A high-yield synthesis of \([m]biphenyl\)-extended pillar\([n]\)arenes for an efficient selective inclusion of toluene and \(m\)-xylene in the solid state†

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[\([m]Bp\)-ExPn with a rigid and nanometer-sized cavity, as an extended version of pillar\([n]\)arene by replacing 1,4-dimethoxybenzene monomers with biphenyl entities, was synthesized for the first time. Intriguingly, toluene and \(m\)-xylene can be stably included within the cavity of \([2]Bp\)-ExP6, which endows these newly developed synthetic receptors with great potential in the purification of petrochemicals.

Inspired by the reports of the first generation of synthetic macrocycles – crown ethers and their host-guest properties toward metal cations,\(^1\) synthetic macrocycles such as cyclodextrins, cucurbiturils, calixarenes and pillar\([n]\)arenes, have gradually become the mainstay of supramolecular chemistry.\(^2\) During the past half century, macrocyclic chemistry has developed rapidly and many synthetic macrocycles were reported one after another like past half century, macrocyclic chemistry has developed rapidly and many synthetic macrocycles were reported one after another like bamboo shoots after a spring rain, which include calixarenes,\(^3\) many synthetic macrocycles were reported one after another like past half century, macrocyclic chemistry has developed rapidly and many synthetic macrocycles were reported one after another like bamboo shoots after a spring rain, which include calixarenes,\(^3\) Ex-Boxes,\(^4\) Ex-Cages,\(^5\) pillararenes\(^6\) and so on.\(^7\) Besides the classical macrocycles mentioned above, there were also several elaborately designed and synthesized new macrocycles, i.e., biphenarene,\(^8\) oxatub[4]arene,\(^9\) thiocalix[2]thienothiophene,\(^10\) hybrid[2]arene,\(^11\) [2]calix[1]biphenyl-type hybrid[3]arene,\(^12\) and S6-corona[3]arene[3]-pyridazine,\(^13\) which have been reported within the last two years. Obviously, these kinds of novel macrocycles as the special oligomers of toluene and \(m\)-xylene in the solid state†

Electronic supplementary information (ESI) available: \(^{1}H\) NMR spectra, \(^{13}C\) NMR spectra, MS spectra, single crystal data. CCDC 1448579 and 1450376. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6cc01892k

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\(^\dagger\) Based on the actuality in the macrocyclic chemistry, we successfully designed and synthesized a kind of a novel macrocycle (Fig. 1). It can be regarded as the replacement of two monomers of the per-methyl-pillar[6]arene, i.e., 1,4-dimethoxybenzenes, by biphenyl, so that the cavity size is on the nanometer scale. The synthetic route contains two steps. First of all, the intermediate, i.e., \(4,4\)'-bis(2,5-dimethoxybenzyl)-1,1\(^{\dagger}\)diphenyl \([\text{MDM for short}]\) containing four methoxyl groups at the para-positions of benzene rings, was synthesized through Friedel–Crafts alkylation reaction catalysed by aluminum chloride in dichloromethane, pre-connecting the 1,4-dimethoxybenzene with biphenyl. Secondly, via the polymerization–cyclization of \([\text{MDM}]\), the extended pillar[6]arene was synthesized by catalysis with boron trifluoride diethyl etherate in dichloromethane at ambient temperature. Because two of the 1,4-dimethoxybenzene units were replaced by two biphenyls compared with traditional pillar[6]arene, these newly synthesised macrocycles were named as \([2]\text{Biphenyl-Extended-Pillar}[6]\)arenes \([\text{[2]Bp-ExPn for short}]\). Biphenyl units and two 1,4-dimethoxybenzene units connect one by one alternately, endowing the symmetric structures.

\([2]Bp\)-ExP6 was characterized using \(^{1}H\) NMR spectroscopy. As compared with that of \([\text{MDM}]\) (Fig. S1, ESI\(^\dagger\)), the appearance of the new peak at 3.88 in the spectrum of \([2]Bp\)-ExP6, corresponding to the methylene protons, and the chemical shift of protons in 1,4-dimethoxybenzene indicates the probable cyclic structure of \([2]Bp\)-ExP6 cyclosed from \([\text{MDM}]\). Meanwhile, the cyclic structure was also confirmed by \(^{13}C\) NMR (Fig. S25, ESI\(^\dagger\)) and MALDI-TOF-MS spectra (Fig. S26, ESI\(^\dagger\)). Dimethoxybenzene in \([2]Bp\)-ExP6 is asymmetric, so there are two sets of protons in the benzene ring \((c1, c2)\) and/or methyl groups \((f1, f2)\) which cannot be assigned in the \(^{1}H\) NMR spectrum. Thus, the 2D NOE NMR spectrum was
measured (Fig. 2). The crosspeak E indicates proton d is adjacent to c2 and crosspeak B indicates proton c2 is adjacent to f2; proton e is adjacent to c1 and proton c1 is adjacent to f1, which leads to the appearance of crosspeaks D and A. Therefore, each peak can be easily assigned to the corresponding proton in \([2]Bp-ExP6\), which confirms the molecular structure of \([2]Bp-ExP6\).

It is worthwhile to mention that BTEX (benzene, toluene, ethylbenzene, and xylenes isomers), not only as antiknocking additives in gasoline, but also as critically important petrochemical feedstocks, are faced with challenging processing and separation problems in the chemical industry. X-ray diffraction indicated that the structure and packing mode of \([2]Bp-ExP6\) in these two crystals are almost the same (Fig. 3). \([2]Bp-ExP6\) has a rigid stretched hexagon structure \((C_{i} \text{ symmetry})\) surrounded by four vertical dimethoxybenzene groups and two cross-biphenyl groups alternately. The cavity is about 12 Å in width and 4 Å in height (Fig. 3a, Fig. S2 and S3, ESI†; the 12 Å is obtained by subtracting twice the van der Waals radius of carbon from the distance between two farthest methylene groups, the 4 Å is the result of subtracting twice the van der Waals radius of hydrogen atoms from the space between them).

\([2]Bp-ExP6\) possesses four chiral planes (four dimethoxybenzene units), which is \((R, R, S, S)\), leading to the meso-form. The two benzene rings of the biphenyl group cross each other with a dihedral angle of 39.06° (Fig. S6, ESI†) in toluene-\([2]Bp-ExP6\) and 45.41° in m-xylene-\([2]Bp-ExP6\) (Fig. S7, ESI†). In the \((1, 1, 0)\) plane, \([2]Bp-ExP6\) rings stacked edge-to-edge in rows, the position of \([2]Bp-ExP6\) molecules in two rows are malposed (Fig. 3b). The distance between two rows is about 3.5 Å. The window of the \([2]Bp-ExP6\) molecule faces the two edges of \([2]Bp-ExP6\) in the adjacent parallel planes (Fig. 4a and b and Fig. S20, ESI†). Each \([2]Bp-ExP6\) molecule strongly interacts with twelve nearest neighbours through C–H···O, π···π and C–H···π interactions (Fig. S8–S19, ESI†), resulting in an exceptional stability.

Meanwhile, there are two parallel toluene or m-xylene molecules residing within the cavity of the \([2]Bp-ExP6\) ring (Fig. 4). The distances between two toluene planes or m-xylene planes are 2.773 Å or 3.525 Å, respectively (Fig. 4c and d). The toluene plane is almost perpendicular to the dimethoxybenzene plane. The dihedral angle of the m-xylene plane and the dimethoxybenzene plane...
The hydrogen atoms at the para-position which is located in the aperture between these [2]Bp-ExP6 molecules in the single crystal of m-xylene and [2]Bp-ExP6, This para-methyl group forms multiple C–H⋯O and C–H⋯π interactions with [2]Bp-ExP6 molecules, which enhances the stability of the host–guest complex.

At the ortho-position, o-xylene has a methyl group which shows steric hindrance to prevent o-xylene stay in the cavity of the [2]Bp-ExP6 ring. At the para-position, p-xylene has a methyl group which has a steric hindrance to remain in the apertures between these [2]Bp-ExP6 rings. Therefore, the crystalline of o-xylene and p-xylene could not be obtained, confirming the potential application of this type of synthetic macrocycles in the purification of petrochemicals.

Moreover, during the purification of [2]Bp-ExP6 using silica-gel column chromatography, we also obtained three other homogeneous macrocycles as by-products, i.e., [2]Bp-ExP5 with a smaller cavity size, [2]Bp-ExP7 and [3]Bp-ExP9 with larger cavity sizes, which were all fully characterized and identified by 1H NMR, 13C NMR, and MALDI-TOF-MS spectra (Fig. S27–S35, ESI†). Similar to the nomenclature of [2]Bp-ExP6 and as shown in Fig. 1, [3]Bp-ExP9 was considered as three 1,4-dimethoxybenzene units of pillar[9]arene replaced by biphenyl units. Similarly, [2]Bp-ExP7 and [2]Bp-ExP5 were regarded as extended pillar[7]arene and extended pillar[5]arene, respectively. The yield of [3]Bp-ExP9 was about 1.2%, while the yields of [2]Bp-ExP7 and [2]Bp-ExP5 were much lower, approximately 0.1%. Acquiring [2]Bp-ExP7 and [2]Bp-ExP5 was out of our expectation, but inspired by the reversible reaction, new 2,5-dimethoxybenzyl radicals could be divorced from MDM molecules, resulting in the formation of [2]Bp-ExP7 and [2]Bp-ExP5.

In conclusion, a series of new macrocycles with rigid and nanometer-sized cavities were designed and synthesized by the cyclization of MDM. [2]Bp-ExP6, as an extended version of pillar[n]arene by replacing two of its 1,4-dimethoxybenzene monomers with biphenyl entities, was obtained via a facile two-step, high-yield reaction. Intriguingly, [2]Bp-ExP7 and [3]Bp-ExP9 with larger cavity sizes, and [2]Bp-ExP5 with a smaller cavity size, were also successfully separated from the same reaction as new synthetic macrocycles. Significantly, toluene and m-xylene can be stably included within the cavity of [2]Bp-ExP6, which makes [m]Bp-ExPn possess a wide array of potential applications in the purification of petrochemicals.

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Notes and references


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Fig. 4  (a) Packing of [2]Bp-ExP6 with toluene in the cavity viewed along the c axis; (b) packing of [2]Bp-ExP6 with m-xylene in the cavity viewed along the c axis; (c), (e) and (g) interactions of toluene with [2]Bp-ExP6; (d), (f) and (h) interactions of m-xylene with [2]Bp-ExP6.

plane is 77.69°. The slight torsion is caused by the steric hindrance of m-xylene. Both toluene and m-xylene molecules have one methyl group located in the [2]Bp-ExP6 cavity, which showed multiple C–H⋯π interactions with [2]Bp-ExP6 (Fig. 4e and f). The hydrogen atom at the ortho-position of toluene has a strong C–H⋯π interaction and a C–H⋯O interaction with [2]Bp-ExP6. The hydrogen atoms at the para-position of toluene and m-xylene show C–H⋯O interactions with one another [2]Bp-ExP6 ring in adjacent layers. While m-xylene has a methyl group at the para-position which is located in the aperture between these [2]Bp-ExP6 molecules in the single crystal of m-xylene and [2]Bp-ExP6, this para-methyl group forms multiple C–H⋯O and C–H⋯π interactions with [2]Bp-ExP6 molecules, which enhances the stability of the host–guest complex.


