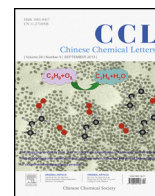




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Original article

A twin-axial[5]pseudorotaxane based on cucurbit[8]uril and α -cyclodextrin[☆]

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ABSTRACT

A twin-axial hetero[5]pseudorotaxane was constructed based on 1-hexyl-4,4'-bipyridinium guest **1** and cucurbit[8]uril (CB[8]) and α -cyclodextrin (α -CD). In its structure, CB[8] included two bipyridinium units to realize the twin-axial mode, and the hexyl chain was threaded into the cavity of α -CD. The [5]pseudorotaxane contains two types of macrocyclic hosts while the single axial and twin axial modes co-exist in its structure. The transformation of [5]pseudorotaxane could be realized by the addition of acid and 2,6-dihydroxynaphthalene (HN).

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1. Introduction

Various supramolecular assemblies, accompanied by novel structures or functions, have been constructed based on macrocyclic compounds [1–4]. As an important member of supramolecular assemblies, pseudorotaxanes have been used in construction of various molecular devices and machines because of their unique structures and stimuli-responsive properties [5,6].

The common [2]pseudorotaxane contains one thread-like component and one macrocyclic component [7]. It seems difficult to obtain the twin-axial pseudorotaxane which contains two guests threading into one macrocyclic component. Furthermore, the pseudorotaxane containing the twin-axial and single-axial mode simultaneously is very rare [8].

Crown ethers [9], cyclodextrins [10] and cucurbiturils [11,12] have been often used in the construction of pseudorotaxanes. To provide the system with more functions, we can introduce two or more kinds of cyclic components into one pseudorotaxane structure through accurate predesign. Both cyclodextrins and cucurbiturils are water soluble, but they exhibit different binding behaviors, which offers a good opportunity for introducing these two macrocycles into one system [13–15]. Cyclodextrins can include a neutral guest through hydrophobic interaction, which

have been applied in various supramolecular assemblies [16]. Cucurbiturils have also attracted great interest because of their unique binding ability toward cationic guests [17–24]. Among them, α -cyclodextrin (α -CD) shows a strong binding affinity toward an aliphatic chain, while cucurbit[8]uril (CB[8]) can accommodate more than one guest because of its large cavity.

Herein, we investigated the self-assembly behavior of 1-hexyl-4,4'-bipyridinium **1** and α -CD and CB[8] (Fig. 1). A novel twin-axial hetero[5]pseudorotaxane was formed, in which CB[8] included two bipyridinium units and α -CD included the hexyl group. Moreover, upon addition of acid and 2,6-dihydroxynaphthalene (HN), the structure of [5]pseudorotaxane can be transformed.

2. Experimental

All chemicals were commercially available unless noted otherwise. NMR data were recorded on Bruker AV400 spectrometer, and chemical shifts were recorded in parts per million (ppm). Mass spectra were recorded using Thermofinnigan LCQ Advantage ESI-MS.

Preparation of compound 1 [25]: 4,4-Dipyridyl (3.1 g, 20 mmol) and 1-bromohexane (5.5 g, 22 mmol) were dissolved in 35 mL acetonitrile, and refluxed for 18 h. After solvent was evaporated under vacuum, the residue was purified by column chromatography over silica gel (eluent: CHCl₃/MeOH = 20/1) to afford **1** as a yellow solid (2.8 g, 44%). ¹H NMR (400 MHz, D₂O): δ 8.87 (d, 2H, *J* = 6.1 Hz), 8.69 (d, 2H, *J* = 4.7 Hz), 8.31 (d, 2H, *J* = 6.1 Hz), 7.82 (d, 2H, *J* = 4.7 Hz), 4.57 (t, 2H, *J* = 7.1 Hz), 1.97 (m, 2H), 1.25 (m, 6H), 0.77 (m, 3H).

[☆] Comment: A nice twin-axial hetero[5]pseudorotaxane constructed from CB[8] and α -CD, could be transformed by the addition of acid and 2,6-dihydroxynaphthalene.

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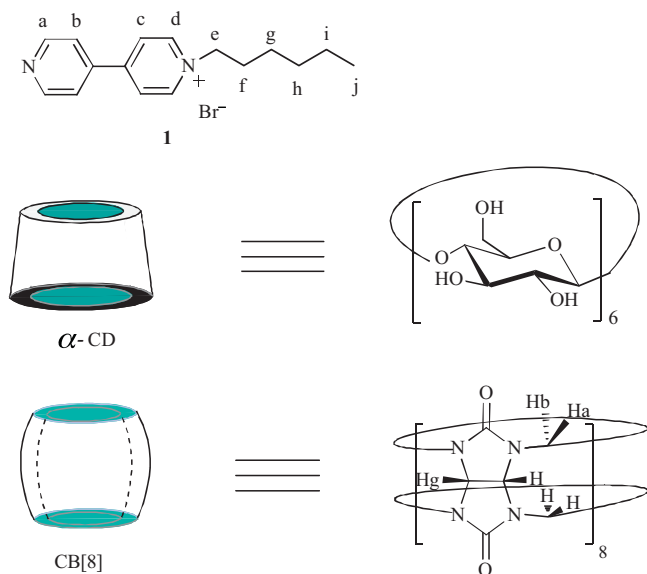


Fig. 1. The structures of guest **1** and hosts CB[8] and α -CD.

3. Results and discussion

3.1. Self-assembly behavior of **1** and CB[8]

In our previous study, we found that the monocharged bipyridinium unit can form 2:1 complex with CB[8] [26,27]. But the complexation was strongly affected by the side chain. If the side chain possessed sufficient hydrophobicity, CB[8] would leave the bipyridinium unit and the twin-axial mode could not be maintained. In the structure of guest **1**, the side chain was a hexyl group (Fig. 2). We initially used ^1H NMR to examine the self-assembly behavior of **1** and CB[8] (Fig. 3). After addition of 0.5 equiv. of CB[8], the signals of the aromatic protons H_a , H_c and H_b all showed obvious upfield shifts, while the hexyl group only exhibited a minor shift. Further addition of 0.5 equiv. of CB[8] did not make any change in the signals of the guest, which suggested that a stable 2:1 complex was formed based on **1** and CB[8].

After **1** was acidified to **1H** (Fig. 4) and upon addition of 1.0 equiv. of CB[8], the proton signals of hexyl group were shifted upfield, while the aromatic signals only showed a minor shift, which suggested that the hexyl group was threaded into the cavity of CB[8]. All the observations indicated that before acidification, CB[8] preferred to include two bipyridinium units to maintain the twin-axial mode. After addition of acid, the monocharged bipyridinium unit acquired another positive charge at the bare N terminal and CB[8] moved to the hexyl group. The ^1H NMR result (Fig. 5) showed that further addition of HN could attract the CB[8] to form a ternary charge transfer (CT) complex with the bipyridinium unit.

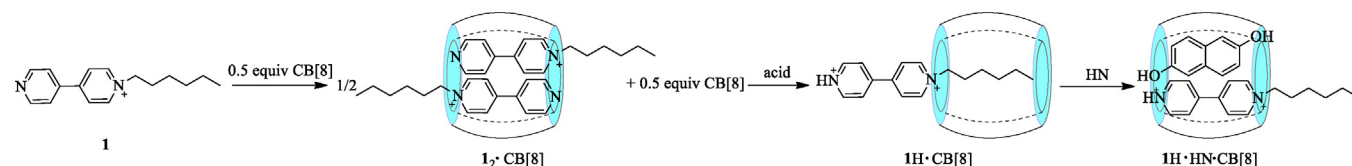


Fig. 2. Schematic representation of the binding modes and the interconversion process of pseudorotaxanes based on **1** and CB[8].

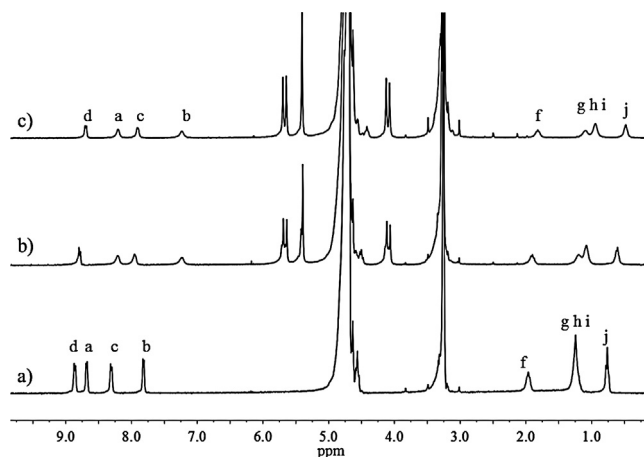


Fig. 3. ^1H NMR spectra of **1** (1.0 mmol/L) upon addition of (a) 0 equiv., (b) 0.5 equiv., and (c) 1.0 equiv. of CB[8] (D_2O , 400 MHz, 298 K).

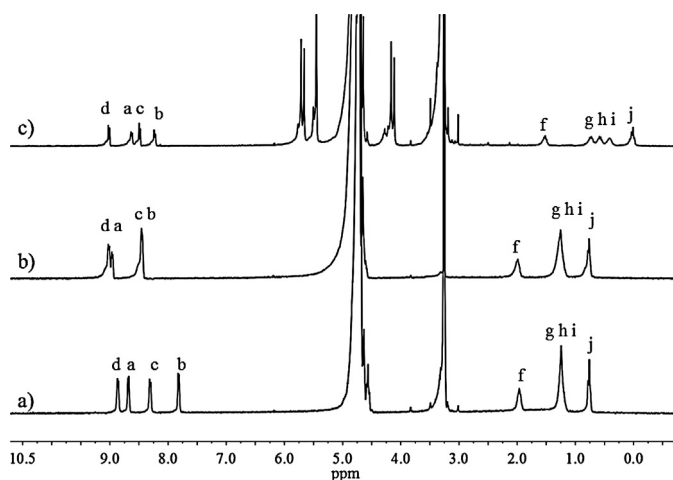


Fig. 4. ^1H NMR spectra of (a) **1** (1.0 mmol/L), (b) **1H** (1.0 mmol/L), (c) **1H** + 1.0 equiv. CB[8] (1.0 mmol/L) (D_2O , 400 MHz, 298 K).

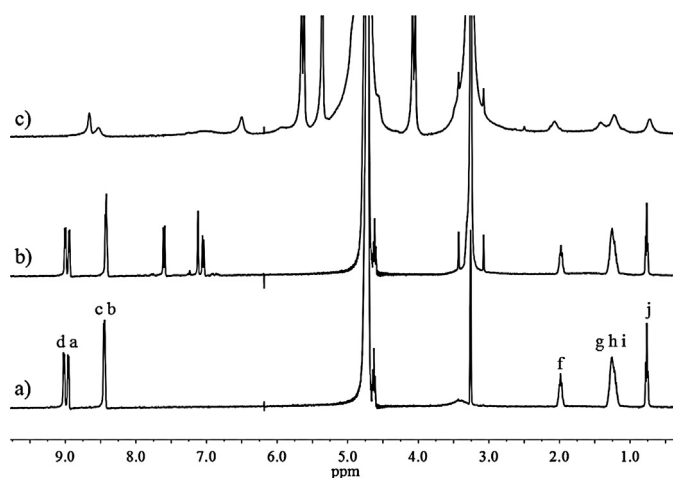


Fig. 5. ^1H NMR spectra (a) **1H** (1.0 mmol/L), (b) **1H** + 1.0 equiv. HN (1.0 mmol/L), and (c) **1H** + 1.0 equiv. HN + 1.0 equiv. CB[8] (1.0 mmol/L) (D_2O , 400 MHz, 298 K).

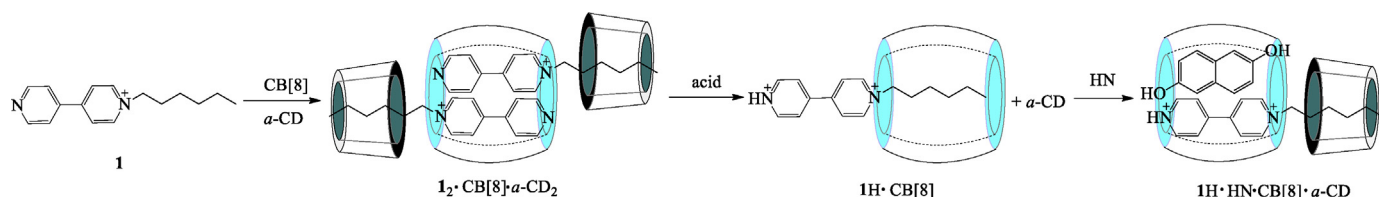


Fig. 6. Schematic representation of the binding modes and the interconversion process of pseudorotaxanes based on **1**, CB[8] and α -CD.

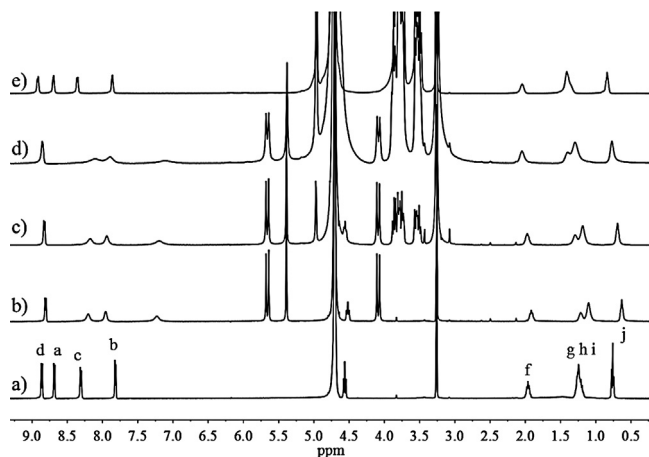


Fig. 7. ^1H NMR spectra (a) **1** (1.0 mmol/L), (b) **1** + 0.5 equiv. CB[8], (c) **1** + 0.5 equiv. CB[8] + 1.0 equiv. α -CD, (d) **1** + 0.5 equiv. CB[8] + 3.0 equiv. α -CD, and (e) **1** + 3.0 equiv. α -CD (D_2O , 400 MHz, 298 K).

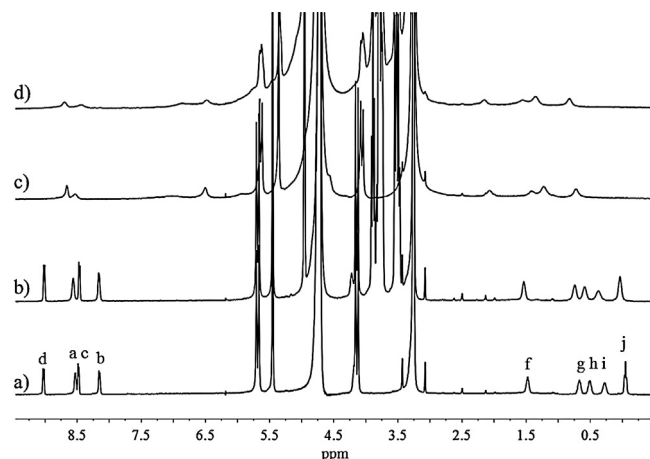


Fig. 9. ^1H NMR spectra (a) **1H** + 1.0 equiv. CB[8] (1.0 mmol/L), (b) **1H** + 1.0 equiv. CB[8] + 3.0 equiv. α -CD, (c) **1H** + 1.0 equiv. CB[8] + 1.0 equiv. HN, (d) **1H** + 1.0 equiv. CB[8] + 1.0 equiv. HN + 3.0 equiv. α -CD (D_2O , 400 MHz, 298 K).

3.2. Self-assembly behavior of CB[8], α -CD and **1**

When CB[8] included the bipyridinium units, the unbound hexyl group became a binding site for α -CD (Fig. 6). Upon

addition of 3.0 equiv. of α -CD (Fig. 7d), the proton signals of the hexyl group shifted downfield, which was similar with the shift of $1\text{-}\alpha\text{-CD}$ (Fig. 7e). Meanwhile, CB[8] was still contained the aromatic units. These observations suggested that a [5]

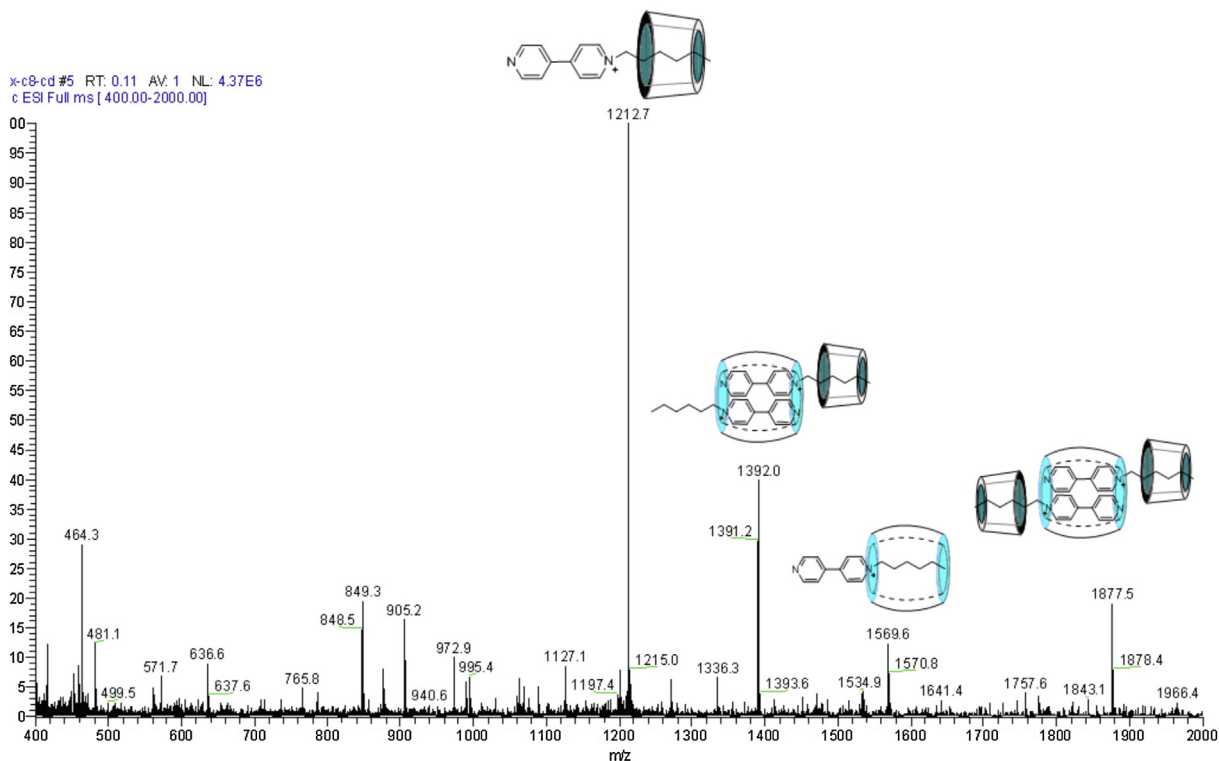


Fig. 8. ESI-MS spectrum of the mixture of **1**, CB[8] and α -CD. The peak at 1212.7 was assigned to $[1\text{-}\alpha\text{-CD}]^+$, 1392.0 was assigned to $[1_2\text{-CB}[8]\text{-}\alpha\text{-CD}]^{2+}$, 1569.6 was assigned to $[1\text{-CB}[8]]^+$, and 1877.5 was assigned to $[1_2\text{-CB}[8]\text{-}\alpha\text{-CD}_2]^{2+}$.

pseudorotaxane, 1_2 -CB[8]- α -CD₂, was formed, in which CB[8] encompassed two bipyridinium units to realize the twin-axial mode, and the hexyl chain of each molecule of **1** was threaded into the cavity of an α -CD (Fig. 6). We further confirmed the formation of the complex by ESI-MS (Fig. 8). The peak at m/z 1212.7 was assigned to $[1-\alpha\text{-CD}]^+$, m/z 1392.0 was assigned to $[1_2\text{-CB[8]-}\alpha\text{-CD}]^{2+}$, m/z 1569.6 was assigned to $[1\text{ CB[8]}]^+$, and m/z 1877.5 was assigned to $[1_2\text{-CB[8]-}\alpha\text{-CD}_2]^{2+}$.

When we added α -CD to the acidified solution containing 1H-CB, the proton signals of guest showed only minor change (Fig. 9b) which indicated α -CD could not drive CB[8] to disassociate the hexyl group. However, upon the addition of HN to 1H-CB, we observed that the signals of aliphatic chain moved downfield. Further addition of α -CD caused the signals of the aliphatic chain to exhibit a more downfield shift. This shift upon the addition of HN could be attributed to CB[8] moving to the bipyridinium unit to form a ternary CT complex, and the hexyl group threaded into α -CD again to form the complex 1H-HN-CB[8]- α -CD (Fig. 6).

4. Conclusion

A novel twin-axial hetero[5]*pseudorotaxane* was constructed based on CB[8], α -CD and guest **1**. In its structure, CB[8] included two bipyridinium units to maintain the twin-axial mode, and the hexyl chain was threaded into the cavity of α -CD to realize the single-axial mode. Further addition of acid and HN could realize the transformation of [5]*pseudorotaxane*. The result presented here realized the co-existence of the single axial and twin axial modes in one *pseudorotaxane* structure, which will be beneficial for the construction of more complicated supramolecular assemblies with well-defined structures and functions.

Acknowledgments

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References

- (a) Z. Wang, D.S. Guo, J. Zhang, et al., Electro-responsive binary hydrogels based on calixarene and viologens, *Acta Chim. Sin.* 70 (2012) 1709–1715;
(b) S.S. Zhai, Y. Chen, Y. Liu, Selective binding of bile salts by β -cyclodextrin derivatives with appended quinolyl arms, *Chin. Chem. Lett.* 24 (2013) 442–446;
(c) C. Yang, Recent progress in supramolecular chiral photochemistry, *Chin. Chem. Lett.* 24 (2013) 437–441;
(d) Z.J. Zhang, H. Wang, H.Y. Zhang, et al., Selectively fluorescent sensing behavior of phenylaza-15-crown-5-triazolyl coumarin for Hg²⁺ and Fe³⁺ in alcohol and aqueous media respectively, *Chin. J. Chem.* 31 (2013) 598–602.
- D.S. Guo, J. Zhang, Y. Liu, Calixarene-based supramolecular polymerization in solution, *Chem. Soc. Rev.* 41 (2012) 5907–5921.
- E.R. Kay, D.A. Leigh, F. Zerbetto, Synthetic molecular motors and mechanical machines, *Angew. Chem. Int. Ed.* 46 (2007) 72–191.
- D.H. Qu, H. Tian, Novel and efficient templates for assembly of rotaxanes and catenanes, *Chem. Sci.* 2 (2011) 1011–1015.
- (a) Z.J. Zhang, H.Y. Zhang, Y. Liu, Artificial molecular devices and machines based on 24-crown-8 macrocyclic compound, *Chem. J. Chin. Univ.* 32 (2011) 1913–1927;
(b) H. Wang, Z.J. Zhang, H.Y. Zhang, et al., Synthesis of a bistable [3]rotaxane and its pH-controlled intramolecular charge-transfer behavior, *Chin. Chem. Lett.* 24 (2013) 563–567.
- (a) Y.L. Sun, Y.W. Yang, D.X. Chen, et al., Mechanized silica nanoparticles based on pillar[5]arenes for on-command cargo release, *Small* 9 (2013), <http://dx.doi.org/10.1002/smll.201300445>;
(b) Y.L. Sun, B.J. Yang, S.X.A. Zhang, et al., Cucurbit[7]uril pseudorotaxane-based photoresponsive supramolecular nanovalve, *Chem. Eur. J.* 18 (2012) 9212–9216;
(c) Y.W. Yang, Towards biocompatible nanovalves based on mesoporous silica nanoparticles, *Med. Chem. Commun.* 2 (2011) 1033–1049;
(d) H. Li, Y.W. Yang, Gold nanoparticles functionalized with supramolecular macrocycles, *Chin. Chem. Lett.* 24 (2013) 545–552;
(e) Y.L. Sun, Y.W. Yang, W. Wu, et al., Supramolecular nanovalve systems based on macrocyclic synthetic receptors, *Chem. J. Chin. Univ.* 33 (2012) 1635–1642;
(f) P. Liu, X.G. Shao, W.S. Cai, Application of pseudorotaxanes/rotaxanes in drug carriers, *Prog. Chem.* 25 (2013) 692–697.
- C. Li, X. Shu, J. Li, et al., Selective and effective binding of pillar[5,6]arenes toward secondary ammonium salts with a weakly coordinating counteranion, *Org. Lett.* 14 (2012) 4126–4129.
- Z.J. Zhang, H.Y. Zhang, H. Wang, et al., A twin-axial hetero[7]rotaxane, *Angew. Chem. Int. Ed.* 50 (2011) 10834–10838.
- Z.J. Zhang, Y. Liu, Construction and function of interpenetrated molecules based on the positively charged axle components, *Synlett* 23 (2012) 1733–1750.
- Y. Liu, X.Y. Li, H.Y. Zhang, et al., Cyclodextrin-driven movement of cucurbit[7]uril, *J. Org. Chem.* 72 (2007) 3640–3645.
- J. Lagona, P. Mukhopadhyay, S. Chakrabarti, et al., The cucurbit[n]uril family, *Angew. Chem. Int. Ed.* 44 (2005) 4844–4870.
- S. Andersson, D.P. Zou, R. Zhang, et al., Selective positioning of CB[8] on two linked viologens and electrochemically driven movement of the host compound, *Eur. J. Org. Chem.* (2009) 1163–1172.
- T. Ooya, D. Inoue, H.S. Choi, et al., pH-Responsive movement of cucurbit[7]uril in a diblock polypseudorotaxane containing dimethyl β -cyclodextrin and cucurbit[7]uril, *Org. Lett.* 8 (2006) 3159–3162.
- C. Yang, Y.H. Ko, N. Selvapalam, et al., Dynamic switching between single- and double-axial rotaxanes manipulated by charge and bulkiness of axle termini, *Org. Lett.* 9 (2007) 4789–4792.
- Z.J. Ding, H.Y. Zhang, L.H. Wang, et al., A heterowheel [3]pseudorotaxane by integrating β -cyclodextrin and cucurbit[8]uril inclusion complexes, *Org. Lett.* 13 (2011) 856–859.
- Y. Chen, Y. Liu, Cyclodextrin-based bioactive nanosupramolecules, *Chem. Soc. Rev.* 39 (2010) 495–505.
- Y.H. Ko, E. Kim, I. Hwang, Supramolecular assemblies built with host-stabilized charge-transfer interactions, *Chem. Commun.* (2007) 1305–1315.
- U. Rauwald, O.A. Scherman, Supramolecular block copolymers with cucurbit[8]uril in water, *Angew. Chem. Int. Ed.* 47 (2008) 3950–3953.
- S. Deroo, U. Rauwald, C.V. Robinson, et al., Discrete, multi-component complexes with cucurbit[8]uril in the gas-phase, *Chem. Commun.* (2009) 644–646.
- J.M. Zayed, F. Biedermann, U. Rauwald, et al., Probing cucurbit[8]uril-mediated supramolecular block copolymer assembly in water using diffusion NMR, *Polym. Chem.* 1 (2010) 1434–1436.
- R.J. Coulston, S.T. Jones, T.C. Lee, et al., Supramolecular gold nanoparticle-polymer composites formed in water with cucurbit[8]uril, *Chem. Commun.* 47 (2011) 164–166.
- F. Tian, N. Cheng, N. Nouvel, et al., Site-selective immobilization of colloids on Au substrates via a noncovalent supramolecular “handcuff”, *Langmuir* 26 (2010) 5323–5328.
- E.A. Appel, F. Biedermann, U. Rauwald, et al., Supramolecular cross-linked networks via host-guest complexation with cucurbit[8]uril, *J. Am. Chem. Soc.* 132 (2010) 14251–14260.
- F. Biedermann, U. Rauwald, J.M. Zayed, et al., A supramolecular route for reversible protein-polymer conjugation, *Chem. Sci.* 2 (2011) 279–286.
- M.F. Pepitone, G.G. Jernigan, J.S. Melinger, et al., Synthesis and characterization of donor-acceptor chromophores for unidirectional electron transfer, *Org. Lett.* 9 (2007) 801–804.
- Z.J. Zhang, Y.M. Zhang, Y. Liu, Controlled molecular self-assembly behaviors between cucurbituril and bipyridinium derivatives, *J. Org. Chem.* 76 (2011) 4682–4685.
- Z.J. Zhang, H.Y. Zhang, L. Chen, et al., Interconversion between [5]pseudorotaxane and pseudorotaxane by pasting/detaching two axle molecules, *J. Org. Chem.* 76 (2011) 8270–8276.