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Mild synthesis of pillar[4]arene[1]*cis*-diepoxy-*p*-dione and guest-assisted formation of 2D network in solid state

Chengyou Han,*[a] Shengyi Dong,[b] Dezhi Zhao,[a] and Daofeng Sun*[a]

Abstract: Herein we have developed an environmentally friendly feasible method to synthesize pillar[4]arene[1]*cis*-diepoxy-*p*-dione. Strikingly, X-ray single crystal analysis between pillar[4]arene[1]*cis*-diepoxy-*p*-dione and 5-chloropentanenitrile indicates an 1 : 2 stoichiometry to form 2D network in solid state.

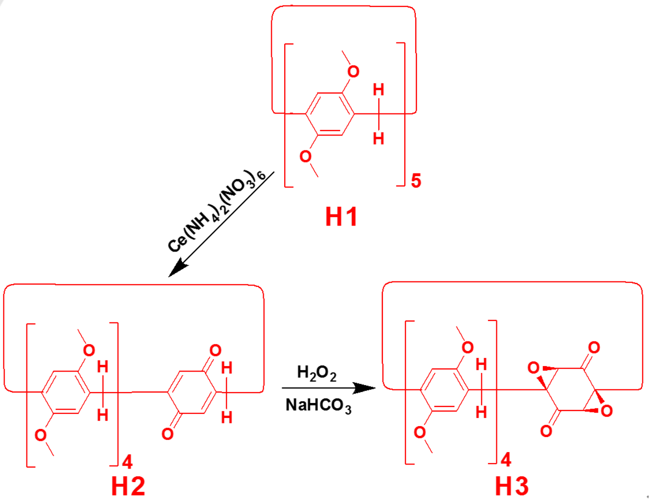
Introduction

More and more attention has been paid to design and synthesis of new macrocyclic hosts since the four well-known classical macrocycles, that are crown ethers,[1] cyclodextrins,[2] calixarenes[3] and cucurbiturils,[4] have played a major role in supramolecular chemistry and are widely applied in different fields. Pillararenes,[5] firstly reported in 2008, are one of leading candidates as a novel kind of macrocyclic host, and they form versatile host–guest complexes with organic and inorganic cations, and with neutral organic guests due to their highly symmetrical rigid architectures.[6] A series of functionalized pillararene derivatives have been prepared to expand their applications in different areas.[7] Recently, we have synthesized a new kind of pillar[5]arene derivative, pillar[4]arene[1]*cis*-diepoxy-*p*-dione, by base-promoted direct addition of molecular oxygen (oxygenation) to the pillararene benzoquinone rings.[8] It showed good complexations with dinitrile molecules in chloroform and in the solid state. However, environmentally unfriendly reagents including *tert*-butyl hydroperoxide as the oxygenation agent and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) as the base are used during the epoxidation. In order to improve the epoxidation in an environmentally friendly way and to further investigate its host–guest property different from pillar[5]arene and pillar[4]arene[1]quinone, it is necessary to develop a feasible method with environmentally friendly reagents and explore its host–guest complexation with different molecules.

Hence, in this communication, we explore the improved synthesis of pillar[4]arene[1]*cis*-diepoxy-*p*-dione by using H_2O_2 as the oxygenation agent and $NaHCO_3$ as the base. Meanwhile, its host–guest properties with the unsymmetrical guest 5-chloropentanenitrile both in solution and in solid state were also investigated.

Results and Discussion

Pillar[4]arene[1]quinone (**H2**) was synthesized according to the reported literature by using $Ce(NH_4)_2(NO_3)_6$ as the oxidizing agent in THF/H_2O solution of DMpillar[5]arene (**H1**) at room temperature (Scheme 1).[9] As reported by us,[8] the pillar[4]arene[1]*cis*-diepoxy-*p*-dione (**H3**) was synthesized by using *tert*-butyl hydroperoxide (*t*-BuOOH) as the oxygenation agent and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) as base in dry CH_2Cl_2 solution in an ice bath. With the current emphasis on "green chemistry", the search for novel oxidation agent and base with environment-friendly affinities is remarkably important. Luckily, we found that H_2O_2, which transforms into H_2O after decomposition, can be used as oxidation agent while $NaHCO_3$, can be used as the inorganic base instead of the organic DBU base in this reaction. Meanwhile, the reaction can be done in ethanol/H_2O at room temperature instead of CH_2Cl_2 in an ice bath. Generally, we successfully synthesized the pillar[4]arene[1]*cis*-diepoxy-*p*-dione (**H3**) under milder and more green conditions than before.



Scheme 1. Synthetic route for pillar[4]arene[1]*cis*-diepoxy-*p*-dione (**H3**)

The host–guest properties of pillar[4]arene[1]*cis*-diepoxy-*p*-dione (**H3**) have been explored, and we found it can effectively complex with dinitrile alkanes in our previous work.[8] After epoxidation, the symmetry of the host molecules have changed from D_{5h} for **H1** into C_2 for **H3**. In order to expand the host–guest properties of **H3** with different guest molecules, the unsymmetrical molecules 5-chloropentanenitrile (**G1**) and 5-azidopentanenitrile (**G2**) were applied. Firstly, the host–guest complexations were

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investigated by ^{1}H NMR spectra. The ^{1}H NMR spectra (spectra b and d in Figure 1) of an equimolar solution of **H3** and **G1**/**G2** in chloroform-*d* show only one group of peaks at NMR time scale, indicating fast-exchange complexation between **H3** and **G1**/**G2** at 22 °C. After complexation with **G1** and **G2**, phenyl protons $H^{3,8}$ methylene protons H^7 and methyl protons H^{12} on **H3** shifted slightly downfield (spectra c and d in Figure 1). Other protons on **H3** also showed minor downfield chemical shift changes after complexation. The significant chemical shift upfield changes of $H^{a\text{-}d}$ from **G1** and $H^{e\text{-}h}$ from **G2** were observed after complexation with **H3**, which showed these methylene protons are located in the shielding region of the cyclic pillar structure. This was indicative of that the linear guest **G1**/**G2** was threaded through the cavity of cyclic host **H3** to form a [2]pseudorotaxane in solution with the methylene protons $H^{a\text{-}d}$ and $H^{e\text{-}h}$ in the cavity of **H3**. The above phenomena suggested the effective bindings between **H3** and guests **G1**/**G2**.

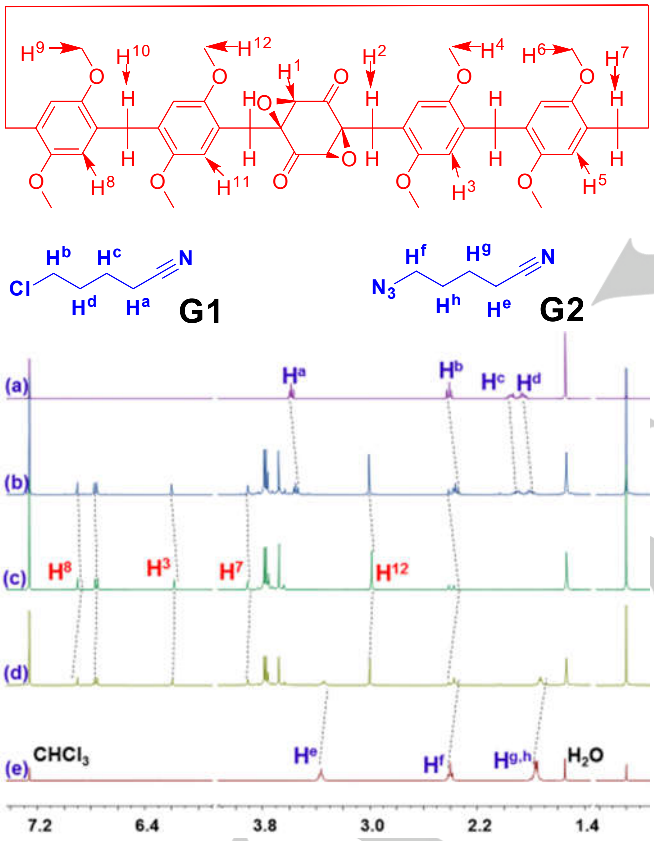


Figure 1. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$, 22 °C) of (a) 2 mmol of **G1**; (b) 2 mmol of **G1**+**H3**; (c) 2 mmol of **H3**; (d) 2 mmol of **G2**+**H3**; (e) 2 mmol of **G2**.

We then turn to study the affinities between different hosts and guests molecules. By an NMR titration method, we investigated the complexations between **Hn** (*n* = 1–3) and **Gn** (*n* = 1–2) in detail (Figure S5–S17). All the association constants were calculated based on NMR data (Table 1) and all the molar ratio plots indicated that the complexation stoichiometries between **Hn** and **Gn** were 1 : 1 to form [2]pseudorotaxanes.

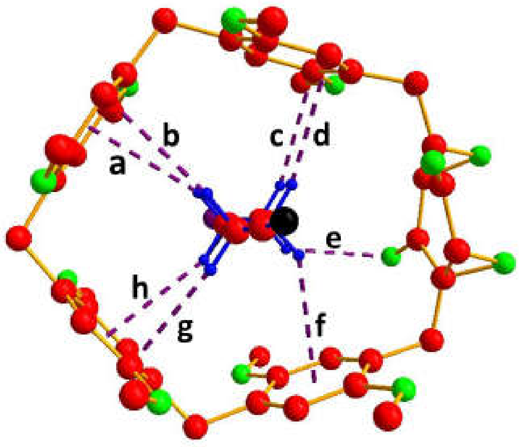
The association constants of these 1:1 complexes **Hn⊃Gn** in chloroform-*d* were also determined. We found that **G1**/**G2** had strong binding affinity with the host DMP5 (**H1**), which were (1.00 ± 0.40) × 10^4 for **G1** and (3.70 ± 1.39) × 10^3 M^{-1} for **G2** in $CDCl_3/CD_3COCD_3$ (9/1, *v*/*v*), indicating the effective complexations of **H1** with **G1**/**G2**. This is reasonable because the host **H1** has strong binding with dinitrile alkane guest molecules which also have the electron-withdrawing cyano groups at the two ends of the alkyl chains as reported by Li et al.[10] Since the host molecule **H2** has an electron-deficient repeating unit benzoquinone, it has an electron-rich cavity with negative electrostatic potential due to the four 1,4-dimethoxybenzene units. Thus, it also can complex with **G1**/**G2** just like pillar[5]arenes. But the association constants between **H2** and **G1**/**G2** are smaller comparing with **H1**. The complexations between **H3** and **G1**/**G2** are the weakest one among these three host molecules, 11.4 ± 2.4 M^{-1} for **G1** and 10.9 ± 4 M^{-1} for **G2**. This may because the host **H3** become flexible after the introduction of the *cis*-diepoxy-*p*-dione unit. These three macrocyclic host molecules showed different host–guest properties although they had similar structures.

Table 1. K_a values for complexations of **G1** and **G2** with **H1**–**H3** at room temperature determined by an NMR titration method.

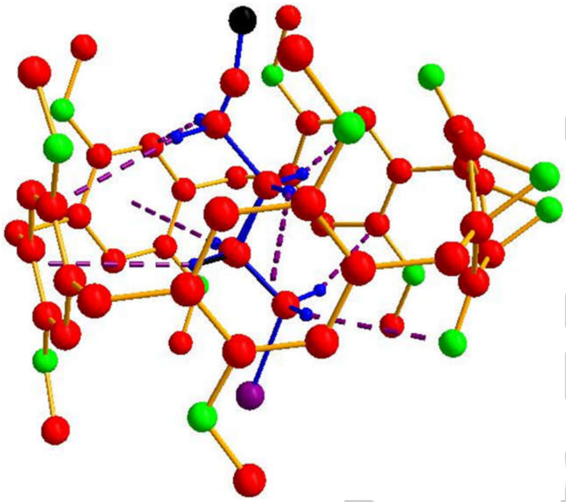
Guests	Hosts	K_a (M^{-1})
G1	**H1**[a]	(1.00 ± 0.40) × 10^4
G1	**H2**[b]	84.5 ± 6.3
G1	**H3**[b]	11.4 ± 2.4
G2	**H1**[a]	(3.70 ± 1.39) × 10^3
G2	**H2**[b]	173.3 ± 10.3
G2	**H3**[b]	10.9 ± 4

[a] The K_a was determined in $CDCl_3/CD_3COCD_3$ (9/1, *v*/*v*) at room temperature. [b] The K_a was determined in $CDCl_3$ at room temperature.

Single crystal analyses are a very powerful tool to reveal the molecular recognition and interactions between hosts and guest molecules in the solid state. Single crystals of **H3⊃G1** were grown by slow evaporation of their dichloromethane/methanol (*v*/*v*, 1/1) solution at room temperature (Figure 2 and Figure 3). The formation of the included [2]pseudorotaxane structure between **H3** and **G1** was verified by the crystal structure. Just like the complexation between **H3** and 1,4-dinitrile butane,[8] **G1** locates in the cavity of **H3**. This is consistent with the proton NMR discussion result that the protons $H_{a\text{-}d}$ show conspicuous upfield chemical shift changes after the occurrence of complexation between **H3** and **G1**. This [2]pseudorotaxane-like structure is stabilized by multiple C-H•••π interactions (Figure 2, **a**–**d**, **f**–**h**) between the methylene protons $H_{b,c}$ on **G1** and the π systems of the benzene rings, and one C-H•••O hydrogen bond interaction (Figure 2, **e**) between proton **H3** on the **G1** and oxygen atom of the C=O double bonds of the *cis*-diepoxy-*p*-dione rings. Because of the existences of the cyano groups in the guest molecules **G1**/**G2**, dipole-dipole forces should also play a significant role in the host–guest binding process. The crystal structure clearly confirmed the formation of the host–guest system based on pillar[4]arene[1]*cis*-diepoxy-*p*-dione (**H3**) and 5-chloropentanenitrile (**G1**).



(A) **H3⊃G1** (Top View)



(B) **H3⊃G1** (Side View)

Figure 2. Ball-stick views of the crystal structure of **H3⊃G1**. Hydrogen atoms on **H3** have been omitted for clarity. Carbon atoms are red, oxygen atoms are green, hydrogen atoms are blue, nitrogen atom are black and chlorine atoms are violet. The guest molecule is blue. The purple dotted lines indicate C-H•••π interactions and C-H•••O hydrogen bond interactions. C-H•••π interaction parameters: C-H•••π distance (Å), C-H•••π angle (deg) **a**, 2.93, 157; **b**, 3.04, 163; **c**, 2.90, 160; **d**, 2.89, 161; **f**, 3.13, 145; **g**, 2.81, 167; **h**, 2.83, 154; C-H•••O hydrogen bond interaction parameters: C-H•••O distance (Å), C-H•••O angle (deg) **e**, 2.86, 134.

Interestingly, to the best of our knowledge, the crystal structure showed another surprising phenomenon that was not observed in other single crystals based on pillararenes or pillararene derivatives. The guest molecules **G1** exist among the host–guest complexation **H3⊃G1** except inclusion in the cavity of **H3**. Every **G1** molecule outside the rings was surrounded by four host–guest systems. Meanwhile, every host–guest system was surrounded by four **G1** guest molecules. Totally, the stoichiometry between **H3** and **G1** was 1 : 2 in the solid states. More interestingly, with the assistance of **G1** molecules among the host–guest system, the crystal showed 2D network in the solid state. The interactions that help the formation of the 2D network are also multiple C-H•••π interactions (Figure 3) between the methylene protons on **G1** and the π systems of the benzene rings, C-H•••O hydrogen bond interactions and C-H•••N hydrogen bond interactions.

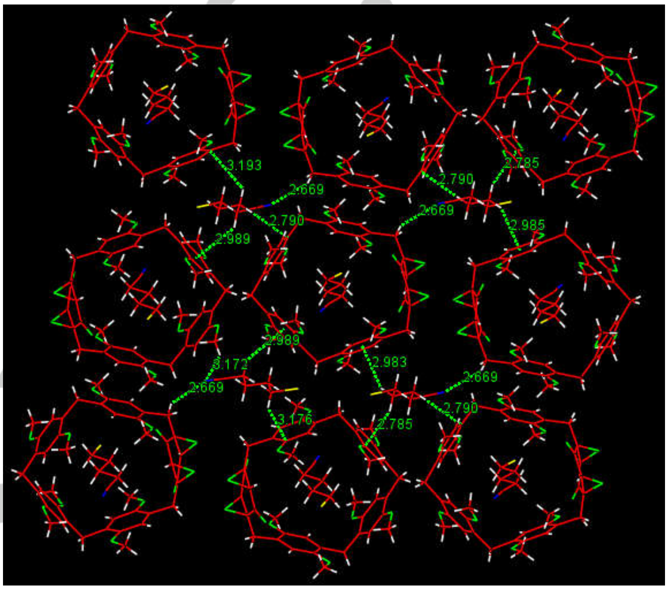


Figure 3. Wireframe views of the crystal structures indicate the existences of **G1** molecules between the host–guest complexation **H3⊃G1**.

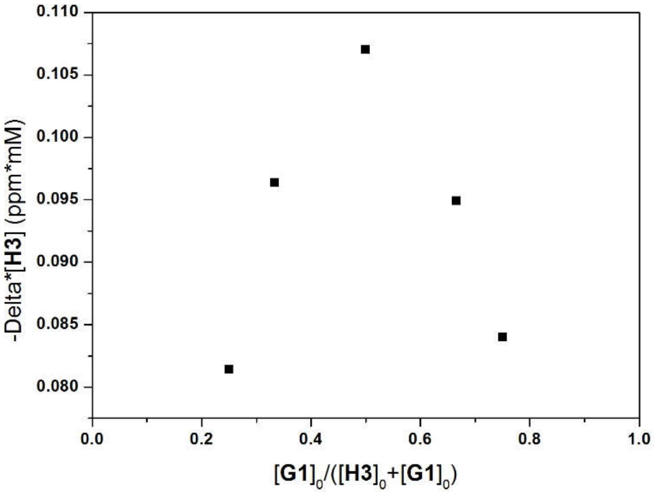


Figure 4. Job plot showing the 1 : 1 stoichiometry of the complex between **H3** and **G1** in CDCl$_3$ solution using data for H^a of **G1**. [**H3**]$_0$ and [**G1**]$_0$ are the initial concentrations of **H3** and **G1**. [**H3**]$_0$ + [**G1**]$_0$ = 5.00 mM.

Job plot of **H3** and **G1** was done to further investigate their complexation stoichiometry and we found they have an 1 : 1

stoichiometry in $CDCl_3$ solution using data for H^a of **G1** at room temperature as expected (Figure 4). This phenomena that complex is 1 : 1 in solution while 1 : 2 in solid state were reported before by Gibson and Huang in the complexes of cryptands and paraquat derivatives.[11]

Conclusions

In summary, we have developed a novel method to synthesize pillar[4]arene[1]*cis*-diepoxy-*p*-dione under mild condition with H_2O_2 as the oxidation agent and $NaHCO_3$ as the base at room temperature. This work is a good supplement for the oxygenated macrocycles such as calixarenes.[12] The differences in complexation between hosts DMpillar[5]arene (**H1**), pillar[4]arene[1]quinone (**H2**), pillar[4]arene[1]*cis*-diepoxy-*p*-dione (**H3**) and guests unsymmetric molecules 5-chloropentanenitrile (**G1**) and 5-azidopentanenitrile (**G2**) were investigated using NMR titration method. The crystal structure **H3**$\supset$**G1** was obtained to prove the complexation between them. More importantly, it was demonstrated that the complexation stoichiometry between **H3** and **G1** was 1 : 2 in solid state while 1 : 1 in solution. Meanwhile, with the assistance of the guest **G1** molecules among the host–guest system, the crystal showed 2D network in the solid state. This host–guest molecular recognition can be used in the fabrication of advanced functional supramolecular systems such as molecular switches, controlled-release systems, and supramolecular polymers.

Experimental Section

Experimental details, characterization data, full NMR spectra, binding constant determination and data for X-ray crystallography are available in the Supporting Information.

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Keywords: host–guest chemistry • self-assembly • pillararenes • pillar[4]arene[1]*cis*-diepoxy-*p*-dione • supramolecular network

[1] a) F. Huang, J. W. Jones, C. Slebodnick, H. W. Gibson, *J. Am. Chem. Soc.* **2003**, *125*, 14458-14464; b) F. Huang, D. S. Nagvekar, C. Slebodnick, H. W. Gibson, *J. Am. Chem. Soc.* **2005**, *127*, 484-485; c) F. Wang, C. Han, C. He, Q. Zhou, J. Zhang, C. Wang, N. Li, F. Huang, *J. Am. Chem. Soc.* **2008**, *130*, 11254-11255; d) Z. Ge, J. Hu, F. Huang, S. Liu, *Angew. Chem.* **2009**, *121*, 1830-1834; *Angew. Chem. Int. Ed.* **2009**, *48*, 1798-1802; e) S. Dong, Y. Luo, X. Yan, B. Zheng, X. Ding, Y. Yu, Z. Ma, Q. Zhao, F. Huang, *Angew. Chem.* **2011**, *123*, 1945-1949; *Angew. Chem. Int. Ed.* **2011**, *50*, 1905-1909; f) K. Zhu, V. N. Vukotic, S. J. Loeb, *Angew. Chem.* **2012**, *124*, 2210-2214; *Angew. Chem. Int. Ed.* **2012**, *51*, 2168-2172; g) K. Zhu, V. N. Vukotic, C. A. O'Keefe, R. W. Schurko, S. J. Loeb, *J. Am. Chem. Soc.* **2014**, *136*, 7403-7409; h) K. Zhu, C. A. O'Keefe, V. N. Vukotic, R. W. Schurko, S. J. Loeb, *Nature Chem.* **2015**, *7*, 514-519; i) P. Wang, Z. Gao, M. Yuan, J. Zhu, F. Wang, *Polym. Chem.* **2016**, *7*, 3664-3668; j) V. N. Vukotic, K. Zhu, G. Baggi, S. J. Loeb, *Angew. Chem.* **2017**, *129*, 6232-6237; *Angew. Chem. Int. Ed.* **2017**, *129*, 6136-6141; k) K. Zhu, G. Baggi, V. N. Vukotic, S. J. Loeb, *Chem. Sci.* **2017**, *8*, 3898-3904.

[2] a) T. Oshikiri, H. Yamaguchi, Y. Takashima, A. Harada, *Chem. Commun.* **2009**, 5515-5517; b) Y. Chen, Y. M. Zhang, Y. Liu, *Chem. Commun.* **2010**, *46*, 5622-5633; c) Y. Chen, Y. Liu, *Chem. Soc. Rev.* **2010**, *39*, 495-505; d) Q. Wang, C. Yang, C. Ke, G. Fukuhara, T. Mori, Y. Liu, Y. Inoue, *Chem. Commun.* **2011**, *47*, 6849-6851; e) S. Peng, K. Wang, D. S. Guo, Y. Liu, *Soft Matter.* **2015**, *11*, 290-296; f) Y. H. Zhang, Y. M. Zhang, Y. Yang, L. X. Chen, Y. Liu, *Chem. Commun.* **2016**, *52*, 6087-6090.

[3] a) J. Rebek, Jr., *Acc. Chem. Res.* **2009**, *42*, 1660-1668; b) S. Liu, H. Gan, A. T. Hermann, S. W. Rick, B. C. Gibb, *Nat. Chem.* **2010**, *2*, 847-852; c) D. S. Guo, V. D. Uzunova, X. Su, Y. Liu, W. M. Nau, *Chem. Sci.* **2011**, *2*, 1722-1734; d) D. Sh. Guo, Y. Liu, *Chem. Soc. Rev.* **2012**, *41*, 5907-5921; e) D. S. Guo, T. X. Zhang, Y. X. Wang, Y. Liu, *Chem. Commun.* **2013**, *49*, 6779-6781; f) D. S. Guo, Y. Liu, *Acc. Chem. Res.* **2014**, *47*, 1925-1934; g) S. Peng, J. Gao, Y. Liu, D. S. Guo, *Chem. Commun.* **2015**, *51*, 16557-16560; g) N. L. Poul, Y. L. Mest, I. Jabin, O. Reinaud, *Acc. Chem. Res.* **2015**, *48*, 2097-2106; h) A. Dondoni, A, Marra in *Glycopolymer Code: Synthesis of Glycopolymers and their Applications*, (Eds.: C. R. Becer, L. Hartmann), RSC publishing, **2015**, pp. 96-148; i) H. Kumari, C. A. Deakyne, J. L. Atwood in *Macrocyclic and Supramolecular Chemistry: How Izatt–Christensen Award Winners Shaped the Field*, (Ed.: R. M. Izatt), Wiley-VCH, Weinheim, **2016**, pp. 325-345; j) Z. Liu, S. K. M. Nalluria, J. F. Stoddart, *Chem. Soc. Rev.* **2017**, *46*, 2459-2478.

[4] a) J. Kim, I. S. Jung, S. Y. Kim, E. Lee, J. K. Kang, S. Sakamoto, K. Yamaguchi, K. Kim, *J. Am. Chem. Soc.* **2000**, *122*, 540-541; b) Y. J. Jeon, S. Y. Kim, Y. H. Ko, S. Sakamoto, K. Yamaguchi, K. Kim, *Org. Biomol. Chem.* **2005**, *3*, 2122-2125; d) Y. H. Ko, E. Kim, I. Hwang, K. Kim, *Chem. Commun.* **2007**, 1305-1315; e) E. Kim, J. Lee, D. Kim, K. E. Lee, S. S. Han, N. Lim, J. Kang, C. G. Park, K. Kim, *Chem. Commun.* **2009**, 1472-1474; f) Y. Liu, K. Liu, Z. Wang, X. Zhang, *Chem. Eur. J.* **2011**, *17*, 9930-9935; g) X. Tan, L. Yang, Y. Liu, Z. Huang, H. Yang, Z. Wang, X. Zhang, *Polym. Chem.* **2013**, *4*, 5378-5381; h) Q. Song, F. Li, Z. Wang, X. Zhang, *Chem. Sci.* **2015**, *6*, 3342-3346; i) H. L. Sun, H. Y. Zhang, Z. Dai, X. Han, Y. Liu, *Chem. Asian j.* **2017**, *12*, 265-270.

[5] a) T. Ogoshi, S. Kanai, S. Fujinami, T. Yamagishi, Y. Nakamoto, *J. Am. Chem. Soc.* **2008**, *130*, 5022-5023; b) Z. Zhang, B. Xia, C. Han, Y. Yu, F. Huang, *Org. Lett.* **2010**, *12*, 3285-3287; c) C. Han, F. Ma, Z. Zhang, B. Xia, Y. Yu, F. Huang, *Org. Lett.* **2010**, *12*, 4360-4363; d) C. Han, Z. Zhang, X. Chi, M. Zhang, G. Yu, F. Huang, *Acta Chim. Sinica* **2012**, *70*, 1775-1778; e) C. Han, L. Gao, G. Yu, Z. Zhang, S. Dong, F. Huang, *Eur. J. Org. Chem.* **2013**, 2529-2532; f) W. Cheng, H. Tang, R. Wang, L. Wang, H. Meier, D. Cao, *Chem. Commun.* **2016**, *52*, 8075-8078; g) J. Ma, F. Shi, D. Tian, H. Li, *Chem. Eur. J.* **2016**, *22*, 13805-13809; h) F. Zhang, J. Ma, Y. Sun, I. Boussouar, D. Tian, H. Li, L. Jiang, *Chem. Sci.* **2016**, *7*, 3227-3233; i) J. Yao, W. Wu, W. Liang, Y. Feng, D. Zhou, J. J. Chruma, G. Fukuhara, T. Mori, Y. Inoue, C. Yang, *Angew. Chem.* **2017**, *129*, 6973-6977; *Angew. Chem. Int. Ed.* **2017**, *56*, 6869-6873.

[6] a) C. Han, G. Yu, B. Zheng, F. Huang, *Org. Lett.* **2012**, *14*, 1712-1715; b) X. Chi, G. Yu, X. Ji, Y. Li, G. Tang, F. Huang, *ACS Macro Lett.* **2015**, *4*, 996-999; c) B. Shi, K. Jie, Y. Zhou, J. Zhou, D. Xia, F. Huang, *J. Am. Chem. Soc.* **2016**, *138*, 80-83; d) S. Dong, J. Heyda, J. Yuan, C. A. Schalley, *Chem. Commun.* **2016**, *52*, 7970-7973; e) X. Wang, L. L. Tan, X. Li, N. Song, Z. Li, J. N. Hu, Y. M. Cheng, Y. Wang, Y. W. Yang, *Chem. Commun.* **2016**, *52*, 13775-13778; f) L. Bai, P. Bose, Q. Gao, Y. Li, R. Ganguly, Y. Zhao, *J. Am. Chem. Soc.* **2017**, *139*, 436-441.

[7] a) Z. Zhang, Y. Luo, J. Chen, S. Dong, Y. Yu, Z. Ma, F. Huang, *Angew. Chem.* **2011**, *123*, 1433-1437; *Angew. Chem. Int. Ed.* **2011**, *50*, 1397-1401; b) C. Han, B. Xia, J. Chen, G. Yu, Z. Zhang, S. Dong, B. Hu, Y. Yu, M. Xue, *RSC Adv.* **2013**, *3*, 16089-16094; c) K. Jie, Y. Zhou, Y. Yao,

B. Shi, F. Huang, *J. Am. Chem. Soc.* **2015**, *137*, 10472-10475; d) W. Si, P. Xin, Z. T. Li, J. L. Hou, *Acc. Chem. Res.* **2015**, *48*, 1612-1619; e) L. Luo, G. Nie, D. Tian, H. Deng, L. Jiang, H. Li, *Angew. Chem.* **2016**, *128*, 12905-12908; *Angew. Chem. Int. Ed.* **2016**, *55*, 12713-12716; f) R. Wang, Y. Sun, F. Zhang, M. Song, D. Tian, H. Li, *Angew. Chem.* **2017**, *129*, 5378-5382; *Angew. Chem. Int. Ed.* **2017**, *56*, 5294-5298.

[8] C. Han, D. Zhao, T. Li, D. Sun, *Chem. Asian J.* **2017**, *12*, 2354-2358.

[9] C. Han, Z. Zhang, G. Yu, F. Huang, *Chem. Commun.* **2012**, *48*, 9876-9878.

[10] X. Shu, S. Chen, J. Li, Z. Chen, L. Weng, X. Jia, C. Li, *Chem. Commun.* **2012**, *48*, 2967-2969.

[11] a) F. Huang, H. W. Gibson, W. S. Bryant, D. S. Nagvekar, F. R. Fronczek, *J. Am. Chem. Soc.* **2003**, *125*, 9367-9371; b) F. Huang, K. A. Switek, L. N. Zakharov, F. R. Fronczek, C. Slebodnick, M. Lam, J. A. Golen, W. S. Bryant, P. E. Mason, A. L. Rheingold, M. Ashraf-Khorassani, H. W. Gibson, *J. Org. Chem.* **2005**, *70*, 3231-3241.

[12] a) Y. Morita, T. Agawa, Y. Kai, N. Kanehisa, N. Kasai, E. Nomura, H. Taniguchi, *Chem. Lett.* **1989**, *18*, 1349-1352; b) Y. Morita, T. Agawa, Y. Kai, E. Nomura, H. Taniguchi, *J. Org. Chem.* **1992**, *57*, 3658-3662; c) P. A. Reddy, R. P. Kashyap, W. H. Watson, C. D. Gutsche, *Isr. J. Chem.* **1992**, *32*, 89-96; d) F. Troisi, L. Citro, C. Gaeta, E. Gavuzzo, P. Neri, *Org. Lett.* **2008**, *10*, 1393-1396.

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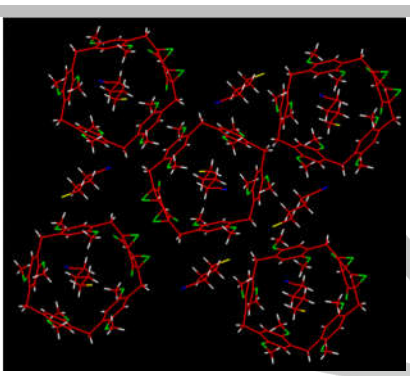
COMMUNICATION

Pillar[4]arene[1]*cis*-diepoxy-*p*-dione was synthesized under environmentally friendly feasible conditions. X-ray single crystal analysis between pillar[4]arene[1]*cis*-diepoxy-*p*-dione and 5-chloropentanenitrile indicates an 1 : 2 stoichiometry to form 2D supramolecular network in solid state.



Supramolecular Chemistry

Chengyou Han, Shengyi Dong, Dezhi Zhao, and Daofeng Sun**

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Mild synthesis of pillar[4]arene[1]*cis*-diepoxy-*p*-dione and guest-assisted formation of 2D network in solid state