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Enantiopure pillar[5]arene active domains within a homochiral metal–organic framework†

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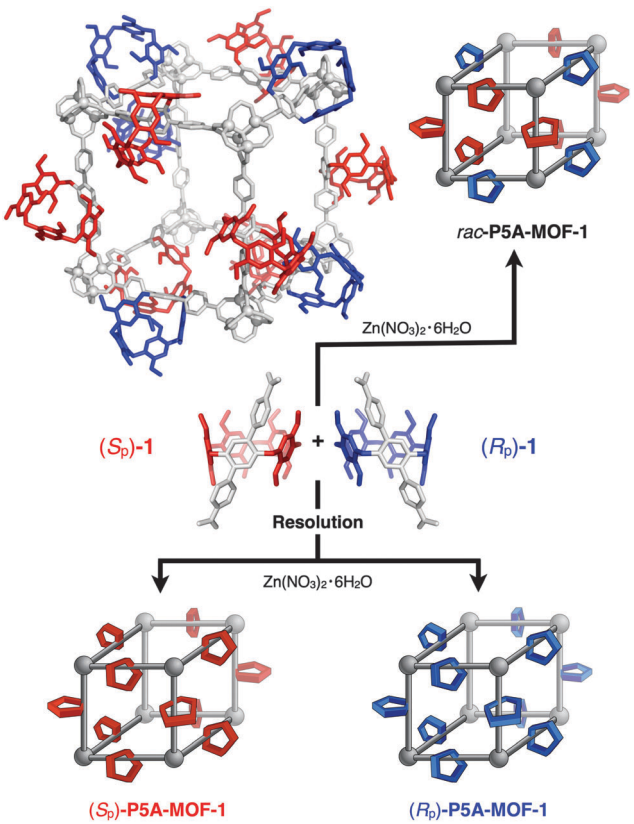
Enantiopure struts containing pillar[5]arenes incorporating planar chirality have been linked together with Zn_4O clusters in order to create metal–organic frameworks that include homochiral active domains and so have the potential to act as a solid support in chiral chromatography.

Pillar[*n*]arenes,[1] macrocycles composed of *n* hydroquinone rings connected through their *para*-positions by methylene bridges, are a new family of cavitands which have quickly become important players in the field of host–guest chemistry[2] since their initial report by Ogoshi and co-workers.[1a] As a result of their novel structures[3] and the tunability of their pendant functional groups,[4] pillar[*n*]arenes have been incorporated into many types of materials including polymers,[1c,5] nanoparticles[6] and liquid crystals.[7] Recently, we have reported[8] the incorporation of a rigid A1/A2-difunctionalised pillar[5]arene strut *rac*-**1** (Scheme 1) into the metal–organic framework (MOF) *rac*-**P5A-MOF-1**. The pillar[5]arene cavities in *rac*-**P5A-MOF-1** served to create active domains[9] within the porous framework wherein an ordered distribution of guests can be maintained through highly specific charge–transfer interactions between the π electron-rich pillar[5]arene hosts and electron-poor guests. These active domains have the ability to take up large amounts of pyridinium cations and *p*-dinitrobenzene, and the pillar[5]arenes were demonstrated to be selective towards guests which are more electron deficient.

The substituents present in the pillar[*n*]arenes oblige them to exhibit planar chirality.[1e] In 1,4-dimethoxypillar[5]arene (DMpillar[5]arene),[1a] there are five planes of chirality which are coplanar with the 1,4-dimethoxybenzene rings and the two contiguous methylene carbons at the 2/5 ring positions. The chiralities in the two lowest energy enantiomeric conformational isomers of DMpillar[5]arene can be described with Cahn–Ingold–Prelog nomenclature as $R_pR_pR_pR_pR_p$ and $S_pS_pS_pS_pS_p$ which we have abbreviated here to R_p and S_p. The R_p and S_p conformational isomers rapidly equilibrate as a result of ring rotations at room temperature, making it impossible to isolate an enantiomerically enriched sample of DMpillar[5]arene. The rate of the inversion process can be curtailed in pillar[*n*]arene derivatives such as in A1/A2-dihydroxy-pillar[5]arene,[10] and arrested completely in some derivatives, such as pillar[5]arenes with



Scheme 1 The organic strut *rac*-**1** can be employed to synthesise *rac*-**P5A-MOF-1** (top) or it can be resolved to give (S_p)-**1** (red) and (R_p)-**1** (blue) which can then be used in separate reactions to form homochiral (S_p)-**P5A-MOF-1** and (R_p)-**P5A-MOF-1**.

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bulky substituents[11] or pillar[5]arenes constituting mechanically interlocked compounds.[12]

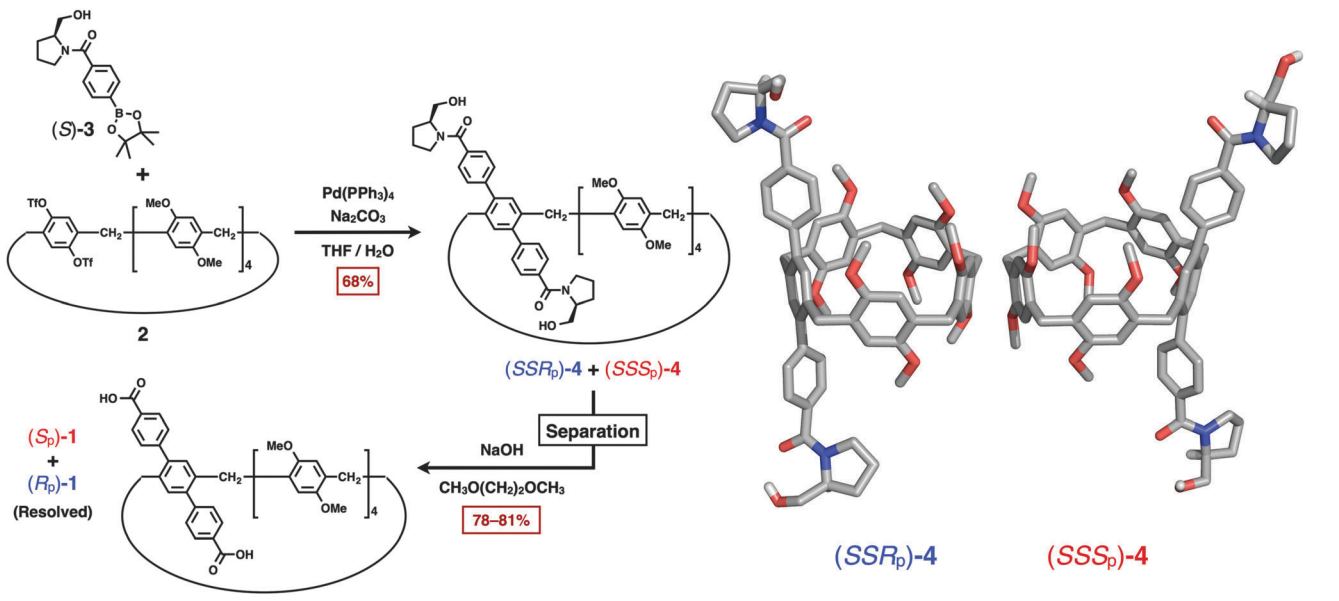
In our previous work[8] a racemic mixture of the organic strut *rac*-**1**, which cannot undergo stereochemical inversion on account of its rigid difunctionalisation, was connected through Zn_4O secondary building units (SBUs) to create *rac*-**P5A-MOF-1**. The active domains in this MOF consist of pillar[5]arene recognition sites with randomly distributed chiralities. Herein, we report the resolution of *rac*-**1** and the incorporation of the enantiopure struts (R_p)-**1** and (S_p)-**1** into the homochiral porous frameworks of (R_p)-**P5A-MOF-1** and (S_p)-**P5A-MOF-1** (Scheme 1).‡ Although there have been many examples of homochiral MOFs reported[13] with components which have either stereogenic centres[14] or axes[15] of chirality, the incorporation of planar chirality into homochiral MOFs is a relatively unexplored phenomenon. Porous frameworks, which contain enantiopure active domains, are also an area of interest as a result of their potential application as highly engineered chiral stationary phases for carrying out the separation of enantiomers by high-performance liquid chromatography (HPLC).

We have demonstrated[8] previously that the methyl ester of strut *rac*-**1** can be resolved on the analytical scale by chiral HPLC. In order to produce homochiral versions of **P5A-MOF-1** and assess the porous frameworks for their ability to separate small molecule racemates, *rac*-**1** must be resolved on a larger scale. While preparative scale chiral HPLC would likely be suitable for the resolution of *rac*-**1**, the technique is cost-prohibitive and not widely available. Therefore, we sought to develop a method to resolve *rac*-**1** which would be operable on the gram scale without the use of chiral chromatography. In order to realize this objective, the enantiomers (S_p)-**1** and (R_p)-**1** can be functionalised with an enantiomerically pure chiral auxiliary, thereby converting the enantiomers into two diastereoisomers which can then be separated using normal phase chromatography. After separation, the chiral auxiliaries can be removed to reveal the enantiomerically pure struts (S_p)-**1** and (R_p)-**1**.

The synthetic protocol we have employed in order to obtain enantiomerically pure struts (S_p)-**1** and (R_p)-**1** (Scheme 2) begins with the previously reported[8] pillar[5]arene ditriflate **2** which can be prepared in three steps from DMpillar[5]arene. Ditriflate **2** can be reacted with the (*S*)-prolinol-substituted 4-carbonylphenylboronic acid pinacol ester **3** in a Pd-catalyzed Suzuki reaction to produce the diastereoisomers (SSS_p)-**4** and (SSR_p)-**4**. This reaction proved to be slightly diastereoselective in favour of (SSR_p)-**4**. The two diastereoisomers of **4** can be easily separated on the hundreds of milligrams scale by employing normal phase silica HPLC (see Fig. S1 in the ESI†). Single crystals of (SSS_p)-**4** and (SSR_p)-**4**, suitable for X-ray crystallography, were obtained from the slow evaporation of CH_2Cl_2. The solid-state structures§ can be used to assign the absolute stereochemistry of the pillar[5]arenes in (SSS_p)-**4** and (SSR_p)-**4** since the absolute configuration of the (*S*)-prolinol is known. The (*S*)-prolinol auxiliaries in (SSS_p)-**4** and (SSR_p)-**4** were easily removed by alkaline amide hydrolysis to give the enantiomerically pure pillar[5]arene struts (S_p)-**1** and (R_p)-**1**.

Circular dichroism (CD) spectroscopy of (S_p)-**1** and (R_p)-**1** (Fig. 1) confirms that the conditions employed for amide hydrolysis do not lead to racemization of the strut. The positive Cotton effect observed for (R_p)-**1** and the negative Cotton effect for (S_p)-**1** agree well with the Cotton effects witnessed for previously reported[11a,16] enantiomerically pure pillar[5]arene derivatives. The optical purities of the methyl esters of (S_p)-**1** and (R_p)-**1** were assessed by analytical scale chiral HPLC¶ (see Fig. S2 in the ESI†) and samples of both enantiomers were shown to have enantiomeric ratios of over 97 : 3.

The homochiral frameworks (S_p)-**P5A-MOF-1** and (R_p)-**P5A-MOF-1** were obtained from (S_p)-**1** and (R_p)-**1**, respectively, and $Zn(NO_3)_2{\cdot}6H_2O$ in DMF at 100 °C (see the ESI†). Crystals of (S_p)-**P5A-MOF-1** and



Scheme 2 Pure enantiomers of the chiral organic strut **1**, (S_p)-**1** and (R_p)-**1** on account of planar chirality can be synthesised from the previously reported[8] ditriflate **2** using chiral auxiliaries in order to aid the separation of the diastereoisomers of intermediate **4**, namely (SSS_p)-**4** and (SSR_p)-**4**. The solid-state structures of (SSS_p)-**4** and (SSR_p)-**4** are shown on the right (C atoms are grey, O atoms are white, N atoms are blue, H atoms have been removed for the sake of clarity).

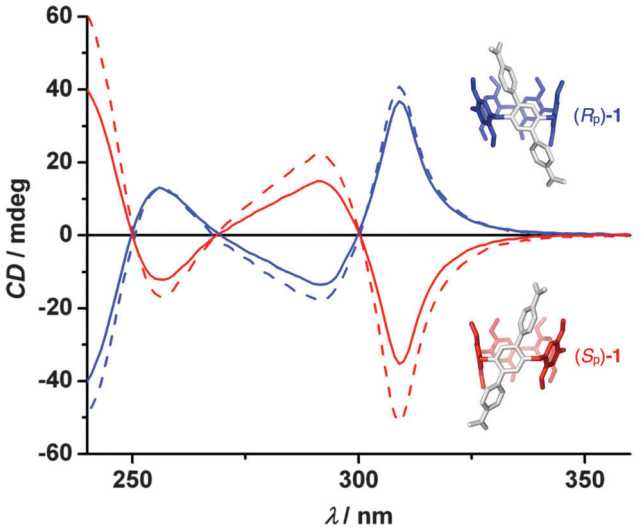


Fig. 1 Circular dichroism (CD) spectroscopy of (S_p)-**1** (red) and (R_p)-**1** (blue). The solid line spectra were collected from (S_p)-**1** and (R_p)-**1** (MeCN, 0.5 mM) as synthesised and the dashed line spectra were collected from digested (S_p)-**P5A-MOF-1** and (R_p)-**P5A-MOF-1** dissolved (~0.5 mM) in MeCN.

(R_p)-**P5A-MOF-1** were large and cubic with approximate average volumes of 0.125 mm^3 (see Fig. S7 in the ESI†). Single-crystal X-ray diffraction analysis of the homochiral MOFs were found to not be well enough resolved to discern individual atoms in the solid-state structure. In common with *rac*-**P5A-MOF-1**, the disorder within the homochiral frameworks is most likely a consequence of the rotational freedom of the pillar[5]arene rings with respect to the terphenylene linker.[8] The powder X-ray diffraction (PXRD) patterns of (S_p)-**P5A-MOF-1** and (R_p)-**P5A-MOF-1** are in almost complete agreement (Fig. 2) and match well with the PXRD pattern of the modelled version[8] of *rac*-**P5A-MOF-1** in a *P*1 space group. The PXRD data indicates that the enantiopure pillar[5]arene active domains in the homochiral frameworks do not change significantly the overall structure of the MOF. CD spectroscopy on samples of digested crystals of (S_p)-**P5A-MOF-1** and (R_p)-**P5A-MOF-1** (Fig. 1) provide evidence that racemization of (S_p)-**1** and (R_p)-**1** does not occur at the elevated temperatures which are required for the synthesis of the MOF.

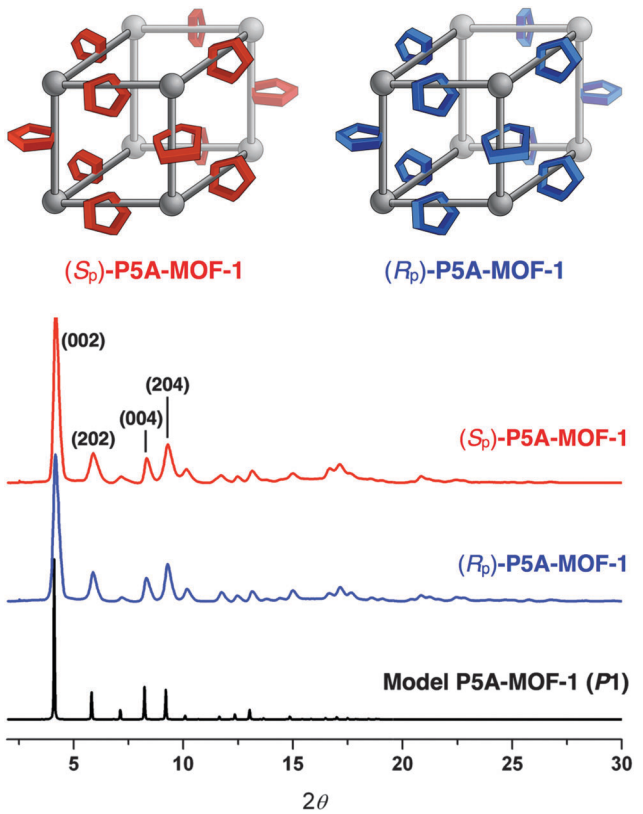


Fig. 2 The powder X-ray diffraction (PXRD) patterns of (S_p)-**P5A-MOF-1** (red) and (R_p)-**P5A-MOF-1** (blue), shown above as graphical representations, match closely those PXRD patterns of the modelled **P5A-MOF-1** structure.

The production of homochiral MOFs which contain enantiopure pillar[5]arene active domains has now been realized. These homochiral MOFs are early examples of porous frameworks incorporating active domains which possess planar chiralities. In the preparation of these homochiral materials, an efficient route to the large-scale resolution of racemic pillar[5]arene derivatives has also been developed. Currently, efforts are underway in our laboratory to investigate the enantioselectivities of these homochiral porous frameworks towards small molecule racemates which we expect to be bound enantioselectively within the pillar[5]arene active domains.

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Notes and references

‡ Since pillar[5]arenes contain five planes of chirality, five stereochemical designators can be used to describe their stereochemistry. We have opted to abbreviate these multiple descriptors to only one, either S_p or R_p, in cases where every plane of chirality has the same absolute stereochemistry, *i.e.*, $S_pS_pS_pS_pS_p$-**1** is abbreviated to S_p-**1**.

§ Crystal data for (*SSS*$_p$)-**4**: $[(C_{67}H_{72}N_2O_{12})_2{\cdot}CH_2Cl_2]$. Colourless plates (0.015 × 0.146 × 0.237 mm). Monoclinic, $P2_1$, a = 12.0918(5), b = 21.3853(9), c = 26.0509(12) Å, α = 90.000, β = 92.817(3), γ = 90.000°, V = 6728.3(5) Å^3, Z = 2, T = 100(2) K, ρ_{calc} = 1.125 g cm^{-3}, μ = 0.972 mm^{-1}. Of a total of 10 925 reflections which were collected, 10 925 were unique (R_{int} = 0.0000). Final R_1 ($F^2 > 2\sigma F^2$) = 0.0824 and wR_2 = 0.2421 (all data). The SQUEEZE function[17] of PLATON was used to remove the contribution of disordered solvent molecules. CCDC 995695. Crystal data for (*SSR*$_p$)-**4**: $[C_{67}H_{72}N_2O_{12}]$; colourless plates (0.011 × 0.09 × 0.173 mm); monoclinic, $P2_1$, a = 12.9346(2), b = 11.7299(1), c = 21.685(3) Å, α = 90.000, β = 97.077(9), γ = 90.000°, V = 3265.1(7) Å^3, Z = 2, T = 100(2) K, ρ_{calc} = 1.116 g cm^{-3}, μ = 0.616 mm^{-1}; of a total of 12 576 reflections which were collected, 6172 were unique (R_{int} = 0.0939); final R_1 ($F^2 > 2\sigma F^2$) = 0.0922 and wR_2 = 0.2501; CCDC 995696.

¶ The diacids S_p-**1** and R_p-**1** are poorly separated using analytical chiral HPLC and therefore the methyl esters of these compounds were prepared and used to determine the enantiomeric ratio by chiral HPLC after resolution.

1 (*a*) T. Ogoshi, S. Kanai, S. Fujinami, T. Yamagishi and Y. Nakamoto, *J. Am. Chem. Soc.*, 2008, **130**, 5022; (*b*) Y. Kou, H. Tao, D. Cao, Z. Fu, D. Schollmeyer and H. Meier, *Eur. J. Org. Chem.*, 2010, 6464; (*c*) Z. Zhang, Y. Luo, J. Chen, S. Dong, Y. Yu, Z. Ma and F. Huang, *Angew. Chem., Int. Ed.*, 2011, **50**, 1397; (*d*) N. L. Strutt, R. S. Forgan,

J. S. Spruell, Y. Y. Botros and J. F. Stoddart, *J. Am. Chem. Soc.*, 2011, **133**, 5668; (*e*) P. J. Cragg and K. Sharma, *Chem. Soc. Rev.*, 2012, **41**, 597; (*f*) M. Xue, Y. Yang, X. Chi, Z. Zhang and F. Huang, *Acc. Chem. Res.*, 2012, **45**, 1294; (*g*) X.-B. Hu, Z. Chen, L. Chen, L. Zhang, J.-L. Hou and Z.-T. Li, *Chem. Commun.*, 2012, **48**, 10999; (*h*) T. Ogoshi and T.-a. Yamagishi, *Eur. J. Org. Chem.*, 2013, 2961; (*i*) H. Zhang and Y. Zhao, *Chem. – Eur. J.*, 2013, **19**, 16862; (*j*) Z. Li, J. Yang, G. Yu, J. He, Z. Abliz and F. Huang, *Chem. Commun.*, 2014, **50**, 2841; (*k*) T. Ogoshi and T. Yamagishi, *Chem. Commun.*, 2014, **50**, 4776; (*l*) T. Ogoshi, N. Ueshima, T. Akutsu, D. Yamafuji, T. Furuta, F. Sakakibara and T.-a. Yamagishi, *Chem. Commun.*, 2014, **50**, 5774; (*m*) X. Hou, C. Ke, C. Cheng, N. Song, A. K. Blackburn, A. A. Sarjeant, Y. Y. Botros, Y.-W. Yang and J. F. Stoddart, *Chem. Commun.*, 2014, **50**, 6196; (*n*) Z. Li, J. Yang, G. Yu, J. He, Z. Abliz and F. Huang, *Org. Lett.*, 2014, **16**, 2066; (*o*) M. Pan and M. Xue, *RSC Adv.*, 2014, **4**, 260; (*p*) Y. Guan, P. Liu, C. Deng, M. Ni, S. Xiong, C. Lin, X.-Y. Hu, J. Ma and L. Wang, *Org. Biomol. Chem.*, 2014, **12**, 1079; (*q*) R. Manoni, P. Neviani, P. Franchi, E. Mezzina and M. Lucarini, *Eur. J. Org. Chem.*, 2014, 147; (*r*) Z.-Y. Li, Y. Zhang, C.-W. Zhang, L.-J. Chen, C. Wang, H. Tan, Y. Yu, X. Li and H.-B. Yang, *J. Am. Chem. Soc.*, 2014, DOI: 10.1021/ja413047r.

2 (*a*) D. J. Cram and J. M. Cram, *Science*, 1974, **183**, 803; (*b*) D. J. Cram, *Angew. Chem., Int. Ed.*, 1988, **27**, 1009.

3 (*a*) C. Han, F. Ma, Z. Zhang, B. Xia, Y. Yu and F. Huang, *Org. Lett.*, 2010, **12**, 4360; (*b*) T. Ogoshi, T. Aoki, K. Kitajima, S. Fujinami, T.-a. Yamagishi and Y. Nakamoto, *J. Org. Chem.*, 2011, **76**, 328; (*c*) Y. Ma, X. Chi, X. Yan, J. Liu, Y. Yao, W. Chen, F. Huang and J.-L. Hou, *Org. Lett.*, 2012, **14**, 1532.

4 (*a*) T. Ogoshi, K. Demachi, K. Kitajima and T.-a. Yamagishi, *Chem. Commun.*, 2011, **47**, 7164; (*b*) T. Ogoshi, R. Shiga, M. Hashizume and T.-a. Yamagishi, *Chem. Commun.*, 2011, **47**, 6927; (*c*) T. Ogoshi, D. Yamafuji, D. Kotera, T. Aoki, S. Fujinami and T.-a. Yamagishi, *J. Org. Chem.*, 2012, **77**, 11146.

5 (*a*) N. L. Strutt, H. Zhang, M. A. Giesener, J. Lei and J. F. Stoddart, *Chem. Commun.*, 2012, **48**, 1647; (*b*) T. Ogoshi, H. Kayama, D. Yamafuji, T. Aoki and T.-a. Yamagishi, *Chem. Sci.*, 2012, **3**, 3221; (*c*) K. Wang, C.-Y. Wang, Y. Wang, H. Li, C.-Y. Bao, J.-Y. Liu, S. X.-A. Zhang and Y.-W. Yang, *Chem. Commun.*, 2013, **49**, 10528; (*d*) L. Gao, Z. Zhang, S. Dong and M. Xue, *Macromol. Rapid Commun.*, 2014, **35**, 987.

6 (*a*) Y. Yao, M. Xue, X. Chi, Y. Ma, J. He, Z. Abliz and F. Huang, *Chem. Commun.*, 2012, **48**, 6505; (*b*) M.-M. Tian, D.-X. Chen, Y.-L. Sun, Y.-W. Yang and Q. Jia, *RSC Adv.*, 2013, **3**, 22111; (*c*) Y. Yao, M. Xue, Z. Zhang, M. Zhang, Y. Wang and F. Huang, *Chem. Sci.*, 2013, **4**, 3667; (*d*) Y.-L. Sun, Y.-W. Yang, D.-X. Chen, G. Wang, Y. Zhou, C.-Y. Wang and J. F. Stoddart, *Small*, 2013, **9**, 3224; (*e*) Y. Yao, Y. Zhou, J. Dai, S. Yue and M. Xue, *Chem. Commun.*, 2014, **50**, 869; (*f*) Y. Yao, K. Jie, Y. Zhou and M. Xue, *Tetrahedron Lett.*, 2014, **55**, 3195; (*g*) Y. Yao, K. Jie, Y. Zhou and M. Xue, *Chem. Commun.*, 2014, **50**, 5072.

7 (*a*) I. Nierengarten, S. Guerra, M. Holler, J.-F. Nierengarten and R. Deschenaux, *Chem. Commun.*, 2012, **48**, 8072; (*b*) I. Nierengarten, S. Guerra, M. Holler, L. Karmazin-Brelot, J. Barberá, R. Deschenaux and J.-F. Nierengarten, *Eur. J. Org. Chem.*, 2013, 3675.

8 N. L. Strutt, D. Fairen-Jimenez, J. Iehl, M. B. Lalonde, R. Q. Snurr, O. K. Farha, J. T. Hupp and J. F. Stoddart, *J. Am. Chem. Soc.*, 2012, **134**, 17436.

9 (*a*) Q. W. Li, W. Y. Zhang, O. S. Miljanić, C. H. Sue, Y. L. Zhao, L. H. Liu, C. B. Knobler, J. F. Stoddart and O. M. Yaghi, *Science*, 2009, **325**, 855; (*b*) C. Valente, E. Choi, M. E. Belowich, C. J. Doonan, Q. Li, T. B. Gasa, Y. Y. Botros, O. M. Yaghi and J. F. Stoddart, *Chem. Commun.*, 2010, **46**, 4911; (*c*) H. Deng, M. A. Olson, J. F. Stoddart and O. M. Yaghi, *Nat. Chem.*, 2010, **2**, 439.

10 N. L. Strutt, S. T. Schneebeli and J. F. Stoddart, *Supramol. Chem.*, 2013, **25**, 596.

11 (*a*) T. Ogoshi, K. Masaki, R. Shiga, K. Kitajima and T.-a. Yamagishi, *Org. Lett.*, 2011, **13**, 1264; (*b*) I. Nierengarten, K. Buffet, M. Holler, S. P. Vincent and J.-F. Nierengarten, *Tetrahedron Lett.*, 2013, **54**, 2398.

12 (*a*) T. Ogoshi, D. Yamafuji, T. Aoki, K. Kitajima, T.-a. Yamagishi, Y. Hayashi and S. Kawauchi, *Chem. – Eur. J.*, 2012, **18**, 7493; (*b*) C. Ke, N. L. Strutt, H. Li, X. Hou, K. J. Hartlieb, P. R. McGonigal, Z. Ma, J. Iehl, C. L. Stern, C. Cheng, Z. Zhu, N. A. Vermeulen, T. J. Meade, Y. Y. Botros and J. F. Stoddart, *J. Am. Chem. Soc.*, 2013, **135**, 17019; (*c*) K. Kitajima, T. Ogoshi and T.-a. Yamagishi, *Chem. Commun.*, 2014, **50**, 2925.

13 (*a*) J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon and K. Kim, *Nature*, 2000, **404**, 982; (*b*) L. Ma, C. Abney and W. Lin, *Chem. Soc. Rev.*, 2009, **38**, 1248; (*c*) M. Yoon, R. Srirambalaji and K. Kim, *Chem. Rev.*, 2011, **112**, 1196.

14 (*a*) J. Zhang, Y.-G. Yao and X. Bu, *Chem. Mater.*, 2007, **19**, 5083; (*b*) Q. Ye, D.-W. Fu, H. Tian, R.-G. Xiong, P. W. H. Chan and S. D. Huang, *Inorg. Chem.*, 2008, **47**, 772; (*c*) M. Banerjee, S. Das, M. Yoon, H. J. Choi, M. H. Hyun, S. M. Park, G. Seo and K. Kim, *J. Am. Chem. Soc.*, 2009, **131**, 7524; (*d*) D. Dang, P. Wu, C. He, Z. Xie and C. Duan, *J. Am. Chem. Soc.*, 2010, **132**, 14321; (*e*) K. Gedrich, M. Heitbaum, A. Notzon, I. Senkovska, R. Fröhlich, J. Getzschmann, U. Mueller, F. Glorius and S. Kaskel, *Chem. – Eur. J.*, 2011, **17**, 2099; (*f*) Q. Li, S. M. Shin, D. Moon, K. S. Jeong and N. Jeong, *CrystEngComm*, 2013, **15**, 10161.

15 (*a*) O. R. Evans, D. R. Manke and W. Lin, *Chem. Mater.*, 2002, **14**, 3866; (*b*) C.-D. Wu, A. Hu, L. Zhang and W. Lin, *J. Am. Chem. Soc.*, 2005, **127**, 8940; (*c*) C.-D. Wu, L. Zhang and W. Lin, *Inorg. Chem.*, 2006, **45**, 7278; (*d*) C.-D. Wu and W. Lin, *Angew. Chem., Int. Ed.*, 2007, **46**, 1075; (*e*) L. Ma, J. M. Falkowski, C. Abney and W. Lin, *Nat. Chem.*, 2010, **2**, 838; (*f*) Y. Peng, T. Gong and Y. Cui, *Chem. Commun.*, 2013, **49**, 8253; (*g*) S. Regati, Y. He, M. Thimmaiah, P. Li, S. Xiang, B. Chen and J. C.-G. Zhao, *Chem. Commun.*, 2013, **49**, 9836; (*h*) P. Li, Y. He, J. Guang, L. Weng, J. C.-G. Zhao, S. Xiang and B. Chen, *J. Am. Chem. Soc.*, 2014, **136**, 547; (*i*) K. Mo, Y. Yang and Y. Cui, *J. Am. Chem. Soc.*, 2014, **136**, 1746.

16 T. Ogoshi, D. Yamafuji, T. Akutsu, M. Naito and T.-a. Yamagishi, *Chem. Commun.*, 2013, **49**, 8782.

17 A. L. Spek, *Acta Crystallogr., Sect. D: Biol. Crystallogr.*, 2009, **65**, 148.

