Tailoring pillararene-based receptors for specific metal ion binding: From recognition to supramolecular assembly

Yuyu Fang ^{a, b}, Yun Deng ^{a*}, Wim Dehaen ^{b*}

^a State Key Laboratory of Southwestern Chinese Medicine Resources, School of Pharmacy, Chengdu University of Traditional Chinese Medicine, Chengdu 611137, China

^b Department of Chemistry, KU Leuven, Celestijnenlaan 200f-bus 02404, 3001 Leuven, Belgium

Corresponding author, e-mail: dengyun2000@hotmail.com; wim.dehaen@kuleuven.be

Abstract: Selective binding towards metal ions has gained significant attention due to the roles this phenomenon plays in diverse fields including biological metabolism, hydrometallurgy, environmental issues, material science and management of nuclear fuel. The obtained binding ability depends mainly on the chemical structure of the specific host molecules, which results in guest recognition through certain optical transduction. Pillararenes, a new class of supramolecular hosts, are akin to calixarenes but consist of (O-substituted) hydroquinone units linked together with methylene bridges at the *para* positions, resulting in a symmetrical pillar-shaped architecture. Due to their unique structure and easy functionalization, these emerging supramolecular macrocycles can be made to display a large array of interesting chemical or physical properties. In this review, we present the progress made so far in applications of pillararene-based receptors for selective binding, recognition and separation of metal ions. Meanwhile, pillararene-based supramolecular systems that have been self-assembled by metal-ligand coordination have also been summarized.

Keywords: Pillararenes; receptor; metal ions; recognition; self-assembly

Contents

1	1. Introduction	3
2	2. Synthesis of pillararenes	5
3	3. Pillararene-based receptor for s-block metal ions	6
4	4. Pillararene-based receptors for transition metal ions.....	9
5	4.1 Alkyl-functionalized pillararene receptors	10
6	4.2 Pillararene receptors functionalized with specific ligands	12
7	4.2.1 Perfunctionalized pillararenes	12
8	4.2.2 Copillararenes	14
9	4.2.3 Monofunctionalized pillararenes	14
10	5. Pillararene-based receptors for f-element metal ions	16
11	6. Pillararene-based self-assembly for metal ion recognition and binding.....	21
12	6.1 One-component self-assembly only caused by pillararenes	21
13	6.1.1 Monofunctionalized pillararenes	21
14	6.1.2 Copillararenes	22
15	6.1.3 Oligomeric pillararenes	24
16	6.2 Two-component self-assembly starting from two different pillararenes.	27
17	6.3 Two-component self-assembly starting from a functionalized pillararene and a specific	
18	guest.....	29
19	7. Pillararene-based polymers for metal ion recognition and binding.....	37
20	8. Pillararene-based self-assembly driven by metal-ligand coordination.....	38
21	8.1 Self-assembly driven by Na^+	38
22	8.2 Self-assembly driven by Cu^{2+}	39
23	8.3 Self-assembly driven by Zn^{2+}	44
24	8.4 Self-assembly driven by Fe^{3+}	48
25	8.5 Self-assembly driven by Ag^+	49
26	8.6 Self-assembly driven by Pd^{2+}	52
27	8.7 Self-assembly driven by Pt^{2+}	54
28	8.8 Self-assembly driven by Cr^{3+}	58
29	8.9 Self-assembly driven by Hg^{2+}	59

1	8.10 Self-assembly driven by Th^{4+}	61
2	9. Summary and outlook.....	62
3	References	63

4

5 **1. Introduction**

6 Host-guest recognition utilizing non-covalent interactions is one of the most important areas in
7 supramolecular chemistry [1]. Among the most widely studied guests, metal ions play a significant role
8 in a wide range of areas such as biological metabolism [2], medicinal chemistry [3], hydrometallurgy
9 [4], environmental issues [5], and material science [6] as well as many other processes [7]. Metal ion
10 recognition chemistry has been firstly brought to the consideration of the broader chemical community
11 as the result of Pedersen's ground-breaking work in the late 1960's about selective binding of crown
12 ethers with alkali metal ions [8]. Compared to other noncovalent interactions (*e.g.*, hydrogen bonding,
13 van der Waals forces, π - π stacking, charge transfer, etc), metal-ligand interactions are relatively strong,
14 directional, and highly versatile by properly modulating and even fine-tuning the ligand(s) and type
15 and/or redox state of metal ions, allowing considerable stability and reversibility as well as various
16 coordination geometries [9]. Notably, metal-ligand interactions may endow the resulting complexes
17 with unique optical, redox, electrochromic, catalytic and magnetic properties [10]. Consequently,
18 efficient binding and selective recognition of metal ions has been continuously receiving considerable
19 attention over the past decades [11].

20 Several factors can influence metal-ligand interactions. The receptors, nature of the metal ions and
21 the environment are generally acknowledged to be three key determinants for achieving efficient metal
22 ion coordination [12]. In terms of the receptors, the obtained binding ability is closely related to their
23 chemical structure. These molecules always contain more than one donor atom (usually nitrogen,
24 oxygen and sulfur), which interact with the metal ion. In addition, steric hindrance of the receptor is an
25 important factor that can have a large influence on the stability and selectivity [13]. To date, a large
26 number of chemosensors capable of selectively recognizing and binding metal ions have been
27 extensively described in many different reviews [14]. These sensors, which are synthetic receptors
28 decorated with chemoluminescent, fluorescent or electrochemical tags, can give a favorable optical and
29 physical response *via* the perturbation of various photoinduced and/or electrochemical processes.
30 Compared to numerous analytical techniques including atomic absorption spectroscopy (AAS), X-ray

fluorescence spectroscopy (XRFS), inductively coupled plasma-mass spectrometry (ICP-MS) and electrochemistry (potentiometric, conductometric or amperometric methods), the use of a synthetic receptor as a sensing and chelating agent offers significant advantages in terms of high selectivity and sensitivity, low cost and localized observation [14, 15].

In many scenarios, efficient binding of metal ions can also be achieved through multiple coordination sites, which can give rise to much higher complexation constants, separation efficiency and selectivity due to the chelate effect (or multivalency effect) [13, 16]. These phenomena have been widely demonstrated in crown ethers, cyclodextrins, calixarenes (considered as the first to the third generation of supramolecular macrocycles, respectively), cucurbiturils, cavitands (Fig. 1a-e) as well as other scaffold systems [17].

Fig. 1. Several types of common supramolecular macrocycles.

Pillararenes, a new class of supramolecular hosts, have aroused extensive attention in the supramolecular chemistry community since they were first reported by Ogoshi and co-workers in 2008 [18]. In contrast to the calixarene analogues that have basket-shaped structures in their cone conformation, pillararenes consist of O-alkylated hydroquinone units linked with methylene bridges at the 2,5-positions, resulting in a symmetrically pillar-shaped architecture (Fig. 1f). Apart from their rigid electron-rich and hydrophobic cavity that is the reason for their use as host molecules for complexing various electron-deficient or certain neutral guests, pillararenes are easy to functionalize

with different substituents including monofunctionalization, difunctionalization, functionalization of only one rim or side, perfunctionalization (on both sides) and even phenylene substitution [19]. Given their unique structure and facile synthesis and functionalization, pillararenes have been widely used in host-guest chemistry [20], self-assembly systems [21], supramolecular polymers [22], artificial transmembrane channels [23], biological-related applications [24] and other supramolecular smart materials [25] in the past decade. However, the reports on pillararene-based receptors for selective binding of metal ions have not been systematically summarized.

In this review, we will focus on the efforts made so far to use pillararenes as platforms to construct various synthetic receptors for selective binding of metal ions. Consequently, different pillararene-based receptors for selective binding towards s-block metal ions, transition metal ions and f-element metal ions will be presented. Additionally, we have summarized the pillararene-based supramolecular self-assembly systems that have been driven by metal-ligand coordination.

2. Synthesis of pillararenes

Generally, pillararenes can be easily synthesized from readily available starting materials using three different, but complementary strategies (Scheme 1), and the cyclopentamers (pillar[5]arenes) are the major products under thermodynamic control conditions. The yield of pillar[n]arenes ($n = 6-15$) with larger sizes which are formed under kinetical control is relatively much lower, although in some cases pillar[6]arenes may be obtained in substantial amounts. Thus, pillar[6]arenes were first synthesized by Cao and coworkers in 2009 with the yields being *ca.* 10% [26]. Hou's group first prepared pillar[7-10]arene homologues with none of the yields being more than 3% [27]. Even larger pillar[11-15]arenes were obtained by Ogoshi *et al* with extremely low yields (<1%) [28]. The reaction temperature and time as well as type of solvent and catalyst are the key factors to get larger pillararenes. With regard to the formation of higher amounts of pillar[6]arenes, template-directed solvent for high-yield synthesis of pillar[6]arene can be achieved in chloroform [29], chlorocyclohexane [30] and polar solvent media [31] in the presence of a proper catalyst. In addition, using templating cationic guests [32] and solvent-free conditions [33] by simply grinding the solid 1,4-dialkoxybenzene and paraformaldehyde in the presence of a catalytic amount of sulfuric acid could also afford a considerable yield of pillar[6]arenes.

Scheme 1. Three different strategies for the synthesis of pillararenes.

3. Pillararene-based receptor for s-block metal ions

The s-block elements, consisting of the alkali and alkaline earth metals, are among the 10 most abundant elements on the planet, which play an essential role in many biological processes [34]. So far, only a few reports of pillararene derivatives have been associated with binding towards alkali metal ions (*vide infra*).

In 2014, the first example of alkali metal ions (Li^+ , Na^+ , K^+ and Cs^+) complexation with pillararene receptors was reported by Stoikov and coworkers [35]. Three perfunctionalized pillar[5]arenes **1-3** were prepared, containing carboxylic, pyrrolidide and morpholide units, respectively (Fig. 2). Intriguingly, only one metal ion was found to bind to each of the three pillararene receptors in methanol solution, in spite of functional groups being present at both of the rims. The pillar[5]arenes **1-3** showed similar binding ability towards the alkali metal cations (except for Li^+) with the association constants ($\log K$) varying between 2.15 and 3.6. However, these three receptors offered the most effective binding strength towards Li^+ , whose corresponding association constants were 10-fold higher than those calculated for other alkali metal ions. K^+ is bonded more strongly than Na^+ and Cs^+ but is still not comparable in binding strength to Li^+ . Subsequently, the alkali metal ion complexation behaviour was investigated by the same team with another three pillar[5]arene receptors **4-6** in the same medium (Fig. 2), which were functionalized with piperidine, glycine and glycylglycine fragments, respectively [36]. Similarly, the three receptors **4-6** could complex with alkali metal ions with a 1:1 stoichiometry with the most effective binding affinity for Li^+ . In contrast, no obvious binding capability toward selected

transition metal ions (Ag^+ , Cu^{2+} , Fe^{3+}) was observed for **4-6**. A decrease in binding efficiency for all the three molecules is observed with increasing cation radius from Li^+ to Cs^+ . Additionally, the receptor **6** bearing the longest glycylglycine units showed the best binding ability towards all of the tested alkali metal ions. Specifically for Li^+ , the association constant of **6** is two orders of magnitude higher than that of **4**.

Fig. 2. Structures of pillar[5]arene-based receptors **1-6** for alkali metal ion binding.

A significant practical application of alkali metal receptors is to construct artificial transmembrane channels (**ATCs**), which are essential to living systems and are involved in many underlying biological functions such as energy metabolism and the excitability of nerves and muscles [23]. Great efforts have been made in fabricating **ATCs** through either the multimolecular self-assembly or unimolecular strategy, not only because these mimics contribute to understand the natural ion channels, but also because they may lead to the development of therapeutic agents and the creation of materials for sensing and separation technologies [23]. The modification of macrocycles has proven itself to be an efficient approach to obtain unimolecular channels with high transport ability for metal ions (particularly K^+ and Na^+), which offers distinctive advantages by combining selective metal ion binding and dynamic behavior for effective functional transport [37]. Specifically for crown ethers, the oxygen atoms in the macrocyclic polyethers are well situated to coordinate with alkali metal ions, depending mainly on the size of the interior of the ring [38].

Barboiu and coworkers envisaged that tethering crown ethers units onto a pillararene framework could induce the formation of highly selective alkali metal ion channels. Consequently, a A1/A2-copillar[5]arene (difunctionalization only at one hydroquinone) **7** was rationally designed and prepared.

1 The host was containing two benzo-15-crown-5 ether cation binding sites at both ends of one
 2 hydroquinone unit, which was spontaneously inserted into lipid bilayers and showed selective K^+ -
 3 channel conductance behavior (Fig. 3) [39]. 1H NMR dilution experiments confirmed the formation of
 4 dimers and oligomers with increasing concentration of compound **7**. The obtained oligomeric
 5 assemblies of **7** with K^+ are more stable than those with Na^+ (as their trifluoromethanesulfonic salts)
 6 probably owing to the synergetic self-assembly of K^+ -(15-crown-5)₂ sandwich aggregates and multiple
 7 anion-thiourea H-bonds. The well-defined channels constructed from **7** showed highly active transport
 8 activity of K^+ and Rb^+ , slightly active transport of Cs^+ and almost inactive transport of Na^+ , reaching a
 9 selectivity of $S_{K^+/Na^+} = 5$ with an initial transport rate of $k_{K^+} = 3.2 \times 10^{-3} \text{ mol} \cdot \text{s}^{-1}$. In contrast, the control
 10 compound **8** without crown binding sites showed nearly no transport activity towards all the alkali
 11 metal ions, demonstrating that the 15-crown-5-ether moieties sites are responsible for the selective K^+ -
 12 binding and transport. This unique artificial selective K^+ -channel is significantly different from other
 13 pillararene-based channels without additional metal ion binding sites, whose cation translocation is
 14 voltage-driven [40] or a secondary process of highly permeable water channels [41].

15

16 **Fig. 3.** (a) Structures of pillar[5]arene-based receptors **7** and **8**; (b) Pseudo first-order rate constants k for the
 17 transport of alkali cations containing 50 μM of **7** in the vesicle stock solution. Reproduced with permission from
 18 Ref. [39]. Copyright 2017 American Chemical Society.

19 Chen and co-workers designed a series of copillar[5]arenes **9-13** anchored with two peptides
 20 consisting of a gramicidin A analogous sequence, which could efficiently insert into lipid bilayers to
 21 form five different unimolecular channels with different lengths (Fig. 4a) [42]. The cation-
 22 transmembrane transport activity was closely related to the lengths of these channels. Longer channels

led to more effective transport of K^+ . This can probably be attributed to the length matching effect of the longest channel molecule **13** (4.0 nm), which agrees well with the thickness of the hydrophobic bilayer (3.0-3.5 nm). Furthermore, it has been demonstrated that the transmembrane transport properties of these artificial channels are in close relation to their antimicrobial activity and inversely correlated with their haemolytic toxicity, providing excellent antibiotic candidates for systematic administration. Subsequently, another class of artificial K^+ -channels has been reported that was consisting of pillar[5]arene- α -cyclodextrin (α -CD) hybrid molecules **14** with three different spacer lengths (Fig. 4b) [43]. All of the three channels could efficiently insert into lipid bilayers and showed high selectivity for K^+ over Na^+ . The obtained high K^+ transport selectivity may be in part due to their α -CD moieties coordinating with hydrated K^+ . Importantly, the cation transport selectivity can be tuned by varying the length of the linkers. Specifically, the channel **14a** with the shortest linker showed preferential transmembrane transport for K^+ among all alkali metal ions with a selectivity sequence of $K^+ > Cs^+ > Rb^+ > Na^+ > Li^+$, which is rarely observed in the reported artificial K^+ channels.

Fig. 4. Artificial K^+ channels constructed by (a) dual helical peptide modified pillar[5]arenes **9-13** (Reproduced with permission from Ref. [42]. Copyright 2017 Royal Society of Chemistry and (b) pillar[5]arene- α -CD hybrid molecules **14** (Reproduced with permission from Ref. [43]. Copyright 2019 John Wiley and Sons.

4. Pillararene-based receptors for transition metal ions

Certain transition metal ions (e.g., Fe^{3+} , Cu^{2+} , Zn^{2+} , Mn^{2+} , Co^{2+}), which are present in small quantities in living creatures, are essential nutrients for the maintenance of a healthy life [44]. Some transition metals cations are hard to remove and they remain in the food chain and ecological systems

indefinitely. Especially, some heavy metal ions, such as Hg^{2+} , Cd^{2+} , Pb^{2+} , and As^{3+} , have strong toxicity by themselves [45]. High intake or long-term contact of these detrimental ions can result in adverse effects and irreversible damage to human health, which leads to strictly defined concentration limits in drinking water.

4.1 Alkyl-functionalized pillararene receptors

On first sight, pillararenes bearing only alkyl groups appear not to be suitable receptors for metal ions binding and/or recognition due to the lack of specific binding sites. However, this is not the case for specific metal ion-pairs conditions or high concentration solutions, which can be demonstrated by the following two examples. Recently, Chen and coworkers reported that a series of perfunctionalized pillar[5]arenes **15a-d** and copillar[5]arenes **16a-b**, only combined of alkoxy functionalities without extra functional groups, showed a strong aggregation induced emission (AIE) both in the solid state and EtOH/ CH_2Cl_2 mixed solution (Fig. 5a-b) [46]. For example, the fluorescence quantum yield of **15a** ($c = 5.0 \times 10^{-4} \text{ M}$) was greatly increased from 0.1% (in pure CH_2Cl_2) to 13.2% (in EtOH/ CH_2Cl_2 , 98:2, v/v) in response to a gradual increment of the solvent polarity. This strong AIE luminescence can be attributed to the restriction of intramolecular phenyl-ring rotations at higher concentration. Importantly, the addition of FeCl_3 to a solution of pillar[5]arene **15a** led to dramatic AIE fluorescence quenching due to the disassociation of the aggregates and/or an energy transfer process, demonstrating its sensing ability for Fe^{3+} with high sensitivity and selectivity. The detection limit (DL) for Fe^{3+} was deduced to be 24.6 μM . Thus, pillararenes in general may hold promise as new promising AIE macrocycles for the construction of various luminescent sensors and materials.

Almost at the same time, Huang's group reported the first examples of an alkyl pillararene-based metal recognition motif by a cooperative metal ion-pair recognition strategy [47]. Peralkylated pillar[5]arenes **15b** and **15c** interacted with CF_3COOAg to form stable [2]pseudorotaxane complexes. As shown in Fig. 5c and 5d, the single crystal X-ray analysis of the two complexes showed that two molecules of CF_3COOAg penetrate into the pillar[5]arene cavity through a combination of silver- π , multiple $\text{C-H}\cdots\text{O}$ and $\text{C-H}\cdots\text{F}$ interactions between the counter ion and the pillar[5]arene. Additionally, **15b** has been demonstrated to be an efficient solid absorbent for solid-liquid extraction of CF_3COOAg from its methanol solution owing to this unique ion-pair recognition motif. More

importantly, the obtained pseudo[2]rotaxane metal-complexes can act as new building blocks in the construction of various advanced topological structures.

Fig. 5. (a) Chemical structure of pillar[5]arenes **15** and **16**; (b) AIE behavior of **15a** in in EtOH/CH₂Cl₂ mixed solution (Reproduced with permission from Ref. [46]. Copyright 2017 Royal Society of Chemistry); (c) Single crystal of the host-guest complexes of peralkylated pillar[5]arenes **15b** and (d) **15c** with the CF₃COOAg. Reproduced with permission from Ref. [47]. Copyright 2019 American Chemical Society.

In most cases, the functionalization on the upper or lower rims of pillararenes is investigated, which has relatively less influence on their electron-rich cavities. Few reports have been associated with phenylene-substituted pillararenes [48]. Yang and co-workers reported a highly efficient method to synthesize mono- and polyorganometallic pillar[5]arene hosts by simple ligand exchange of the cationic transition metal complexes [(Cp*)M(acetone)₃](OTf)₂, Cp* = pentamethylcyclopentadienyl and M = Ir or Rh) with pillar[5]arene **15a** (Fig. 6a) [49]. Single crystal X-ray analysis demonstrated that the charged transition metal cations were directly bound to the outer π -surface of aromatic rings of pillar[5]arene. Intriguingly, one of the triflate anions was deeply embedded in the cavity of trimetallic pillar[5]arenes *via* anion- π interactions due to the reduction of the electron density inside the cavity after coordination of the benzene rings with the metal centers (Fig. 6b and 6c), which is significantly different from the host-guest properties of commonly known pillararenes. This is the first example of pillar[5]arenes metallated at the π -surfaces with anion binding behavior *via* anion- π interactions.

Fig. 6. (a) Synthesis of mono- and polyorganometallic pillar[5]arene complexes; X-ray crystal structures of (b) **15a-3Rh** and (c) **15a-3Ir** with top view (H-atoms and TfO⁻ outside the cavity are omitted for clarity). Reproduced with permission from Ref. [49]. Copyright 2017 John Wiley and Sons.

4.2 Pillararene receptors functionalized with specific ligands

4.2.1 Perfunctionalized pillararenes

It is commonly known that the mercury ion is highly reactive and toxic, as exemplified by certain mercury species including methylmercury readily transporting across the blood-brain barrier, resulting in irreversible damage to nervous organs and tissues [50]. Various types of organic receptors that are capable of forming Hg^{2+} -complexes or selective binding, recognition and separation of Hg^{2+} have been created [51]. In 2014, Yuan and coworkers prepared pillar[5]arenes **17** bearing ten phosphine oxide groups with different spacer length (Fig. 7a), which could efficiently bind and recognize Hg^{2+} and represents the first example of pillararene-based receptors for transition metal ions [52]. In $\text{C}_2\text{H}_5\text{OH-H}_2\text{O}$ (3/2, v/v) solution, the binding constants (K_a) of **17a-e** for Hg^{2+} varied from $1.77 \times 10^3 \text{ M}^{-1}$ to $4.47 \times 10^3 \text{ M}^{-1}$, each of whose binding stoichiometries was determined to be 1:1. Solvent extraction results further demonstrated the pronounced selective binding and recognition for Hg^{2+} as indicated by the increasing extractability with increasing spacer length. However, their acyclic species did not show an

efficient binding for Hg^{2+} , highlighting the importance of the pillar[5]arene platform. The receptor **17c** was successfully applied for separation and analyzing Hg^{2+} in real environmental samples.

The toxicity of mercury *in vivo* is attributed to blocking the potassium ion channels. It is extremely difficult to design a simple and efficient artificial system to mimic this complicated biological process. In 2016, Li and coworkers reported a tunable artificial Hg^{2+} -nanochannel constructed from carboxymethylsulfanyl perfunctionalized pillar[5]arene **18** to mimic the sophisticated biological process of mercury poisoning (Fig. 7b) [53]. Firstly, the authors investigated the host-guest complexing behaviour of **18** with model guest 1,6-hexanediamine (**G1**) and Hg^{2+} . Driven by hydrophobic interaction, **G1** could insert into the cavity of **18** to form a host-guest complex with 1:1 stoichiometry in water. The addition of Hg^{2+} (acetate as the counter anion) led to the release of **G1** due to the stronger binding affinity between Hg^{2+} and **18**. The poly(ethylene terephthalate) planar film modified with **G1** and **18** demonstrated excellent reversibility of the **18-G1** complex toward Hg^{2+} at least for six cycles. More importantly, the reversible “on-off” switching of the **18**-immobilized nanochannel could be realized in the absence and presence of mercury ions, which allowed the potassium ion transport either to proceed or be blocked, respectively, thus providing a new strategy for better understanding of the mercury toxicity in physiological processes and biomedical research. The nanochannel functionalized with **18** could selectively distinguish mercury ions from other metal ions with a DL of 1 nM.

Fig. 7. Chemical structure of perfunctionalized pillar[5]arene receptors (a) **17**; (b) **18**. Reproduced with permission from Ref. [53]. Copyright 2016 Royal Society of Chemistry; (c) **19** and (d) **20**.

Recently, Yang and coworkers reported amino-pillar[5]arene **19** as a fluorescent probe for the highly selective recognition and detection of Au^{3+} ions in aqueous solutions (Fig. 7c) [54]. The binding ratio was determined to be 2:1 (L:M) under the specific conditions with DL of 7.59×10^{-8} M. The

recognition event of the fluorescent probe was not significantly affected by other coexisting metal ions and could occur in a wide pH range of 1-13.5. In the same manner, quinoline functionalized pillar[5]arene **20** has been demonstrated to be a fluorescent sensor for selective recognition of Fe^{3+} (DL = 157 ppm) in aqueous-acetonitrile (1:1, v/v) solution (Fig. 7d) [55]. The quenching of the fluorescence of *in-situ* formed **20**- Fe^{3+} complex can be enhanced by addition of F^- , arginine and lysine.

4.2.2 Copillararenes

In 2015, Huang and co-workers designed and synthesized a novel anthracene-appended 2:3 copillar[5]arene **21** (Fig. 8), which was found to be a Fe^{3+} -selective fluorescent on-off chemosensor in the presence of a wide range of other transition metal ions (quenching efficiency *ca.* 75%) in DMSO solution [56]. Molecular dynamics (MD) and DFT calculations supported the formation of a 1:2 (ligand:metal) complex between **21** and Fe^{3+} , indicating that the five oxygen atoms at each rim formed a planar binding core which binds one Fe^{3+} . Later, Wei and co-workers prepared A1/A2-difunctionalized copillar[5]arene **22** with 2-mercaptobenzothiazole substitution at both ends of only one hydroquinone unit, which displayed a selective and sensitive fluorescence on-off response for Fe^{3+} over other common metal cations with 1 : 1 stoichiometry in DMSO/THF (1 : 4, v/v) [57]. The DL was found to be 1.25×10^{-8} M. Additionally, the resulting **22**-Fe(III) ensemble could serve as an off-on sensor for H_2PO_4^- in the same solution due to its competitive binding process.

Fig. 8. Chemical structure of anthracene-appended 2:3 copillar[5]arene **21** and A1/A2-difunctionalized copillar[5]arene **22**.

4.2.3 Monofunctionalized pillararenes

1 Monofunctionalized pillar[5]arene **23** (Fig. 9) anchored with only one 2-aminobenzimidazole
2 functional group had an excellent selective fluorescence recognition for Cu^{2+} with the DL of 5.84×10^{-7}
3 M in DMSO solution [58]. The resulting **23**- Cu^{2+} ensemble could serve as an outstanding sensitive and
4 selective fluorescent off-on sensor for CN^- with the DL of 9.03×10^{-7} M in the same medium.
5 Analogously, receptor **23** was demonstrated to be a prominent sequential fluorescence sensor for Fe^{3+}
6 followed by F^- with high selectivity in DMSO solution [59]. These two recognition mechanisms can
7 also be explained by the competitive binding by removal of the metal cations from their complexes by
8 specific anions.

9 Pillar[5]arene **24** monofunctionalized with a 2-(hydroxy)-naphthylimino group could cause selective
10 recognition of Fe^{3+} in $\text{H}_2\text{O}/\text{DMSO}$ (1/9, v/v) solution with a DL of 1.21×10^{-7} M [60]. The recognition
11 process can be ascribed to the coordination with Fe^{3+} via 'O' and 'N' heteroatoms in a 1:1
12 stoichiometry, leading to a turn-off fluorescence process. This molecule could efficiently separate Fe^{3+}
13 from aqueous solution and the separation ratio was up to 98.25%. The resulting **24**- $\text{Fe}(\text{III})$ complex
14 could selectively exhibit turn-on fluorescence on sensing F^- (DL = 1.34×10^{-7} M) due to F^-
15 competitively binding with Fe^{3+} to form a more stable complex $[\text{FeF}_6]^{3-}$.

16 Mono-quinoline functionalized pillar[5]arene **25** showed strong AIE in $\text{DMF}/\text{H}_2\text{O}$ (8:2, v/v)
17 solution, which can selective and sensitive recognition of Hg^{2+} in a fluorescence quenching manner due
18 to the Hg^{2+} -coordination and the inhibition of the $\pi \cdots \pi$ stacking of the quinoline moieties [61]. A test
19 kit upon loading **25** on a silica gel plate has been proposed for the convenient detection of Hg^{2+} . The
20 resultant Hg^{2+} -**25** complex could act as a fluorescence off-on sensor for CN^- with a high selectivity and
21 sensitivity through competitive coordinating interactions. The DL of Hg^{2+} and CN^- was found to be
22 2.53×10^{-8} M and 7.71×10^{-8} M, respectively.

23 Wei and co-workers designed and synthesised a novel monofunctionalized pillar[5]arene **26** linked
24 only one 2-aminobenzothiazole binding site, which could act as an on-off fluorescence sensor for Fe^{3+}
25 with high sensitivity and selectivity in $\text{DMSO}/\text{H}_2\text{O}$ (8:2, v/v) solution [62]. The DL of the receptor for
26 Fe^{3+} was 9.0×10^{-7} M, which is much below the limit concentration level Fe^{3+} ($2 \text{ mg} \cdot \text{L}^{-1}$) in drinking
27 water according to the World Health Organization (WHO). The resulting **26**- Fe^{3+} ensemble could also
28 act as a turn-on fluorescent sensor for F^- over other anions in the same media without interference. The
29 DL of F^- was determined to be 2.59×10^{-8} M, which is much lower than the limit concentration level
30 ($4.00 \text{ mg} \cdot \text{L}^{-1}$) of F^- in drinking water set by United States Environmental Protection Agency (USEPA).

The fluorescence on-off-on recognition process can be ascribed to unique competitive host-guest interactions by removal of Fe^{3+} from the 1:1 (ligand: metal) **26**- Fe^{3+} complex by F^- , resulting in the formation of a more stable species $[\text{FeF}_6]^{3-}$ and release of the free receptor **26**.

Fig. 9. Chemical structure of monofunctionalized pillar[5]arene receptors **23-26**.

5. Pillararene-based receptors for f-element metal ions

f-Block elements located at the bottom of the modern periodic table, consisting of lanthanides (Ln) and actinides (An), play an irreplaceable role in a wide range of areas owing to their extensive applications in green and sustainable products in material, military, energy and manufacturing. Ln have been widely used to construct magnetic and optical materials, which have been applied in luminescent sensors, nuclear medicine, chelation therapy, magnetic resonance imaging (MRI) contrast agents and so on [63]. On the other hand, An are closely related to nuclear processes and especially minor actinides (MA) are considered to be among the most dangerous components due to their long-lived radionuclides ($T_{1/2} = 10^3$ - 10^6 years). However, selective recognition and separation of these f-elements is not an easy task because of the similar identical oxidation states and nearly similar ionic radii resulted from the lanthanide contraction. Preorganizing chelating groups onto a platform or scaffold (*i.e.* calixarenes, resorcinarenes, tripodands) has aroused intense research interest owing to the increased complexation constants, much higher extraction efficiency and separation factors [64].

Organophosphorus species are well-known ligands for efficient binding of f-block element cations [65]. Yuan and co-workers reported pillar[5]arene-based phosphine oxides **17** that showed noticeable efficient and selective extraction for Th^{4+} and UO_2^{2+} in 1 M nitric acid solution [66]. The highest extraction efficiencies that reached 72% for Th^{4+} and 94% for UO_2^{2+} were obtained for **17e**. In sharp

contrast, the extractability for lanthanides is less than 30%. Compared with acyclic monovalent analogs dimethylpillar[5]arene **15a** and industrial extractant tri-*n*-octylphosphine oxide (TOPO), the remarkable efficiency and selectivity for Th⁴⁺ and UO₂²⁺ highlights the importance of preorganization of the chelating groups onto the pillararene platform. Log-log plot analysis indicated the 1:1 stoichiometry (ligand/metal) for the extracted Th⁴⁺ or UO₂²⁺ complex. These ligands also showed better affinity towards Eu³⁺ than Am³⁺ at the specified conditions in the presence of a synergist (Br₆-COSAN). This is the first example of functionalized pillararenes to explore the complexation behavior towards metal ions. Afterwards, the effects of phosphorous-based pillar[5]arenes with different substituents on extraction for UO₂²⁺ were studied [67], indicating that phosphine oxides have better affinity towards UO₂²⁺ than phosphinates, while phosphonates are even less effective. Recently, the thermodynamic behaviour and effect of organic diluents on solvent extraction of UO₂²⁺ by **17** from nitric acid (1 M) solution has been investigated in detail [68]. The longer spacer of the extractant offered a better extractability for all the tested diluents and UO₂²⁺ extraction was more favorable at lower temperature. In contrast to dichloromethane, in which the UO₂²⁺ extraction process is synergistically driven by enthalpy and entropy, the extraction in 1,2-dichloroethane, 1-nitro-3-(trifluoromethyl)benzene and nitropropane is enthalpy driven whereas the entropy factor counteracts. Particularly, halogenated solvents have better extraction ability than non-halogenated solvents.

In order to improve performance in extraction separation of trivalent lanthanide and actinide cations, a novel series of pillar[5]arenes **27** tethered with dense bidentate carbamoylmethylphosphine oxides (CMPO) ligating groups on both sides of the pillar were designed and synthesized (Fig. 10) [69]. As confirmed by NMR titration, fluorescence spectroscopy titration, time-resolved laser fluorescence spectroscopy (TRLFS), FT-IR spectra and HR-ESIMS, the host-guest complexing process was revealed to proceed in a stepwise manner to form a bimetallic complex. These CMPO-pillar[5]arenes **27** also exhibited increased distribution (D) values for both Am³⁺ and Eu³⁺ with increasing nitric acid concentration in the range of 0.1 to 1.0 M in a mixed solvent system consisting of *m*-nitro(trifluoromethyl)benzene and *n*-octanol (*m*-NTFB/*n*-octanol = 95:5, v/v). In contrast, the industrial extractant (N,N-diisobutylcarbamoylmethyl)phenyloctylphosphine oxide and pillar[5]arene-based phosphine oxides **17**, even at the ligand concentration with the phosphine oxide functionalities being equal to that of **27**, only showed very poor extractability under the same conditions, highlighting the importance of the preorganization of the pillar[5]arene platform. Importantly, the D values for

1 Am^{3+} were generally greater than those for Eu^{3+} over all the acid concentrations examined and a
 2 remarkable selectivity of Am^{3+} over Eu^{3+} ($\text{SF}_{\text{Am/Eu}} = 13.1$) was observed in 1 M HNO_3 . This work
 3 represents the first example in which minor actinides separation from lanthanides is realized by using
 4 pillararene-based receptors as extractants in the extraction process. Thus, CMPO-pillararenes may hold
 5 good potential as promising candidates for actinide partitioning. Sengupta *et al.* then investigated the
 6 local environment and photo-physical parameters including the Judd-Offelt parameter, radiative and
 7 non-radiative lifetimes, branching ratio, quantum efficiency, magnetic and electric dipole transition
 8 probabilities of Eu^{3+} -**27** complexes by TRLFS [70]. This gives more metal-ligand coordinating
 9 information about the bonding energy and stereochemical crowding around the coordinating sites,
 10 further explaining the results obtained from the liquid-liquid extraction process.

11
 12 **Fig. 10.** (a) Structures of CMPO-functionalized pillar[5]arenes **27a–c** and CMPO; (b) representation of the host-
 13 guest recognition process with **27a–c** to form a bimetallic complex in a stepwise fashion. Reproduced with
 14 permission from Ref. [69]. Copyright 2015 Royal Society of Chemistry.

15 Diglycolamides (DGAs), containing ether linkages between two amide groups, have been recognized
 16 as some of the most efficient ligands for actinide partitioning from acidic waste solutions [71].
 17 Appending DGA species to calixarene and tripodal platforms leads to efficient f-block metal ion
 18 binding and extraction due to the preorganization effect [72]. Yuan and co-workers synthesized three
 19 novel pillar[5]arenes **28a–c** functionalized with ten DGA groups on both sides of the pillar (Fig. 11)

[73]. Even at highly acidic conditions (4 M HNO₃), remarkably efficient extraction and separation abilities towards partitioning of Eu³⁺ and Am³⁺ were observed by these molecules with 1-octanol as the diluent. TRLFS studies and slope analysis results showed the strong complexation of the trivalent f-block ions. The stoichiometry of the extracted species was 1:1 (M:L) without inner-sphere water molecules for **28b** and **28c**, while with one water molecule for **28a**, suggesting that pillararene-based DGAs **28** may hold potential for the efficient separation of Eu³⁺ and Am³⁺ from radioactive liquid nuclear waste. The local environment and photo-physical parameters of the Eu³⁺-**28** complexes further indicated that preorganization of DGA moieties on the pillararene platform favoured the covalency of the metal-ligand bond, which gave rise to high extractability of Eu³⁺ [74].

Fig. 11. Structures of pillar[5]arene receptors **28a-c** and schematic representation of the solvent extraction process.

Reproduced with permission from Ref. [73]. Copyright 2014 Royal Society of Chemistry

Apart from conventional organic solvent-based diluents, room temperature ionic liquids (RTILs), which are considered to be “designer solvents”, are a class of organic salts with high thermal stability, negligible vapour pressure, low melting points, adjustable miscibility and polarity as well as high ionic conductivity [75]. Accordingly, RTILs-based extraction is regarded as a promising strategy for the extraction of f-block metal ions [76]. Yuan and co-workers first proposed a supramolecular extraction system utilizing RTIL of 1-*n*-octyl-3-methylimidazolium bis(trifluoromethane)sulfonamide (C₈mimNTf₂) as both the guest and the solvent. When ligands **28** were dissolved in C₈mimNTf₂, they could form host-guest complexes. The larger binding affinities of receptors **28** toward f-block metal ions facilitate a unique competitive metal ion-mediated displacement of C₈mim⁺, resulting in unusual extraction abilities towards UO₂²⁺ and Am³⁺ [77]. Subsequently, the thermodynamics and radiolytic stability of **28** for highly efficient extraction of PuO₂²⁺ and Pu⁴⁺ in the same RTIL was evaluated by

1 Sengupta *et al.* [78]. Additionally, much remarkable extraction abilities of actinide ions (*e.g.*, UO_2^{2+} ,
2 Pu^{4+} , Th^{4+} and Am^{3+}) with pillar[5]arene-based phosphine oxides **17** [79] and CMPO-pillar[5]arenes
3 **27** [80] in RTILs were observed, further demonstrating the importance of RTILs and the
4 preorganization of the pillararene platform.

5 Thorium (Th), which is regarded as a potential nuclear fuel, is a naturally occurring radioactive
6 actinide. Thorium not only has radiotoxicity, but also has high physiological toxicity. Accordingly, the
7 selective recognition of thorium is of considerable significance both in nuclear industry and
8 environmental monitoring. Yuan and co-workers designed and synthesized a novel non-symmetric
9 pillar[5]arene **29** anchored with five triazole-linked 8-oxyquinolines only at one rim and five alkyl
10 chains at the other (Fig. 12) [81]. The recognition behavior of the receptor towards various metal ions
11 was investigated. As confirmed by UV-vis, fluorescence, NMR and mass spectroscopic techniques, the
12 receptor **29** showed high sensitivity and selectivity toward Th^{4+} among the 18 metal ions tested. The
13 DL was found to be $5.35 \times 10^{-7} \text{ M}$ ($124 \mu\text{g} \cdot \text{L}^{-1}$), which is lower than the maximum level for Th^{4+} (246
14 $\mu\text{g} \cdot \text{L}^{-1}$) in drinking water specified by WHO guidelines. The recognition mechanism is probably
15 involving a metal ligand charge transfer (MLCT) effect by the electron transfer from the quinoline
16 nitrogen to the Th^{4+} , resulting in the formation of a weakly fluorescent **29**- Th^{4+} complex of 1:1
17 stoichiometry. In sharp contrast, its acyclic monomeric analog only showed very poor fluorescence
18 quenching for Th^{4+} under the same conditions, highlighting the importance of the preorganization of
19 the pillar[5]arene platform for the recognition of Th^{4+} by providing cooperative coordination in the
20 supramolecular complex. In addition, the resulting **29**- Th^{4+} can further act as a turn-on fluorescent
21 sensor for F^- over other halides in the same media without interference, which can be ascribed to the
22 removal of Th^{4+} from its chelated complexes by F^- , resulting in the formation of more stable species
23 $[\text{ThF}_x^{4-x}]$ and the release of free ligand. This receptor is the first example for selective fluorescent
24 recognition of f-block metal ions in the field of pillararene chemistry, which lays the foundation for the
25 design of pillararene-based fluorescent sensors for other metal cations with tailored properties.

Fig. 12. A non-symmetric pillar[5]arene **29** based on triazole linked 8-oxyquinolines served as fluorescent chemosensor for Th^{4+} . Reproduced with permission from Ref. [81]. Copyright 2015 Royal Society of Chemistry

6. Pillararene-based self-assembly for metal ion recognition and binding

6.1 One-component self-assembly only caused by pillararenes

6.1.1 Monofunctionalized pillararenes

Mono-naphthalimide functionalized pillar[5]arene **30** could self-assemble into a stable supramolecular organogel in cyclohexanol with strong AIE properties via exo-wall π - π interactions of the naphthalimide motifs (Fig. 13) [82]. The obtained supramolecular organogel showed high selectivity and ultrasensitivity towards Fe^{3+} followed by H_2PO_4^- with detection limits of 0.145 nM and 10.3 nM, respectively. The reversible fluorescent response process can be ascribed to the Fe^{3+} -competition between cation- π and exo-wall π - π interactions. In addition, the xerogel of **30**-assembly also showed a potentially practical application in Fe^{3+} separation, providing a new and facile methodology for constructing smart responsive supramolecular materials.

Fig. 13. Supramolecular organogel constructed from mono-naphthalimide functionalized-pillar[5]arene **30** for ultrasensitive and selective recognition of Fe^{3+} followed by H_2PO_4^- . Reproduced with permission from Ref. [82].

Copyright 2018 Royal Society of Chemistry

6.1.2 Copillararenes

Although copillar[5]arene **16b** has been demonstrated to show a strong AIE in EtOH/ CH_2Cl_2 mixed solution, Wei, Lin and coworkers found that **16b** could spontaneously self-assemble into a strongly fluorescent [c2]daisy-chain dimer between the pillar[5]arene units and $\text{Br}(\text{CH}_2)_4-$ units in the H_2O -DMSO (1:9, v/v) medium [83]. The addition of Fe^{3+} can lead to significant fluorescence on-off response with a detection limit of 1.65×10^{-8} M. When F^- was added to **16b**- Fe^{3+} solution, the fluorescence recovery was due to the renewed formation of supramolecular [c2]daisy self-assembly. Interestingly, the practical utility of the probe **16b** in a daily life sample was also evaluated using Fe^{3+} in tap water and F^- in toothpastes. Subsequently, it was found that receptor **16b** was also a highly selective and sensitive sensor for Hg^{2+} and I^- in the same medium through a novel iodination-triggered competitive coordination mechanism, which was further utilized to form a molecular NAND logic gate [84]. The receptor **16b** could not directly sense Hg^{2+} or I^- , however, after adding I^- to the **16b** solution, the iodized solution can recognize Hg^{2+} with high selectivity and sensitivity ($\text{DL} = 3.73 \times 10^{-8}$ M). The resulting solution system consisting of Hg^{2+} and iodized-**16b** can exhibit high selectivity and sensitive recognition towards I^- ($\text{DL} = 3.51 \times 10^{-7}$ M).

1 Substitution of the bromine atoms of copillar[5]arene **16b** by iodine atoms can result in a iodine-
 2 functionalized copillar[5]arene **31** (Fig. 14a), which can further self-assemble into a supramolecular
 3 organogel with a sheet-like structure in cyclohexanol [85]. This gel can selective recognize Hg^{2+} and
 4 Ag^+ signaled by fluorescence quenching, with a detection limit of 2.07×10^{-8} M and 3.66×10^{-8} M,
 5 respectively. Reaction of **16b** with triethylamine could result in another copillar[5]arene **32** (Fig. 14b),
 6 which self-assembled into [c2]daisy chain dimers via intermolecular hydrogen bonds [86]. This
 7 [c2]daisy chain dimer could further self-assemble to form a fluorescent supramolecular hydrogel at
 8 high concentrations with self-healing capacity and multi-stimuli responsiveness including temperature,
 9 pH, anion and competitive guest. Additionally, only Fe^{3+} could induce the blue fluorescence quenching
 10 of the hydrogel, implying its highly selective and sensitive recognition of Fe^{3+} cations ($\text{DL} = 7.86 \times 10^{-10}$
 11 M).

13 **Fig. 14.** (a) Chemical structure of iodine-functionalized copillar[5]arene **31**. (b) Supramolecular hydrogel
 14 constructed by copillar[5]arene **32** for fluorescent sensing for Fe^{3+} . Reproduced with permission from Ref. [86].

15 Copyright 2018 Royal Society of Chemistry

16 Zhang and co-workers reported a supramolecular gel, which was constructed from a bis-
 17 naphthalimide functionalized copillar[5]arene **33**, for selective fluorescence sensing Fe^{3+} followed by
 18 L-Cys (Fig. 15) [87]. Compound **33** could self-assemble into a stable supramolecular gel driven by π - π
 19 interaction of the naphthalimide groups with AIE in cyclohexanol. The obtained supramolecular gel
 20 also showed excellent thermal responsiveness, acid and base responsiveness, cation and amino acid
 21 responsiveness. Particularly, this supramolecular π -gel could act as a successively selective
 22 fluorescence sensor for Fe^{3+} ($\text{DL} = 6.06 \times 10^{-8}$ M) and L-Cys ($\text{DL} = 1.0 \times 10^{-8}$ M) as well as to
 23 efficiently remove Fe^{3+} from water. The distinctive recognition process can be ascribed to the

1 competition of π - π stacking and cation- π interactions between Fe^{3+} and the naphthalimide moiety as
 2 well as competitive binding of L-Cys with Fe^{3+} .

3

4 **Fig. 15.** Supramolecular gel constructed from a bis-naphthalimide functionalized copillar[5]arene **33** acts as a
 5 selective fluorescence sensing for Fe^{3+} followed by L-Cys. Reproduced with permission from Ref. [87]. Copyright
 6 2018 Royal Society of Chemistry

7 6.1.3 Oligomeric pillararenes

8 Bispillar[5]arene **34** (Fig. 16), linked with diacylhydrazone, showed strong aggregation-induced
 9 emission (AIE) in DMSO/ H_2O solutions (fluorescence quantum yield is 21%) [88]. This AIE property
 10 is probably due to the intermolecular hydrogen bonds involving the diacylhydrazone group and $\pi\cdots\pi$
 11 stacking interactions of the phenyl moiety, which reduced the restriction of intramolecular motion.
 12 Addition of Hg^{2+} could result in significant fluorescence quenching of the AIE luminogen (AIEgen) **34**
 13 owing to the disrupting the intermolecular hydrogen bonds through coordination of Hg^{2+} with the
 14 acylhydrazone groups. Thus, the receptor can selectively recognize Hg^{2+} over other metal cations with
 15 a detection limit of 4.3×10^{-8} M. The binding ratio and bonding constant was found to 2:1 (metal:ligand)
 16 and $2.5 \times 10^3 \text{ M}^{-2}$ in DMSO/ H_2O (v/v=1:1), respectively.

Fig. 16. A novel bispillar[5]arene-based AIEgen **34** for highly selective recognition towards Hg^{2+} . Reproduced with permission from Ref. [88]. Copyright 2018 Elsevier.

A novel tripodal organic gelator **35** (Fig. 17), which was constructed by connecting a pillar[5]arene skeleton and a benzene group *via* a dihydrazide group, could self-assemble into a supramolecular polymer within 0.5 minutes in cyclohexanol driven by C–H $\cdots\pi$, $\pi\cdots\pi$ stacking, Van der Waals' force and hydrogen bonding interactions [89]. Interestingly, the obtained supramolecular polymer presented strong blue aggregation-induced emission (AIE) and multiple external stimuli-responsive behaviors, and showed a high sensitivity for selective recognition and sensing of Hg^{2+} based on fluorescence on-off switching with a detection limit of 1.02×10^{-8} M. The xerogel could also effectively remove Hg^{2+} from aqueous solution with a separation ratio of 81.3%. In addition, a thin film based on this gel was demonstrated to be a convenient test kit for Hg^{2+} detection.

Liu *et al.* reported another SOF gel constructed from a novel tripodal pillar[5]arene-based supramolecular polymer network [90]. As shown in Fig. 18a, the tripodal trispillar[5]arene **36** could self-assemble into supramolecular polymer networks in DMF-H₂O (1:1, v/v) solution, which further formed a stable organogel with strong AIE properties simultaneously through multiple CH- π , π - π and hydrogen bonds. Intriguingly, the obtained organogel showed high sensitivity in its response for Fe^{3+} , Cu^{2+} , Cr^{3+} , Ag^{+} signaled by fluorescence quenching. Particularly, obvious fluorescence color changes varying from light-blue to yellow and pink for Tb^{3+} and Eu^{3+} respectively can be observed, leading to the formation of a series of metallogels which could further act as a sequential sensor for specific

anions and amino acids. The DLs of the sensor array for the corresponding multianalytes ranged from 6.80×10^{-10} M to 1.20×10^{-8} M. Importantly, the obtained xerogel could serve for efficient adsorption of the above-mentioned six metal cations (absorption percentages > 98%).

Fig. 17. Tripodal organic gelator constructed from tris-pillar[5]arene **35** for fluorescence recognition and separation of Hg^{2+} . Reproduced with permission from Ref. [89]. Copyright 2018 Royal Society of Chemistry.

Fig. 18. Chemical structure of tris-pillar[5]arenes (a) **36** and (b) **37**.

Wei and coworkers reported another AIE-SOF constructed from tris-pillar[5]arene **37** (Fig. 18b) [91]. The compound **37** self-assembled into stable three-dimensional (3D) SOF gels, which showed a fluorescence quenching response for Fe^{3+} , Hg^{2+} and Cr^{3+} with the limits of detection ranging from 9.40

$\times 10^{-10}$ to 1.86×10^{-9} M. The obtained xerogel with porous mesh structures showed excellent adsorption separation of these metal cations (adsorption percentages > 92%). Additionally, Fe^{3+} - and Cr^{3+} -coordinated supramolecular organic frameworks (SOFs) also can exhibit a fluorescence turn-on recognition for CN^- (DL = 2.12×10^{-9} M) and H_2PO_4^- (DL = 1.78×10^{-9} M).

6.2 Two-component self-assembly starting from two different pillararenes.

Pillar[5]arenes **33** and **38** could assemble into a novel supramolecular polymer, which was able to form a SOF through π - π stacking interactions and then further formed a stable supramolecular gel in cyclohexanol with strong AIE (Fig. 19a) [92]. Importantly, the obtained supramolecular gels could successively recognize Fe^{3+} followed by H_2PO_4^- through the competition of cation- π and π - π stacking interactions in their gel states with the detection limits of 7.54×10^{-9} M and 4.21×10^{-9} M respectively. Their xerogels showed good potential for practical applications in the adsorption of Fe^{3+} and construction of fluorescent display materials as well as sensitive logic gates.

Wei and co-workers have reported a novel supramolecular polymer gel constructed by combination of copillar[5]arene **38** and mono-naphthalimide functionalized pillar[5]arene **39** for sequential fluorescent detection of Hg^{2+} followed by I^- in DMSO solution (Fig. 19b) [93]. The supramolecular gel, driven by π - π stacking interactions of each naphthalene moiety and C-H $\cdots\pi$ interaction of the alkyl chains of **38** threaded into the cavity of **39**, displayed no fluorescence. However, neither **38** nor **39** could self-assemble into a supramolecular gel in DMSO. The obtained supramolecular polymer gel could cause a selective fluorescent turn-on recognition for Hg^{2+} via cation- π interactions with high selectivity and sensitivity (DL = 1.65×10^{-9} M), which induced the supramolecular polymer gel to change into a metallogel. The Hg^{2+} -coordinating gel can furthermore selectively recognize I^- (DL = 1.84×10^{-8} M) over other anions, leading to the recovery of the supramolecular polymer gel.

Another supramolecular polymer was constructed by connecting copillar[5]arene **38** and mono-phthalimide functionalized pillar[5]arene **40** (Fig. 19c), which could further self-assemble into a stable supramolecular gel via “exo-wall” π - π interactions and host-guest interactions in cyclohexanol solution with strong AIE properties (quantum yield: 60%) [94]. Importantly, the obtained supramolecular gel could selectively sense Fe^{3+} , Hg^{2+} , and Ag^+ signaled by fluorescence on-off switching, with detection limits of 1.78, 9.5, and 3.17 nM, respectively. These three metal cations could also be effectively adsorbed from aqueous solution by the gel, leading to formation of the

corresponding metallogel. Analogously, the resultant metallogels (Fe^{3+} and Hg^{2+}) could act as fluorescence off-on sensors for selective recognition of F^- (DL = 1.51 nM) and Br^- (DL = 0.73 nM) through the competition between “exo-wall” π - π interactions and cation- π interactions, respectively.

Fig. 19. (a) SOF gel constructed from pillar[5]arenes **38** and **33** for ultrasensitive recognition of Fe^{3+} ; (b) Supramolecular polymer gel consisting of functionalized pillar[5]arenes **38** and **39** for sequential fluorescent detection of Hg^{2+} followed by I^- ; (c) Multianalyte response properties of supramolecular AIE gels constructed from pillar[5]arenes **38** and **40**; (d) Multi-guest-response properties of SOF gel constructed from pillar[5]arenes **38** and **41**; (e) SOF gel constructed from pillar[5]arenes **38** and **42** for ultrasensitive recognition of Fe^{3+} in water.

Copillar[5]arene **38** and bis-thioacetylhydrazine functionalized copillar[5]arene **41** could also assemble into a novel SOF in cyclohexanol solution (Fig. 19d), which could further form a stable gel. Interestingly, the obtained xerogel showed excellent fluorescent on-off response for Hg^{2+} , Cr^{3+} , Cu^{2+} and Fe^{3+} with the detection limit in the range of 1.0×10^{-7} M to 1.0×10^{-6} M [95]. The xerogel could also efficiently separate these metal ions and the absorption rates were up to 99.29%. Importantly, the

1 rational addition of these metal ions (Fe^{3+} , Hg^{2+} and Cu^{2+}) into the supramolecular gel could result in a
2 series of metal ion coordinating SOF, which could selectively and sensitively sense F^- , Br^- , and L-Cys
3 by fluorescence off-on switching (detection limits were about 10^{-8} M), respectively.

4 Similarly, another SOF gel with AIE enhancement behavior has been fabricated by bis-8-
5 hydroxyquinoline functionalized copillar[5]arene **42** and copillar[5]arene **38** in aqueous-cyclohexanol
6 (85:15, v/v) solution (Fig. 19e) [96]. The fluorescence of the gel was remarkably quenched selectively
7 by addition of Fe^{3+} ions with DL of 0.102 nM. Restoring the emission from the strongly quenched Fe^{3+} -
8 coordinated metallogel could be achieved by the addition of F^- owing to the competitive coordination
9 of F^- with metal cations. Importantly, the supramolecular gel and the resultant Fe^{3+} -coordinating
10 metallogel had excellent feasibility for selective separation and detection of Fe^{3+} and F^- in aqueous
11 solution.

12 6.3 Two-component self-assembly starting from a functionalized pillararene and a specific 13 guest

14 Lin and co-workers reported a novel supramolecular sensor based on a cationic water-soluble
15 pillar[5]arene **43** for highly selective recognition of Fe^{3+} ions in water [97]. Compound **43** bearing ten
16 trimethylammonium groups at both rims, and the aromatic acid derivative guest **G2** could self-
17 assemble into a stable host-guest complex through electrostatic and π - π stacking interactions with a
18 stoichiometry of 1:2 (host:guest) in water (Fig. 20a). This ensemble was further used for highly
19 selective and sensitive detection of Fe^{3+} with a DL of 8.24×10^{-7} M. The sensing mechanism could be
20 attributed to Fe^{3+} coordination to **G2**, resulting in the fluorescence quenching of the host-guest
21 complex. The *in situ* generated **43**-(**G2**)₂- Fe^{3+} ensemble could serve as an outstandingly sensitive and
22 selective fluorescent off-on sensor for F^- over other anions in the same medium with a DL of 4.07×10^{-8} M.
23

24 Subsequently, another guest **G3** (Fig. 20b) and pillar[5]arene **43** could also self-assemble into a 1:2
25 host-guest complex in the same manner, which was demonstrated to be a sequential fluorescence on-off
26 sensor for Al^{3+} (DL = 9.93×10^{-8} M) followed by off-on fluorescence sensing by the CN^- (DL = $2.29 \times$
27 10^{-6} M) with high sensitivity and selectivity in water [98]. Phenazine imidazole guest **G4** (Fig. 20c) and
28 **43** could also self-assemble into a stable pseudo[2]rotaxane through C-H $\cdots\pi$ interaction of the alkyl
29 chain and the pillar[5]arene cavity as well as π - π stacking interactions of the cavity and

phenazineimidazole in DMSO/H₂O (1 : 1, v/v). The pseudorotaxane could also act as a supramolecular sensor for selective and sensitive fluorescence on-off recognition of Ag⁺ (DL = 1.2 × 10⁻⁸ M) and Hg²⁺ (DL = 5.0 × 10⁻⁷ M) respectively [99]. Pillar[5]arene **43** also showed AIE properties with increasing concentration in DMSO solution, which can serve as an outstanding chemosensor for the successive fluorescent recognition of Fe³⁺ (DL = 7.49 × 10⁻⁸ M) followed by F⁻/H₂PO₄⁻ (DL = 2.53 × 10⁻⁸ M and 5.04 × 10⁻⁸ M, respectively) [100]. Some of the positively charged trimethylammonium heads of **43** threaded into the cavity of the other **43**, and further self-assembled into an AIE supramolecular system. The Fe³⁺ could coordinate with **43** via cation-π interactions, leading to the disassembly of the aggregates of **43** accompanied by complete fluorescent quenching. The binding mode of **43** towards Fe³⁺ was found to be 1:2 (L:M). The AIE of **43** could be recovered upon addition of F⁻/H₂PO₄⁻ due to the competitive coordination of these anions toward Fe³⁺.

Fig. 20. (a) Self-assembled supramolecular sensor based on water soluble cationic pillar[5]arene **43** and aromatic acid derivative guest **G2** for selective recognition towards Fe³⁺. Reproduced with permission from Ref. [97].

Copyright 2017 Royal Society of Chemistry; (b) Chemical structure of organic guests **G3** and (c) **G4**.

Lin *et al* reported that another mono-naphthalimide functionalized-pillar[5]arene **44** and bis-pyridinium derivative guest **G4** could self-assemble into a linear fashion, affording a one-dimensional supramolecular polymer in DMSO-H₂O (9:1, v/v) solution through host-guest interactions and π-π

stacking interactions (Fig. 21) [101]. Importantly, when iodine was introduced into the self-assembled solution where the self-assembly took place, it could not only control the optical properties and self-assembly states of the **44-G5** ensemble *via* an electronic donor-acceptor effect, but also control the molecular recognition properties by competitive redox reactions. Accordingly, the **44-G5** ensemble showed selective fluorescent off-on recognition towards CN^- ($\text{DL} = 4.1 \times 10^{-8} \text{ M}$), Hg^{2+} ($\text{DL} = 1.0 \times 10^{-7} \text{ M}$), and L-Cys ($\text{DL} = 3.3 \times 10^{-8} \text{ M}$) both in supramolecular polymer gels, DMSO- H_2O water solutions and living cells with high sensitivities.

Fig. 21. Iodine-induced multiresponsive supramolecular polymer constructed from mono-naphthalimide functionalized-pillar[5]arene **44** and bis-pyridinium derivative guest **G5** for fluorescence recognition of CN^- , Hg^{2+} , and L-Cys. Reproduced with permission from Ref. [101]. Copyright 2017 American Chemical Society.

A novel fluorescent supramolecular pseudo[2]rotaxane, constructed from a water-soluble copillar[5]arene host **45** and a naphthaleneimide guest **G6** (Fig. 22a), could further self-assemble into a supramolecular polymer gel *via* multiple intermolecular hydrogen bonds, C-H- π interactions, exo-wall π - π interactions and van der Waals forces in DMSO- H_2O (1:1, v/v) solution [102]. The obtained supramolecular polymer gel showed multiple external stimuli-responsiveness including temperature, competitive guest, acid-base stimuli and mechanical stress due to the dynamic and reversible nature of non-covalent interactions. Particularly, the gel exhibited fluorescent on-off response for Fe^{3+} and Cu^{2+} , while its xerogel could effectively remove Fe^{3+} and Cu^{2+} from aqueous solution with adsorption rates

up to 98.07% and 95.38%, respectively. Additionally, the resultant formation of Fe^{3+} and Cu^{2+} metallogels could selectively and sensitively fluorescence turn on sensing for F^- and CN^- with the detection limits about 1×10^{-8} M.

Similarly, anionic water soluble-copillar[5]arene **46** bearing disulfonated arms and tetraphenylethene (TPE)-based tetratopic guest **G7** could self-assemble into supramolecular AIE system in water solution through host-guest complexation (Fig. 22b) [103]. The obtained inclusion complex, having excellent tolerance to a wide range of pH values (pH = 3.0-13), showed strong blue emission, high quantum yield and long fluorescence lifetime due to the restriction of intramolecular motions of the **G7**. Additionally, the supramolecular host-guest complex can recognize Fe^{3+} (DL = 0.86 μM) with high sensitivity and selectivity in a fluorescent quenching manner owing to the coordination of **46** with Fe^{3+} and release of the free **G7**.

Fig. 22. (a) Supramolecular gel constructed by copillar[5]arene **45** and **G6** for efficient detection and separation of Fe^{3+} and Cu^{2+} . (b) Supramolecular assembly-induced AIE constructed by copillar[5]arene **46** and **G7** for selective recognition of Fe^{3+} .

Wei and co-workers constructed a linear supramolecular polymer based on acylhydrazone functionalized bispillar[5]arenes **47** and bipyridinium salt **G8** through host-guest interactions in DMSO solution (Fig. 23), which could further self-assemble into a supramolecular gel at high concentration *via* intermolecular hydrogen bonding and π - π stacking interactions of the acylhydrazone linkers [104]. The obtained supramolecular gel showed reversible gel-sol phase transitions upon heating and cooling. In contrast, adding the competitive ligand of adiponitrile resulted in the irreversible transformation due to the higher binding affinity of adiponitrile with pillararenes in comparison to

pyridinium salt derivatives, leading to the destruction of the linear supramolecular polymer. The supramolecular gel could also selectively and sensitively recognize Fe^{3+} cations with a detection limit of $1.56 \times 10^{-7} \text{ M}$.

Fig. 23. Supramolecular gel constructed from bispillar[5]arene **47** and a bipyridinium salt derivative **G8** for highly selective and sensitive recognition of Fe^{3+} followed by H_2PO_4^- . Reproduced with permission from Ref. [104].

Copyright 2017 Royal Society of Chemistry

Wei and co-workers constructed multi-functional spongy supramolecular polymer gels through assembly of tripodal guest **G9** and mono-naphthalimide functionalized-pillar[5]arene **48** via multi-non-covalent interactions such as host-guest inclusion, C-H- π , π - π and hydrogen bonds, which showed multi-responsiveness toward outer stimuli such as heating-cooling, pH, competitive agents and mechanical shaking and resting (Fig. 24) [105]. Importantly, the supramolecular polymer gels have a strong AIE, which could be applied to efficiently separate and detect Fe^{3+} with the DL of 0.9 nM and binding constant of $2.34 \times 10^6 \text{ M}^{-1}$. The selective recognition of Fe^{3+} may be ascribed to the supramolecular assembly binding with Fe^{3+} via cation- π interactions.

Fig. 24. Spongy supramolecular polymer assembled from tripodal guest **G9** and mono-naphthalimide functionalized-pillar[5]arene **48**. Reproduced with permission from Ref. [105]. Copyright 2019 Royal Society of Chemistry.

Another supramolecular self-assembly sensor was constructed for specific and ratiometric recognition of Fe^{3+} ion by Yin's group [106]. Water-soluble quaternized perylenediimide derivative **G10** alone exhibited irregular aggregates with strong fluorescence in aqueous solution. As shown in Fig. 25, water-soluble pillar[5]arene **49** and **G10** could form a host-guest complex due to the hydrophobic effect and electrostatic interaction, leading to morphological transformation and fluorescence turn-off properties due to supramolecular photoinduced electron transfer (PET). The obtained supramolecular host-guest system could serve as a sensitive and selective turn-on fluorescent probe for Fe^{3+} ions ($\text{DL} = 2.13 \times 10^{-7} \text{ M}$) through the perturbing of the microenvironment of the host-guest systems and the inhibition of the supramolecular PET process.

Fig. 25. A supramolecular host-guest system based on water-soluble pillar[5]arene **49** and water-soluble quaternized perylenediimide derivative **G10** served as a turn-on fluorescent probe for Fe^{3+} . Reproduced with permission from Ref. [106]. Copyright 2017 American Chemical Society.

Recently, Lin and coworkers reported a 3D supramolecular polymer network gel constructed by the assembly of **50** and 4,4'-bipyridinium salt guest **G8**, and this gel had a spongy structure and AIE properties (Fig. 26) [107]. Intriguingly, the gel could not only serve as a fluorescence on-off chemosensor for Fe^{3+} and Hg^{2+} with a DL of 9.19×10^{-9} and 3.95×10^{-8} M respectively, but also act as an adsorbent for efficient separation of various pollutants including metal ions, oxometallates, various organic dyes and organic compounds (separation rates > 99%). Additionally, the corresponding xerogel also showed highly selective response for pyridine vapor. The resulting Fe^{3+} -metallogel and Hg^{2+} -metallogel can selectively recognize F^- (DL = 3.38×10^{-8} M) and Br^- (DL = 8.17×10^{-7} M) respectively, with a fluorescence off-on response.

Fig. 26. AIE supramolecular polymer network constructed by assembling a bisnaphthalimide functionalized-pillar[5]arene **50** and a 4,4'-bipyridinium salt guest **G8** serves as a fluorescence on-off chemosensor for Fe^{3+} and Hg^{2+} . Reproduced with permission from Ref. [107]. Copyright 2019 American Chemical Society.

Very recently, Zhang, Lin and coworkers have reported a supramolecular polymer network for the selective recognition of Ag^+ followed by I^- through a mechanism involving *in situ* generation of AgI quantum dots (Fig. 27) [108]. Bis-8-hydroxyquinoline functionalized pillar[5]arene **42** and bis-pyridinium guest **G11** could self-assemble into a supramolecular polymer network with AIE properties in DMSO/ H_2O solution ($f_{\text{water}} > 20\%$), and this network showed selective fluorescence off-on recognition of Ag^+ ($\text{DL} = 7.44 \times 10^{-9} \text{ M}$) and efficiently separated Ag^+ in water (separation rate $> 95\%$). Unexpectedly, only sequential addition of I^- to the [**42** + **G11** + Ag^+] system can lead to strong warm white fluorescence emission owing to the *in situ* formation of AgI quantum dots. Control experiments further demonstrated that the confinement effect of the supramolecular polymer network plays a vital role in the formation of AgI quantum dots.

Fig. 27. Supramolecular polymer network, constructed from bis-8-hydroxyquinoline functionalized pillar[5]arene **42** and bis-pyridinium guest **G11**, showed selective recognition of Ag^+ , which could selectively recognize I^- due to the *in situ* generation of AgI quantum dots. Reproduced with permission from Ref. [108]. Copyright 2019 John

Wiley and Sons.

7. Pillararene-based polymers for metal ion recognition and binding

A novel pillar[5]arene-based thioacetohydrazone fluorescent polymer **51** was prepared by Wei and co-workers (Fig. 28), which exhibited highly selective sensing and effective removal of Hg^{2+} ions [109]. The pillar[5]arene units served as the fluorophore and thioacetohydrazone groups acted as the ionophore for cation binding sites through coordination with S and N atoms. Selectively, addition of Hg^{2+} led to significant fluorescence quenching with a detection limit of 8.12×10^{-7} M in DMSO/ H_2O (1:1, v/v). The fluorescence of polymer **50** could be easily recovered upon addition of 5 equivalent of Na_2S due to the formation of more stable complexes $[\text{HgS}_2]^{2-}$. In addition, this polymer could also act a potent sorbent for efficient removal of Hg^{2+} with an average adsorption capacity of $108 \text{ mg} \cdot \text{g}^{-1}$ at room temperature.

Fig. 28. Pillar[5]arene-based fluorescent polymer **51** for selective sensing and effective removal of Hg^{2+} .

Reproduced with permission from Ref. [109]. Copyright 2017 Royal Society of Chemistry.

Another fluorescent polymer, constructed from ditriflate functionalized copillar[5]arene **52** and 1,1,2,2-tetrakis(4-ethynylphenyl)ethylene through Sonogashira-Hagihara cross-coupling reactions, was reported by Yang and co-workers (Fig. 29) [110]. The luminescent polymer material could act as a two-photon fluorescent sensor for selective and sensitive recognition of Fe^{3+} and 4-amino azobenzene dye with remarkable insolubility, stability and recyclability, signaling *via* fluorescence quenching. The unique sensing mechanism could be mainly attributed to the good specificity of the methoxy groups and the size matching effect of pillar[5]arene toward Fe^{3+} . This work provides a new strategy for enhancing the properties of porous organic polymers through the introduction of supramolecular macrocycles.

Fig. 29. Luminescent conjugated macrocycle polymer constructed from ditriflate functionalized copillar[5]arene **52** and 1,1,2,2-tetrakis(4-ethynylphenyl)ethylene. Reproduced with permission from Ref. [110]. Copyright 2019

John Wiley and Sons.

8. Pillararene-based self-assembly driven by metal-ligand coordination

The metal-ligand bonds possess relatively modest bond energies, which can be useful for creating hierarchical assemblies. Actually, coordination-driven self-assembly not only offers a simple, bottom-up and efficient approach for constructing various metal-organic supramolecular materials [111], but also provides diverse suprastructures with unique spatial arrangements including gels, vesicles, micelles, ribbons, films, fibers, tubes and so forth [112]. Metal-ligand coordination also has numerous advantages as exemplified by its distinctive magnetic, redox, optical, and electrochromic properties. Considering that pillararenes have electron-donating cavities, these macrocycles are ideal for complexing with different kinds of complementary guests. Thus, the orthogonal self-assembly based on combination of host-guest interaction and metal-ligand coordination not only gives unprecedented complexity and diverse functions but also endows the obtained assemblies with multi-responsiveness in a controlled manner [9, 113].

8.1 Self-assembly driven by Na^+

Among the numerous types of mechanically interlocked molecules, pseudo[1]rotaxane has its unique structure, with a wheel threaded reversibly by a connected axle. Hu and coworkers prepared three mono-alkyl-functionalized pillar[5]arenes **53a-c** tethered with alkyl chains as the end group and different length of ethylene glycol (EG) groups as a flexible linker (Fig. 30), which exhibited different dynamic self-inclusion behavior in strongly polar solvent DMSO solution [114]. Compounds **53a** and

53b showed self-inclusion behavior in DMSO solution, leading to the formation of stable pseudo[1]rotaxanes. However, compounds **53c** with longer and more flexible side chain exhibited concentration-dependent pseudorotaxane formation only at high concentration (at least 10 mM). This different self-inclusion behavior of compounds **53** could be attributed to the random movement of their flexible side chains that hinders the alkyl side chain from threading into the cavity of the pillar[5]arene. The addition of Na^+ (as BF_4^- salt) to the pseudo[1]rotaxane formed by **53a** or **53b** could cause tightening of the inclusion structures due to the cooperative coordination of the EG groups with Na^+ .

Fig. 30. Dynamic self-inclusion behavior of pseudo[1]rotaxanes displayed by pillar[5]arene derivatives **53a-c** in the presence of NaBF_4 .

8.2 Self-assembly driven by Cu^{2+}

In 2015, Ji and co-workers reported a novel supramolecular polymer gel constructed by crosslinking pillar[5]arene-based supramolecular polymers through Cu^{2+} -ligand coordination [115]. A heteroditopic monofunctionalized-pillar[5]arene **54** was prepared, bearing both a Schiff base group and a trimethylammonium unit, which could self-organize into linear supramolecular polymers at high concentration, utilizing host-guest interactions of the pillar[5]arene cavity and trimethylammonium guest (Fig. 31). The solution of **54** in CHCl_3 changed from fluidity to gel-like viscous liquids. Specifically, the linear supramolecular polymer chains could be crosslinked and entangled upon addition of equimolar amounts of Cu^{2+} ion due to the metal-ligand coordination between bidentate Schiff base moieties and metal cations, leading to the formation of a 3D network and a supramolecular

polymer gel. Additionally, dramatic fluorescence quenching was also observed, indicating that this self-organized supramolecular polymer can be used as a novel fluorescent sensor for the recognition of Cu^{2+} .

Fig. 31. Self-assembly process of heteroditopic monofunctionalized-pillar[5]arene **54** and the formation of supramolecular polymer gel driven by metal-ligand interactions. Reproduced with permission from Ref. [115].

Copyright 2015 Royal Society of Chemistry.

Yao and co-workers reported a Cu^{2+} -specific metallohydrogel constructed from a terpyridine based low molecular weight ligand **G12** [116]. Upon coordination with Cu^{2+} , the **G12**- Cu^{2+} complex could lead to the formation of a hydrogel under slightly acidic conditions while other divalent metal ions did not cause gelation (Fig. 32). This metallohydrogel showed multistimuli responsiveness towards gel-to-sol transition including physical and chemical triggers such as temperature, thixotropy, and addition of alkali or sodium L-ascorbate. More interestingly, the metallogel collapsed to a sol upon addition of equal equivalent water-soluble pillar[5]arene **49**. This is because **G12** was threaded into the cavity of cyclic host **49** to form a stable host-guest complex with its positive ammonium salt head located to the negative carboxylate groups of **49**, resulting in the formation of a supra-amphiphile. Accordingly, the rigid pillar[5]arene framework hindered the gelation. The morphology of the material was changed from nanofibers to bilayer vesicles with a diameter of 300 nm.

Fig. 32. Cu^{2+} -specific metallohydrogel and water-soluble pillar[5]arene **49** induced nanofiber-to-vesicle morphology transformation. Reproduced with permission from Ref. [116]. Copyright 2015 Royal Society of Chemistry.

Another Cu^{2+} -responsive self-assembly in aqueous media based on a water-soluble pillar[5]arene **55** and an amphiphilic rhodamine B derivative **G13** containing a triethylammonium bromide group was reported by Shi and co-workers (Fig. 33) [117]. Amphiphilic **G13** could self-assemble into micelles in aqueous media, which further changed to irregular aggregates upon addition of Cu^{2+} ion due to the coordination of **G13** and Cu^{2+} . Simultaneously, the **G13**- Cu^{2+} solution changed from colorless to red, accompanied with a fluorescence off-on behaviour. Interestingly, when one equivalent of **55** was added into the solution of **G13**, these micelles transformed to vesicles owing to the formation of a supra-amphiphile **55-G13** through host-guest interactions. Furthermore, after introduction of Cu^{2+} ion into the solution of supra-amphiphile **55-G13**, the vesicles were destroyed and turned into solid nanoparticles along with the same color changes and fluorescence responses, suggesting their potential applications in sensors, controlled release, drug delivery and so on.

Fig. 33. Cu^{2+} -responsive self-assembly based on a water-soluble pillar[5]arene **55** and a rhodamine B-containing amphiphile guest **G13** in aqueous media. Reproduced with permission from Ref. [117]. Copyright 2016 American Chemical Society.

Wen and co-workers prepared a novel supramolecular metallo(organo)gel constructed from copillar[5]arene **56** through Cu^{2+} -ligand coordination (Fig. 34) [118]. Upon addition of 2.0 equivalents of Cu^{2+} to **56**, a stable metallo(organo)gel was obtained in DMF/toluene (2:1, v/v) at 0 °C, which showed reversible gel-sol transition by heating and cooling. A xerogel with hydrangea flower-like rugate layer-structure was observed by field emission scanning electron microscopy (FE-SEM), while a sheet-like structured gel-precipitate was formed from **56**- Cu^{2+} gel upon shaking or sonication. In addition, the obtained supramolecular metallo(organo)gel could extract Sudan III from its ethanol solution.

Fig. 34. Supramolecular metallo(organo)gel constructed from bipyridyl functionalized copillar[5]arene **56** through Cu^{2+} -ligand coordination and its FE-SEM image of (a) the xerogel (inset, hydrangea flower) and (b) the gel-precipitate. Reproduced with permission from Ref. [118]. Copyright 2017 John Wiley and Sons.

In 2017, Xia and co-workers reported another metallosupramolecular polypseudorotaxane constructed by pillararene-based host-guest interaction and Cu^{2+} coordination (Fig. 35), which showed triple responsiveness to pH-, light and CN^- [119]. Firstly, *trans*-4,4'-vinylenedipyridine guest **G14** could be threaded into the cavity of pillar[5]arene **57**, per-substituted with morpholine groups, leading to a dual-responsive [2]pseudorotaxane due to the photoresponsive property of **G14** and pH-responsive behaviour of pyridine groups. The addition of Cu^{2+} to the solution of the [2]pseudorotaxane could ultimately lead to the formation of a metallosupramolecular polypseudorotaxane, which could be further cleaved by CN^- owing to its competitive coordination to Cu^{2+} . This work represented the first example of triple stimuli-responsive metallosupramolecular polypseudorotaxane and enriched the field of metallosupramolecular polymers.

Fig. 35. Metallosupramolecular polypseudorotaxane fabricated by a pH-sensitive pillar[5]arene **57** and guest **G14**. Reproduced with permission from Ref. [119]. Copyright 2018 American Chemical Society.

A linear supramolecular polymer constructed by a salicylaldehyde azine-containing pillar[5]arene dimer **58** and a homoditopic guest **G15** was reported by Wang and coworkers (Fig. 36), which showed strong AIE fluorescence at high concentration in chloroform [120]. After the addition of Cu^{2+} , the linear supramolecular polymer could be cross-linked accompanied with dramatical quenching of the

- 1 fluorescence emission due to the coordination of the salicylaldehyde azine group with Cu^{2+} .
- 2 Additionally, sequential addition of CN^- led to the recovery of the linear AIE supramolecular polymer.

3

4 **Fig. 36.** Linear AIE supramolecular polymer based on a salicylaldehyde azine-containing pillararene **58** and **G15**

5 and its reversible cross-linking by Cu^{2+} and CN^- . Reproduced with permission from Ref. [120]. Copyright 2019

6 American Chemical Society.

7

8 8.3 Self-assembly driven by Zn^{2+}

9 A1/A2-thioacetohydrazide functionalized copillar[5]arene **41** could self-assemble into a linear

10 supramolecular metal-organic polymer upon addition of Zn^{2+} through metal-ligand coordination (Fig.

11 37) [121]. The obtained supramolecular polymer could further self-assemble into a fluorescent

12 supramolecular metal-organic gel in cyclohexanol at high concentration ($[\mathbf{41}] = [\text{Zn}^{2+}] = 150 \text{ mM}$). The

13 gelation process was driven by the intermolecular hydrogen bonding of the hydrazide motifs and π - π

14 stacking interactions of pillar[5]arene framework. The supramolecular gel also showed reversible gel-

15 sol phase transitions upon heating and cooling. On the contrary, irreversible sol-gel phase transition

16 was observed after the addition of tetrabutylammonium hydroxide (TBAOH) owing to the reversal of

17 the coordination between the hydrazide groups and Zn^{2+} and the formation of inorganic $\text{Zn}(\text{OH})_2$. In

addition, the strong blue fluorescence of the gel was significantly quenched selectively upon the addition of Hg^{2+} , which was successfully applied to remove Hg^{2+} from water samples.

Fig. 37. Pillar[5]arene-based fluorescent supramolecular Zn^{2+} -organic gel for efficient removal of Hg^{2+} .

Reproduced with permission from Ref. [121]. Copyright 2017 Royal Society of Chemistry.

Another novel linear metallosupramolecular polypseudorotaxane has been constructed *via* Zn^{2+} -coordination with pseudo[3]rotaxane which was prepared from thioacetylhydrazine functionalized pillar[5]arene **59** and pillar[5]arene **32** through host-guest interactions (Fig. 38) [122]. The obtained polypseudorotaxane could further self-assemble into a metallosupramolecular polypseudorotaxane gel at a high concentration ($[\mathbf{32}] \cdot \mathbf{Zn} \cdot 2[\mathbf{59}] = 75 \text{ mM}$) in cyclohexanol. Interestingly, the polypseudorotaxane gel showed multiple stimuli-responsive gel-sol phase transitions such as temperature, sulfide, formaldehyde, competitive guests and so on, due to the nature of the metal-ligand bonds, host-guest interactions and hydrogen bonding interactions. This metallosupramolecular gel also showed fluorescence on-off responses for selective recognition of Fe^{3+} and Cu^{2+} with a detection limit of 0.893 nM and 45.7 nM, respectively. The authors claimed this is the first example of pillararene-based supramolecular polypseudorotaxanes constructed for highly sensitive and selective fluorescence recognition of metal ions.

Fig. 38. Linear metallosupramolecular polypseudorotaxane constructed by self-assembly of a pillar[5]arene-based pseudo[3]rotaxane *via* Zn^{2+} -coordination. Reproduced with permission from Ref. [122]. Copyright 2018 Royal Society of Chemistry.

Gong and Ning's group designed and synthesized a new copillar[5]arene **60** functionalized with a terpyridine (TPY) moiety which is regarded as a versatile and well-known building block to construct various smart materials due to its high binding affinity towards metal cations (Fig. 39) [123]. Owing to the orthogonal self-assembly of the host-guest interaction of pillar[5]arene with neutral guest **G16** and the well-defined coordination of TPY towards Zn^{2+} , a cross-linked dimeric hexagonal supramolecular polymer was successfully constructed. Interestingly, changing the adding order of Zn^{2+} and **G16** could lead to totally different self-assembled morphologies of the supramolecular polymer. When **G16** was first added, laminar sheets with a regular width of about 650 nm were obtained, which is quite different from the spherical clusters formed when Zn^{2+} was introduced first, indicating that the first step plays a crucial role in the generation of the morphology and the nanostructure control. In addition, the supramolecular polymer showed an excellent reversible transition upon addition of the competitive ligand 1,4,7,10-tetrazacyclododecane (cyclen). However, the inherent rigid structure of the host molecule **60** and poor solubility of the formed three component supramolecular complex may restrict its characterization and further applications.

Fig. 39. Fluorescent cross-linked supramolecular polymer based on copillar[5]arene **60** and **G16** driven by orthogonal host-guest interaction and metal-ligand coordination. Reproduced with permission from Ref. [123].

Copyright 2016 John Wiley and Sons.

Shi and co-workers reported the first example of catenane-based supramolecular polymers constructed by orthogonal pillar[5]arene-based host-guest interaction and metal ion coordination [124]. The [2]catenane guest **G17** bearing two cyano groups worked as a homoditopic guest monomer. Monofunctionalized-pillar[5]arene **61** containing only one TPY group was introduced to interact with Zn^{2+} and **G17**, further self-assembling to form a linear supramolecular ternary main-chain polymer in $\text{CH}_3\text{CN}/\text{CHCl}_3$ (1/1, v/v) medium (Fig. 40a). The obtained supramolecular polycatenane showed dual-stimuli responsiveness to both temperature and OH^- due to the reversibility of metal-ligand and host-guest interactions. Upon increasing the temperature, the glue-like viscous liquid gradually changed to a turbid solution because of the decomplexation of **61-G17**. The glue-like gel of supramolecular main-chain polycatenanes could dissociate into a transparent solution within a short time of 1 min when TBAOH was added to the solution owing to the much higher binding ability of OH^- towards Zn^{2+} . Interestingly, compared with traditional supramolecular polymers, the supramolecular main-chain polycatenanes showed a better viscoelastic behavior.

In the same manner, changing the linker of [2]catenane guest **G17** to neutral ditopic guest **G18** (Fig. 40b) could lead to another stimulus responsive fluorescent supramolecular polymer by orthogonal

pillar[5]arene **61** based host-guest interaction and Zn^{2+} -coordination in the same medium [125]. The guest **G18** and 2,2'-bipyridine-bridged pillar[5]arene dimer **62** can also self-assemble into a linear supramolecular polymer through host-guest interactions in chloroform, and this polymer could be further transformed into a cross-linked supramolecular polymer network gel upon addition of Zn^{2+} ions via metal-ligand interactions [126]. Similarly, the obtained supramolecular gel showed reversible gel-sol transition upon dual-external stimuli of heating/cooling and the addition of the competitive guest adiponitrile.

Fig. 40. (a) Supramolecular main-chain polycatenanes constructed by monofunctionalized-pillar[5]arene **61** and [2]catenane derivative **G17** via orthogonal metal-ligand coordination and host-guest interaction. Reproduced with permission from Ref. [124]. Copyright 2016 Royal Society of Chemistry; Chemical structure of (b) neutral ditopic guest **G18** and (c) 2,2'-bipyridine-bridged pillar[5]arene dimer **62**.

8.4 Self-assembly driven by Fe^{3+}

Another novel supramolecular polymer network has been constructed by monofunctionalized pillar[5]arene **63** binding with the homoditopic guest **G18** through host-guest complexation and a coordination interaction between Fe^{3+} and the catechol groups of pillararene **63** (Fig. 41) [127]. Thus, the supramolecular polymer gel ($[\text{63-Fe}^{3+}\text{-G18}] = 150 \text{ mM}$) could be obtained in $\text{CHCl}_3/\text{CH}_3\text{OH}$ ($v : v = 10:1$), and showed responsiveness to multistimuli such as pH, H_2S and temperature, owing to orthogonal non-covalent interactions.

Fig. 41. Cross-linked supramolecular polymer network constructed by monofunctionalized-pillar[5]arene **63** and guest **G18**. Reproduced with permission from Ref. [127]. Copyright 2018 Royal Society of Chemistry.

8.5 Self-assembly driven by Ag^+

Shi and co-workers reported a supramolecular polymer network gel fabricated by orthogonal Ag^+ -coordination and pillar[5]arene-based host-guest molecular recognition [128]. Firstly, a linear supramolecular polymer was prepared, driven by Ag^+ -coordination between pillar[5]arene derivative **64** containing two pyridyl groups and Ag^+ in a 1:1 stoichiometric ratio in CHCl_3 (Fig. 42a). Then, introduction of a ditopic connector **G18** led to the formation of a supramolecular polymer network, which could further gelate rapidly at a higher concentration of 30.0 mM. The obtained cross-linked supramolecular polymer network gel exhibited reversible gel-sol-gel transitions by heating and cooling. In contrast, irreversible gel-sol transition was observed upon addition of I^- due to the destruction of the supramolecular polymer **64**- Ag^+ and formation of more stable AgI .

Similarly, a H_2S and I^- dual-responsive supramolecular polymer was constructed via pillar[5]arene-based host-guest interactions and Ag^+ -coordination [129]. Mono-functionalized pillar[5]arene **65** containing only one pyridine group has high coordinating affinity towards Ag^+ (Fig. 42b), leading to

the fabrication of a pillararene dimer. Subsequent addition of another homoditopic guest **G15** in chloroform afforded the expected supramolecular polymer. The unique H₂S and I⁻ dual-stimuli responsiveness could be ascribed to the removal of Ag⁺ from the coordinated supramolecular polymer, resulting in the formation of more stable precipitates.

Fig. 42. (a) Supramolecular polymer network constructed by orthogonal Ag⁺-coordination and pillar[5]arene-based host-guest recognition. Reproduced with permission from Ref. [128]. Copyright 2017 Royal Society of Chemistry; (b) Chemical structure of neutral ditopic guest **G15** and mono-functionalized pillar[5]arene **65**.

Lee and coworkers constructed a tricyclic pillar[5]-bis-thiacrown **66** whose conformation is rigidified by dimetal coordination followed by recognition and binding of organic guests with high selectivity (Fig. 43a) [130]. The tricyclic pillararene **66** could bind with a broad range of linear dinitrile guests **G19a-f** through host-guest interactions, regardless of their lengths. However, after addition of Ag⁺ to result in the disilver(I) complex with an Ag⁺-Ag⁺ distance of 9.976 Å, the conformation changed from semi-flexible to rigid, which caused selective recognition for the guest **G19a**. The length-selective recognition could be attributed to the size-matching of **G19a** which linked two Ag⁺ centers to give a specific Ag⁺-**G19a**-Ag⁺ arrangement via Ag⁺-CN bond formation.

Considering the specific binding of linear dinitrile with two Ag⁺, a two-dimensional (2D) poly-pseudo-rotaxane was reported, self-assembled by the A1/A2-thiopyridyl copillar[5]arene **67** and

CF₃COOAg in the presence of linear dinitrile guests (Fig. 43b) [131]. The assembly was driven by an adaptive rearrangement of the components that minimizes the stereochemical crowding, not only between the threaded guests but also between the threaded and crosslinking guests. This is the first example of a 2D poly-pseudo-rotaxane in which the same guest (**G19g**) both threads and crosslinks, providing the opportunity to construct higher dimensional poly-pseudo-rotaxanes and inorganic-organic hybrid materials incorporating macrocyclic components.

Fig. 43. (a) Pillar[5]-bis-thiacrown **66** serves as an adaptive tricyclic host for selectively recognizing an organic guest by dimetalation. Reproduced with permission from Ref. [130]. Copyright 2019 John Wiley and Sons; (b) Pillar[5]arene-based two-dimensional poly-pseudo-rotaxane by threading and crosslinking by the same guest.

Reproduced with permission from Ref. [131]. Copyright 2019 John Wiley and Sons.

Despite numerous reports on supramolecular self-assembly of functionalized pillar[5]arene, the use of metal-coordination involving larger pillararenes remains very limited. In 2019, Xia *et al.* reported the first example of pillar[6]arene-based metallosupramolecular polypseudorotaxanes [132]. As shown in Fig. 44, pseudo[2]dorotaxane based on a mono(ethylene oxide) substituted pillar[6]arene **68** and a paraquat derivative guest **G20** was firstly prepared, whose energy-minimized structure confirmed that the cyano groups of guest **G20** were located outside of the cavity of **68** and were able to coordinate with metal ions. Thus, a metallosupramolecular polypseudorotaxane was formed upon addition of Ag⁺.

Fig. 44. Metallosupramolecular polypseudorotaxane constructed by Ag^+ -coordination and pillar[6]arene-based molecular recognition. Reproduced with permission from Ref. [132]. Copyright 2019 Royal Society of Chemistry.

8.6 Self-assembly driven by Pd^{2+}

Wang and coworkers reported a novel linear supramolecular polyrotaxane (Fig. 45), consisting of a pseudo[2]rotaxane formed between dimethoxypillar[5]arene **15a** host and an amide-functionalized pyridine derivative guest **G21** with Pd^{2+} (AcO^- as the counter anion) as the linkage in chloroform [133]. The resulting polyrotaxanes could further self-assemble into a supramolecular polymeric network gel at high concentration ($[\text{G21}] = 15 \text{ mM}$, $[\text{G21}]/[\text{15a}]/[\text{Pd}^{2+}] = 1:5:1$) by multiple intermolecular hydrogen bonding interactions. Interestingly, the obtained supramolecular gel showed reversible gel-sol-gel phase transitions upon heating and cooling, as well as diluting and concentrating. However, adding the competitive ligand triphenylphosphine (PPh_3) led to irreversible transformation due to the competitive binding of PPh_3 with Pd^{2+} , resulting in the destruction of the polyrotaxanes.

Fig. 45. Stimuli-responsive supramolecular polymeric network gel consisting of pillar[5]arene-based pseudo[2]rotaxanes via orthogonal Pd^{2+} -ligand coordination and multiple hydrogen bonding interactions.

Reproduced with permission from Ref. [133]. Copyright 2016 Royal Society of Chemistry.

Shi and coworkers reported a novel organo- Pd^{2+} cross-linked polymer constructed by the complexation between imidazolium-derived pillar[5]arene **69** and $\text{Pd}(\text{OAc})_2$ (Fig. 46), which could act as an excellent heterogeneous catalyst for the Suzuki-Miyaura coupling reaction [134]. This catalyst could be reused at least five times without significant loss of activity, suggesting its outstanding stability and reusability. The work shown here presents a new perspective of using pillararenes for construction of multicomponent catalytic machinery.

Fig. 46. Pillar[5]arene-based organo- Pd^{2+} cross-linked polymer for heterogeneous catalysis of Suzuki-Miyaura coupling reaction.

1

2 Huang and co-workers prepared a $\text{Pd}_2\text{Ligand}_4$ metallacage $[\text{Pd}_2 \cdot \mathbf{70}]_4(\text{BF}_4)_4$, containing four
 3 appendant pillar[5]arene units by utilizing dynamic metal coordination (Fig. 47). The metallacage
 4 could further self-assemble into a cross-linked supramolecular polymer gel in chloroform solution upon
 5 addition of a ditopic guest **G18** through host-guest interactions [135]. The obtained supramolecular gel
 6 showed temperature and acid responsivities due to the nature of the two orthogonal non-covalent
 7 interactions. Controlled release of different cargos demonstrated the ability of the supramolecular gel to
 8 differentiate emodin, which was encapsulated in the cavities of the metallacage, from methylene blue
 9 molecules that were located in the pores of the supramolecular gel.

10

11 **Fig. 47.** Crosslinked supramolecular polymer network constructed by hierarchical self-assembly of Pd^{2+} -
 12 coordination and pillar[5]arene-based host-guest interaction. Reproduced with permission from Ref. [135].

13

Copyright 2018 John Wiley and Sons.

14

15 8.7 Self-assembly driven by Pt^{2+}

16 In 2014, Yang's group reported the construction of two different sized hexakis-pillar[5]arene
 17 metallacycles by metal–ligand coordination between two linear di-Pt(II) acceptors of different length
 18 and monofunctionalized pillar[5]arene receptor **71** mounted with one dipyridyl unit (Fig. 48a) [136].

These discrete hexakis-pillar[5]arene metallacycles could be further used to construct cross-linked supramolecular polymers by host-guest interactions between the pillar[5]arene cavities and neutral ditopic guests which played an important role in “cross-linking agents”. Interestingly, the obtained supramolecular polymers could further convert to stable supramolecular gels in acetone with continuous increase of concentration to a relatively high level when special guests were used. Notably, those gels exhibited reversible gel-sol transitions stimulated by multiple stimuli such as competitive guests, temperature and halide owing to the dynamic nature of the hierarchical self-assembly involving metal-ligand coordination and host-guest interactions. For example, when bromide anions were added, gel to sol transition behavior was observed due to the dissociation of the metal-ligand bonds and formation of Pt-Br complexes. The supramolecular gels could recover after removal of the Br⁻ because of the reformation of metal-ligand bonds.

Fig. 48. (a) The self-assembled hexakis-pillar[5]arene metallacycles constructed by metal-ligand coordination between two linear di-Pt(II) acceptors and monofunctionalized pillar[5]arene **71**. Reproduced with permission from Ref. [136]. Copyright 2014 American Chemical Society; (b) Two novel supramolecular metallogels constructed by Pt²⁺-coordination and pillar[5]arene-based host-guest interactions. Reproduced with permission from Ref. [137]. Copyright 2017 Royal Society of Chemistry.

After changing the monofunctionalized pillar[5]arene receptor **71** to A1/A2-copillar[5]arene derivative **72** bearing two pyridyl groups, two kinds of Pt²⁺ acceptors (180° organic di-Pt(II) and 120° tri-arm Pt(II)) were introduced to coordinate with **72** to afford linear or 2D supramolecular polymers (Fig. 48b) [137]. Upon addition of neutral guest **G22**, two 3D cross-linked networks were obtained, which further self-assembled into supramolecular metallogels *via* host-guest interaction and metal coordination. These two supramolecular metallogels not only exhibited distinct rheological behaviors but also showed external stimuli-induced gel-sol transitions. The stimuli investigated were heating and cooling or addition of a competitive guest such as tetrabutylammonium bromide (TBABr) or silver trifluoromethanesulfonate (AgOTf).

Subsequently, Yang and coworkers reported a organometallic [2]rotaxane constructed from per-ethyl functionalized pillar[5]arene **15b** and an organic axle tethered with a platinum-acetylide capping stopper (Fig. 49) [138]. The organometallic [2]rotaxane showed dimethylsulfoxide (DMSO) or acetate anion stimulus-switchable properties due to the competitive hydrogen bonding between the urea moiety and DMSO, acetate as well as the ethoxy group of pillararene macrocycle. More importantly, rotaxane-branched dendrimers, containing 21 switchable [2]rotaxane moieties located on each branch, were successfully obtained through a triple deprotection-coupling process, which also exhibited amplified reversible switching responsiveness upon solvent or anion external stimuli. This work paved a new way for in-depth investigation of rotaxane dendrimers as dynamic supramolecular materials. Subsequently, after preparing a fourth generation dendrimer through a similarly controllable divergent approach, a new family of Type III-C rotaxane-branched dendrimers was successfully constructed with 45 switchable [2]rotaxane units dispersing within the dendrimer skeleton, which is regarded as the largest member of the proposed rotaxane-branched dendrimer family [139]. Importantly, the Type III-C rotaxane-branched dendrimers also showed AcO⁻-induced dimension modulation features as indicated by a collective expansion–contraction motion on each branch.

Fig. 49. Rotaxane-branched dendrimers based on [2]rotaxane upon the addition or removal of external solvent and acetate anion stimuli.

In 2018, Champness's group reported restricted shuttling [2]rotaxanes constructed by metal coordination to rod-like imidazolium salts *via* metal-carbene bonds [140]. A series of [2]rotaxanes **73a-c** composed of permethylpillar[5]arene **15a** and bis-imidazolium rods with varying lengths were primarily prepared in high yields, and were further used as proligands for N-heterocyclic carbenes and effective coordination to Ag⁺ and Pd²⁺ at either end of the rod (Fig. 50). More importantly, the shuttling behaviour of the pillar[5]arene **15a** along the full length of the rod could be restricted to the centre of the rod as a result of Ag⁺ and Pd²⁺ coordination. Specifically for **73a**, mono-Pt²⁺-metalation could be observed by reaction of the corresponding Ag⁺-coordinated [2]rotaxane with Pd(CH₃CN)₂Cl₂ probably due to the shorter linker between the two imidazolium groups which does not allow two sterically bulky Pd²⁺ complexes and the pillar[5]arene on the same rod. Ulteriorly, the Ag⁺-coordinated [2]rotaxanes can be reacted with trifluoroacetic acid, removing the Ag-carbene species to recreate the parent [2]rotaxane. This work provides a simple approach to influencing and restricting shuttling motion in macrocycle-based mechanically-interlocked molecules.

Fig. 50. Metal coordination to the imidazolium rotaxanes as N-heterocyclic carbenes leads to restriction of the pillar[5]arene shuttling.

8.8 Self-assembly driven by Cr^{3+}

Yang and Wu reported a fluorescent pillar[5]arene-based coordination polymer *via* a simple hydrothermal synthesis of a dicarboxylic acid-containing copillar[5]arene **74** and chromium(III) nitrate nonahydrate [141]. The copillar[5]arene acts as the organic linker and Cr^{3+} with an octahedral spatial configuration acts as the node (Fig. 51). The obtained coordination polymer showed significant fluorescence enhancement and crystal ordering, as compared with sole copillar[5]arene and counterpart coordination polymer without pillararene rings. Intriguingly, the fluorescent coordination polymer can serve as an “on-off” fluorescence chemosensor for recognition of Fe^{3+} , acetone, and nitrophenols with highly sensitivity and selectivity. The dramatic fluorescence quenching caused by Fe^{3+} could be ascribed to ion exchange of Cr^{3+} with Fe^{3+} , and energy transfer between the sensor and Fe^{3+} as well as the interaction between Fe^{3+} and the pillar[5]arene skeleton. Acetone caused significant fluorescence quenching could be attributed to destruction of the coordination polymer and strong energy absorption in the presence of acetone solvent. The nitrophenols quenching the fluorescence may be explained by a donor-acceptor electron-transfer mechanism from the electron-rich pillar[5]arene moieties to the electron-deficient nitrophenol analytes.

Fig. 51. Fluorescent pillar[5]arene-based Cr^{3+} -coordination polymer served as a multifunctional chemosensor for the recognition of Fe^{3+} , acetone, and nitrophenols. Reproduced with permission from Ref. [141]. Copyright 2019

Royal Society of Chemistry.

8.9 Self-assembly driven by Hg^{2+}

In 2017, Wu and co-workers reported a new supramolecular polymer driven by orthogonal host-guest interaction of thymine-substituted copillar[5]arene **75** and TPE derivative **G23** together with metal-ligand coordination of **75** towards Hg^{2+} (Fig. 52) [142]. The aim was to achieve Hg^{2+} sensing and removal with one action. Copillar[5]arene **75** could tightly coordinate with Hg^{2+} through thymine- Hg^{2+} -thymine pairings, leading to the formation of linear wires. After addition of the guest **G23** to the solution, a cross-linked supramolecular polymer, which eventually wrapped into spherical nanoparticles (*ca.* 200-300 nm), was obtained in acetone solution. On the other hand, when Hg^{2+} was introduced into the pseudorotaxane **75-G23** solution which exhibited weak fluorescence, the supramolecular cross-linked **75-G23-Hg²⁺** polymer showed strong fluorescence due to the AIE of **G23**. Consequently, pseudorotaxane **75-G23** could serve as an off-on fluorescent sensor for selective recognition of Hg^{2+} with a DL of 2.3 μM . In addition, the assembled cross-linked polymer precipitate can be readily isolated by centrifugation, which could be also recycled by a simple treatment with Na_2S in acetone/dichloromethane (v/v = 15:1).

Fig. 52. Cross-linked supramolecular polymer constructed by copillar[5]arene **75** and TPE derivative guest **G23** via orthogonal Hg^{2+} -ligand coordination and host-guest interaction. Reproduced with permission from Ref. [142].

Copyright 2017 American Chemical Society.

In 2018, Lee and coworkers presented the planar-chiral inversion of pillar[5]thiacrown **76** driven by Hg^{2+} controlled by anions (Fig. 53) [143]. The bulky thiacycrown substituents hindered the rotation of aromatic units of pillar[5]arene **76**, providing the opportunity to obtain two stable enantiomers (*pS* and *pR*). The *in-pS-76* could selectively recognize Hg^{2+} to trigger the chiral inversion to *out-pR-76* (*endo*-coordination) only in the presence of ClO_4^- or NO_3^- due to its weak coordinating ability towards Hg^{2+} as compared to thiacycrown. Expectedly, the removal of Hg^{2+} upon addition of S^{2-} or anion-exchange from ClO_4^- to I^- resulted in reversible chiral inversion, highlighting the importance of the anion coordination mode. In addition, the other enantiomer *in-pR-76* also afforded identical results. This work presented the first example of chiral inversion triggered by a unique combination of metal ion and anion.

Fig. 53. Planar chiral inversion of pseudo[1]catenane-type pillar[5]thiacrown **76** triggered by Hg^{2+} -coordination and controlled by anions. Reproduced with permission from Ref. [143]. Copyright 2018 American Chemical Society.

8.10 Self-assembly driven by Th^{4+}

So far, few reports have been associated with the self-assembly driven by Th^{4+} . In 2017, Yuan and coworkers rationally designed and synthesized oxime-functionalized pillar[5]arene **77** which showed 1:1 binding mode even in the presence of excess Th^{4+} (Fig. 54) [144]. Intriguingly, the Th^{4+} -**77** complex could be further self-assembled to vesicles due to the nature of the amphiphilic mono- Th^{4+} complex which impedes the binding of a second Th^{4+} on the other rim of **77**. The vesicles could be disassembled when F^- was added to the aggregates owing to the removal of Th^{4+} from the chelated complexes by F^- , leading to insoluble ThF_4 . Intriguingly, the addition of Cu^{2+} could also disrupt the vesicles, resulting in formation of unusual heterobinuclear complexes with the homoditopic pillar[5]arene **77**. This work represents the first example of binding two different metal cations located at each of the rims of pillar[5]arene.

Fig. 54. Th^{4+} -driven self-assembled vesicle and its disassembly process in the presence of F^- or a second Cu^{2+} .

Reproduced with permission from Ref. [144]. Copyright 2017 Royal Society of Chemistry.

9. Summary and outlook

In summary, we summarized the recent advances in the past seven years in the construction of various synthetic pillararene receptors for selective recognition and binding of metal ions together with the pillararene-based supramolecular self-assembly systems driven by metal-ligand coordination. The above-mentioned examples provided strong evidence that more and more attention has been paid to the fields of pillararene-based receptors for metal ion binding. Nevertheless, many issues have not been addressed and there are extensive challenges and opportunities that ought to be noted in this emerging research field.

(a) For the guest part, it is of great importance to involve more kinds of metal ions in pillararene complexing due to the fact that there is still only a relatively small variety of metal ions that have been used until the present time. For example, the complexation of alkaline earth metal ions with pillararene-based receptors has not been explored to date. Highly selective binding affinity of certain rare earth ions has not been achieved. Only nine different metal ions have been introduced in the coordination-driven pillararene-based self-assembly. For the host part, no examples of functionalized pillar[n]arenes ($n \geq 6$) with larger sizes directly designed for metal ions recognition and binding, and their binding properties ought to be quite different (*e.g.* homo- and hetero- bimetallic and/or polymetallic complexes).

(b) In view of metal complexes, it will be interesting to design molecular switches based on pillararene-metal complexes, in which electron and energy transfer processes as well as externally

1 stimuli including electrical, magnetic, photo- and redox-responsiveness can be significantly modulated.
2 More well-defined crystal structures of pillararene-metal complexes are expected to obtain, which
3 could give a better understanding of the binding mechanism. It is also tempting to construct versatile
4 pillararene-metal complexes acting as efficient catalysts for various reactions. Hitherto, uncovering
5 potential application of pillararene-based metal complexes for physiological activity (*e.g.* antibacterial,
6 anticancer, etc.) has also not been addressed.

7 (c) In terms of pillararene-based fluorescent receptors, most reported metal ions recognition events
8 involve signaling by fluorescence on-off behavior, which is not comparable to fluorescence
9 enhancement. The recognition of metal ions shown by other fluorescence mechanisms (*e.g.* ICT, PET,
10 excimer/exciple formation or extinction, FRET) has not been reported yet in pillararene chemistry.
11 Furthermore, no near infrared (NIR) emissive fluorophores based on pillararene skeleton for metal ions
12 recognition are described although this would have distinct advantages for *in vivo* imaging. More
13 efforts should be paid towards the construction of water-soluble fluorescent receptors.

14 Undoubtedly, it can be concluded that the research area of pillararene-based receptors for specific
15 metal ion recognition and binding is still in its infancy. We firmly believe that this review may
16 contribute to facilitating new discoveries based on functionalized pillararene receptors for metal ions in
17 the near future. Therefore, great achievements can be expected with continuous and collaborative
18 efforts dedicated to the field, which will boost this emerging area to a new level.

19 20 Acknowledgments

21 The authors thank the National Natural Science Foundation of China (No. 81973460 and
22 U19A2011), the fellowship from China Scholarship Council (CSC), Sichuan Provincial Youth Science
23 and Technology Innovation Team (2016TD0006), Natural Science Foundation of Sichuan Province
24 Department of Education (No. 18ZB0184) and Foundation of Chengdu University of Traditional
25 Chinese Medicine (No. QNXZ2018012 and ZRYY1715) for financial support.

26 27 References

- [1] J. M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, Wiley-VCH, Weinheim (Germany), 1995.
- [2] (a) S.M. Yannoni, S. Hartung, A.L. Menon, M.W.W. Adams, J.A. Tainer, *Curr. Opin. Biotech.* 23 (2012) 89-95. (b) R.J. Williams, *Biol. Rev.* 28 (1953) 381-412.
- [3] (a) K.H. Thompson, C. Orvig, *Science*, 300 (2003) 936-939; (b) G. Gasser, N. Metzler-Nolte, *Curr. Opin. Chem. Biol.* 16 (2012) 84-91.
- [4] (a) M.K. Jha, A. Kumari, R. Panda, J. Rajesh Kumar, K. Yoo, J.Y. Lee, *Hydrometallurgy*, 165 (2016) 2-26. (b) Y. Yao, M. Zhu, Z. Zhao, B. Tong, Y. Fan, Z. Hua, *ACS Sustainable Chem. Eng.* 6 (2018) 13611-13627.
- [5] (a) Y. Wu, H. Pang, Y. Liu, X. Wang, S. Yu, D. Fu, J. Chen, X. Wang, *Environ. Pollut.* 246 (2019) 608-620. (b) Y. Ge, Z. Li, *ACS Sustainable Chem. Eng.* 6 (2018) 7181-7192.
- [6] (a) N.A.A. Rusman, M. Dahari, *Int. J. Hydrogen Energ.* 41 (2016) 12108-12126. (b) S.K. Lalmuan, S. Das, M. Chandrasekaran, S.K. Tamang, *Mater. Today* 4 (2017) 8167-8175.
- [7] (a) H. Wang, Q.-L. Zhu, R. Zou, Q. Xu, *Chem.* 2 (2017) 52-80. (b) Y. Cui, B. Li, H. He, W. Zhou, B. Chen, G. Qian, *Acc. Chem. Res.* 49 (2016) 483-493.
- [8] C.J. Pedersen, *J. Am. Chem. Soc.* 89 (1967) 7017-7036.
- [9] P. Wei, X. Yan, F. Huang, *Chem. Soc. Rev.* 44 (2015) 815-832.
- [10] (a) S. Shaw, J.D. White, *Chem. Rev.* 119 (2019) 9381-9426. (b) J. Liu, A.M. Kaczmarek, R. Van Deun, *Chem. Soc. Rev.* 47 (2018) 7225-7238. (c) Y. Park, Y. Kim, S. Chang, *Chem. Rev.* 117 (2017) 9247-9301. (d) Y.-Z. Zheng, G.-J. Zhou, Z. Zheng, R.E. Winpenny, *Chem. Soc. Rev.* 43 (2014) 1462-1475. (e) X.-Y. Wang, C. Avendaño, K.R. Dunbar, *Chem. Soc. Rev.* 40 (2011) 3213-3238.
- [11] (a) P.R. Sahoo, K. Prakash, S. Kumar, *Coordin. Chem. Rev.* 357 (2018) 18-49. (b) B. Kaur, N. Kaur, S. Kumar, *Coordin. Chem. Rev.* 358 (2018) 13-69. (c) W. Zhou, R. Saran, J. Liu, *Chem. Rev.* 117 (2017) 8272-8325.
- [12] L. Chen, Y. Cai, W. Feng, L. Yuan, *Chem. Commun.* 55 (2019) 7883-7898.
- [13] R.D. Hancock, *Chem. Soc. Rev.* 42 (2013) 1500-1524.
- [14] (a) S.-H. Park, N. Kwon, J.-H. Lee, J. Yoon, I. Shin, *Chem. Soc. Rev.* 49 (2020) 143-179. (b) D. Cao, Z. Liu, P. Verwilst, S. Koo, P. Jangjili, J.S. Kim, W. Lin, *Chem. Rev.* 119 (2019) 10403-10519. (c) D. Wu, L. Chen, W. Lee, G. Ko, J. Yin, J. Yoon, *Coordin. Chem. Rev.* 354 (2018) 74-97. (d) G.

- Sivaraman, M. Iniya, T. Anand, N.G. Kotla, O. Sunnapu, S. Singaravadivel, A. Gulyani, D. Chellappa, *Coordin. Chem. Rev.* 357 (2018) 50-104. (e) R. Balamurugan, J.-H. Liu, B.-T. Liu, *Coordin. Chem. Rev.* 376 (2018) 196-224. (f) D. Wu, A.C. Sedgwick, T. Gunnlaugsson, E.U. Akkaya, J. Yoon, T.D. James, *Chem. Soc. Rev.* 46 (2017) 7105-7123.
- [15] (a) Y. Yue, F. Huo, F. Cheng, X. Zhu, T. Mafireyi, R.M. Strongin, C. Yin, *Chem. Soc. Rev.* 48 (2019) 4155-4177. (b) H. Singh, K. Tiwari, R. Tiwari, S.K. Pramanik, A. Das, *Chem. Rev.* 119 (2019) 11718-11760. (c) L. You, D. Zha, E.V. Anslyn, *Chem. Rev.* 115 (2015) 7840-7892. (d) Y. Zhou, J.F. Zhang, J. Yoon, *Chem. Rev.* 114 (2014) 5511-5571.
- [16] (a) E.J. Werner, S.M. Biro, *Org. Chem. Front.* 6 (2019) 2067-2094. (b) H.H. Dam, D.N. Reinhoudt, W. Verboom, *Chem. Soc. Rev.* 36 (2007) 367-377.
- [17] (a) Q. He, G.I. Vargas-Zuniga, S.H. Kim, S.K. Kim, J.L. Sessler, *Chem. Rev.* 119 (2019) 9753-9835. (b) S. Nardis, F. Mandoj, M. Stefanelli, R. Paolesse, *Coordin. Chem. Rev.* 388 (2019) 360-405. (c) A. Jana, S. Bähring, M. Ishida, S. Goeb, D. Canevet, M. Sallé, J.O. Jeppesen, J.L. Sessler, *Chem. Soc. Rev.* 47 (2018) 5614-5645. (d) H. Lee, K.-I. Hong, W.-D. Jang, *Coordin. Chem. Rev.* 354 (2018) 46-73. (e) B. Das, J.N. McPherson, S.B. Colbran, *Coordin. Chem. Rev.* 363 (2018) 29-56. (f) I. Ling, C.L. Raston, *Coordin. Chem. Rev.* 375 (2018) 80-105. (g) Z. Liu, S.K.M. Nalluri, J.F. Stoddart, *Chem. Soc. Rev.* 46 (2017) 2459-2478.
- [18] T. Ogoshi, S. Kanai, S. Fujinami, T.-a. Yamagishi, Y. Nakamoto, *J. Am. Chem. Soc.* 130 (2008) 5022-5023.
- [19] N.L. Strutt, H. Zhang, S.T. Schneebeli, J.F. Stoddart, *Acc. Chem. Res.* 47 (2014) 2631-2642.
- [20] For selected reviews: (a) M. Xue, Y. Yang, X. Chi, Z. Zhang, F. Huang, *Acc. Chem. Res.* 45 (2012) 1294-1308. (b) T. Ogoshi, T.A. Yamagishi, Y. Nakamoto, *Chem. Rev.* 116 (2016) 7937-8002.
- [21] For selected reviews: (a) S. Fa, T. Kakuta, T.-a. Yamagishi, T. Ogoshi, *CCS Chem.* 1 (2019) 50-63. (b) T. Xiao, L. Qi, W. Zhong, C. Lin, R. Wang, L. Wang, *Mater. Chem. Front.* 3 (2019) 1973-1993. (c) T. Kakuta, T.A. Yamagishi, T. Ogoshi, *Acc. Chem. Res.* 51 (2018) 1656-1666. (d) H. Zhang, Z. Liu, Y. Zhao, *Chem. Soc. Rev.* 47 (2018) 5491-5528.
- [22] For selected reviews: (a) H. Li, Y. Yang, F. Xu, T. Liang, H. Wen, W. Tian, *Chem. Commun.* 55 (2019) 271-285. (b) C. Li, *Chem. Commun.* 50 (2014) 12420-12433.
- [23] (a) W. Si, P. Xin, Z.T. Li, J.L. Hou, *Acc. Chem. Res.* 48 (2015) 1612-1619. (b) W.-X. Feng, Z. Sun,

- M. Barboiu, *Isr. J. Chem.* 58 (2018) 1209-1218.
- [24] For selected reviews: (a) N. Song, X.Y. Lou, L. Ma, H. Gao, Y.W. Yang, *Theranostics*, 9 (2019) 3075-3093. (b) W. Feng, M. Jin, K. Yang, Y. Pei, Z. Pei, *Chem. Commun.* 54 (2018) 13626-13640. (c) C. Sathiyajith, R.R. Shaikh, Q. Han, Y. Zhang, K. Meguellati, Y.-W. Yang, *Chem. Commun.* 53 (2017) 677-696. (d) X. Wu, L. Gao, X.Y. Hu, L. Wang, *Chem. Rec.* 16 (2016) 1216-1227.
- [25] (a) J. Chen, Y. Wang, C. Wang, R. Long, T. Chen, Y. Yao, *Chem. Commun.* 55 (2019) 6817-6826. (b) K. Jie, Y. Zhou, E. Li, F. Huang, *Acc. Chem. Res.* 51 (2018) 2064-2072. (c) N. Song, T. Kakuta, T.-a. Yamagishi, Y.-W. Yang, T. Ogoshi, *Chem*, 4 (2018) 2029-2053.
- [26] D. Cao, Y. Kou, J. Liang, Z. Chen, L. Wang, H. Meier, *Angew. Chem. Int. Ed.* 48 (2009) 9721-9723.
- [27] X.B. Hu, Z. Chen, L. Chen, L. Zhang, J.L. Hou, Z.T. Li, *Chem. Commun.* 48 (2012) 10999-11001.
- [28] T. Ogoshi, N. Ueshima, F. Sakakibara, T.A. Yamagishi, T. Haino, *Org. Lett.* 16 (2014) 2896-2899.
- [29] (a) S. Mirzaei, D. Wang, S.V. Lindeman, C.M. Sem, R. Rathore, *Org. Lett.* 20 (2018) 6583-6586. (b) H. Tao, D. Cao, L. Liu, Y. Kou, L. Wang, H. Meier, *Sci. China Chem.* 55 (2012) 223-228.
- [30] T. Ogoshi, N. Ueshima, T. Akutsu, D. Yamafuji, T. Furuta, F. Sakakibara, T.A. Yamagishi, *Chem. Commun.* 50 (2014) 5774-5777.
- [31] S. Santra, I. Kovalev, D. Kopchuk, G. Zyryanov, A. Majee, V. Charushin, O. Chupakhin, *RSC Adv.* 5 (2015) 104284-104288.
- [32] M. Da Pian, O. De Lucchi, G. Strukul, F. Fabris, A. Scarso, *RSC Adv.* 6 (2016) 48272-48275.
- [33] S. Santra, D.S. Kopchuk, I.S. Kovalev, G.V. Zyryanov, A. Majee, V.N. Charushin, O.N. Chupakhin, *Green Chem.* 18 (2016) 423-426.
- [34] D. Banerjee, J.B. Parise, *Cryst. Growth Des.* 11 (2011) 4704-4720.
- [35] D.N. Shurpik, L.S. Yakimova, L.I. Makhmutova, A.R. Makhmutova, I.K. Rizvanov, V.V. Plemenkov, I.I. Stoikov, *Macroheterocycles*, 7 (2014) 351-357.
- [36] L.S. Yakimova, D.N. Shurpik, A.R. Makhmutova, I.I. Stoikov, *Macroheterocycles*, 10 (2017) 226-232.
- [37] N. Sakai, S. Matile, *Langmuir*, 29 (2013) 9031-9040.
- [38] Z. Liu, S.K.M. Nalluri, J.F. Stoddart, *Chem. Soc. Rev.* 46 (2017) 2459-2478.
- [39] W.X. Feng, Z. Sun, Y. Zhang, Y.M. Legrand, E. Petit, C.Y. Su, M. Barboiu, *Org. Lett.* 19 (2017)

1438-1441.

- [40] W. Si, Z.T. Li, J.L. Hou, *Angew. Chem. Int. Ed.* 53 (2014) 4578-4581.
- [41] (a) X.B. Hu, Z. Chen, G. Tang, J.L. Hou, Z.T. Li, *J Am Chem Soc*, 134 (2012) 8384-8387. (b) Y.-x. Shen, W. Si, M. Erbakan, K. Decker, R. De Zorzi, P.O. Saboe, Y.J. Kang, S. Majd, P.J. Butler, T. Walz, *Pro. Nat. Acad. Sci. U. S. A.* 112 (2015) 9810-9815.
- [42] P. Xin, Y. Sun, H. Kong, Y. Wang, S. Tan, J. Guo, T. Jiang, W. Dong, C.P. Chen, *Chem. Commun.* 53 (2017) 11492-11495.
- [43] P. Xin, H. Kong, Y. Sun, L. Zhao, H. Fang, H. Zhu, T. Jiang, J. Guo, Q. Zhang, W. Dong, C.P. Chen, *Angew. Chem. Int. Ed.* 58 (2019) 2779-2784.
- [44] G. Bertini, H. Gray, H.B. Gray, E. Stiefel, J.S. Valentine, E.I. Stiefel, *Biological inorganic chemistry: structure and reactivity*, University Science Books, 2007.
- [45] D.T. Quang, J.S. Kim, *Chem. Rev.* 110 (2010) 6280-6301.
- [46] J.-F. Chen, G. Meng, Q. Zhu, S. Zhang, P. Chen, *J. Mater. Chem. C*, 7 (2019) 11747-11751.
- [47] B. Hua, L. Shao, Z. Zhang, J. Liu, F. Huang, *J. Am. Chem. Soc.* 141 (2019) 15008-15012.
- [48] N.L. Strutt, S.T. Schneebeli, J.F. Stoddart, *Supramol. Chem.* 25 (2013) 596-608.
- [49] B. Jiang, W. Wang, Y. Zhang, Y. Lu, C.W. Zhang, G.Q. Yin, X.L. Zhao, L. Xu, H. Tan, X. Li, G.X. Jin, H.B. Yang, *Angew. Chem. Int. Ed.* 56 (2017) 14438-14442.
- [50] J. Aaseth, O.P. Ajsuvakova, A.V. Skalny, M.G. Skalnaya, A.A. Tinkov, *Coord. Chem. Rev.* 358 (2018) 1-12.
- [51] (a) M. Saleem, M. Rafiq, M. Hanif, *J. Fluoresc.* 27 (2017) 31-58. (b) H.N. Kim, W.X. Ren, J.S. Kim, J. Yoon, *Chem. Soc. Rev.* 41 (2012) 3210-3244.
- [52] Y. Jia, Y. Fang, Y. Li, L. He, W. Fan, W. Feng, Y. Yang, J. Liao, N. Liu, L. Yuan, *Talanta*, 125 (2014) 322-328.
- [53] F. Zhang, J. Ma, Y. Sun, I. Boussouar, D. Tian, H. Li, L. Jiang, *Chem. Sci.* 7 (2016) 3227-3233.
- [54] J.L. Yang, Y.H. Yang, Y.P. Xun, K.K. Wei, J. Gu, M. Chen, L.J. Yang, *ACS Omega*, 4 (2019) 17903-17909.
- [55] R. Joseph, A. Asok, K. Joseph, *Spectrochim. Acta A*, 224 (2020) 117390.
- [56] P. Wei, D. Li, B. Shi, Q. Wang, F. Huang, *Chem. Commun.* 51 (2015) 15169-15172
- [57] T.-B. Wei, J.-F. Chen, X.-B. Cheng, H. Li, Q. Lin, H. Yao, Y.-M. Zhang, *RSC Adv.* 6 (2016)

65898-65901.

- [58] Y.-M. Zhang, J.-X. Su, Q. Li, W.-J. Qu, X. Zhu, Y.-L. Leng, S.-F. Xin, H. Yao, Q. Lin, T.-B. Wei, *Supramol. Chem.* 29 (2017) 411-416.
- [59] Y. Zhang, J. Su, Q. Li, W. Li, G. Liang, H. Li, H. Ma, Q. Lin, H. Yao, T. Wei, *Chinese J. Chem.* 34 (2016) 1263-1267.
- [60] W. Zhu, H. Fang, J.-X. He, W.-H. Jia, H. Yao, T.-B. Wei, Q. Lin, Y.-M. Zhang, *New J. Chem.* 42 (2018) 11548-11554.
- [61] X.-Q. Ma, Y. Wang, T.-B. Wei, L.-H. Qi, X.-M. Jiang, J.-D. Ding, W.-B. Zhu, H. Yao, Y.-M. Zhang, Q. Lin, *Dyes Pigments* 164 (2019) 279-286.
- [62] T.-B. Wei, X.-B. Cheng, H. Li, F. Zheng, Q. Lin, H. Yao, Y.-M. Zhang, *RSC Adv.* 6 (2016) 20987-20993.
- [63] (a) J. Xu, A. Gulzar, P. Yang, H. Bi, D. Yang, S. Gai, F. He, J. Lin, B. Xing, D. Jin, *Coordin. Chem. Rev.* 381 (2019) 104-134. (b) T.I. Kostelnik, C. Orvig, *Chem. Rev.* 119 (2019) 902-956. (c) A. Gautam, P. Komal, *Coordin. Chem. Rev.* 376 (2018) 393-404. (d) M.T. Kaczmarek, M. Zabiszak, M. Nowak, R. Jastrzab, *Coordin. Chem. Rev.* 370 (2018) 42-54. (e) J. Liu, A.M. Kaczmarek, R. Van Deun, *Chem. Soc. Rev.* 47 (2018) 7225-7238. (f) L. Sun, R. Wei, J. Feng, H. Zhang, *Coordin. Chem. Rev.* 364 (2018) 10-32. (g) M.L. Aulsebrook, B. Graham, M.R. Grace, K.L. Tuck, *Coordin. Chem. Rev.* 375 (2018) 191-220. (h) D.C. Schmitt, B.L. Drake, G.T. McCandless, J.Y. Chan, *Acc. Chem. Res.* 48 (2015) 612-618.
- [64] A. Leoncini, J. Huskens, W. Verboom, *Chem. Soc. Rev.* 46 (2017) 7229-7273.
- [65] F.T. Edelmann, J.H. Farnaby, F. Jaroschik, B. Wilson, *Coordin. Chem. Rev.* 398 (2019) 113005.
- [66] Y. Fang, L. Wu, J. Liao, L. Chen, Y. Yang, N. Liu, L. He, S. Zou, W. Feng, L. Yuan, *RSC Adv.* 3 (2013) 12376-12383.
- [67] B. Bai, Y. Fang, Q. Gan, Y. Yang, L. Yuan, W. Feng, *Chinese J. Chem.* 33 (2015) 361-367.
- [68] X. Yuan, Y. Cai, L. Chen, S. Lu, X. Xiao, L. Yuan, W. Feng, *Sep. Purif. Technol.* 230 (2020) 115843.
- [69] Y. Fang, X. Yuan, L. Wu, Z. Peng, W. Feng, N. Liu, D. Xu, S. Li, A. Sengupta, P.K. Mohapatra, L. Yuan, *Chem. Commun.* 51 (2015) 4263-4266.
- [70] A. Sengupta, Y. Fang, X. Yuan, L. Yuan, *J. Lumin.* 166 (2015) 187-194.
- [71] S.A. Ansari, P. Pathak, P.K. Mohapatra, V.K. Manchanda, *Chem. Rev.* 112 (2012) 1751-1772.

- [72] (a) S.A. Ansari, P.K. Mohapatra, A. Leoncini, S.M. Ali, J. Huskens, W. Verboom, *Inorg. Chem.* 58 (2019) 8633-8644. (b) H. Huang, S. Ding, N. Liu, Y. Wu, D. Su, S. Huang, *Sep. Purif. Technol.* 123 (2014) 235-240. (c) P.K. Mohapatra, A. Sengupta, M. Iqbal, J. Huskens, S.V. Godbole, W. Verboom, *Dalton Trans.* 42 (2013) 8558-8562.
- [73] L. Wu, Y. Fang, Y. Jia, Y. Yang, J. Liao, N. Liu, X. Yang, W. Feng, J. Ming, L. Yuan, *Dalton Trans.* 43 (2014) 3835-3838.
- [74] A. Sengupta, L. Wu, W. Feng, L. Yuan, V. Natarajan, *J. Lumin.* 158 (2015) 356-364.
- [75] F. Javed, F. Ullah, M.R. Zakaria, H.M. Akil, *J. Mol. Liq.* 271 (2018) 403-420.
- [76] X. Sun, H. Luo, S. Dai, *Chem. Rev.* 112 (2012) 2100-2128.
- [77] C. Li, L. Wu, L. Chen, X. Yuan, Y. Cai, W. Feng, N. Liu, Y. Ren, A. Sengupta, M.S. Murali, P.K. Mohapatra, G. Tao, H. Zeng, S. Ding, L. Yuan, *Dalton Trans.* 45 (2016) 19299-19310.
- [78] A. Sengupta, X. Yuan, W. Feng, N.K. Gupta, L. Yuan, *Sep. Sci. Technol.* 52 (2017) 2767-2776.
- [79] (a) L. Chen, Y. Wang, X. Yuan, Y. Ren, N. Liu, L. Yuan, W. Feng, *Sep. Purif. Technol.* 192 (2018) 152-159. (b) S.A. Ansari, P.K. Mohapatra, L. Chen, L. Yuan, W. Feng, *Eur. J. Inorg. Chem.* 2018 (2018) 4022-4030.
- [80] A. Sengupta, P.K. Mohapatra, Y. Fang, X. Yuan, W. Feng, L. Yuan, *Sep. Purif. Technol.* 195 (2018) 224-231.
- [81] Y. Fang, C. Li, L. Wu, B. Bai, X. Li, Y. Jia, W. Feng, L. Yuan, *Dalton Trans.* 44 (2015) 14584-14588.
- [82] Y.-M. Zhang, W. Zhu, W.-J. Qu, K.-P. Zhong, X.-P. Chen, H. Yao, T.-B. Wei, Q. Lin, *Chem. Commun.* 54 (2018) 4549-4552.
- [83] J.-F. Chen, X.-B. Cheng, H. Li, Q. Lin, H. Yao, Y.-M. Zhang, T.-B. Wei, *New J. Chem.* 41 (2017) 2148-2153.
- [84] J.-F. Chen, X.-B. Cheng, H. Li, B.-B. Han, Q. Lin, Y.-M. Zhang, H. Yao, T.-B. Wei, *New J. Chem.* 41 (2017) 12707-12712.
- [85] C. Jinfa, L. Xi, H. Bingbing, D. Jindong, Z. Youming, L. Qi, Y. Hong, W. Taibao, *Chinese J. Org. Chem.* 38 (2018) 2741-2746.
- [86] J.-F. Chen, Q. Lin, H. Yao, Y.-M. Zhang, T.-B. Wei, *Mater. Chem. Front.* 2 (2018) 999-1003.
- [87] Y.-M. Zhang, Y.-F. Li, K.-P. Zhong, W.-J. Qu, H. Yao, T.-B. Wei, Q. Lin, *New J. Chem.* 42 (2018)

16167-16173.

- [88] Q. Lin, X.-M. Jiang, X.-Q. Ma, J. Liu, H. Yao, Y.-M. Zhang, T.-B. Wei, *Sensor. Actuat. B Chem.* 272 (2018) 139-145.
- [89] X.-M. Jiang, X.-J. Huang, S.-S. Song, X.-Q. Ma, Y.-M. Zhang, H. Yao, T.-B. Wei, Q. Lin, *Poly. Chem.* 9 (2018) 4625-4630.
- [90] J. Liu, Y.-Q. Fan, S.-S. Song, G.-F. Gong, J. Wang, X.-W. Guan, H. Yao, Y.-M. Zhang, T.-B. Wei, Q. Lin, *ACS Sustainable Chem. Eng.* 7 (2019) 11999-12007.
- [91] T.-B. Wei, X.-Q. Ma, Y.-Q. Fan, X.-M. Jiang, H.-Q. Dong, Q.-Y. Yang, Y.-F. Zhang, H. Yao, Q. Lin, Y.-M. Zhang, *Soft Matter.* 15 (2019) 6753-6758.
- [92] Y.-M. Zhang, Y.-F. Li, K.-P. Zhong, W.-J. Qu, X.-P. Chen, H. Yao, T.-B. Wei, Q. Lin, *Soft Matter*, 14 (2018) 3624-3631.
- [93] Q. Lin, P.-P. Mao, Y.-Q. Fan, L. Liu, J. Liu, Y.-M. Zhang, H. Yao, T.-B. Wei, *Soft Matter*, 13 (2017) 7085-7089.
- [94] Y.-M. Zhang, W. Zhu, X.-J. Huang, W.-J. Qu, J.-X. He, H. Fang, H. Yao, T.-B. Wei, Q. Lin, *ACS Sustainable Chem. Eng.* 6 (2018) 16597-16606.
- [95] Q. Lin, Y.Q. Fan, P.P. Mao, L. Liu, J. Liu, Y.M. Zhang, H. Yao, T.B. Wei, *Chem. -Eur. J.* 24 (2018) 777-783.
- [96] Y.M. Zhang, J.X. He, W. Zhu, Y.F. Li, H. Fang, H. Yao, T.B. Wei, Q. Lin, *Mater. Sci. Eng. C* 100 (2019) 62-69.
- [97] Q. Lin, F. Zheng, L. Liu, P.-P. Mao, Y.-M. Zhang, H. Yao, T.-B. Wei, *RSC Adv.* 6 (2016) 111928-111933.
- [98] Q. Lin, L. Liu, F. Zheng, P.-P. Mao, J. Liu, Y.-M. Zhang, H. Yao, T.-B. Wei, *Tetrahedron*, 73 (2017) 5307-5310.
- [99] Y.-M. Zhang, X.-P. Chen, G.-Y. Liang, K.-P. Zhong, Q. Lin, H. Yao, T.-B. Wei, *New J. Chem.* 42 (2018) 10148-10152.
- [100] H. Yao, Q. Zhou, J. Wang, Y.Y. Chen, X.T. Kan, T.B. Wei, Y.M. Zhang, Q. Lin, *Spectrochim. Acta A*, 221 (2019) 117215.
- [101] Q. Lin, K.-P. Zhong, J.-H. Zhu, L. Ding, J.-X. Su, H. Yao, T.-B. Wei, Y.-M. Zhang, *Macromolecules*, 50 (2017) 7863-7871.

- [102] Y.-M. Zhang, Y.-F. Li, H. Fang, J.-X. He, B.-R. Yong, H. Yao, T.-B. Wei, Q. Lin, *Soft Matter*, 14 (2018) 8529-8536.
- [103] X. Wang, X.-Y. Lou, X.-Y. Jin, F. Liang, Y.-W. Yang, *Research*, 2019 1454562.
- [104] T.-B. Wei, J.-F. Chen, X.-B. Cheng, H. Li, B.-B. Han, H. Yao, Y.-M. Zhang, Q. Lin, *Poly. Chem.* 8 (2017) 2005-2009.
- [105] X.-W. Guan, Q. Lin, Y.-M. Zhang, T.-B. Wei, J. Wang, Y.-Q. Fan, H. Yao, *Soft Matter*, 15 (2019) 3241-3247.
- [106] Q. Yao, B. Lu, C. Ji, Y. Cai, M. Yin, *ACS App. Mater. Interfaces*, 9 (2017) 36320-36326.
- [107] Q. Lin, X.-W. Guan, Y.-M. Zhang, J. Wang, Y.-Q. Fan, H. Yao, T.-B. Wei, *ACS Sustainable Chem. Eng.* 7 (2019) 14775-14784.
- [108] Y.M. Zhang, J.X. He, W. Zhu, W.J. Qu, Z. Zhang, H. Fang, H. Yao, T.B. Wei, Q. Lin, *Chem.-Asian J.* 14 (2019) 3274-3278.
- [109] J.-F. Chen, B.-B. Han, J.-F. Ma, X. Liu, Q.-Y. Yang, Q. Lin, H. Yao, Y.-M. Zhang, T.-B. Wei, *RSC Adv.* 7 (2017) 47709-47714.
- [110] X. Li, Z. Li, Y.W. Yang, *Adv Mater.* 30 (2018) 1800177.
- [111] A. Goswami, S. Saha, P.K. Biswas, M. Schmittl, *Chem. Rev.* (2019) DOI: 10.1021/acs.chemrev.9b00159.
- [112] Y. Sun, C. Chen, P.J. Stang, *Acc. Chem. Res.* 52 (2019) 802-817.
- [113] For selected reviews: (a) B. Li, T. He, Y. Fan, X. Yuan, H. Qiu, S. Yin, *Chem. Commun.* 55 (2019) 8036-8059. (b) G.-Y. Wu, L.-J. Chen, L. Xu, X.-L. Zhao, H.-B. Yang, *Coordin. Chem. Rev.* 369 (2018) 39-75. (c) S.-L. Li, T. Xiao, C. Lin, L. Wang, *Chem. Soc. Rev.* 41 (2012) 5950-5968.
- [114] X. Wu, L. Gao, J. Sun, X.-Y. Hu, L. Wang, *Chinese Chem. Lett.* 27 (2016) 1655-1660.
- [115] P. Wang, H. Xing, D. Xia, X. Ji, *Chem. Commun.* 51 (2015) 17431-17434.
- [116] K. Jie, Y. Zhou, B. Shi, Y. Yao, *Chem. Commun.* 51 (2015) 8461-8464.
- [117] D. Xia, P. Wang, B. Shi, *Org. Lett.* 19 (2017) 202-205.
- [118] W.-B. Hu, H.-R. Cai, W.-J. Hu, X.-L. Zhao, Y.A. Liu, J.-S. Li, B. Jiang, K. Wen, *Eur. J. Inorg. Chem.* (2017) 3551-3554.
- [119] D. Xia, L. Wang, X. Lv, J. Chao, X. Wei, P. Wang, *Macromolecules*, 51 (2018) 2716-2722.
- [120] P. Wang, B. Liang, D. Xia, *Inorg. Chem.* 58 (2019) 2252-2256.

- [121] J.-F. Chen, X. Liu, J.-F. Ma, B.-B. Han, J.-D. Ding, Q. Lin, H. Yao, Y.-M. Zhang, T.-B. Wei, *Soft Matter*, 13 (2017) 5214-5218.
- [122] J.-D. Ding, J.-F. Chen, Q. Lin, H. Yao, Y.-M. Zhang, T.-B. Wei, *Poly. Chem.* 9 (2018) 5370-5376.
- [123] X. Qian, W. Gong, X. Li, L. Fang, X. Kuang, G. Ning, *Chem. -Eur. J.* 22 (2016) 6881-6890.
- [124] H. Xing, B. Shi, *Poly. Chem.* 7 (2016) 6159-6163.
- [125] B. Shi, K. Jie, Y. Zhou, D. Xia, Y. Yao, *Chem. Commun.* 51 (2015) 4503-4506.
- [126] L. Shao, J. Yang, B. Hua, *Poly. Chem.* 9 (2018) 1293-1297.
- [127] Y. Liu, L. Shangguan, B. Shi, *Chem. Commun.* 54 (2018) 12230-12233.
- [128] Y. Liu, L. Shangguan, H. Wang, D. Xia, B. Shi, *Poly. Chem.* 8 (2017) 3783-3787.
- [129] P. Wang, J. Ma, D. Xia, *Org. Chem. Front.* 5 (2018) 1297-1302.
- [130] E. Lee, H. Ryu, H. Ju, S. Kim, J.E. Lee, J.H. Jung, S. Kuwahara, M. Ikeda, Y. Habata, S.S. Lee, *Chem. -Eur. J.* 25 (2019) 949-953.
- [131] E. Lee, I.H. Park, H. Ju, S. Kim, J.H. Jung, Y. Habata, S.S. Lee, *Angew. Chem. Int. Ed.* 58 (2019) 11296-11300.
- [132] D. Xia, X. Lv, K. Chen, P. Wang, *Dalton Trans.* 48 (2019) 9954-9958.
- [133] X. Wu, Y. Yu, L. Gao, X.-Y. Hu, L. Wang, *Org. Chem. Front.* 3 (2016) 966-970.
- [134] Y. Liu, B. Lou, L. Shangguan, J. Cai, H. Zhu, B. Shi, *Macromolecules*, 51 (2018) 1351-1356.
- [135] Y. Liu, B. Shi, H. Wang, L. Shangguan, Z. Li, M. Zhang, F. Huang, *Macromol. Rapid Commun.* 39 (2018) 1800655.
- [136] Z.Y. Li, Y. Zhang, C.W. Zhang, L.J. Chen, C. Wang, H. Tan, Y. Yu, X. Li, H.B. Yang, *J. Am. Chem. Soc.* 136 (2014) 8577-8589.
- [137] Z. Li, H. Xing, B. Shi, *Poly. Chem.* 8 (2017) 2747-2751.
- [138] X.Q. Wang, W. Wang, W.J. Li, L.J. Chen, R. Yao, G.Q. Yin, Y.X. Wang, Y. Zhang, J. Huang, H. Tan, Y. Yu, X. Li, L. Xu, H.B. Yang, *Nat. Commun.* 9 (2018) 3190.
- [139] X.Q. Wang, W.J. Li, W. Wang, J. Wen, Y. Zhang, H. Tan, H.B. Yang, *J. Am. Chem. Soc.* 141 (2019) 13923-13930.
- [140] P. Langer, L. Yang, C.R. Pfeiffer, W. Lewis, N.R. Champness, *Dalton Trans.* 48 (2018) 58-64.
- [141] M.-X. Wu, Y.-W. Yang, *Poly. Chem.* 10 (2019) 2980-2985.
- [142] H.B. Cheng, Z. Li, Y.D. Huang, L. Liu, H.C. Wu, *ACS Appl. Mater. Interfaces*, 9 (2017) 11889-

11894.

[143] E. Lee, H. Ju, I.H. Park, J.H. Jung, M. Ikeda, S. Kuwahara, Y. Habata, S.S. Lee, J. Am. Chem. Soc. 140 (2018) 9669-9677.

[144] X. Yuan, Y. Jia, Y. Cai, W. Feng, Y. Li, X. Li, L. Yuan, Chem. Commun. 53 (2017) 2838-2841.