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ARTICLE TYPE

A cationic water-soluble pillar[5]arene: synthesis and host-guest complexation with long linear acids

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A cationic water-soluble pillar[5]arene has been synthesized and revealed to encapsulate linear acids in neutral, alkaline, and acidic conditions, driven by the hydrophobic and hydrogen bond interactions. The higher guest hydrophobicity contributes to the higher host affinity. Methanoic acid (A1) and acetic acid (A2) do not show any affinity for the host at all, because they are too hydrophilic for the host to compete with water.

Pillararenes are a new class of supramolecular hosts after crown ethers, cyclodextrins, calixarenes and cucurbiturils.[1] They have shown interesting properties in host-guest chemistry.[2] Compared with traditional hosts, they have some advantages. First, they were selective binding to specially designed guests, which attributed to highly symmetrical and rigid compared to crown ethers, calixarenes and cyclodextrins. Second, they are easier to functionalize by different substituents on the benzene rings than cucurbiturils; this enables their host-guest binding properties to be tuned easily.[3] Therefore, pillararenes are good and necessary supplements to these traditional hosts. A lot of host-guest complexes have been fabricated on the basis of their recognition to various guests based on their rigid symmetrical pillar structures.[4] But, the studies about the host-guest chemistry of pillar[5]arenes have been usually carried out in organic media, which is in sharp contrast to the case of cyclodextrins and cucurbiturils, resulting from the poor solubility of pillar[5]arenes in aqueous media. Therefore, in order to investigate the inclusion properties of pillar[5]arenes in water, water-soluble pillar[5]arenes were prepared. In 2010, the first water-soluble pillar[5]arene was synthesized by the introduction of carboxylate anions at both upper and lower rims,[5] which could bind cationic viologen salt in water; the second one, a pillar[5]arene decaamine was synthesized in 2011 and revealed to encapsulate linear diacids in neutral, alkaline and acidic conditions.[6] Later, Huang et al. synthesised a cationic water-soluble pillar[5]arene, which forms a stable 1 : 1 host-guest complex with sodium 1-octanesulfonate in water.[7] These water-soluble pillar[5]arene contains negative anion groups, carboxylate anions, neutral groups, amino groups and cationic groups. The length of columnar conformation of the former water-soluble pillar[5]arene stay in a relatively shorter. Consequently, in this study, we reported the preparation of a cationic water-soluble pillar[5]arene **P** with four carbons alkyl chain and it could strongly bind adipic acid in water, mainly driven by hydrophobic and hydrogen hond interactions.

We designed and synthesized a pillar[5]arene **P**. It was characterized by ^{1}H NMR, ^{13}C NMR and HRESIMS (Fig. S1-S9).[7] HRESIMS of **P** revealed peaks at m/z 772.3, 557.75, 433.97 and 349.70, 288.47 corresponding to $[M\text{-}3Br]^{3+}$, $[M\text{-}4Br]^{4+}$, $[M\text{-}5Br+Na^+]^{5+}$, $[M\text{-}6Br+Na^+]^{6+}$ and $[M\text{-}7Br+Na^+]^{7+}$, respectively (Fig. S9). This shows that **P** can lose different numbers of bromide anions to form a series of fragments containing different numbers of positive charges.

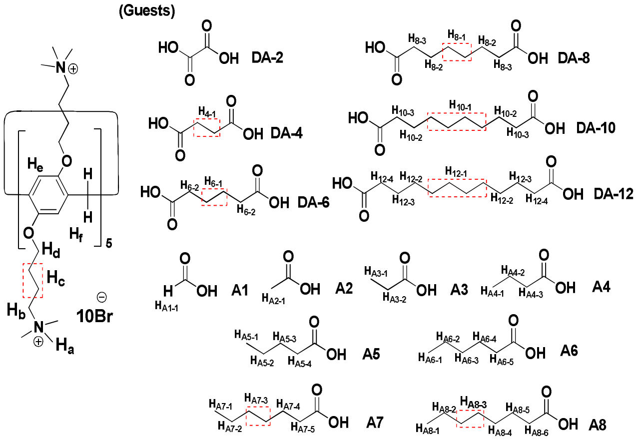

Fig. 1 Chemical structures of cationic water-soluble pillar[5]arene **P** and guests studied here.

Host **P** possesses a hydrophobic cavity,[8] which are open and thus different from the space exhibited by Rebek's closed molecular capsules.[9] Herein, **P** can strongly complex linear adipic acid in water driven by hydrophobic and hydrogen bonds interactions. Thus, the complexation of **P** for 5 equiv. of a,ω-diacids (DA-n, n:carbon number, n = 2, 4, 6, 8, 10, 12) and n-monoacids (A-n, n:carbon number, n = 1, 2, 3, 4, 5, 6, 7, 8) were then investigated in D_2O by ^{1}H NMR (Fig. 2 and Fig.3). For the mixture of DA-2 (Fig. S10), protons H_a, H_b and H_e on the pillar[5]arene **P** slightly shifted upfield while no obvious chemical shift changes were observed for H_f after complexation. This phenomenon suggested that DA-2 did not thread through the cavity of **P**. Furthermore, peaks of H_c and H_d of the free **P** were further shift upfield two new peaks (H_c' 3.45 and H_d' 0.97, respectively.) after the addition of 5 equiv. of DA-2. Meanwhile, slightly upfield shift changes for the methylene protons H_c and H_d of host were also observed compared to the free host, which suggests their involvement in the intermolecular hydrogen bonding between the carboxylic acid moieties and the methylene protons (H_c and H_d). The interior of the cavity is an electron-rich space, thus the methylene protons (H_c and H_d) located in the inner and outer spaces were shielded and deshielded, respectively.[5] Consequently, the split should reflect the low conformational freedom of the cavity. Upon mixing with DA-4 (Fig. S11 and Table S1), the results show that the variation of the signal of DA-4 and **P** were quite similar to that of the complex of **P** with DA-2 in the D_2O, indicating that it did not thread through the cavity of **P**.

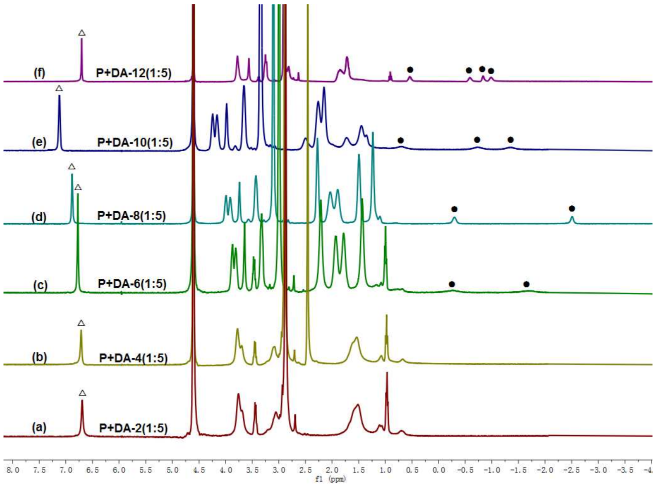

Fig. 2 Partial ^1H NMRspectra (400MHz, 298K) of **P** (10.0 mM) with diacids (50.0 mM) in D_2O (△: signal of ArH of **P** from complexes, ●: signals from methylenes of encapsulated diacids).

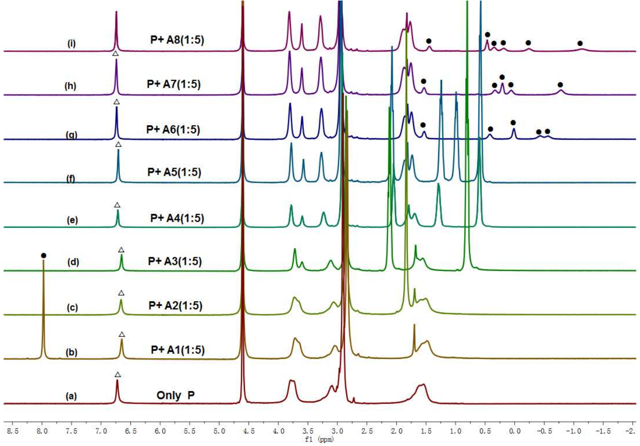

Fig. 3 Partial ^1H NMRspectra (400MHz, 298K) of **P** (10.0 mM) with n-monoacids (A-n, n: 1, 2, 3, 4, 5, 6, 7, 8) (50.0 mM) in D_2O (△: signal of ArH of **P** from complexes, ●: signals from methylenes of encapsulated monoacids).

When host **P** was mixed with DA-6 in water, a host-guest complex was formed. The complexation of **P** for DA-6 was then investigated in D_2O by ^1H NMR (Fig. S12). Upon mixing with 5 equiv. of DA-6, protons H_a, H_b, H_c, H_d and H_e on the pillar[5]arene **P** shifted downfield after complexation. Especially both of the peaks for H_c and H_d were further split into two separate peaks. Meanwhile, upfield shift changes (H_c'' and H_d'') for the host methylene protons H_c and H_d were also observed compared to the free host, corresponding to the H_c and H_d protons close to the carboxylic acid moieties of DA-6 to form the intermolecular hydrogen bond. However, there were no interaction between trimethylammonium protons with the carboxylic acid moieties of DA-6. Furthermore, in the upfield area, two new signals ($H_{6\text{-}1}$ and $H_{6\text{-}2}$) were also exhibited (δ=-1.69 and -0.27 ppm) (Table S3), because only the strong shielding effect by the tubular cyclophane could lead to such large upfield.[7] Thus, these phenomenon suggested that DA-6 was threaded through the cavity of columnar host **P** to form a [2]pseudorotaxane with its carboxyl groups close to the H_c and H_d protons of **P** and the middle four methylene groups ($H_{6\text{-}1}$ and $H_{6\text{-}2}$) located in the cavity of **P** (Fig.4). The formation of the complex might be mainly driven by hydrophobic and hydrogen bond interactions, because the hydrophobic cavity of **P** could hold the hydrophobic alkyl chain of DA-6 and the H_c and H_d protons of **P** could bind the carboxyl groups of DA-6 via hydrogen bond interaction. From ^1H NOESY spectroscopy analysis (Fig. 5), NOE correlations were observed between the four methylene protons ($H_{6\text{-}1}$ and $H_{6\text{-}2}$) of DA-6 and the aromatic protons of **P**, which also confirmed the interpenetrated geometry (Fig. S13).[10]

The ability of **P** to form a 1 : 1 complex with DA-6 was assessed by ^1H NMR titration of **P** into a 15.00 mM solution of DA-6 in water (Fig. S15). Addition of 0.2 equiv. of **P** resulted in an upfield shift of -0.27 ppm ($H_{6\text{-}2}$) for the methylene protons of DA-6 while protons $H_{6\text{-}1}$ on DA-6 shifted upfield even more. Meanwhile protons H_a-H_f on the pillar[5]arene **P** slightly shifted downfield and both of the peaks for H_c and H_d were split into two separated peaks. Additionally, the two new signals (H_c'' and H_d'') were found at δ 0.984 and 3.47, these were ascribed to hydrogen bonds between the H_c and H_d of **P** and the carboxylic acid moieties of DA-6. Upon addition of 1.0 equiv. of **P**, the signals of $H_{6\text{-}1}$ and $H_{6\text{-}2}$ on DA-6 have almost disappeared, other two signals (H_c'' and H_d'') remained and the intensity of peak (H_c'' and H_d'') increased. However, when the concentration of **P** was higher than 1 equiv., chemical shifts of protons H_a-H_d hardly changed and the $H_{6\text{-}1}$ and $H_{6\text{-}2}$ signals of DA-6 were completely upfield shifts, indicating the formation of a 1:1 complex between pillar[5]arene **P** and DA-6 in water. Further evidence for the formation of the desired complex was obtained by HRESIMS, revealing a peak at m/z 817.28, corresponding to $[H \supset DA\text{-}6 - 3Br]^{3+}$ (Fig. S14).

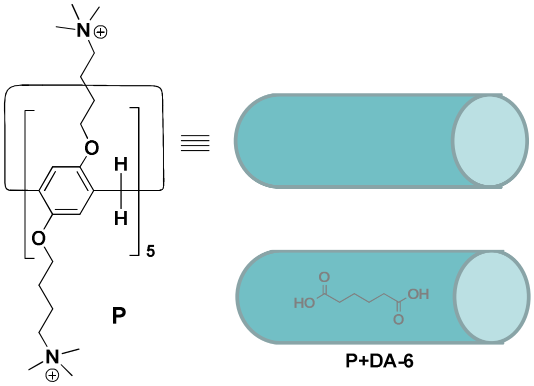

Fig. 4 Models for the formation of a highly stable inclusion complex.

Remarkably, longer DAs of up to 12 carbons, could also be encapsulated in the cavity of **P**. Upon mixing with 5 equiv. of DA-8 and DA-10, protons H_a, H_b, H_c, H_d, H_e and H_f on the pillar[5]arene **P** shifted downfield after complexation (Fig. S16-

S17). More interestingly, both of the peaks for H_c and H_d were not further split into two separate peaks. These phenomena suggested that the length of DA-8 and DA-10 were greater than DA-6. Consequently, the carboxylic acid moieties of DA-8 and DA-10 were far away from the methylene protons H_c, H_d of **P** after DA-8 and DA-10 threaded through the cavity of columnar host **P**. Thus, no intermolecular hydrogen bond between the carboxylic acid moieties of DA-8 and DA-10 with the methylene protons H_c, H_d existed. Even so, DA-8 and DA-10 were always wrapped by hydrophobic interactions in the cavity of **P** (Fig. 5a and Fig. 5b), because the length of the hydrophobic alkanes of DA-8 and DA-10 is shorter than the hydrophobic cavity of **P**. On the contrary, for the mixture of DA-12 (Fig. S18), protons H_e and H_f of the pillar[5]arene **P** slightly shifted upfield after complexation, while protons H_a, H_b and H_c of the pillar[5]arene **P** shifted downfield (Table S1). Meanwhile both of the peaks for H_c and H_d were further split into two separate peaks. These phenomena suggested that the alkyl chain lengths of DA-12, DA-10 and DA-8 followed the order DA-12> DA-10> DA-8. Therefore, the formation of a strong intermolecular hydrogen-bonding system occurred between one of the carboxylic acid moieties of DA-12 and the methylene protons (H_c, H_d), meanwhile, another the carboxylic acid moieties of DA-12 had interaction with solvent (water) (Fig. 5c).

Many n-monoacids (A-n, n = 1, 2, 3, 4, 5, 6, 7, 8) could be considered for further study the complexation of **P** with linear acids (Fig. 3). All of the guests A1-A8 bear acid groups, but they have alkyl chains with different lengths, giving them different hydrophobicities. Consequently, **P** exhibited different affinities for them. A1 and A2 did not show evidence for binding in the presence of **P**. The chemical shift of all the protons of A1 and A2 in D_2O did not change at all (Fig. S19-S20). The reason for this phenomenon might be that even though **P** was present, A1 and A2 remains what it has always been in the solvent due to their good solubility in water. Simply stated, A1 and A2 were too hydrophilic for **P** to compete with water. Upon mixing with A3 (Fig. S21 and Table S2), protons H_d and H_f on the pillar[5]arene **P** slightly shifted upfield after complexation. We speculated that the formation of the complex between **P** and A3 was mainly driven by hydrophobic interaction. Upon mixing with A4, A5, A6, A7 and A8, which could be bound by **P** in water (Fig. S22-S26 and Table S2), protons H_a, H_b, H_d, H_e on the pillar[5]arene **P** distinctly shifted downfield after complexation (Fig. 5d), and their association constants with **P** followed the order A8> A7> A6> A5> A4 (Table 2). Because the alkyl chain lengths of A4, A5, A6, A7 and A8 follow the order A8> A7> A6> A5> A4, A8 is slightly more hydrophobic than A7 which is a little more hydrophobic than A6, A5 and A4. The higher hydrophobicity guests have, the higher affinity they may contribute to the host. It seems that the complexation of **P** with the monoacids is dependent on the alkyl chain length and arises from hydrophobic interactions between the alkyl part of guest and the host interior. An interesting point: both of the peaks for H_c and H_d were not further split into two separate peaks after n-monoacids (A-n, n= 1, 2, 3, 4, 5, 6, 7, 8) and **P** were mixed together. These findings indicate that the host-guest complexation by **P** for amphiphilic guests in water will be strongly decreased not only because of the small contribution of hydrophobic interactions instead of no intermolecular hydrogen bond between the carboxylic acid moieties and the methylene protons (H_c and H_d), but also a substantial competitive influence of the solvent.

Table 1 Association constant Ka values (M^{-1}) for host-guest complexes of DA-6, DA-8, DA-10 and DA-12 with **P** in D_2O at 298 K.

Guests	Ka($\times 10^5 M^{-1}$)
DA-6	0.96
DA-8	1.92
DA-10	3.88
DA-12	3.37

Table 2 Association constant Ka values (M^{-1}) for host-guest complexes of A4, A5, A6, A7 and A8 with **P** in H_2O at 298 K.

Guests	Ka($\times 10^3 M^{-1}$)
A4	0.97
A5	1.09
A6	3.5
A7	8.82
A8	10.49

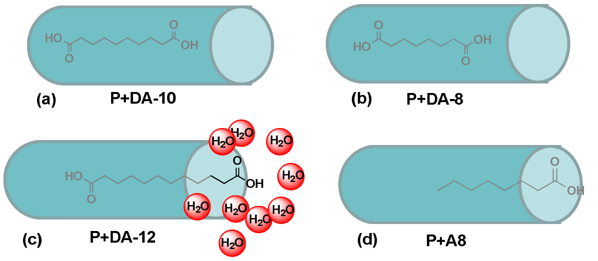

Fig. 5 Models for the formation of a highly stable inclusion complex.

To investigate the effect of F_3CCOOH on the stability of the complexes, the ^1H NMR spectra of the 1 : 1: 6 solution of **P**, the a,ω-diacids (DA-n, n: carbon number, n = 6, 8, 10, 12) and n-monoacids (A-n, n = 3, 4, 5, 6, 7, 8) with F_3CCOOH in D_2O were also recorded (Fig. 6 and Fig.7). The complexes of all the acids were still formed. Especially, adding F_3CCOOH caused their α- and central CH_2 and ArH of **P** from complexes signals to shift upfield considerably (Table S3-S4). These results indicated that F_3CCOOH remarkably enhanced the stability of the complexes. More interestingly, when the subsequent addition of 6 equivalents TEA to the 1 : 1 solution of **P** and all the acids caused the complexes of DA-10, DA-12, A3, A4 and A5 to decompose completely. The peak of the protons H_b, H_d, H_f backed to the location of the origin, which were blamed that DA-10, DA-12, A3, A4 and A5 were too hydrophilic for **P** to compete with water in TEA environment. On the contrary, the signals of methylenes encapsulated DA-6 and DA-8 shifted upfield (Fig. 8 and Table S5). However, the complexe from DA-8 had weaker signal strength than the DA-6. We surmised that the alkyl chain lengths of DA-6 was the shortest and the intramolecular hydrogen bond between the carboxylic acid moieties of DA-6 with the methylene protons H_c, H_d of **P** existed. In addition, A7 and A8 could be bound with **P** because the alkyl chain length of A7, A8 were too hydrophobic for water to compete with **P** in TEA environment (Fig. 9 and Table S6). In addition, in order to investigate the influence of F_3CCOOH and TEA for **P**, F_3CCOOH and TEA with **P** were studied in D_2O, we found protons H_a, H_b, H_c, H_d, H_e and H_f on the pillar[5]arene **P** shifted upfield (Fig. S27-S28). But the F_3CCOOH and TEA were not threaded within the cavity of **P**.

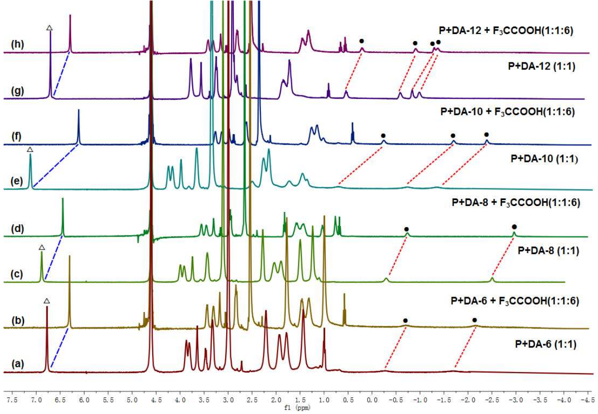

Fig. 6 Partial ^{1}H NMR (400 MHz, 298 K) spectra of **P** (10.0 mM) with (a) DA-6; (c) DA-8; (e) DA-10 and (g) DA-12. (b), (d), (f) and (h) correspond to the spectra after adding F_3CCOOH to the solution of (a), (c), (e) and (g) (Δ: signal of ArH of **P** from complexes, ●: signals from methylenes of encapsulated diacids).

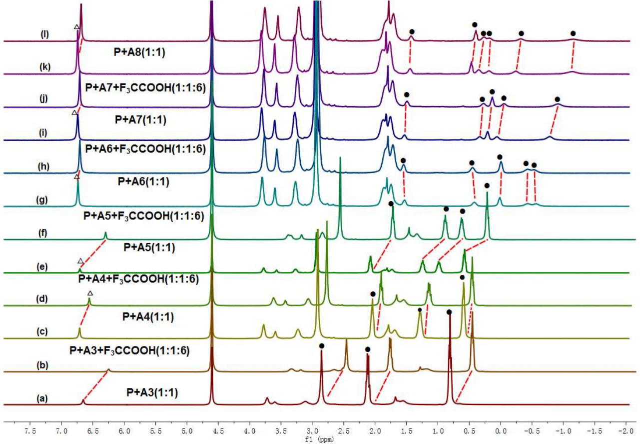

Fig. 7 Partial ^{1}H NMR (400 MHz, 298 K) spectra of **P** (10.0 mM) with (a) A3; (c) A4; (e) A5; (g) A6; (i) A7 and (k) A8. (b), (d), (f), (h), (j) and (l) correspond to the spectra after adding F_3CCOOH to the solution of (a), (c), (e), (g), (i) and (k) (Δ: signal of ArH of **P** from complexes, ●: signals from methylenes of encapsulated diacids).

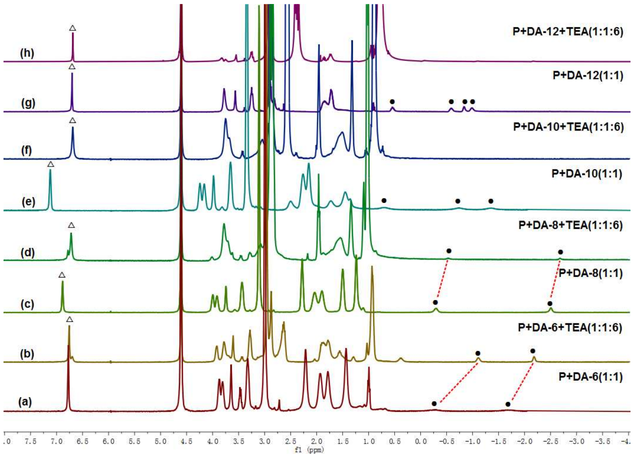

Fig. 8 Partial ^{1}H NMR (400 MHz, 298 K) spectra of **P** (10.0 mM) with (a) DA-6; (c) DA-8; (e) DA-10 and (g) DA-12. (b), (d), (f) and (h) correspond to the spectra after adding TEA to the solution of (a), (c), (e) and (g) (Δ: signal of ArH of **P** from complexes, ●: signals from methylenes of encapsulated diacids).

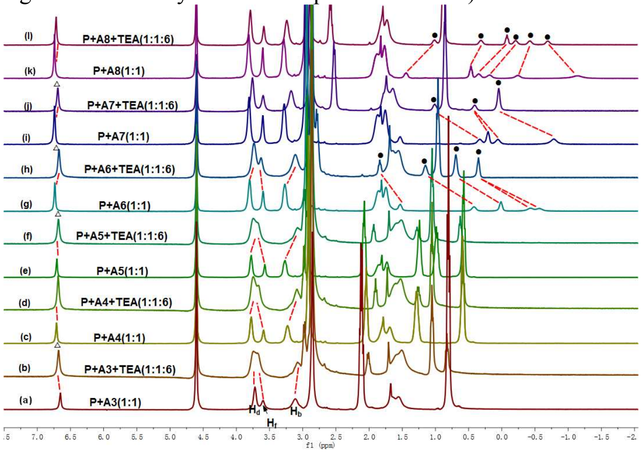

Fig. 9 Partial ^{1}H NMR (400 MHz, 298 K) spectra of **P** (10.0 mM) with (a) A3; (c) A4; (e) A5; (g) A6; (i) A7 and (k) A8. (b), (d), (f), (h), (j) and (l) correspond to the spectra after adding TEA to the solution of (a), (c), (e), (g), (i) and (k) (Δ: signal of ArH of **P** from complexes, ●: signals from methylenes of encapsulated diacids).

In order to investigate the a,ω-diacids (DA-n, n: carbon number, n = 2, 4, 6, 8, 10, 12) and n-monoacids (A-n, n: 1, 2, 3, 4, 5, 6, 7, 8) complex abilities of the **P** in H_2O solution, we carried out a series of Host-Guest experiments (Fig. S29-S30). The colorimetric and fluorimetric sensing abilities were primarily investigated by adding H_2O solution of acids to the H_2O (pH = 7.0) solutions of **P** , respectively. As shown in Fig. S29 and Fig. S30, absorption bands at 293 nm for **P** were attributed primarily to the phenyl based π-π* transition. When 20 equivalents of DA-2, A2, A3 and A4 were added to a solution of **P**, it did not cause any significant changes. However, when 20 equivalents of DA-4 were added to a solution of **P**, it may lead to the intensity of UV absorption peak became slightly weak at 293 nm. These phenomena are due to DA-2 and DA-4 did not thread through the cavity of **P**. When 20 equivalents of DA-6, DA-8, DA-10, DA-12, A5, A6, A7 and A8 were added to a solution of **P** (2.0×10^{-5} M), a notable red-shift was observed (from 292 nm to 295 nm) on account of the formation of a stable charge transfer after coordinating between **P** and them.[11] These results attributed to the methylene groups of DA-6, DA-8, DA-10, DA-12, A5, A6, A7 and A8 threaded within the cavity of **P**.

In order to investigate the binding properties of the pillar[5]arene **P** towards DA-6, DA-8, DA-10, DA-12, A4, A5, A6, A7 and A8, the UV-vis titration of **P** (2×10^{-5} mol/L) with their in the solution of H_2O (pH=7.00) was carried out (Fig. S31-S39). The Benesie-Hildebrand[12] analysis of these changes gave their binding constant, see Table 1 and Table 2.

The fluorescence spectral properties of the pillar[5]arene **P** with DA-6 were also examined. Free the pillar[5]arene **P** exhibited an emission maximum at 330 nm upon excitation at 293 nm, when 20 equivalents of DA-6, DA-8, DA-10 and DA-12 were added to the H_2O solutions of the pillar[5]arene **P**, it led to a prominent fluorescence enhancement (Fig. 10). However, when 20 equivalents of DA-2 were added to a solution of **P**, it may lead to weaken the fluorescence intensity of **P**. When 20 equivalents of DA-4 were added to a solution of **P**, it did not cause any significant changes. This phenomenon provided further evidence for the methylene groups of DA-6, DA-8, DA-10 and DA-12 threaded within the cavity of **P**. The fluorescence titration of the pillar[5]arene **P** toward DA-6 was also carried out. As shown in Fig. S40, free pillar[5]arene **P** showed a board emission band situated between 300 nm and 425 nm. The fluorescent intensity remarkably increased as the DA-6 concentration increased from 0 to 1.3 equivalents. When 20 equivalents of A1, A2, A3, A4, A5, A6, A7 and A8 were added to a solution of **P** (2.0×10^{-5} M), it did enhance the fluorescent intensity of **P** at 330nm (Fig. S41).

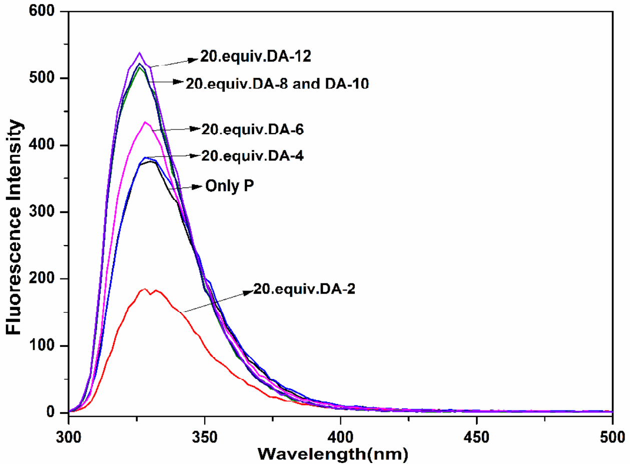

Fig. 10 Fluorescence spectra response of **P** (20 μM) upon addition of DA-2, DA-4, DA-6, DA-8, DA-10 and DA-12 (20 equiv.) in H_2O (pH = 7.0), (λ_{ex} = 293 nm).

More importantly, the resulting inclusion complex between DA-6 and **P** was then studied by cyclic voltammetry experiments. Fig. S42 shows the CV curves recorded at different scan rates for **P**. The current under the curve slowly increases with scan rate. This shows that the voltammetric currents are directly proportional to the scan rate and thereby display capacitive behavior.[11] Because DA-6 could be tightly included in the cavity of **P**, as proved by cyclic voltammetry experiments (Fig. S43), the reduction and oxidation processes of **P** changed significantly upon complexation with DA-6, which makes generation of their radical cations more easily, suggesting the formation of a stable chargetransfer complex between them as mentioned above.

Conclusions

In summary, we have demonstrated a cationic water-soluble pillar[5]arene offering a well-defined cavity with hydrophobic inner surface and it can capture linear acids guests driven by the hydrophobic and hydrogen bond interactions. The methylene groups of DA-6, DA-8, DA-10, DA-12, A4, A5, A6, A7 and A8 threaded within the cavity of **P**. In addition, the stability of the complexes can be further enhanced by the addition of F_3CCOOH, while complex between pillar[5]arene **P** and DA-6 was the most stable in TEA environment. In addition, the colorimetric, ratiometric fluorescent response and cyclic voltammetry experiments to DA-6 was realized through the complexation of Host **P** with linear acids. This new molecular recognition motif between **P** and linear acids can be further used in the preparation of new functional supramolecular systems, including molecular machines, molecular switches, chemosensors, delivery systems and responsive supramolecular polymers, which can be operated in water.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details, synthesis of **P**, and other materials. See DOI: 10.1039/b000000x/

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