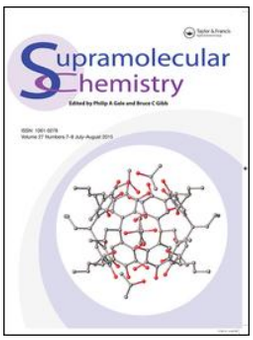


Supramolecular Chemistry

ISSN: 1061-0278 (Print) 1029-0478 (Online) Journal homepage: http://www.tandfonline.com/loi/gsch20

Pyridine-incorporated cyclo[6]aramide for recognition of urea and its derivatives with two different binding modes

Kang Kang, Wei Huang, Yonghong Fu, Lixi Chen, Jinchuan Hu, Yi Ren, Wen Feng & Lihua Yuan

To cite this article: Kang Kang, Wei Huang, Yonghong Fu, Lixi Chen, Jinchuan Hu, Yi Ren, Wen Feng & Lihua Yuan (2017): Pyridine-incorporated cyclo[6]aramide for recognition of urea and its derivatives with two different binding modes, Supramolecular Chemistry, DOI: 10.1080/10610278.2017.1282614

To link to this article: http://dx.doi.org/10.1080/10610278.2017.1282614

SUPRAMOLECULAR CHEMISTRY, 2017
http://dx.doi.org/10.1080/10610278.2017.1282614

Taylor & Francis
Taylor & Francis Group

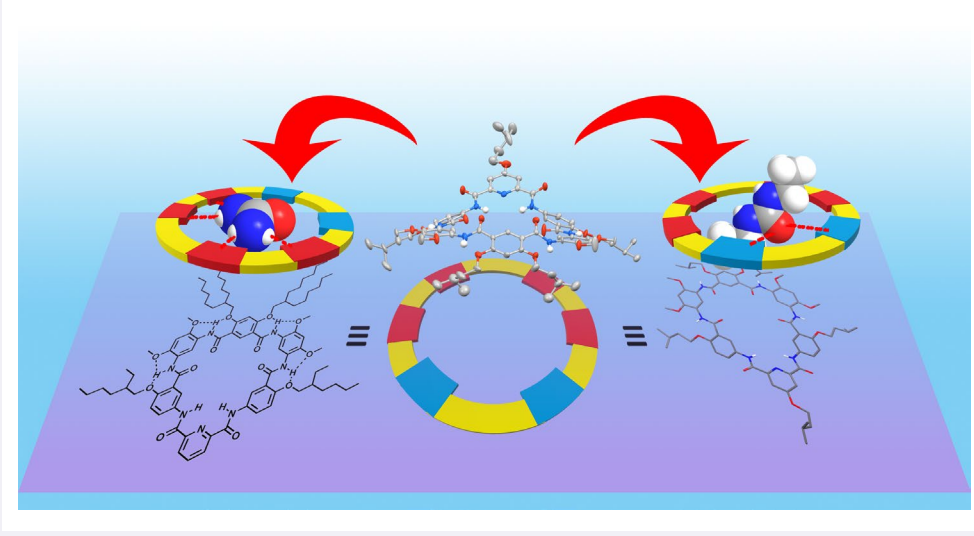
Pyridine-incorporated cyclo[6]aramide for recognition of urea and its derivatives with two different binding modes

Kang Kang, Wei Huang, Yonghong Fu, Lixi Chen, Jinchuan Hu, Yi Ren, Wen Feng and Lihua Yuan

Key Laboratory for Radiation Physics and Technology of Ministry of Education, Institute of Nuclear Science and Technology, College of Chemistry, Sichuan University, Chengdu, China

ABSTRACT

A novel pyridine-incorporated cyclo[6]aramide is designed and synthesised for recognition of urea and its derivatives. Analysis of its single crystal structure reveals the presence of introverted amide NH protons and amide carbonyl groups that are supposed to contribute to the subsequent accommodation of neutral urea-related guest molecules via multiple hydrogen bonding interactions. Thiourea is found to be superior to urea in binding to the receptor. Particularly interesting is the observation of two binding modes in complexing urea/thiourea (contact mode) and ethylurea/diethylurea (threading mode) as supported by both NMR experiments and computational simulations. The finding of the threading mode may open up new opportunities for the development of pesudorotaxanes and related mechanically interlocked structures.



ARTICLE HISTORY
Received 17 October 2016
Accepted 7 January 2017

KEYWORDS
Cyclo[6]aramide; urea; host–guest complexation; hydrogen bonding

1. Introduction

One-pot H-bonding-directed macrocyclisation (*1*) boasts high production of cyclic compounds and synthetic simplicity and atom economy. Particularly appealing is its utility in generating various classes of aromatic amide macrocycles that result from such macrocyclisation (*2*). The resultant macrocycles, termed H-bonded aromatic amide macrocycles (*3*), have demonstrated a unique structural feature of two-dimensional shape-persistency (non-collapsiblility) (*4*) that differentiates them from nowadays popular macrocyclic compounds such as crown ethers (*5*), calixarenes (*6*), cyclodextrins (*7*), cucurbiturils (*8*), pillararenes (*9*) and other artificial cycles (*10*). Simultaneous with the shape-persistency of their molecular backbones is the preorganisation of functionalities or amide carbonyl groups that allow follow-up implementation of host–guest (H–G) interactions. These H-bonded macrocycles have found a variety of applications in catalysis (*11*), sensors (*12*), separation technology (*13*), molecular recognition (*14*) and transmembrane channels (*15*), etc.

CONTACT Lihua Yuan lhyuan@scu.edu.cn
Supplemental data for this article can be accessed http://dx.doi.org/10.1080/10610278.2017.1282614.

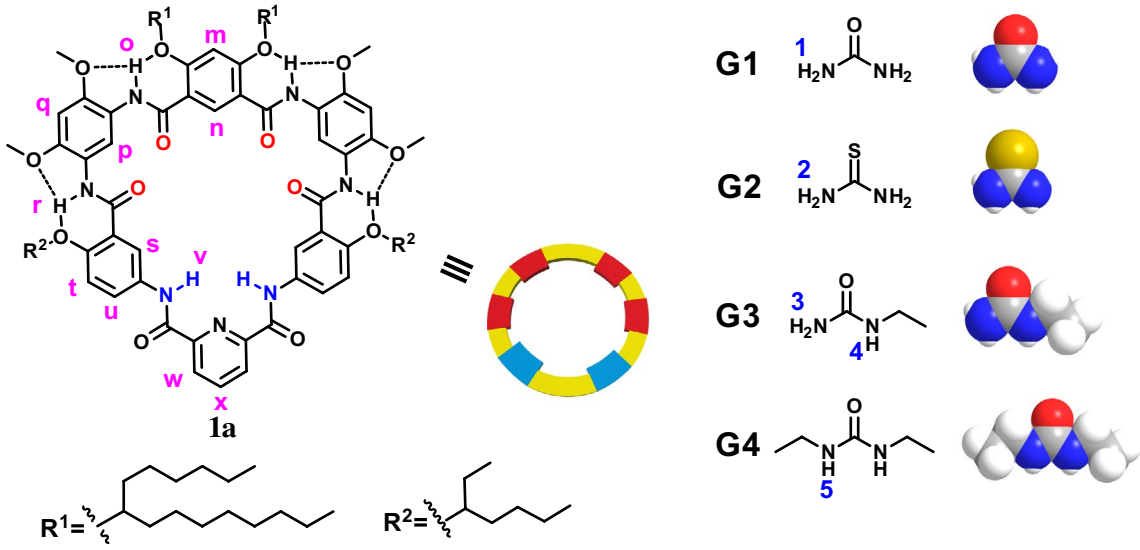


Figure 1. Chemical structures of pyridine-incorporated cyclo[6]aramide **1a** and guest **G1**,**G2**,**G3** and **G4**.

Among them, H-bonded aromatic amide macrocycles bearing introverted carbonyl oxygens in their interiors (*16*) dubbed cycloaramides, and their derivatives, are especially intriguing due to their rich H–G chemistry (*17*). Our recent work has revealed the strong ability of cyclo[6]aramides, the smallest member of this class of H-bonded aromatic amide macrocycles to bind organic cations (*18*) such as dialkylammonium ions and diquat, and even to recognise amino acids (*19*). Cyclo[6]aramide with a larger cavity could accommodate a depsipeptide antibiotic valinomycin or its potassium complex on a highly oriented pyrolytic graphite surface (*20*). Interestingly, these macrocycles are able to serve as a class of macrocyclic mesogens that cover a wide spectrum of phases as liquid crystalline materials, whose inter-phase transition is tunable via H–G interactions (*21*). However, the presence of all six carbonyl groups preorganised inside the cavity prevents these cyclic compounds from being used in binding ion-pair or neutral guest species.

Recently, we have developed a strategy by depleting partial internal H-bonds to construct convergent heteroditopic cyclo[6]aramides as ion-pair receptor (*22*). The design exploits the synergistic action by both anion- and cation-binding groups, and therefore significantly enhances the binding affinity (>10^5 M^{-1} in $CDCl_3$) towards binding dibutylammonium chloride, leading to an increase in association constant (K_a) in chloroform by two orders of magnitude. Analysis of the single crystal structure of the receptor shows that one of the two carbonyl groups from the phenyl ring absent of intramolecular hydrogen bonds orients outwards and the other carbonyl group points inwards. This prompted us to consider an alternative design by incorporating a pyridine unit rather than a phenyl ring to give receptor **1a** (Figure 1). In this molecule, two amide groups are predisposed on the same side due to the presence of intramolecular three-centre H-bonds formed by the nitrogen atom and two NH protons, partially hindering its rotation around two rotatable amide bonds. With this conformation, we envisioned that **1a** would be able to easily accommodate a neutral guest, urea or thiourea. More importantly, the installation of an electro-deficient pyridyl ring relative to a phenyl ring should increase the acidity of NH protons, and thus may likely improve the binding ability of the receptor for the guest.

Urea represents a typical guest molecule in host–guest chemistry that has arrested considerable attention during the past years. This is largely due to the importance of urea as a metabolism product (*23*) for detecting purposes (*24*) and protein denaturant (*25*), and its use as a thread component (*26*) in constructing mechanically interlocked molecules (*27*). Numerous receptors on recognising urea and its derivatives have been reported since 1971 (*28*), among which most of their structures are based on pyridine- or its analogue-based aromatic oligoamides (*29*), but few are associated with macrocyclic hosts (*30*). Crown ethers and their derivatives are one of the very few examples that have demonstrated the complexation of urea though their host–guest interactions are pretty weak in water (*31*). Therefore, there is still need to search for artificial macrocycles that would recognise urea or its derivatives. H-bonded aromatic amide macrocycles with removal of partial H-bonds are likely to be the right candidates because their interior cavities are decorated with amide functionalities available for the formation of multiple hydrogen bonds. Despite the progress made in recent years in utilising cyclo[6]aramides for binding various

guests, the complexation of a neutral guest like urea is still lacking. Herein, we report the recognition of urea and its derivatives (thiourea, ethylurea and diethylurea) **G1–G4** by a pyridine-incorporated cyclo[6]aramide **1a**. The presence of the intramolecular H-bonding for restricting rotation of amide bonds is corroborated by X-ray crystallography. Two different binding modes are proposed according to the data collected from NMR techniques.

2. Results and discussion

2.1. Synthesis and solid state structure

Receptor **1a** was synthesised according to the synthesis route as shown in Figure 2. Hydrogenation of pentamer **5a** in the presence of 20% Pd/C in $CHCl_3/CH_3OH$ led to its reduced form **5b**, which was used for the immediate coupling reaction with acid chloride **6a'** prepared from pyridine dicarboxylate **6a**. Purification by chromatography on silica gel (CH_2Cl_2/MeOH = 30:1) provided the pyridine-incorporated cyclo[6]aramide **1a** as a white solid in a yield of 44.2%. To grow single crystals, compound **1b**, which shares the same backbone but bears shorter side chains, was synthesised according to the same procedure above in 30% yield. Syntheis of pentamer **5a** and **5b** and control compound **2** was accomplished following the previously describeded method (*22*). All the target molecules and intermediates were characterised by ^{1}H NMR, ^{13}C NMR and high resolution mass spectroscopy (HRMS) techniques.

Crystals suitable for the X-ray analysis were obtained by slow evaporation of a solution of **1b** in a mixed solvent of dichloromethane and methanol (20:1). A summary of the crystallographic data and structure refinement of **1b** is listed in Table S1 and detailed labelling of major atoms are shown in supporting information (Figure S23). The crystal belongs to the space group P2(1)/c (Table S1), and the unit cell contains four macrocyclic molecules. Surprisingly, analysis of the single crystal structure clearly shows that macrocycle **1b** adopts a chair-like conformation seen from side view (Figure 3(b)), which considerably deviates from the shallow bowl conformation of its analogue (*22*) or the almost flat conformation of classical cyclo[6]aramide **2** with the fully H-bonded backbone (*21*). Detailed inspection of the crystal structure reveals a pyridyl ring-localised conformation where two intramolecular hydrogen bonds, N2C–H2C···N4C (105.931°, 2.3267 Å) and N1C–H1C···N4C (106.653°, 2.3807 Å), each comprising one five-membered ring, predispose two amide NH hydrogens orienting inside (Figure 3(a)). The observed orientation of amide hydrogens as H-bond donor is crucial to the subsequent formation of hydrogen bonds with H-bond acceptor (guest). This local conformation constitutes the 'chair' back of the defined chair conformation, while the four phenyl rings (phenyls 2, 3 and 5, 6, see Figure S23) adjacent to the pyridyl ring construct the 'seat' flanked by two side chains as 'chair' feet. The dihedral angle between the chair back and the chair seat is 151.8°. We attribute this to diminished strains caused by depletion of two intramolecular three-centre H-bonds in **2** that leads to considerable conformational distortion in **1a**. Interestingly, the plane (phenyl 3 and 5, see Figure S23) along with its side chains is twisted away from the 'seat', actually constituting two front feet of the chair conformation. This suggests that even locally rigidified backbone enforced by the presence of intramolecular three-centre H-bonds (*32*) may still be subject to the fluctuation of regional conformation change, which is supposed to be otherwise impossible with fully H-bonded cyclo[6]aramide (*21*). The diameter of cavity in **1a** measures 6.82 Å, which is large enough to engulf a guest molecule like urea with a size of only 3.82 Å (*33*). Selected bond lengths and angles for **1b** from X-ray diffraction experiment are given in Table 1.

In the packing diagram, the pyridyl ring in one macrocyclic molecule of **1b** interacts with a phenyl ring in another molecule via *π*–*π* stacking interactions (right side, Figure

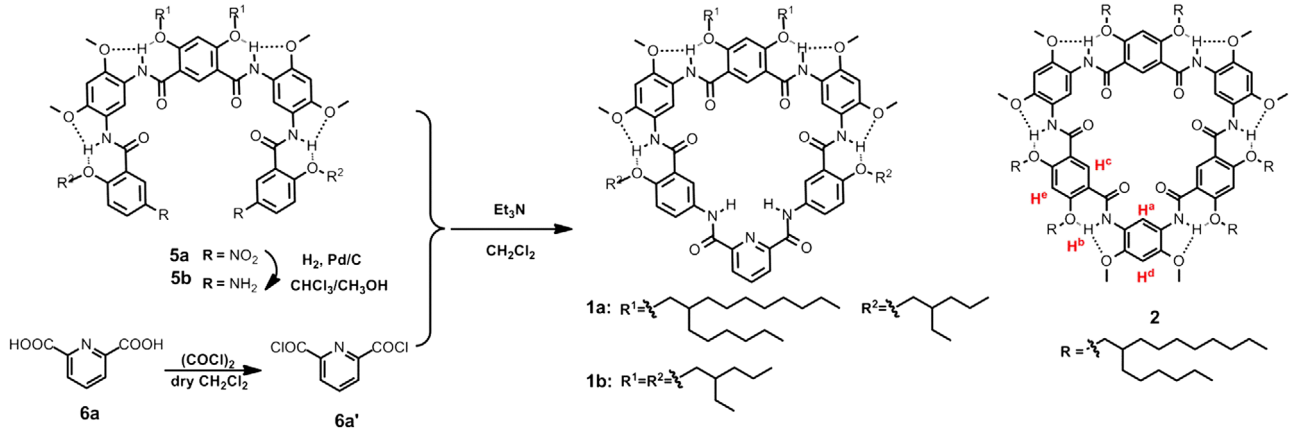


Figure 2. Synthesis of pyridine-incorporated cyclo[6]aramide **1a**.

3(c)). The interplanar distance between the two adjacent macrocycles is 3.583 Å with the dihedral angle of 7.68° between the phenyl ring and the pyridyl ring. At the same time, two phenyl rings, each of which comes from a macrocyclic constituent of two different macrocycles, stack upon each other with a *π–π* stacking distance of 3.680 Å (left side, Figure 3(c)). Noticeably, these two phenyl rings orient in the same direction with the dihedral angle of 6.73°. The observation that a phenyl ring (phenyl 4) protrudes out of a regional plane comprising two phenyl rings (phenyl 3, 5) is quite unusual because it is less likely for a rigidified backbone enforced by two three-centre H-bonds to twist to such an extent (*23*). The concurrent formation of two very close dihedral angles (7.68° and 6.73°) as a result of intermolecular *π–π* stacking interactions explains why one of the five phenyl rings and the pyridyl ring in a single macrocyclic molecule are oriented in the same orientation, leading to the observed stacking mode and subsequent linear arrangement of macrocycles (Figure 3(c)). Therefore, the stacking interaction is considered here as a major non-covalent linking bridge to another macrocycle in the molecular packing.

2.2. Host–guest complexation

With two predisposed amide functionalities as H-bond donor and carbonyl oxygen atoms as H-bond acceptor, **1a** is expected to bind urea and its derivatives. Control compound **2**, which bears the same number of carbonyl oxygens but whose oxygen atoms are all pointing inwards, serves as a control to see if there is any difference in complexation as compared to partially H-bonded cyclo[6]aramide **1a**.

Urea (**G1**) has high affinity for water and is insoluble in chloroform (*34*); however, upon adding 0.2 equiv. of **G1** to a 1.0 mM solution of cyclo[6]aramide **1a**, the ^{1}H NMR spectra of the mixture containing **1a** and urea in $CDCl_3$ showed an appreciable change of chemical shifts associated mainly with the amide protons H_v of the host (Figure 4). Protons H_1 of **G1** were identified to appear at 5.5 ppm. Further addition of **G1** up to 1.0 equiv. led to finally the downfield shifting of signals of amide protons H_v by 0.88 ppm. Contrary to the downfield shifting, Protons H_1 on urea experienced an upfield shift by 0.17 ppm. This indicates that **G1** interacts with the macrocycle possibly as a result of the formation of hydrogen bonds via both amide protons and urea protons. It should be noted that the sample used was sonicated for ca. 1 h followed by filtration to remove excess solid urea before NMR experiments.

In the presence of thiourea (Figure 5), receptor **1a** experienced significant downfield shifts for both two introverted amide protons H_v and interior aromatic protons H_p, H_n and H_s, (0.32, 0.32 and 0.71 ppm, respectively), in sharp contrast to the case of urea where only a minor change in chemical shifts was observed for aromatic protons H_p, H_n and H_s (0.03, 0.04, 0.04 ppm, respectively). This suggests a stronger interaction of the receptor with thiourea than urea. Indeed, the titration experiments for binding thiourea reveals the association constant of $(3.1 \pm 1.0) \times 10^4$ M^{-1} in $CDCl_3$–2%CD_3CN, which is more than one order of magnitude larger than the value of $(6.2 \pm 1.9) \times 10^3$ M^{-1} observed for urea in $CDCl_3$ (vide post). With ethylurea **G3**, beyond our expectation, a much larger downfield shift of protons H_v (1.66 ppm) was observed. However, other interior aromatic protons (H_p, H_n and H_s) were only marginally influenced by the binding of this guest. Concomitant with the change of proton chemical shifts on the receptor, aliphatic protons of the guest also experience a change of both upfield shifts of protons H_4 and H_5. Diethylurea **G4**, which is a diethylated derivative of urea, showed a similar downfield shift behaviour (1.59 ppm). These results indicate that two amide protons in **1a** should involve the formation of much stronger H-bonding interactions with **G3** and **G4** than with **G1** and **G2**. This drives us to propose a unique 'threading mode' for these two guests, as compared to the 'contact mode' with **G1** and **G2** as the interacting guest species (also see Computational simulations).

The information of the binding stoichiometry of **G1**–**G4** was retrieved from Job's plot and mole ratio method. In all cases, results from NMR titration experiments indicate a 1:1 stoichiometry for each host–guest pair. It is worth noting that both interior aromatic protons (H_p, H_n, H_s) experience a significant change of chemical shifts upon stepwise addition of a guest, For example, addition of 2.0 equiv of **G2** to a solution of **1a** led to the downfield shifting of signals of protons H_p, H_n and H_s on **1a** by 0.20, 0.30 and 0.57 ppm in $CDCl_3$–2%CD_3CN (Figure 6). The mixed solvent is chosen for increasing the complex solubility. Beyond 1.0 equiv. of the guest, these protons are subjected to a small change, indicating the relatively stronger binding of **G2** by the macrocycle **1a**. In the meanwhile, there are only one set of signals for the protons of the host and the guest with increasing concentrations of the

Table 1. Hydrogen bonds in the crystal structure of **1b**.

D-H···A	Bond angle/°	Bond length/Å
N1A–H1A···O1A	91.410	2.5070
N1A–H1A···O5A	132.783	2.0709
N1B–H1B···O3B	97.395	2.3848
N1B–H1B···O6A	135.767	2.0106
N2A–H2A···O2A	107.929	2.1960
N2A–H2A···O4C	138.509	2.1960
N2B–H2B···O4B	106.737	2.2310
N2B–H2B···O5B	139.227	1.9300
N2C–H2C···N4C	105.931	2.3267
N1C–H1C···N4C	106.653	2.3807

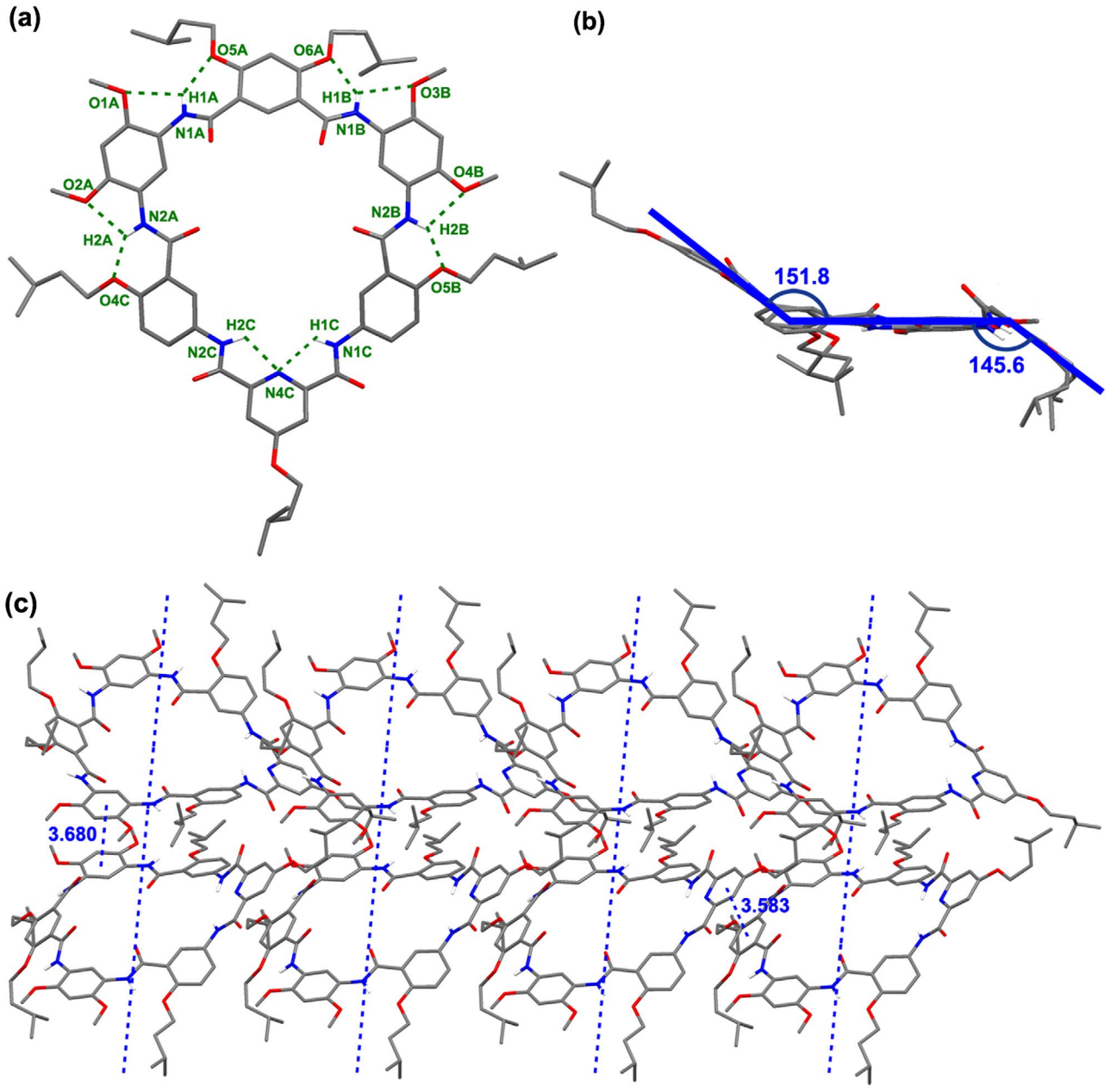


Figure 3. X-ray crystal structure of pyridine-incorporated cyclo[6]aramide **1b**: (a) top view with crystallographic numbering, (b) side view, illustrating a chair conformation with dihedral angles, (c) molecular stacking viewed along the axis with the dashed blue lines drawn passing through the cavities of the macrocycles. Only hydrogen atoms involved in H-bonds are shown for clarity.

guest. All these results, taken in concert, suggest a fast exchange in the complexation process on NMR time scale. The resulting Job's plot from NMR and UV–vis experiments also corroborates the 1:1 stoichiometry. For example, the maximum value which is obtained through mole fraction multiplying by $\Delta\delta$ is observed at 0.5 for **G1**, indicating a host–guest ratio of 1:1 in the complex (Figure 7). In line with the results above, HRMS of an equimolar mixture of **1a** and guest **G1** (or **G2**) also showed the presence of the 1:1 complex at m/z = 1634.0743, corresponding to $[\mathbf{1a} + \mathbf{G1} + H]^+$ (Figure S5), and at m/z = 1650.0201, corresponding to $[\mathbf{1a} + \mathbf{G2} + H]^+$ (Figure S6), respectively.

On the basis of 1:1 stoichiometry and ^{1}H NMR titrations data (Figure S9–S22), the association constants of **1a** for **G1**-**G4** are obtained using nonlinear curve fitting method (Table 2). The binding affinities of these guest by **1a** increase in the order of **G2** > **G1** > **G3** > **G4**. This indicates that the binding event is favourable for **G2**, and thus **1a** shows better selectivity towards thiourea in the recognition process.

To evaluate the importance of preorganised amide NH protons in the binding event, compound **2** (Figure 2) was used as a control for comparing its binding affinity with urea. The association constant with **2** for binding **G1** was

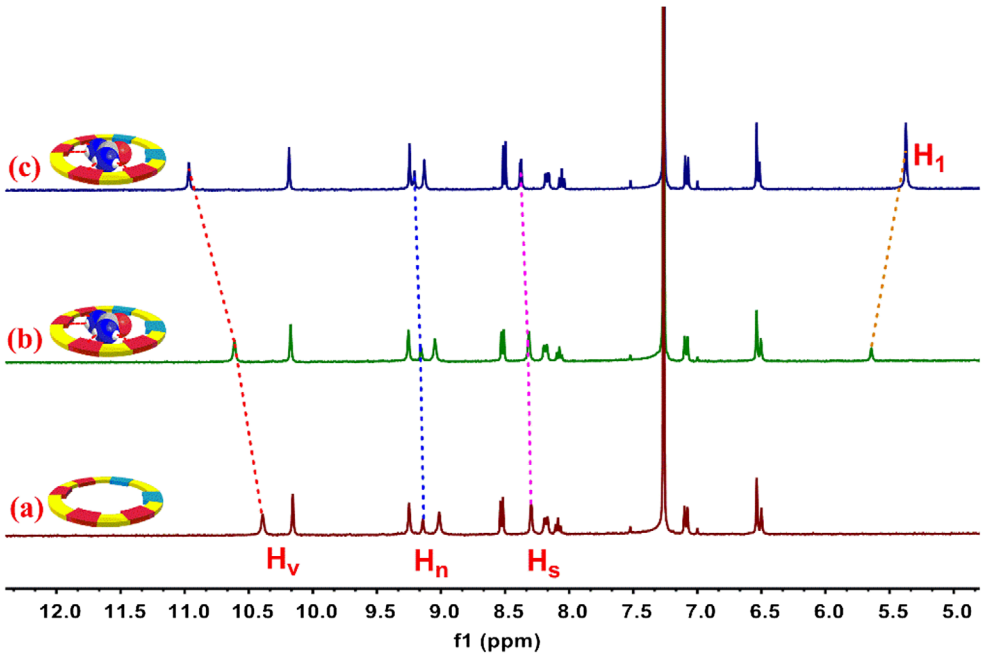


Figure 4. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) showing chemical shift changes after host–guest complexation in chloroform: (a) 1.0 mM cyclo[6]aramide **1a**, (b) 1.0 mM **1a** and 0.2 equiv. urea, (c) 1.0 mM **1a** and 1.0 equiv. urea.

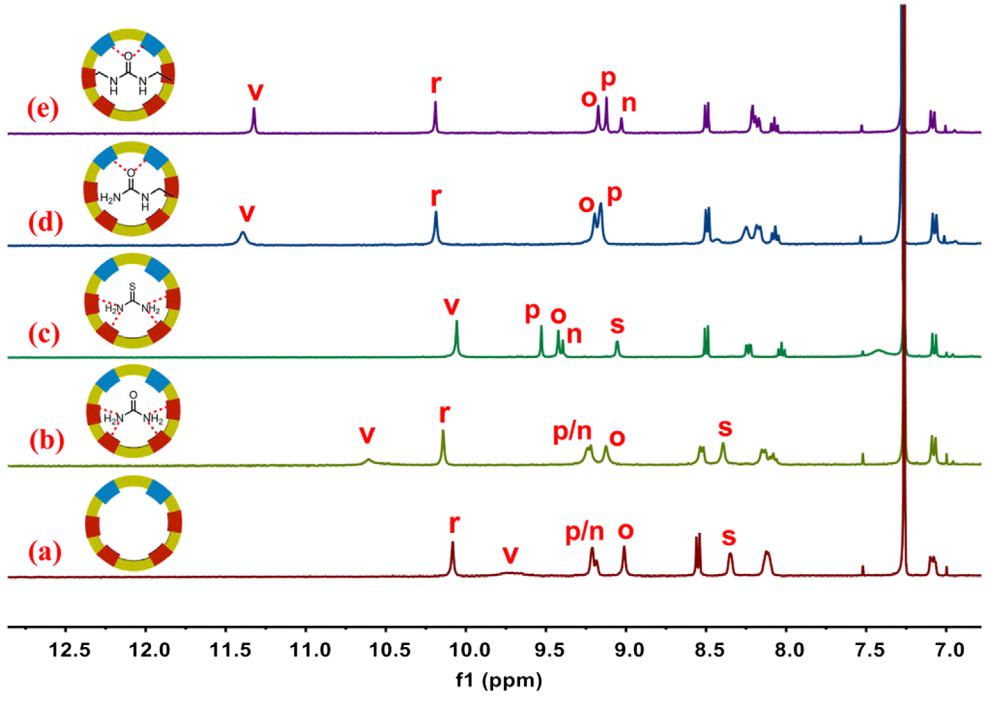


Figure 5. Partial ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectra of (a) **1a** (2.5×10^{-3} M), (b) complex of **1a** with urea, (c) complex of **1a** with thiourea, (d) complex of **1a** with ethylurea, (e) complex of **1a** with diethylurea.

found to be considerably reduced to $(4.2 \pm 3.4) \times 10^2$ M^{-1} in $CDCl_3$ (Figure S22) as compared to the K_a value of $(6.2 \pm 1.9) \times 10^3$ M^{-1} with **1a**. This result is significant because it demonstrates the importance of the pyridyl ring in directing carbonyl groups to point inwards for efficient guest binding.

2.3. Binding modes aided by computational simulations

To gain insight into the binding site, two-dimensional NOESY experiments were performed in $CDCl_3/CD_3CN$ (9:1, v/v) with **1a** and **G2**. **G1** is only sparsely soluble in the

Table 2. Association constants (K_a/M^{-1})[a] for the complexation of guests by **1a** and **2** at 298 K.

Host	Guest	Solvent	Association constant
1a	**G1**	$CDCl_3$	$(6.2 \pm 1.9) \times 10^3$
2	**G1**	$CDCl_3$	$(4.2 \pm 3.4) \times 10^2$
1a	**G2**	$CDCl_3$–2%CD_3CN	$(3.1 \pm 1.0) \times 10^4$
1a	**G3**	$CDCl_3$	$(3.4 \pm 0.9) \times 10^2$
1a	**G4**	$CDCl_3$	$(8.8 \pm 4.4) \times 10$

[a]This association constants values were obtained by ^{1}H NMR titration experiments. For full details, see the Supporting Information.

chosen solvent system at higher concentrations, and thus **G2** was used for the experiments. Correlations between the signals attributable to the interior aromatic protons of **1a** (denoted as H_p, H_n and H_s) and protons of thiourea (denoted as H_2) are observed (Figure S8); meanwhile, no cross-peaks associated with the contact between peripheral alkyl protons and protons H_2 appear. This strongly implicates that the complexation of the neutral guest species should most likely occur in the macrocyclic cavity.

To further clarify the observed binding properties, a series of molecular modelling simulations based on density functional theory (DFT) method were performed for the host–guest system comprising pyridine-incorporated cyclo[6]aramide **1a** and guests **G1**–**G4**. The computational

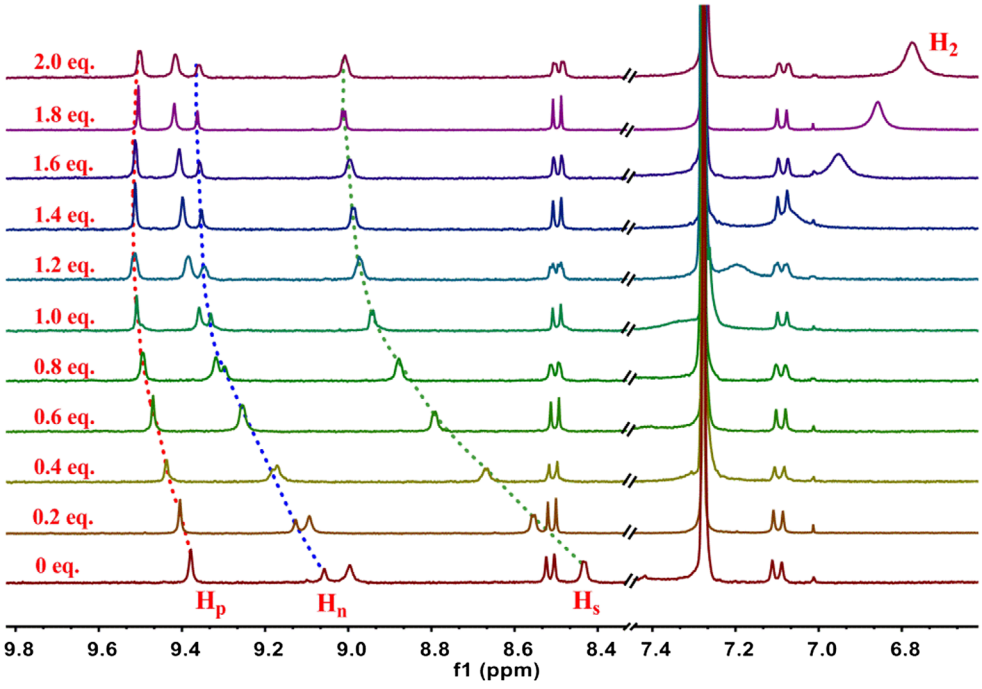


Figure 6. Stacked partial ^{1}H NMR (400 MHz, 298 K) titration spectra of **1a** (1.0 mM) with **G2** in $CDCl_3$–2%CD_3CN.

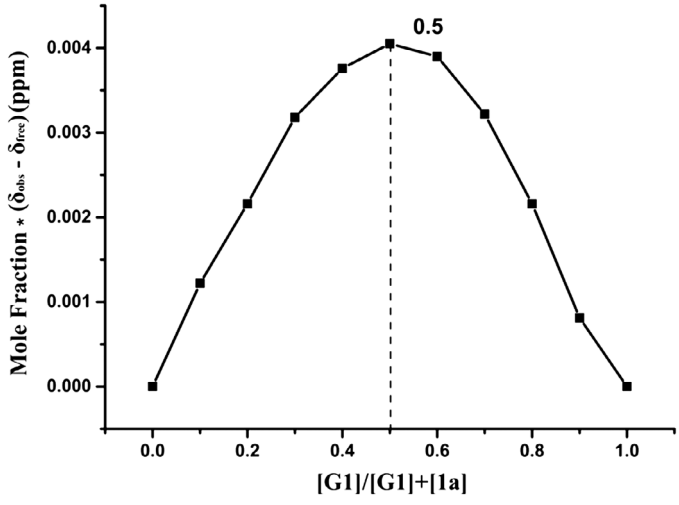


Figure 7. Job's plot for the determination of stoichiometry in the complex formed by **1a** and **G1** from ^{1}H NMR experiments in $CDCl_3$.

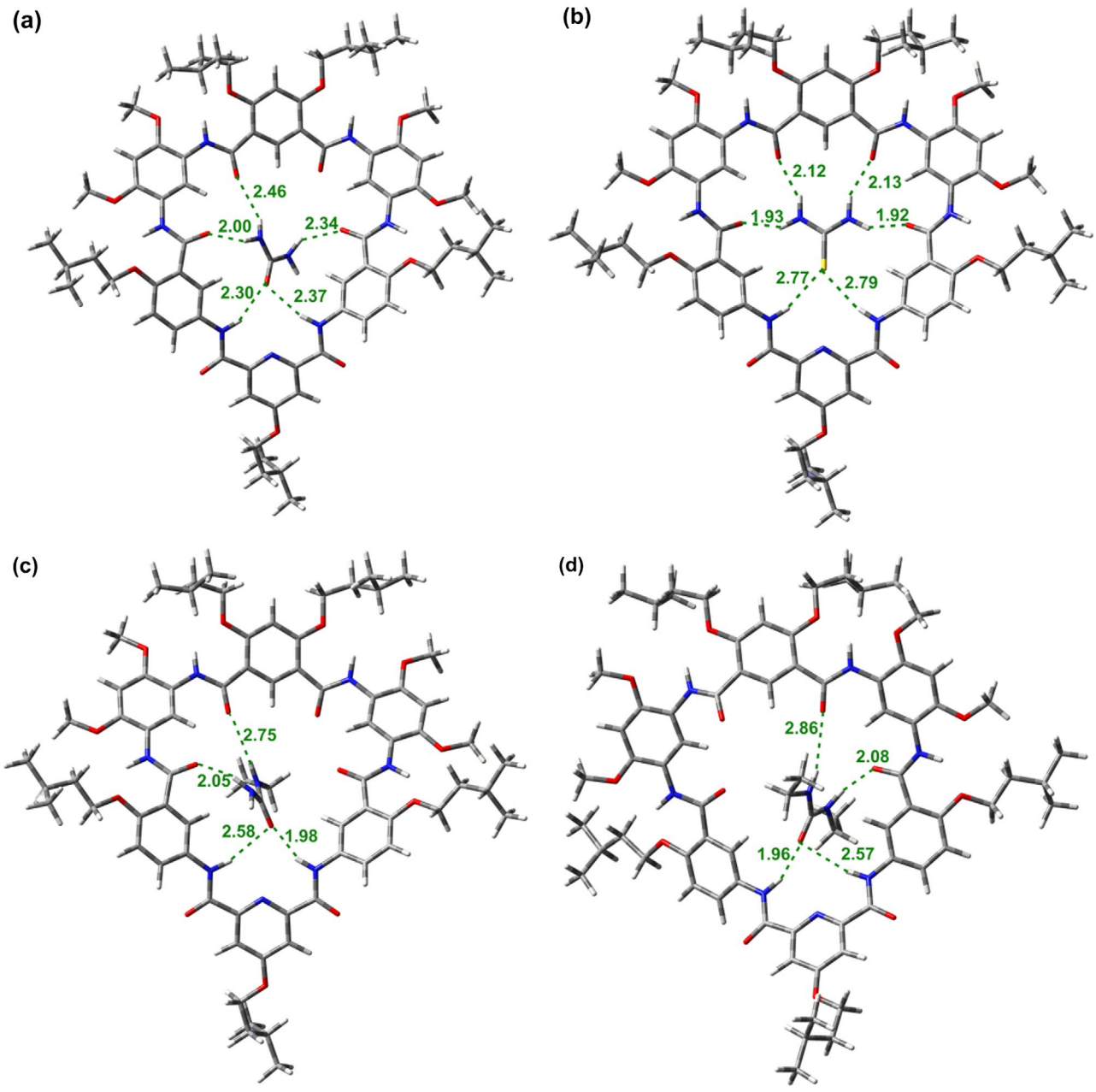


Figure 8. The complex structure of (a) **1a**·urea, (b) **1a**·thiourea, (c) **1a**·ethylurea, (d) **1a**·diethylurea optimised by the DFT method.

results based on the calculated binding energies reveal that each guest resides in the cavity of the macrocycle via multiple hydrogen bonding interactions (Figure 8). In general, the macrocycle in each complex shows a chair-like geometry (Figure S24–S27), which is very similar to the conformation of the parent framework of cyclo[6]aramides as observed in the single crystal structure. In the presence of **G1**, the guest urea engages in five intermolecular hydrogen bonds (Figure 8(a)), among which one NH_2 group of urea is bound to two carbonyl oxygens, and the other NH_2 group forms a single hydrogen bond with one carbonyl oxygen at 2.43 Å. The amide NH_2 protons of macrocycle **1a** are bound by a carbonyl oxygen of urea (2.43 and 2.37 Å). It should be noted that the urea molecule looks slightly protruding out of the macrocyclic plane. The complex involving **G2** is stabilised by six hydrogen bonds with the optimised structure of the complex **1a**·**G2** in inclusive conformation (Figures 8(b), and S25). The inter-H bonding distance for each hydrogen bond which is formed between four carbonyl oxygen groups of **1a** and NH_2 of urea is less than 2.20 Å. As for the sulphur atom, it binds two amide protons through hydrogen bonds at 2.77 and 2.79 Å, each of which is more than 2.70 Å, suggesting that the H-bonding interaction between sulphur atom and amides is relatively less stronger. So, we presume that carbonyl oxygens play a more important role in binding urea and thiourea rather than amide protons. The

superior binding affinity with **G2** over **G1** is supported by the Gibbs free energy difference of −61.0 kJ/mol of complex **1a**·**G2** being smaller compared to that of −39.7 kJ/mol of complex **1a**·**G1** (Table S2). With **G3**, which bears additional ethyl group, the complex is stabilised by only four inter-H bonds. Different from **G1** and **G2**, the optimised structure of the complex **1a**·**G3** clearly shows that **G3** threads the cavity of the macrocycle because of steric repulsion from the substitution of an ethyl group on urea. Interestingly, when two ethyl groups are installed on urea, the binding mode of **1a** with **G4**, is very similar to that of **G3** in terms of both the number of hydrogen bonds and the length of bonds. Furthermore, this guest also penetrates threads the cavity to form a pseudo[2]rotaxane-like complex. However, this host–guest complex ($\Delta G = -26.1$ kJ/mol) is less stable than complex **1a**·**G3** ($\Delta G = -27.5$ kJ/mol) as a result of larger steric effect. These computational results are consistent with the observations from NMR experiments (vide ante). Based on all these results above, we propose two different binding modes that may operate in the binding of urea and its derivatives, i.e., 'contact mode' for **G1** and **G2**, and 'threading mode' for **G3** and **G4**. The 'threading mode' is more intriguing in terms of the possibility of using cyclo[6]aramide-based host–guest system for constructing pesudorotaxanes and rotaxanes.

3. Conclusions

In summary, we have shown that a novel pyridine-incorporated cyclo[6]aramide **1a** binds strongly and selectively urea and its derivatives in 1:1 stoichiometry. Among four guests examined, the thiourea offers the highest binding affinity in a mixed solution of chloroform-2% acetonitrile ($K_a = 3.1 \times 10^4$ M^{-1}) in forming the host–guest complex. The single crystal structure of **1a** evidences the presence of introverted amide groups that are supposed to play an important role in enhancing the binding ability for urea-related compounds. The interplay of multiple H-bonds and guest size should be responsible for the stability of the complex as compared to classical fully H-bonded cyclo[6]aramide. Importantly, NMR experiments reveal two different binding modes, i.e., 'contact mode' and 'threading mode', that are operative in the recognition process, which is further corroborated by computational modelling. The finding of 'threading mode' holds promise for applications in constructing mechanically interlocked structures.

4. Experimental section

4.1. Materials and reagents

Compound **1a** was synthesised following the reported procedure (*22*). $CDCl_3$ and CD_3CN were purchased from Cambridge Isotope Laboratories, used for the titration experiments without further drying. Dichloromethane, chloroform and methanol were purchased from Chengdu Kelong Chemical Factory. CH_2Cl_2 was dried over CaH_2. Column chromatography was carried out using silica gel (300–400 mesh). All other solvents and chemicals used for the synthesis were of reagent grade and used as received. The complex samples for ESI-MS determination were prepared by mixing a MeOH solution.

4.2. Synthese

Receptor **1a** was synthesised according to Figure 2. Pentamer **5a** (400 mg, 0.27 mmol) was hydrogenated in the presence of 20% Pd/C (80 mg) in $CHCl_3$/CH_3OH (70 mL, v/v = 7:1) for 14 h at 45 °C. The solution was filtered in darkness as fast as possible followed by immediate removal of the solvent. The reduced diamine was used for the immediate coupling reaction. DMF (5 μL) was added to a suspension of compound **6a** (82 mg, 0.28 mmol) and oxalyl chloride (105 mg, 0.84 mmol) in CH_2Cl_2. The mixture was stirred for 40 min at room temperature. The solvent was evaporated and the resulting acid chloride was dried in vacuum at room temperature for 30 min to get compound **6a'**. Compound **6a'** was dissolved in CH_2Cl_2 (60 mL) and added dropwise to a mixture of the above **5a'** and Et_3 N (162 mg, 1.60 mmol) in CH_2Cl_2 (20 mL) at 0 °C. The solution was stirred under N_2 for 10 min. The organic layer was washed with water (20 mL × 3). The crude product was purified by chromatography on silica gel (CH_2Cl_2/MeOH = 30:1) to provide the product **1a** as a white solid. **1a**: yield 44.2%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 10.67 (s, 2H), 10.16 (s, 2H), 9.27 (s, 2H), 9.12 (s, 1H), 9.02 (s, 2H), 8.51 (d, J = 7.74 Hz, 2H), 8.29 (s, 1H), 8.19 (d, J = 9.06 Hz, 2H), 8.10 (t, J = 7.74 Hz 1H), 7.05 (d, J = 9.06 Hz, 2H), 6.52 (s, 2H), 6.50 (s, 1H), 4.10 (m, 10H), 3.90 (m, 15H), 2.82 (m, 15H), 1.99 (m, 5H), 1.56–1.28 (m, 85H), 0.94–0.85 (m, 31H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 163.50, 163.10, 162.58, 159.97, 153.85, 149.69, 147.10, 146.24, 138.33, 138.00, 131.60, 127.46, 125.59, 122.03, 121.00, 119.34, 117.90, 116.15, 112.54, 96.33, 94.91, 72.55, 72.27, 55.89, 55.79, 38.58, 37.89, 31.88, 31.86, 30.99, 30.05, 29.88, 29.71, 29.62, 29.52, 29.34, 28.72, 26.70, 26.66, 23.28, 23.06, 22.83, 22.67, 14.11, 14.10, 14.05, 10.47. HRESI-MS m/z: $[M + Na]^+$ Calcd for $C_{93}H_{133}N_7O_{14}Na$ 1594.9803, found 1594.9811.

4.3. Instruments and apparatus

^{1}H and ^{13}C NMR spectra were recorded on Bruker AVANCE AV II-400 MHz (^{1}H: 400 MHz; ^{13}C: 100 MHz). High resolution mass data were collected by WATERS Q-TOF Premier. Chemical shifts are reported in δ values in ppm using tetramethylsilane. The geometry optimisations were carried out in gas phase by employing the Gaussian09

program. Crystallographic study was performed on compounds **1b**. Data were collected on a Xcalibur E diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.7107 Å).

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported by the National Natural Science Foundation of China [grant number 21572143], the Doctoral Programme of the Ministry of Education of China [grant number 20130181110023] and Open Project of State Key Laboratory of Supramolecular Structure and Materials [grant number SKLSSM201629]. Comprehensive Training Platform of Specialized Laboratory, College of Chemistry, Sichuan University, is acknowledged for NMR analyses.

References

(1) (a) Adams, H.; Carver, F.J.; Hunter, C.A.; Osborne, N.J. *Chem. Commun.* **1996**, *56*, 2529–2530. (b) Hunter, C.A.; Thomas, J.; Bernad, P. Jr *Chem. Commun.* **1998**, *58*, 2449–2450.

(2) (a) Jiang, H.; Léger, J.M.; Guionneau, P.; Huc, I. *Org. Lett.* **2004**, *6*, 2985–2988. (b) Ren, C.L.; Xu, S.Y.; Xu, J.; Chen, H.Y.; Zeng, H.Q. *Org. Lett.* **2011**, *13*, 3840–3843. (c) Ren, C.; Maurizot, V.; Zhao, H.; Shen, J.; Zhou, F.; Ong, W.Q.; Du, Z.; Zhang, K.; Su, H.; Zeng, H.Q. *J. Am. Chem. Soc.* **2011**, *133*, 13930–13933. (d) Zhang, D.W.; Zhao, X.; Hou, J.L.; Li, Z.T. *Chem. Rev.* **2012**, *112*, 5271–5316. (e) Ferrand, Y.; Chandramouli, N.; Kendhale, A.M.; Aube, C.; Kauffmann, B.; Grélard, A.; Laguerre, M.; Dubreuil, D.; Huc, I. *J. Am. Chem. Soc.* **2012**, *134*, 11282–11288. (f) Gong, B.; Shao, Z. *Acc. Chem. Res.* **2013**, *46*, 2856–2866. (g) Fu, H.L.; Liu, Y.; Zeng, H.Q. *Chem. Commun.* **2013**, *49*, 4127–4144.

(3) (a) Zhu, Y.-Y.; Li, C.; Li, G.-Y.; Jiang, X.-K.; Li, Z.-T. *J. Org. Chem.* **2008**, *73*, 1745–1751. (b) Qin, B.; Ren, C.; Ye, R.; Sun, C.; Chiad, K.; Chen, X.; Li, Z.; Xue, F.; Su, H.; Chass, G.A.; Zeng, H.Q. *J. Am. Chem. Soc.* **2010**, *132*, 9564–9566. (c) Kline, M.; Wei, X.; Gong, B. *Org. Lett.* **2013**, *15*, 4762–4765. (d) Wu, Z.; Hu, T.; He, L.; Gong, B. *Org. Lett.* **2012**, *14*, 2504–2507.

(4) (a) Zhang, J.S.; Moore, J.S. *J. Am. Chem. Soc.* **1994**, *116*, 2655–2656. (b) Shetty, A.S.; Fischer, P.R.; Stork, K.F.; Bohn, P.W.; Moore, J.S. *J. Am. Chem. Soc.* **1996**, *118*, 9409–9414. (c) Zhang, W.; Moore, J.S. *Angew. Chem. Int. Ed.* **2006**, *45*, 4416–4439.

(5) (a) Cooper, S.R. *Acc. Chem. Res.* **1988**, *21*, 141–146. (b) Power, P.P. *Acc. Chem. Res.* **1988**, *21*, 147–153. (c) Dye, J.L. *Acc. Chem. Res.* **2009**, *42*, 1564–1572. (d) Zheng, B.; Wang, F.; Dong, S.Y.; Huang, F.H. *Chem. Soc. Rev.* **2012**, *41*, 1621–1636. (e) Hu, X.Y.; Xiao, T.X.; Lin, C.; Huang, F.H.; Wang, L.Y. *Acc. Chem. Res.* **2014**, *47*, 2041–2051.

(6) (a) Gutsche, C. D. In *Calixarenes Revisited*; Stoddart, J.F., Ed.; The Royal Society of Chemistry: Cambridge, **1998**; Chapter 2. (b) Casnati, A.; Sansone, F.; Ungaro, R. *Acc. Chem. Res.* **2003**, *36*, 246–254. (c) Zhao, Y.; Ryu, E.H. *J. Org. Chem.* **2005**, *70*, 7585–7591. (d) Guo, D.S.; Liu, Y. *Acc. Chem. Res.* **2014**, *47*, 1925–1934.

(7) (a) Chen, G.; Jiang, M. *Chem. Soc. Rev.* **2011**, *40*, 2254–2266. (b) Ortiz Mellet, C.; Garcia Fernandez, J.M.; Benito, J. M. *Chem. Soc. Rev.* **2011**, *40*, 1586–1608. (c) Ma, X.; Tian, H. *Acc. Chem. Res.* **2014**, *47*, 1971–1981.

(8) (a) Lee, J.W.; Samal, S.; Selvapalam, N.; Kim, H.-J.; Kim, K. *Acc. Chem. Res.* **2003**, *36*, 621–630. (b) Ni, X.L.; Xiao, X.; Cong, H.; Zhu, Q.J.; Xue, S.F.; Tao, Z. *Acc. Chem. Res.* **2014**, *47*, 1386–1395. (c) Isaacs, L. *Acc. Chem. Res.* **2014**, *47*, 2052–2062. (d) Lin, F.; Zhan, T.G.; Zhou, T.Y.; Zhang, K.D.; Li, G.Y.; Wu, J.; Zhao, X. *Chem. Commun.* **2014**, *50*, 7982–7985. (e) Zhang, Y.; Zhou, T.Y.; Zhang, K.D.; Dai, J.L.; Zhu, Y.Y.; Zhao, X. *Chem. Asian J.* **2014**, *9*, 1530–1534.

(9) (a) Duan, Q.P.; Cao, Y.; Li, Y.; Hu, X.Y.; Xiao, T.X.; Lin, C.; Pan, Y.; Wang, L.Y. *J. Am. Chem. Soc.* **2013**, *135*, 10542–10549. (b) Chen, L.; Si, W.; Zhang, L.; Tang, G.; Li, Z.T.; Hou, J.-L. *J. Am. Chem. Soc.* **2013**, *135*, 2152–2155. (c) Yang, Y.W.; Sun, Y.L.; Song, N. *Acc. Chem. Res.* **2014**, *47*, 1950–1960. (d) Strutt, N.L.; Zhang, H.; Schneebeli, S.T.; Stoddart, J.F. *Acc. Chem. Res.* **2014**, *47*, 2631–2642. (e) Cao, Y.; Hu, X.Y.; Li, Y.; Zou, X.; Xiong, S.H.; Lin, C.; Shen, Y.Z.; Wang, L.Y. *J. Am. Chem. Soc.* **2014**, *136*, 10762–10769. (f) Wu, L.; Fang, Y.Y.; Jia, Y.M.; Yang, Y.Y.; Liao, J.L.; Liu, N.; Yang, X.S.; Feng, W.; Ming, J.L.; Yuan, L.H. *Dalton Trans.* **2014**, *43*, 3835–3838. (g) Fang, Y.Y.; Yuan, X.Y.; Wu, L.; Peng, Z.Y.; Feng, W.; Liu, N.; Xu, D.G.; Li, S.J.; Sengupta, A.; Mohapatra, P.K.; Yuan, L.Y. *Chem. Comm.* **2015**, *51*, 4263–4266. (h) Bai, B.; Fang, Y.Y.; Gan, Q.; Yang, Y.Y.; Yuan, L.H.; Feng, W. *Chem. Comm.* **2015**, *33*, 361–367.

(10) (a) Jiang, H.; Léger, J.-M.; Guionneau, P.; Huc, I. *Org. Lett.* **2004**, *6*, 2985–2988. (b) Cho, H.; Widanapathirana, L.; Zhao, Y. *J. Am. Chem. Soc.* **2010**, *133*, 141–147. (c) Pareek, Y.; Ravikanth, M.; Chandrashekar, T.K. *Acc. Chem. Res.* **2012**, *45*, 1801–1816. (d) Pang, T.; Shang, J.; Yang, Q.-W.; Sun, Y.; Wu, A.-X.; Jiang, H. *CrystEngComm.* **2012**, *14*, 5170–5173. (e) Otis, F.; Auger, M.; Voyer, N. *Acc. Chem. Res.* **2013**, *46*, 2934–2943. (f) Chapin, J.C.; Purse, B.W. *Supramol. Chem.* **2014**, *26*, 517–520. (g) Kim, S.K.; Sessler, J.L. *Acc. Chem. Res.* **2014**, *47*, 2525–2536. (h) Han, Y.; Meng, Z.; Ma, Y.X.; Chen, C.F. *Acc. Chem. Res.* **2014**, *47*, 2026–2040. (i) Guo, Q.H.; Fu, Z.D.; Zhao, L.; Wang, M.X. *Angew. Chem. Int. Ed.* **2014**, *53*, 13548–13552. (j) Qi, Z.; Schalley, C.A. *Acc. Chem. Res.* **2014**, *47*, 2222–2233. (k) Ghale, G.; Nau, W.M. *Acc. Chem. Res.* **2014**, *47*, 2150–2159. (l) Guo, Q.H.; Zhao, L.; Wang, M.X. *Angew. Chem. Int. Ed.* **2015**, *54*, 8386–8389.

(11) Zhao, H.Q.; Shen, J.; Guo, J.J.; Ye, R.; Zeng, H.Q. *Chem. Commun.* **2013**, *49*, 2323–2325.

(12) (a) Lim, J.Y.; Cunningham, M.J.; Davis, J.J.; Beer, P.D. *Dalton Trans.* **2014**, *43*, 17274–17282. (b) Liu, J.Q.; Sun, C.; Ma, W.L.; Lu, Y.-J.; Yu, L.; Zhang, K.; Zeng, H.Q. *RSC Adv.* **2014**, *4*, 54469–54473. (c) Zhang, Z.; Kim, D.S.; Lin, C.-Y.; Zhang, H.C.; Lammer, A.D.; Lynch, V.M.; Popov, I.; Miljanić, O.S.; Anslyn, E.V.; Sessler, J.L. *J. Am. Chem. Soc.* **2015**, *137*, 7769–7774.

(13) Zhong, L.J.; Chen, L.; Feng, W.; Zou, S.L.; Yang, Y.Y.; Liu, N.; Yuan, L.H. *J. Inclusion Phenom. Macrocyclic Chem.* **2012**, *72*, 367–373.

(14) (a) Li, Z.T.; Hou, J.L.; Li, C.; Yi, H.P. *Chem. Asian. J.* **2006**, *1*, 766–778. (b) Zhao, X.; Li, Z.T. *Chem. Commun.* **2010**, *46*, 1601–1616.

(15) Helsel, A.J.; Brown, A.L.; Yamato, K.; Feng, W.; Yuan, L.H.; Clements, A.J.; Harding, S.V.; Szabo, G.; Shao, Z.; Gong, B. *J. Am. Chem. Soc.* **2008**, *130*, 15784–15785.

(16) (a) Yuan, L.H.; Feng, W.; Yamato, K.; Sanford, A.R.; Xu, D.G.; Guo, H.; Gong, B. *J. Am. Chem. Soc.* **2004**, *126*, 11120–

11121. (b) Zou, S.L.; He, Y.Z.; Yang, Y.A.; Zhao, Y.; Yuan, L.H.; Feng, W.; Yamato, K.; Gong, B. *Synlett* **2009**, *9*, 1437–1440. (c) Yang, L.Q.; Zhong, L.J.; Yamato, K.; Zhang, X.H.; Feng, W.; Deng, P.C.; Yuan, L.H.; Zeng, X.C.; Gong, B. *New J. Chem.* **2009**, *33*, 729–733. (d) Yang, Y.A.; Yuan, L.H.; Hu, J.C.; Zou, S.L.; Feng, W.; Gong, B. *Acta Phys. Chim. Sin.* **2010**, *26*, 1557–1564. (e) Yang, Y.A.; Feng, W.; Hu, J.C.; Zou, S.L.; Gao, R.-Z.; Yamato, K.; Kline, M.; Cai, Z.-H.; Gao, Y.; Wang, Y.-B.; Li, Y.-B.; Yang, Y.L.; Yuan, L.H.; Zeng, X.C.; Gong, B. *J. Am. Chem. Soc.* **2011**, *133*, 18590–18593. (f) Wei, X.X.; Zhang, G.Q.; Shen, Y.; Zhong, Y.L.; Liu, R.; Yang, N.; Al-mkhaizim, F.Y.; Kline, M.A.; He, L.; Li, M.F.; Lu, Z.-L.; Shao, Z.F.; Gong, B. *J. Am. Chem. Soc.* **2016**, *138*, 2749–2754. (g) Feng, W.; Yamato, K.; Yang, L.Q.; Ferguson, J.S.; Zhong, L.J.; Zou, S.L.; Yuan, L.H.; Zeng, X.C.; Gong, B. *J. Am. Chem. Soc.* **2009**, *131*, 2629–2637.

(17) (a) Sanford, A.R.; Yuan, L.H.; Feng, W.; Yamato, K.; Flowers, R.A.; Gong, B. *Chem. Commun.* **2005**, *41*, 4720–4722. (b) Jiang, Q.; He, L.T.; Luo, S.Z.; Yang, Y.Q.; Yang, L.; Feng, W.; Yuan, L.H. *Chin. Chem. Lett.* **2013**, *24*, 881–884. (c) He, L.T.; Jiang, Q.; Jia, Y.M.; Fang, Y.Y.; Zou, S.L.; Yang, Y.Y.; Liao, J.L.; Liu, N.; Feng, W.; Luo, S.Z.; Yang, Y.Q.; Yang, L.; Yuan, L.H. *J. Chem. Technol. Biotechnol.* **2013**, *88*, 1930–1936. (d) Yang, X.S.; Chen, L.; Yang, Y.A.; He, Y.Z.; Zou, S.L.; Feng, W.; Yang, Y.; Liu, N.; Liao, J.; Yuan, L.H. *J. Hazard. Mater.* **2012**, *217*, 171–176. (e) Gao, R.Z.; Hu, J.C.; Zhang, K.; He, Y.Z.; Liu, P.; Luo, S.Z.; Yang, Y.Q.; Yang, L.; Feng, W.; Yuan, L.H. *Chin. J. Chem.* **2013**, *31*, 689–694. (f) He, L.T.; Jiang, Q.; Gao, R.Z.; Yang, X.S.; Feng, W.; Luo, S.Z.; Yang, Y.Q.; Yang, L.; Yuan, L.H. *Sci. China. Chem.* **2014**, *57*, 1246–1256. (g) Chen, L.; Yuan, X.Y.; Wang, Z.X.; Luo, Y.R.; Huang, W.; Zhang, S.; Yuan, W.-Y.; Qin, S.; Tao, G.-H.; Yuan, L.Y. *Asian J. Org. Chem* **2016**, *5*, 966–970. (h) Shi, S.S.; Zhu, Y.M.; Li, X.W.; Yuan, X.Y.; Ma, T.; Yuan, W.-L.; Tao, G.-H.; Feng, W.; Yuan, L.H. *RSC Adv.* **2016**, *6*, 39839–39845.

(18) (a) Hu, J.C.; Chen, L.; Ren, Y.; Deng, P.C.; Li, X.W.; Wang, Y.J.; Jia, Y.M.; Luo, J.; Yang, X.S.; Feng, W.; Yuan, L.H. *Org. Lett.* **2013**, *15*, 4670–4673. (b) Chen, L.; Peng, Z.Y.; Liu, S.; Li, X.W.; Chen, R.Z.; Ren, Y.; Feng, W.; Yuan, L.H. *Org. Lett.* **2015**, *17*, 5950–5953. (c) Xu, M.; Chen, L.; Jia, Y.M.; Mao, L.J.; Feng, W.; Ren, Y.; Yuan, L.H. *Supramol. Chem.* **2015**, *27*, 436–443.

(19) He, Y.Z.; Xu, M.; Gao, R.Z.; Li, X.W.; Li, F.X.; Li, Wu, X.; Xu, D.G.; Zeng, H.Q.; Yuan, L.H. *Angew. Chem. Int. Ed.* **2014**, *53*, 11834–11839.

(20) Li, Y.B.; Liu, C.H.; Xie, Y.Z.; Li, X.; Fan, X.L.; Yuan, L.H.; Zeng, Q.D. *Chem. Commun.* **2013**, *49*, 9021–9023.

(21) Li, X.W.; Li, B.; Chen, L.; Hu, J.C.; Wen, C.D.Y.; Zheng, Q.D.; Wu, L.X.; Zeng, H.Q.; Gong, B.; Yuan, L.H. *Angew. Chem. Int. Ed.* **2015**, *54*, 11147–11152.

(22) Hu, J.C.; Chen, L.; Shen, J.; Luo, J.; Deng, P.C.; Ren, Y.; Zeng, H.Q.; Feng, W.; Yuan, L.H. *Chem. Commun.* **2014**, *50*, 8024–8027.

(23) (a) Ghosh, K.; Adhikari, S.; Fröhlich, R. *Tetrahedron Lett.* **2008**, *49*, 5063–5066. (b) Dixit, N.; Shukla, P.; Mishra, P.; Mishra, L.; Roesky, H.W. *J. Phys. Chem. A* **2009**, *114*, 97–104.

(24) Wu, M.-H.; Cheng, C.-H.; Lai, C.-S.; Pan, T.-M. *Sens. Actuators, B* **2009**, *138*, 221–227. (b) Khan, M.; Kim, Y.; Lee, J.H.; Kang, I.-K.; Park, S.-Y. *Anal. Methods* **2014**, *6*, 5753–5759.

(25) Greene, R.F.; Pace, C.N. *J. Biol. Chem.* **1974**, *249*, 5388–5393. (b)Wallqvist, A.; Covell, D.; Thirumalai, D. *J. Am. Chem. Soc.* **1998**, *120*, 427–428. (c)Bennion, B.J.; Daggett, V. *Proc. Natl. Acad. Sci. USA* **2003**, *100*, 5142–5147. (d) Guinn, E.J.; Pegram, L.M.; Capp, M.W.; Pollock, M.N.; Record, M.T. *Proc. Natl. Acad. Sci. USA* **2011**, *108*, 16932–16937.

(26) (a) Allwood, B.L.; Méndez, L.; Stoddart, J.F.; Williams, D.J.; Williams, M.K. *J. Chem. Soc., Chem. Commun.* **1992**, 331–333. (b) Akae, Y.; Okamura, H.; Koyama, Y.; Arai, T.; Takata, T. *Org. Lett.* **2012**, *14*, 2226–2229. (c) Lu, T.-W.; Chang, C.-F.; Lai, C.-C.; Chiu, S.-H. *Org. Lett.* **2013**, *15*, 5742–5745. (d) Chang, J.C.; Lai, C.C.; Chiu, S.H. *Molecules* **2015**, *20*, 1775–1787.

(27) (a) Jiang, Q.; Zhang, H.-Y.; Han, M.; Ding, Z.-J.; Liu, Y. *Org. Lett.* **2010**, *12*, 1728–1731. (b) Belowich, M.E.; Valente, C.; Smaldone, R.A.; Friedman, D.C.; Thiel, J.; Cronin, L.; Stoddart, J.F. *J. Am. Chem. Soc.* **2012**, *134*, 5243–5261. (c) Bruns, C.J.; Stoddart, J.F. *Acc. Chem. Res.* **2014**, *47*, 2186–2199. (d) Dong, S.; Yuan, J.; Huang, F. *Chem. Sci.* **2014**, *5*, 247–252. (e) Fu, X.; Zhang, Q.; Rao, S.-J.; Qu, D.-H.; Tian, H. *Chem. Sci.* **2016**, *7*, 1696–1701. (f) Cakmak, Y.; Erbas-Cakmak, S.; Leigh, D.A. *J. Am. Chem. Soc.* **2016**, *138*, 1749–1751. (g) Marcos, V.; Stephens, A.J.; Jaramillo-Garcia, J.; Nussbaumer, A.L.; Woltering, S.L.; Valero, A.; Lemonnier, J.-F.; Vitorica-Yrezabal, I.J.; Leigh, D.A. *Science* **2016**, *352*, 1555–1559. (h) Meng, Z.; Xiang, J.-F.; Chen, C.-F. *J. Am. Chem. Soc.* **2016**, *138*, 5652–5658.

(28) Pedersen, C.J. *J. Org. Chem.* **1971**, *36*, 1690–1693.

(29) (a) Bell, T.W.; Liu, J. *J. Am. Chem. Soc.* **1988**, *110*, 3673–3674. (b)Hegde, V.; Madhukar, P.; Madura, J.D.; Thummel, R.P. *J. Am. Chem. Soc.* **1990**, *112*, 4549–4550. (c)Hung, C.Y.; Hopfner, T.; Thummel, R.P. *J. Am. Chem. Soc.* **1993**, *115*, 12601–12602. (d)Bell, T.W.; Hou, Z. *Angew. Chem. Int. Ed.* **1997**, *36*, 1536–1538. (e)Goswami, S.; Dey, S. *J. Org. Chem.* **2006**, *71*, 7280–7287. (f)Chetia, B.; Iyer, P.K. *Tetrahedron Lett.* **2006**, *47*, 8115–8117. (g)Ghosh, K.; Sen, T. *J. Inclusion Phenom. Macrocyclic Chem.* **2010**, *67*, 271–280. (h) María, D.S.; Farrán, M.Á.; García, M.Á.; Pinilla, E.; Torres, M.R.; Elguero, J.; Claramunt, R.M. *J. Org. Chem.* **2011**, *76*, 6780–6788.

(30) Chang, S.K.; Hamilton, A.D. *J. Am. Chem. Soc.* **1988**, *110*, 1318–1319. (b)Ray, J.K.; Haldar, M.K.; Gupta, S.; Kar, G.K. *Tetrahedron* **2000**, *56*, 909–912. (c)Ghosh, K.; Masanta, G. *New J. Chem.* **2009**, *33*, 1965–1972.

(31) Staveren, C.J.V.; Aarts, V.M.L.J.; Grootenhuis, P.D.J.; Droppers, W.J.H.; Eerden, J.V.; Harkema, S.; Reinhoudt, D.N. *J. Am. Chem. Soc.* **1989**, *20*, 8134–8144.

(32) (a)Parra, R.D.; Zeng, H.; Zhu, J.; Zheng, C.; Zeng, X.C.; Gong, B. *Chem. Eur. J.* **2001**, *7*, 4352–4357. (b)Gong, B. *Chem. Eur. J.* **2001**, *7*, 4336–4342.

(33) Mahapatra, A.K.; Sahoo, P.; Hazra, G.; Goswami, S.; Fun, H.-K. *J. Lumin.* **2010**, *130*, 1475–1480.

(34) Goswami, S.; Mukherjee, R. *Tetrahedron Lett.* **1997**, *38*, 1619–1622.