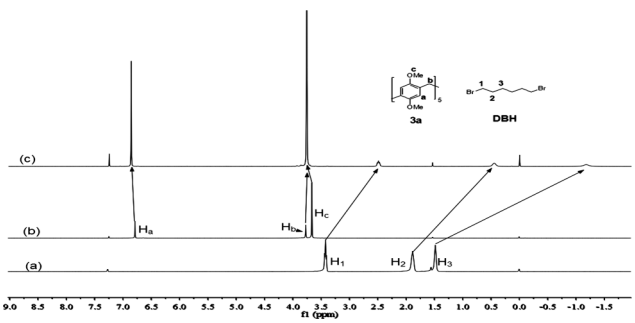


Fig. 1 The ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of (a) DBH, (b) **3a**, and (c) an equimolar mixture of **3a** and DBH (18.8 mM).

Table 1 Optimization of reaction conditions

Entry	Molar Ratio (**1**/**2b**)	Yield[a] (**3a**)	Yield[b] (**3b**)	Yield[b] (**4b**)	Molar Ratio (**3b**/**4b**)
1	4/1	24%	27%	11%	5/1
2	8/1	47%	64%	7%	18.6/1
3	16/1	59%	85%	None	—

[a] Isolated yields, calculated based on the feed amount of compound **1**. [b] Isolated yields, calculated based on the feed amount of compound **2b**.

or pyridinium salts.[10] Fig. 2 shows the crystal structure of **3a** in whose cavity a 1,6-dibromohexane is symmetrically threaded. There are two interesting interactions for the inclusion of 1,6-dibromohexane, documented by the short distances O . . . H_2CBr and CH_2 . . . π cloud (benzene).

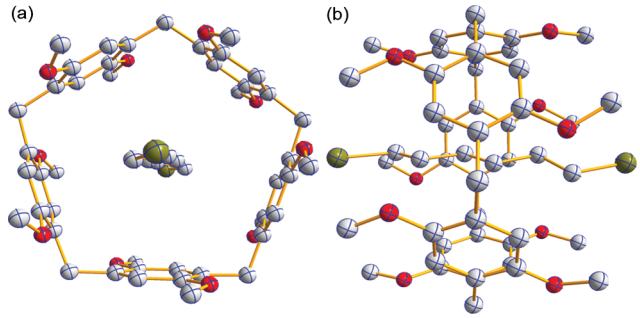


Fig. 2 The host-guest system of **3a** and DBH: (a) view from above, (b) view from the side.

Some 1 : 1 complexes are so strong that they can be observed in the ESI-MS. For **3f**-DBB the cation [**3f**-DBB-NH_3-K]$^+$ with m/z = 1061.8 could be found.

Based on these results, we can say pillar[5]arenes such as **3a** have excellent host-guest properties. To examine the influence of pendants on the binding interaction, we studied the complexation of 1,4-dibromobutane (DBB) and the (co)pillar[5]arenes **3a**, **3b**, **3d–3h**. Table 2 shows the chemical shifts of DBB in $CDCl_3$ and its changes Δδ in the presence of approximately 1 equiv of the different hosts. According to the size of the Δδ values, the binding interactions of **3a**, **3b**, **3f** and **3h** are high, whereas they are low for **3d**, **3e** and **3g**. Further experiments have to clarify this effect of different side chains.

In order to investigate the binding selectivity of dibromoalkanes to different hosts, we also examined the interaction of **DBH** with 1,4-bis(ethoxy)pillar[6]arene (**BEOP6**).[2] The results show that no complexation between **BEOP6** and **DBH** in $CDCl_3$ occurs. Fig. 3 shows the ^{1}H NMR spectrum of an equimolar solution of **BEOP6** and **DBH** and the spectra of the corresponding compounds. The distance of the cavity of **BEOP6** is too large: 9.5 ± 0.5 Å in comparison to 8.1 Å for pillar[5]arenes.[4]

Conclusion

In summary, an efficient method for the synthesis of copillar[5]arenes has been developed with $FeCl_3$ as catalyst (yields: 50–85%). Surprisingly strong host-guest interactions between the copillar[5]arenes and dibromoalkanes were found and studied by

Table 2 Upfield shifts of 1,4-dibromobutane guest molecules ([G-DBB] = 18.8 mM, $CDCl_3$, 298 K) in different host-guest complexation

Compound	δ (H1)/ppm	Δδ (H1)/ppm	δ (H2)/ppm	Δδ (H2)/ppm
DBB	3.45	0	2.04	0
3a + DBB	1.55	1.90	–0.46	2.5
3b + DBB	1.55	1.90	–0.21	2.25
3d + DBB	3.15	0.30	1.70	0.34
3e + DBB	3.22	0.23	1.77	0.27
3f + DBB	1.37	2.08	–0.67	2.70
3g + DBB	3.31	0.14	1.80	0.24
3h + DBB	2.04	1.40	–1.14	3.18

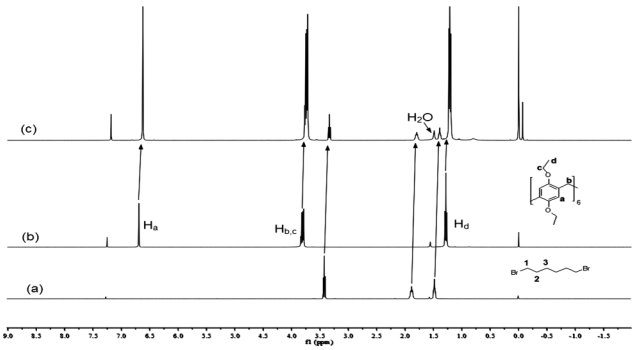


Fig. 3 The ^{1}H NMR spectra ($CDCl_3$) of (a) DBH, (b) BEOP6, and (c) an equimolar mixture of BEOP6 and DBH (18.8 mM).

^{1}H NMR spectroscopy. A crystal structure analysis proved that the dibromoalkane is symmetrically threaded in the pillar[5]arene cavity. 6-Bromohexyl pendants on the copillar[5]arene lead to a self-complexation. The cavity of pillar[6]arene is too large and therefore not suitable to complex dibromoalkanes. Such a complete selectivity has a highly interesting aspect for sensor techniques. Furthermore, the bromoalkyl pendants opens the door to many functionalized hosts and their supramolecular chemistry.

Experimental section

Reagents and instruments

Pillar[5]arene **3a** and 1,4-bis(ethoxy)pillar[6]arene were synthesized according to the literature procedure.[2] Solvents were either employed as purchased or dried according to procedures described in the literatures. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded with a Bruker DRX 400 spectrometer by using $CDCl_3$ as solvent and TMS as an internal standard. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass measurements were performed with an Autoflex III smart-beam spectrometer. Thin layer chromatography was performed by using commercial Merck silica gel plates (GF254), and visualization was carried out at 254 nm.

General procedure for the preparation of copillar[5]arenes

To a solution of **1** (0.55 g, 4.0 mmol) and **2** (0.25 mmol) in CH_2Cl_2 (80 mL), paraformaldehyde (0.36 g, 12 mmol) was added in a nitrogen atmosphere. Then, anhydrous ferric chloride (103.25 mg, 0.64 mmol) was added to the solution and the mixture was stirred at 25–30 °C. After the completion of the reaction, water (63 mL) was added and the product was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phase was dried over with anhydrous Na_2SO_4. The crude mixture was chromatographed over silica gel column using a mixture of ethyl acetate and petroleum ether.

Copillar[5]arene **3b**: colorless crystals, in 85% yield (191 mg), m.p. 202–203 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.84–7.11 (m, 10H), 3.70–3.91 (m, 40H), 1.56 (m, 1H), 1.24–1.35 (d, 2H), 0.31–1.14 (m, 2H), (–0.34)–0.30 (m, 2H), (–1.73)–(–0.50) (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 151.11, 150.71, 150.38, 150.31, 150.20, 150.15, 149.53, 128.18, 128.11, 127.95, 127.74, 115.62, 115.58, 114.25, 114.04, 113.28, 113.00, 112.96, 112.88, 112.76, 68.89, 57.06, 56.47, 55.31, 55.28, 55.18, 55.14, 33.06, 30.67, 30.44, 29.64, 29.19, 29.13, 28.92, 27.69, 23.99. MS (MALDI-TOF)

calcd for $C_{50}H_{59}BrO_{10}$ 898.329, found 898.334 $[M]^+$, 921.322 $[M + Na]^+$, 937.342 $[M + K]^+$. Anal. Calc. for $C_{50}H_{59}BrO_{10}$: C, 66.73; H, 6.61. Found: C, 66.80; H, 6.71.

Copillar[5]arene **3c**: colorless crystals, in 78% yield (170 mg), m.p. 161–162 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.77 (s, 10H), 3.77 (s, 10H), 3.65 (s, 29H), 3.40 (s, 2H), 0.88–0.99 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 150.86, 150.82, 150.80, 150.77, 150.71, 150.67, 149.91, 128.33, 128.30, 128.24, 128.22, 128.15, 114.83, 114.37, 114.11, 114.04, 114.00, 113.84, 113.77, 67.45, 56.07, 55.95, 55.79, 55.77, 55.76, 55.71, 33.24, 29.78, 29.72, 29.69, 29.60, 29.38, 28.97, 28.36. MS (MALDI-TOF) calcd for $C_{48}H_{55}BrO_{10}$ 870.298, found 870.080 $[M]^+$, 893.117 $[M + Na]^+$. Anal. Calc. for $C_{48}H_{55}BrO_{10}$: C, 66.13; H, 6.36. Found: C, 66.21; H, 6.30.

Copillar[5]arene **3d**: colorless crystals, in 50% yield (97 mg), m.p. 129–130 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.80–6.83 (m, 10H), 3.76–3.82 (m, 13H), 3.68–3.69 (d, 24H), 3.43 (s, 2H), 1.75–1.83 (dd, 2H), 1.01–1.05 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 150.65, 150.61, 150.50, 149.95, 128.48, 128.45, 128.36, 128.32, 128.26, 128.23, 114.59, 113.78, 69.94, 55.73, 55.69, 55.68, 52.37, 29.56, 29.53, 29.47, 29.43, 29.35, 23.15, 10.91. MS (MALDI-TOF) calcd for $C_{47}H_{54}O_{10}$ 778.372, found 778.524 $[M]^+$, 801.517 $[M + Na]^+$. Anal. Calc. for $C_{47}H_{54}O_{10}$: C, 72.47; H, 6.99. Found: C, 72.41; H, 6.93.

Copillar[5]arene **3e**: colorless crystals, in 54% yield (105 mg), m.p. 101–103 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.51–6.75 (m, 10H), 4.12–4.18 (m, 1H), 3.67–3.70 (m, 11H), 3.58–3.63 (m, 23H), 3.54 (s, 3H), 0.90–0.91 (d, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 150.77, 150.73, 150.71, 150.70, 150.64, 150.32, 148.54, 128.47, 128.40, 128.30, 128.26, 128.24, 128.21, 115.88, 114.21, 114.05, 114.04, 113.93, 113.89, 113.73, 114.69, 113.66, 69.33, 55.80, 55.72, 55.66, 52.52, 30.14, 29.64, 29.59, 29.48, 29.45, 21.81. MS (MALDI-TOF) calcd for $C_{47}H_{54}O_{10}$ 778.372, found 778.530 $[M]^+$, 801.523 $[M + Na]^+$. Anal. Calc. For $C_{47}H_{54}O_{10}$: C, 72.47; H, 6.99. Found: C, 72.44; H, 6.89.

Copillar[5]arene **3f**: colorless crystals, in 62% yield (127 mg), m.p. 139–140 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.77–6.80 (m, 10H), 3.82–3.86 (t, 2H), 3.77–3.79 (m, 10H), 3.66 (s, 27H), 1.71–1.77(m, 2H), 1.48–1.53(m, 2H), 0.93–0.97 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 150.76, 150.73, 150.14, 128.31, 128.28, 128.24, 128.19, 128.15, 128.13, 114.11, 68.11, 55.72, 55.71, 55.64, 31.80, 29.63, 19.50, 13.97. MS (MALDI-TOF) calcd for $C_{48}H_{56}O_{10}$ 792.387, found 792.402 $[M]^+$, 815.395 $[M + Na]^+$. Anal. Calc. for $C_{48}H_{56}O_{10}$: C, 72.70; H, 7.12. Found: C, 72.64; H, 7.05.

Copillar[5]arene **3g**: colorless crystals, in 71% yield (186 mg), m.p. 191–192 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.90–7.99 (m, 10H), 3.78–3.90 (m, 39H), 0.86–1.71 (m, 18H), –1.21(s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 150.67, 150.65, 150.47, 150.22, 150.18, 149.62, 128.83, 128.13, 128.09, 128.06, 127.82, 114.07, 113.66, 113.08, 112.88, 68.27, 55.91, 55.29, 55.22, 33.49, 30.10, 29.74, 29.30, 29.10, 27.85, 24.65. MS (MALDI-TOF) calcd for $C_{55}H_{68}Br_2O_{10}$ 1046.318, found 1046.538 $[M]^+$, 1069.551 $[M + Na]^+$.. Anal. Calc. for $C_{55}H_{68}Br_2O_{10}$: C, 62.98; H, 6.53. Found: C, 62.90; H, 6.63.

Copillar[5]arene **3h**: colorless crystals, in 52% yield (105 mg), m.p. 94–95 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.802 (s, 10H), 3.78(s, 15H), 3.68–3.69(d, 23H), 1.75 (t, 4H), 1.00–1.02 (d, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 150.75, 150.70, 149.95, 128.44, 128.29, 128.24, 128.14, 128.11, 114.89, 114.03, 113.97, 113.89, 69.96, 55.73, 55.68, 31.73, 31.44, 29.68, 29.59, 29.07, 23.05, 22.63, 14.15, 10.82. MS (MALDI-TOF) calcd for $C_{49}H_{58}O_{10}$ 806.403, found 829.234 $[M + Na]^+$, 845.209 $[M + K]^+$. Anal. Calc. for $C_{49}H_{58}O_{10}$: C, 73.02; H, 7.13. Found: C, 72.93; H, 7.19.

Copillar[5]arene **3i**: colorless crystals, in 63% yield (129 mg), m.p. 147–148 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.82–7.01 (m, 10H), 3.68–3.80 (m, 39H), 1.38–1.75 (m, 6H), 1.12(m, 2H), 0.78–0.87(t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 150.49, 128.26, 128.17, 128.11, 115.27, 114.62, 113.58, 68.43, 55.54, 31.74, 29.72, 29.38, 26.09, 22.80, 14.37. MS (MALDI-TOF) calcd for $C_{50}H_{60}O_{10}$ 820.419, found 820.443 $[M]^+$, 843.432 $[M + Na]^+$. Anal. Calc. for $C_{50}H_{60}O_{10}$: C, 73.15; H, 7.37. Found: C, 73.11; H, 7.48.

Acknowledgements

We are grateful to the National Natural Science Foundation of China (20872038, 21072064) and the Natural Science Foundation of Guangdong Province, China (10351064101000000) for the financial support.

Notes and references

1 T. Ogoshi, S. Kanai, S. Fujinami, T.-a. Yamagishi and Y. Nakamoto, *J. Am. Chem. Soc.*, 2008, **130**, 5022–5023.
2 D. Cao, Y. Kou, J. Liang, Z. Chen, L. Wang and H. Meier, *Angew. Chem. Int. Ed.*, 2009, **48**, 9721–9723.
3 T. Ogoshi, K. Umeda, T.-A. Yamagishi and Y. Nakamoto, *Chem. Commun.*, 2009, 4874–4876.
4 Y. Kou, H. Tao, D. Cao, Z. Fu, D. Schollmeyer and H. Meier, *Eur. J. Org. Chem.*, 2010, 6464–6470.
5 T. Ogoshi, M. Hashizume, T.-a. Yamagishi and Y. Nakamoto, *Chem. Commun.*, 2010, **46**, 3708–3710.
6 T. Ogoshi, K. Kitajima, T. Aoki, T.-a. Yamagishi and Y. Nakamoto, *J. Phys. Chem. Lett.*, 2010, **1**, 817–821.
7 C. Li, Q. Xu, J. Li, Y. Feina and X. Jia, *Org. Biomol. Chem.*, 2010, **8**, 1568–1576.
8 C. Li, L. Zhao, J. Li, X. Ding, S. Chen, Q. Zhang, Y. Yu and X. Jia, *Chem. Commun.*, 2010, **46**, 9016–9018.
9 Z. Zhang, B. Xia, C. Han, Y. Yu and F. Huang, *Org. Lett.*, 2010, **12**, 3285–3287.
10 T. Ogoshi, T. Aoki, K. Kitajima, S. Fujinami, T.-a. Yamagishi and Y. Nakamoto, *J. Org. Chem.*, 2011, **76**, 328–331.
11 W. Si, X.-B. Hu, X.-H. Liu, R. Fan, Z. Chen, L. Weng and J.-L. Hou, *Tetrahedron Lett.*, 2011, **52**, 2484–2487.
12 Z. Zhang, Y. Luo, J. Chen, S. Dong, Y. Yu, Z. Ma and F. Huang, *Angew. Chem., Int. Ed.*, 2011, **50**, 1397–1401.
13 N. L. Strutt, R. S. Forgan, J. M. Spruell, Y. Y. Botros and J. F. Stoddart, *J. Am. Chem. Soc.*, 2011, **133**, 5668–5671.
14 X.-B. Hu, L. Chen, W. Si, Y. Yu and J.-L. Hou, *Chem. Commun.*, 2011, **47**, 4694–4696.
15 C. Han, F. Ma, Z. Zhang, B. Xia, Y. Yu and F. Huang, *Org. Lett.*, 2010, **12**, 4360–4363.
16 T. Ogoshi, R. Shiga, T.-a. Yamagishi and Y. Nakamoto, *J. Org. Chem.*, 2011, **76**, 618–622.
17 T. Ogoshi, K. Masaki, R. Shiga, K. Kitajima and T.-a. Yamagishi, *Org. Lett.*, 2011, **13**, 1264–1266.
18 Z. Zhang, Y. Luo, B. Xia, C. Han, Y. Yu, X. Chen and F. Huang, *Chem. Commun.*, 2011, **47**, 2417–2419.
19 D. Wang, L.-J. Wan and C.-L. Bai, *Mater. Sci. Eng., R*, 2010, **70**, 169–187.

