



# Macrocycles containing azo groups: recognition, assembly and application

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Received: 29 May 2018 / Accepted: 7 July 2018 / Published online: 2 August 2018  
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## Abstract

Macrocyclic compounds play an important role in supramolecular chemistry accounting for their unique recognition and self-assembly properties and potential applications in biomedicine and material science. Azo compounds display promising capability in fields of molecular switches, polymers, smart materials and molecular machines because of their photoactive and electroactive properties. Introducing azo groups into macrocycles gives them signal moieties, additional recognition sites, photo-responsive properties, and so on. Herein, we comprehensively review the structures of azo-containing macrocyclic compounds reported up to now. Then we describe representative works on azo macrocycles with their molecular recognition, self-assembly and application emphasized.

**Keywords** Supramolecular chemistry · Macrocycles · Azo group · Molecular recognition · Self-assembly

## Introduction

Macrocyclic chemistry has become a major topic of supramolecular chemistry because of the unique recognition properties [1], serving as self-assembly building blocks [2–4] and potential applications in biomedicine [5–7], and material science [8–11]. A lot of macrocycles, typically crown ethers, cyclodextrins, calixarenes, and cucurbiturils, have been developed and investigated extensively [12]. In recent years, stimuli-responsive molecular recognition and self-assembly have gained more and more attention, and demonstrated abundant applications in various fields. Conventional stimulating modalities include temperature, pH, light, electric, enzyme, and so on. Among these stimuli, light is especially appealing for its cleanness, non-invasion and high spatiotemporal resolution [13, 14]. The most commonly used

photo-responsive molecules include azobenzene, stilbene, and spiropyran and diarylethene derivatives.

Azo compounds represent more than half of the world production of industrial dyes [15] and most of them displayed reversibly light-driven *trans*- to *cis*-isomerization. *Cis*-isomer is substantially different from *trans*-isomer in many aspects: larger dipole moment, weaker  $\pi$ - $\pi^*$  and stronger  $n$ - $\pi^*$  absorption, more bent geometry and typically less thermodynamically stable. Therefore, they have been widely used to drive photo-responsive molecular switches [16, 17], polymers [18], metal-organic materials [19], liquid crystals [20], and molecular machines [21].

Decorating azo groups on macrocycles is a convenient and powerful way to endow macrocycles with additional physical and chemical properties, such as larger cavity for efficient recognition, guest induced color change for optical sensing, and more importantly, photo-responsive switch of binding affinity, self-assembly behavior and function [22]. Several excellent reviews have summarized the progress in this field [23, 24], but no review summarized the azo-containing macrocycles comprehensively and highlighted their recognition, assembly and application. In this review, we will summarize the structures of azo-containing macrocyclic compounds reported up to now and focus our special attention on their recognition, self-assembly and application. The structure of this review will be such that we first summarize and comprehensively list the structures of different classes of

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azo macrocycles, including azo crown ether, azo cyclodextrin, azo calixarene, azo resorcinarene, azo calixpyrrole, azo benzenophane, azo porphyrin and others. Then we describe selectively a series of representative works on azo macrocycles with their molecular recognition, self-assembly and application.

## Structures of azo macrocycles

### Azo crown ethers

Crown ethers, cyclic chemical compounds containing a ring with several ether groups, are the first generation of macrocyclic compounds. In 1967, Pedersen discovered crown ethers and found their binding with alkali metal cation [25]. Crown ethers are represented as  $[m]$ crown- $n$ , where  $m$  is the total number of atoms and  $n$  is the number of oxygen atoms. Crown ethers have been applied in phase transfer catalysis, the decontamination of nuclear waste, and so on [12] (Schemes 1, 2, 3, 4, 5, 6, 7, 8, 9; Tables 1, 2, 3, 4, 5, 6, 7, 8, 9).

### Azo cyclodextrins

Cyclodextrins, the second generation of macrocyclic compounds, are cyclic oligosaccharides consisting of D-glucose units linked by  $\alpha$ -(1,4)-glucose bonds. The most common cyclodextrins consist 6, 7, and 8 glucose units, and are called  $\alpha$ -,  $\beta$ -, and  $\gamma$ -cyclodextrins, respectively. They are cylinder shaped and possess hydrophobic inner cavity and hydrophilic outer surface, resulting in their unique complex ability with a variety of lipophilic molecules [164] (Schemes 10, 11; Tables 10, 11).

### Azo calixarenes

Calixarenes are the third generation of macrocyclic compounds composed of phenolic units bridged with methylene groups at *o*-positions of phenolic hydroxyl groups. Calixarenes with  $n$  phenolic units are represented as calix[ $n$ ]arene and the most studied calixarenes have  $n = 4, 5, 6,$  and  $8$ . Calixarenes are facily modified to introduce various kinds of functional groups and to adjust cavity sizes, which have been described as having “(almost) unlimited possibilities” [213]. Properly modified calixarenes can bind with both metal ions like crown ethers, and hydrophobic molecules like cyclodextrins. A unique property of calixarene is its various conformation. The smallest calix[4]arene have four typical conformations: cone, partial cone, 1,2-alterative, 1,3-alterative [214], while other larger calixarenes have more complex conformational space (Schemes 12, 13, 14, 15, 16, 17, 18; Tables 12, 13, 14, 15, 16, 17, 18).

### Azo resorcinarenes

Resorcinarenes are a class of macrocycles which are structurally similar to calixarenes. In contrast to calixarenes, the repeat unit of resorcinarenes is resorcinol instead of phenol. Resorcinarenes with  $n$  repeat units are represented as resorcin[ $n$ ]arenes and the most studied resorcinarenes are the resorcin[4]arene [399]. In general, resorcinarenes can be synthesized by acid-catalyzed condensation of resorcinol or its derivatives with aldehyde [400]. Various methods were developed for their functionalization to synthesize sophisticated derivatives [399] (Schemes 19; Table 19).

### Azo calixpyrroles

Calixpyrroles are a class of hetero-calixarenes containing pyrrole units linked by meso-carbon bridges. Calixpyrroles can be obtained by the condensation of pyrrole and ketones. Sessler and co-workers first found they can bind anion guests [424] and be used to construct ion-pair receptors [425]. They have been utilized for sensing [426], extracting [427] and transporting [428] of anions (Scheme 20, Table 20).

### Azobenzenophanes

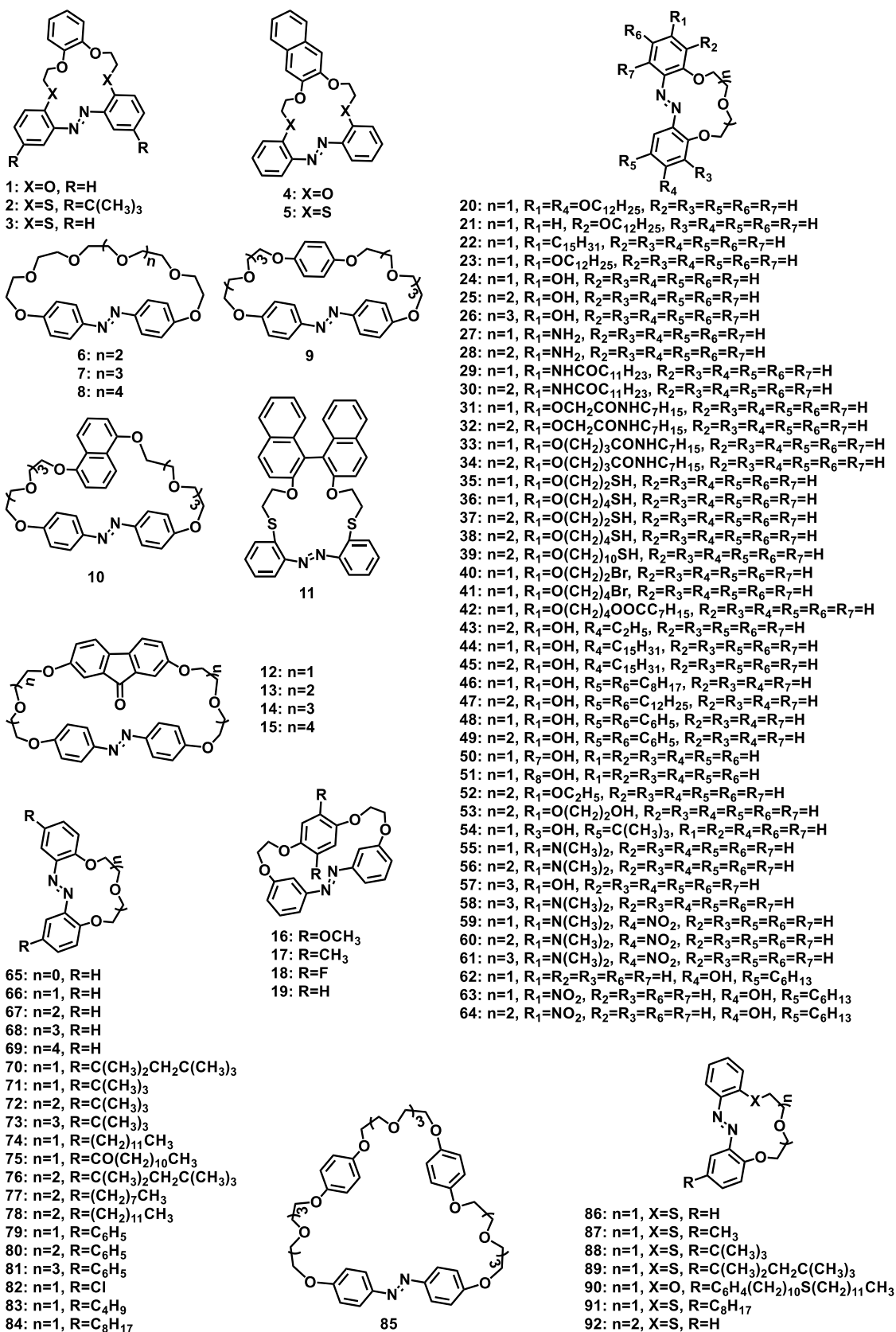
Azobenzenophanes are cyclic oligomer of azobenzenes with unique isomerization properties [22]. They have potential applications in constructing multistate switches and overcoming the instability of *Z*-isomer of azobenzene (Scheme 21, Table 21).

### Azo porphyrins

Porphyrins are a class of planar macrocycle with four pyrrolic subunits bridged by methine units. Porphyrins are involved in various biological processes, such as oxygen binding, photosynthesis and electron transfer. They are also used as photosensitizer in photodynamic therapy and artificial light harvesting system (Scheme 22, Table 22).

### Others

Although the above compounds covered most of azo macrocycles, some azo containing macrocyclic molecules not belong to derivatives of typical macrocycles. Here, we classified these compounds as others (Schemes 23, 24, 25, 26, 27; Tables 23, 24, 25, 26, 27).



Scheme 1 Structures of crown ethers with one azo group in a simple ring

**Table 1** Azo crown ethers in Scheme 1

Compound	References	Compound	References	Compound	References	Compound	References
1	[26]	24	[27–29]	47	[30]	70	[26, 31–33]
2	[34]	25	[27, 29, 30, 35]	48	[30, 36]	71	[37]
3	[34]	26	[35]	49	[30, 36]	72	[38]
4	[39]	27	[40]	50	[30]	73	[41, 42]
5	[34]	28	[40]	51	[30]	74	[33, 43]
6	[44]	29	[40]	52	[30]	75	[45]
7	[44]	30	[40]	53	[30]	76	[46]
8	[44]	31	[40]	54	[28]	77	[47]
9	[48]	32	[40]	55	[27, 29]	78	[26, 32]
10	[48]	33	[40]	56	[27, 29]	79	[36]
11	[34]	34	[40]	57	[29]	80	[36]
12	[49]	35	[50]	58	[29]	81	[41, 51]
13	[49]	36	[50]	59	[29]	82	[43, 52]
14	[49]	37	[50]	60	[29]	83	[43]
15	[49]	38	[50]	61	[29]	84	[37, 43, 46, 47, 53]
16	[54, 55]	39	[50]	62	[35]	85	[48]
17	[55]	40	[56]	63	[35]	86	[57]
18	[55]	41	[56]	64	[35]	87	[57]
19	[55]	42	[56]	65	[58]	88	[57]
20	[27]	43	[30]	66	[31]	89	[57]
21	[27]	44	[30]	67	[26, 29, 30, 32, 50, 58–65]	90	[66]
22	[27]	45	[30]	68	[29, 62–64, 67]	91	[68, 69]
23	[27]	46	[30]	69	[70]	92	[71]

## Recognition, self-assembly and application

In this section, we describe selectively the following 30 representative works on azo-containing macrocycles to demonstrate their recognition, self-assembly and application.

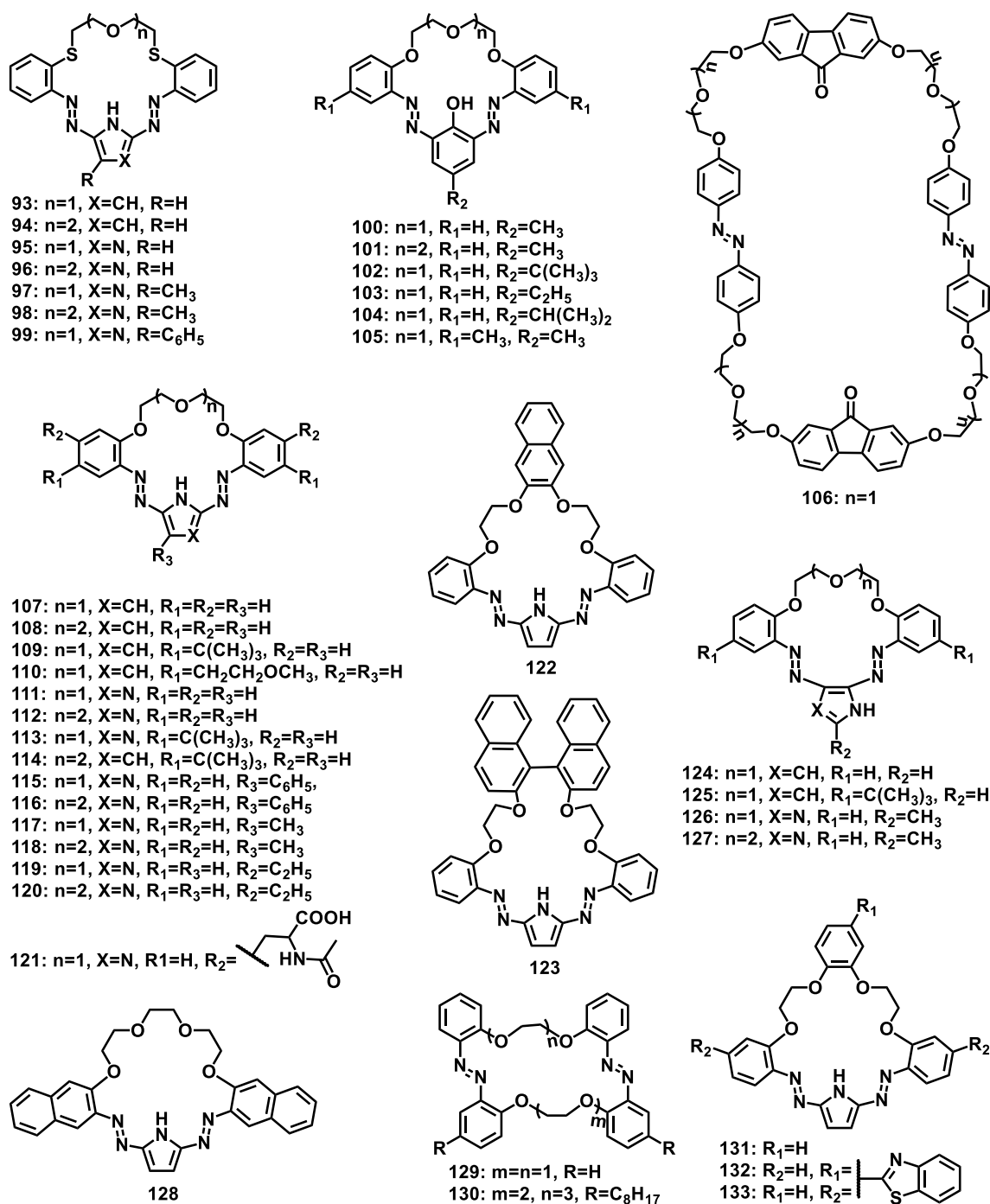
### Recognition

Early in 1979, Ueno et al. reported an azobenzene-capped  $\beta$ -cyclodextrin ( $\beta$ -CD) that can regulate the 1:2 host–guest complexation and its binding ability by *cis/trans* photoisomerization of azobenzene in response to light stimulus (Fig. 1) [191]. Reaction of  $\beta$ -CD with 4,4'-bis(chlorocarbonyl)-*trans*-azobenzene afforded compound **349** (see Scheme 10) in 20% yield. Upon irradiation, **349** was converted into its *cis*-isomer with a much larger cavity. For most of tested aromatic and olefinic guests, the cavity of *cis*-isomer is large enough to encapsulate two guests. All tested guests show higher binding affinities with the *cis*-isomer than with the *trans*-isomer. The most striking feature took place in binding 4,4'-bipyridine. **349** cannot bind 4,4'-bipyridine when the azobenzene group is in its *trans* form. However, upon irradiation with UV light, it converts to *cis*-isomer, and then the host includes 4,4'-bipyridine in its expanded cavity, as indicated by circular dichroism

experiments. When *cis* **349** reverses to its *trans*-isomer in the dark, 4,4'-bipyridine is ejected from the cavity.

In 1992, the same group synthesized a color change indicator in acidic solution **325** (see Scheme 10) by appending one methyl red dye to 6-deoxy-6-amino- $\beta$ -CD (Fig. 2) [165]. Methyl red shows color change depending on the pH conditions. The dye moiety is included in the hydrophobic cavity of  $\beta$ -CD, which protects it from protonation. Therefore, the dye-appended  $\beta$ -CD remains yellow in acidic solution. The color change will occur when an organic guest displaces the methyl red dye from the interior of  $\beta$ -CD, which makes the dye moiety available to protonation. It should be possible to exploit the molecular recognition capability of  $\beta$ -CD to develop a range of such indicators.

In 2017, Hayashita and co-workers reported an azobenzene bearing  $\gamma$ -CD derivative **350** (see Scheme 10) for recognizing phosphoric acid derivatives (Fig. 3) [194]. Compound **350** shows high selectivity towards adenosine triphosphate (ATP) over other tested phosphoric acid derivatives: monophosphate, pyrophosphate, triphosphate, adenosine monophosphate and adenosine diphosphate. Moreover, the absorption spectrum of **350** responds to ATP specifically even if other analogues existed. The  $\text{Cu}^{2+}$  complex of compound **350** forms 1:1 complex towards ATP with binding constant  $6640 \text{ M}^{-1}$ , accompanied with remarkable blue shift



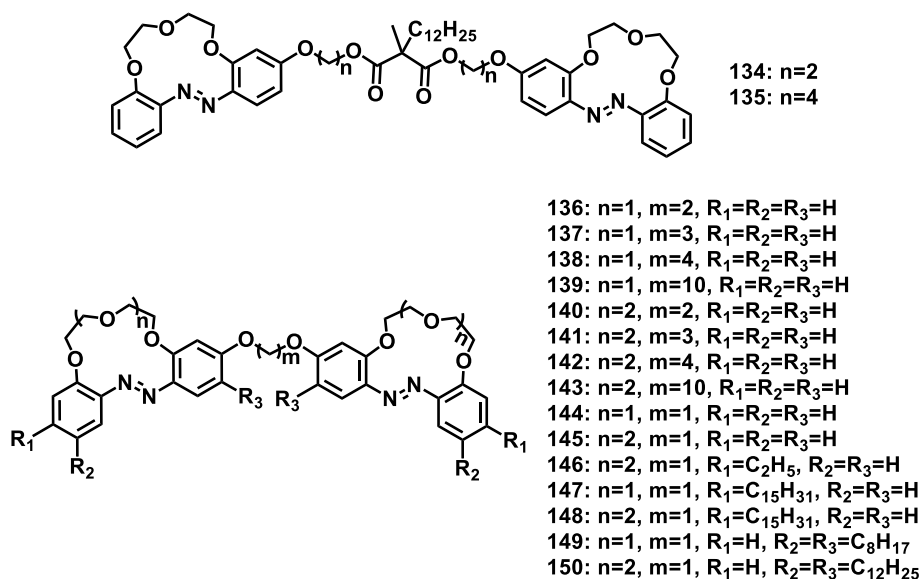
**Scheme 2** Structures of crown ethers with two azo groups in a simple ring

in the absorption spectrum.  $^1H$  NMR experiments revealed that adenine moiety of ATP existed in the  $\gamma$ -CD cavity. Dipicolylamine moiety provides additional recognition site for phosphoric groups of ATP. The cooperation of these interactions probably results in the high selectivity to ATP.

In 2006, Chun et al. reported a nitroazophenolic crown ether **219** (see Scheme 6) with asymmetric centers for enantiomeric recognition of amines [135]. Spectrophotometric method verified that the binding of amines resulted in changes of the absorption spectrum of the host, and that two

**Table 2** Azo crown ethers in Scheme 2

Compound	References	Compound	References	Compound	References	Compound	References
93	[72]	104	[73]	115	[74–76]	126	[74]
94	[72]	105	[73]	116	[75, 76]	127	[76]
95	[72, 77]	106	[49]	117	[76]	128	[78]
96	[72, 77]	107	[51, 72, 76, 79]	118	[76]	129	[80]
97	[72]	108	[72, 76, 79]	119	[76]	130	[81, 82]
98	[72]	109	[83]	120	[76]	131	[76]
99	[72, 77]	110	[83]	121	[41, 51]	132	[78]
100	[73, 84, 85]	111	[72, 74–76]	122	[76, 78, 79]	133	[78]
101	[73, 84]	112	[72, 76]	123	[78]		
102	[73]	113	[83]	124	[83]		
103	[73]	114	[79]	125	[83]		

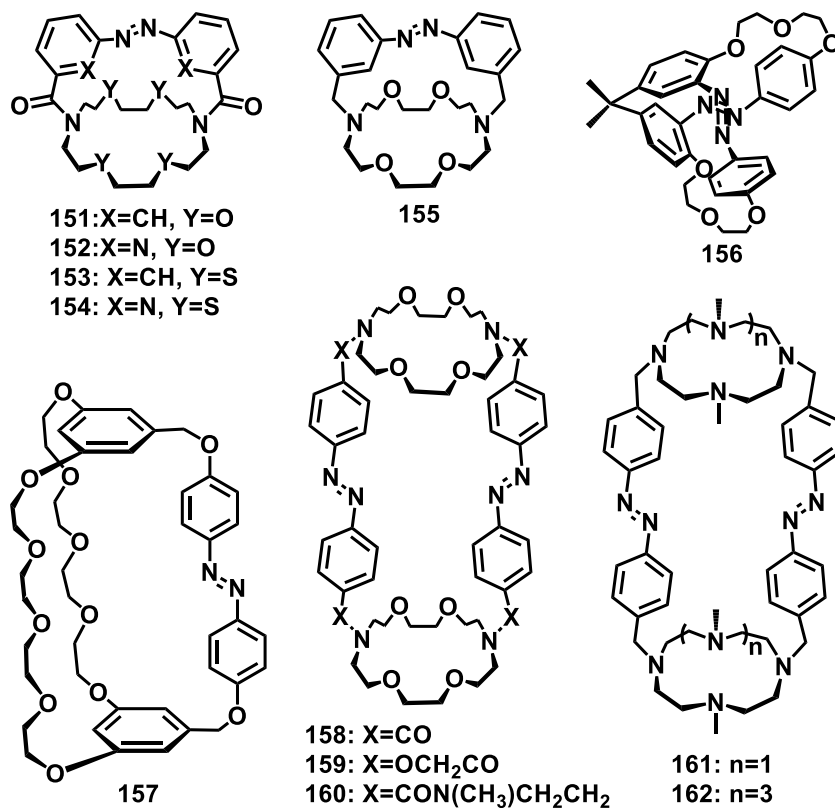
**Scheme 3** Structures of bis(crown ethers) with one azo group in a simple ring**Table 3** Azo crown ethers in Scheme 3

Compound	References	Compound	References	Compound	References	Compound	References
134	[56]	139	[86]	144	[30]	149	[30]
135	[56]	140	[86]	145	[30]	150	[30]
136	[86]	141	[86]	146	[30]		
137	[86]	142	[86]	147	[30]		
138	[86]	143	[86]	148	[30]		

enantiomers formed complexes with different stabilities. The recognition process can also be monitored by cyclic voltammetry. The oxidation of the phenol group of **219** shows a single peak at voltammograms. The addition of an alkyl amine is accompanied by a new oxidation wave at potentials that are different for each enantiomer. The difference between the oxidation potentials of the complexes formed by **219** with

two enantiomers of 2-amino-2-phenylethanol is 44 mV. This method allows quantifying the ratio of enantiomers in an R/S mixture because the peak potential of **219** varied linearly with the enantiomer ratio.

In 1998, Kim and Chang reported a calix[4]arene chromophore **928** (see Scheme 18) with two distal azophenol moieties [391]. NMR data showed **928** adopted a syn-oriented

**Scheme 4** Structures of bis(crown ethers) with azo groups in complex ring**Table 4** Azo crown ethers in Scheme 4

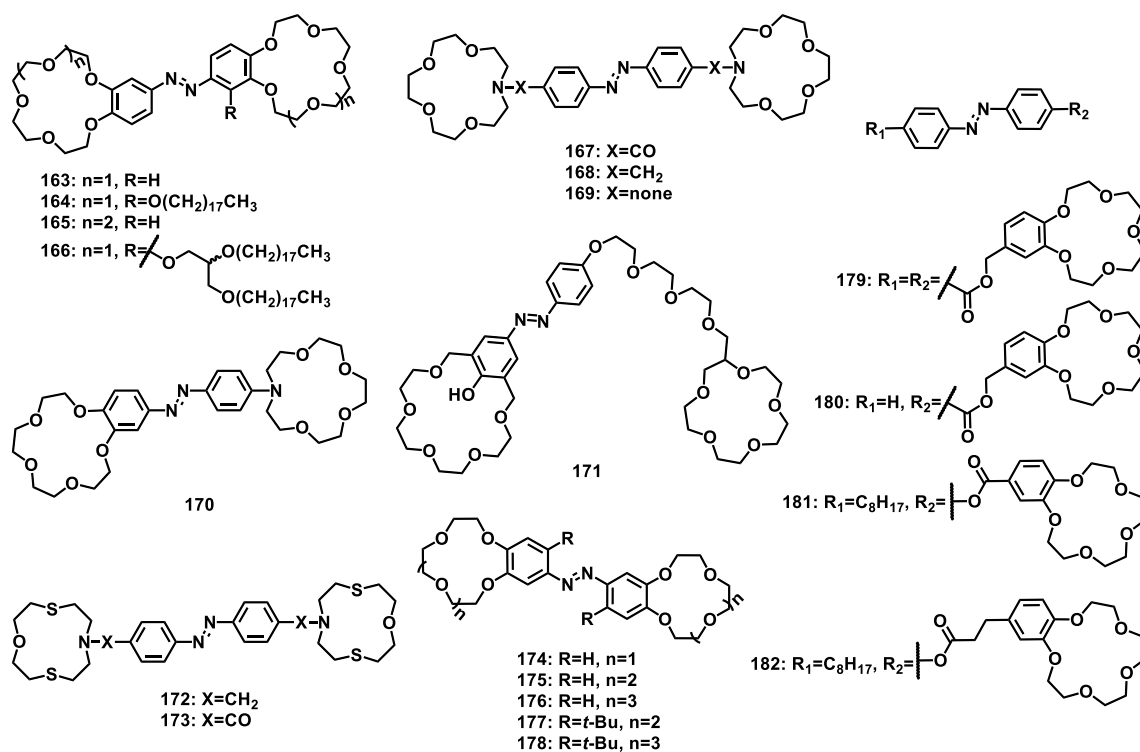
Compound	References	Compound	References	Compound	References	Compound	References
151	[87]	154	[88]	157	[89]	160	[90]
152	[88]	155	[91]	158	[92]	161	[93]
153	[88]	156	[41, 42]	159	[94]	162	[95]

conformation. Binding of Ca<sup>2+</sup> by **928** was determined by extraction between CaCl<sub>2</sub> solution at pH 7 and CHCl<sub>3</sub> contain host **928**. A bathochromic shift from 437 to 605 nm was observed (Fig. 4) and the solution color changed from yellow to greenish blue. Other similar cations induced no shift at comparable concentrations and the selectivity to Ca<sup>2+</sup> over them were 195 (Sr<sup>2+</sup>), 725 (Mg<sup>2+</sup>) and 680 (Na<sup>+</sup>). The nitrogen atoms on **928** are important for both binding at neutral condition and Ca<sup>2+</sup> selectivity.

In 2012, Pulpoka and co-workers described a selective fluoride sensor based on an azo calix[4]arene-strapped calix[4]pyrrole **473** (see Scheme 17) [269]. The color modulation of CH<sub>3</sub>CN solution of **473** was observed in the presence of certain anions, which was also reflected in distinctive absorption changes. Upon addition of six equivalents of F<sup>-</sup>, a bathochromic shift from 395 nm to about 600 nm in the absorption spectrum of **473** was observed. Other

tested anions only imparted much smaller, if not negligible, absorption changes. The spectroscopic changes upon basic anions complexation were ascribed to the modulation of charge transfer from the oxygen of azophenol moieties to the nitrophenyl chromophores. Spectroscopic analyses showed the formation of both 1:1 and 1:2 complexes for F<sup>-</sup>. By adding Ca(NO<sub>3</sub>)<sub>2</sub> into a solution of the **473**·F<sup>-</sup> complex, the F<sup>-</sup> ions were salted out in the form of CaF<sub>2</sub>, which resulted in the recovery of the original orange color of free receptor **473** (Fig. 5). In contrast, when Ca(NO<sub>3</sub>)<sub>2</sub> was added to the corresponding CH<sub>3</sub>COO<sup>-</sup>, BzO<sup>-</sup>, or H<sub>2</sub>PO<sub>4</sub><sup>-</sup> complexes, ion-pair complexes were formed without noticeable color changes.

In 1985, Kaneda et al. developed a series of novel spherand azophenol dyes **1236** (see Scheme 26), displaying Li<sup>+</sup>-specific colouration [560]. The crystal structure of **1236a** (Fig. 6), an analogue of **1236**, showed that the radius



**Scheme 5** Structures of bis(crown ethers) linked by azo group

**Table 5** Azo crown ethers in Scheme 5

Compound	References	Compound	References	Compound	References	Compound	References
163	[96]	168	[97]	173	[98]	178	[99]
164	[100]	169	[101]	174	[99]	179	[102–106]
165	[107]	170	[97]	175	[96]	180	[105]
166	[100]	171	[108]	176	[99, 109]	181	[110]
167	[97]	172	[98]	177	[99]	182	[52]

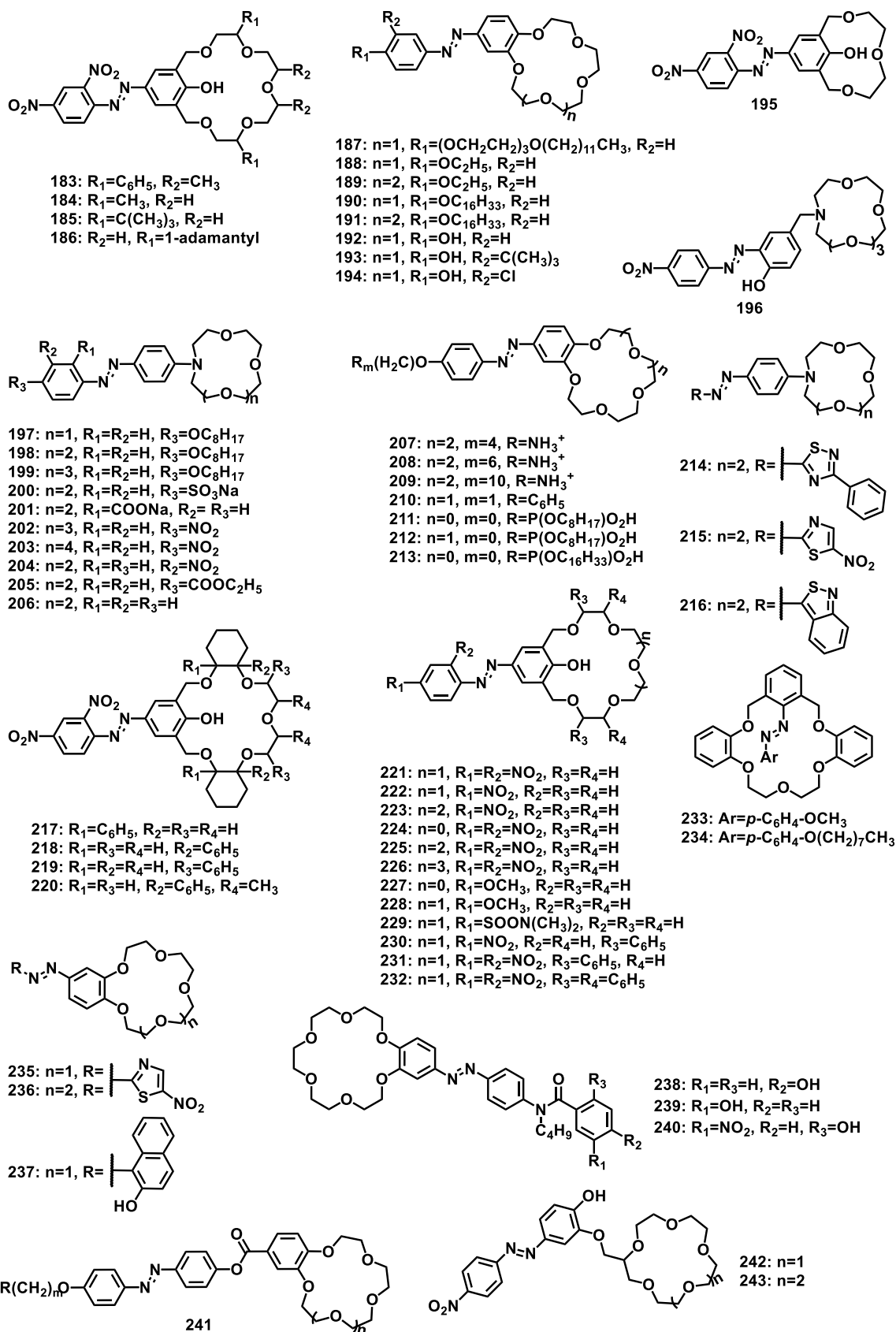
of the cavity is 0.68 Å. This radius is compatible with the ionic radius of  $Li^+$  (0.60 or 0.73 Å) and is smaller than that of  $Na^+$  (0.95 or 1.16 Å). In chloroform, only lithium salt in 63 kinds of salts leads to the change in absorption spectrum in the presence of excess piperidine as base, with a remarkable color change from yellow to violet. The “perfect” selectivity is obtained due to the steric effect caused by the narrow entrance to the cavity rejects larger cations.

In 1988, the same group studied the binding properties of azophenol crown ether **255** (see Scheme 6) containing a benzoic acid moiety [116]. The solution of **255** was yellow and showed absorption maxima at 400 nm in chloroform. Large red shift of its UV–Vis spectrum could be observed when **255** formed complexes with amines. The solution color turned to blue with monoamines while to pink with

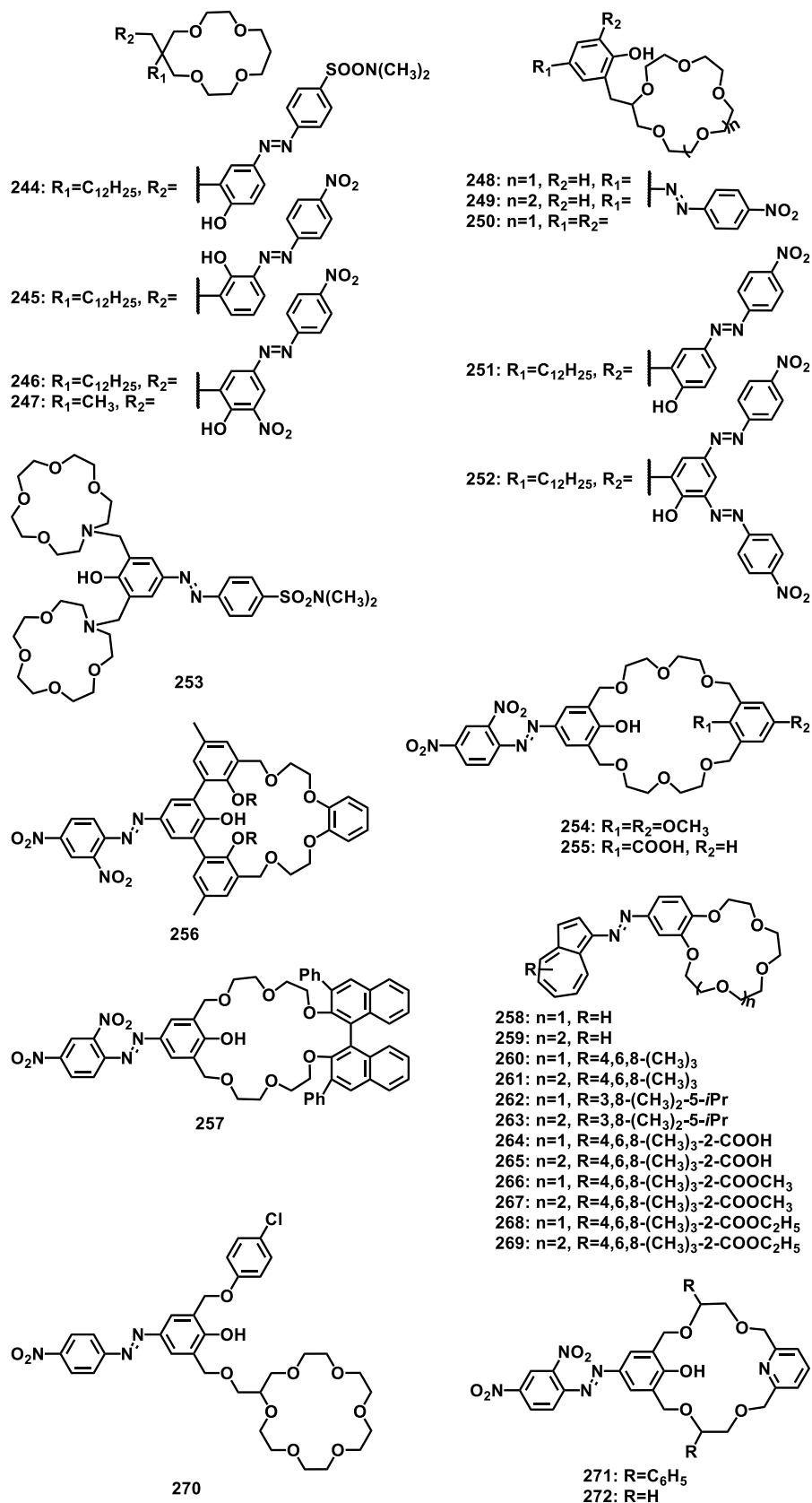
diamines, indicating a very different coloration based on the two ionic binding sites in the crown cavity. Titration experiments show that **255** forms a 1:1 complexes with some equivalents of diamines and 1:2 complexes with large excess of diamines. The molecular structure of the salt complex between **255** and piperazine was determined by X-ray crystal analysis (Fig. 7). In the **255**-piperazine complex, the protonated piperazine is sandwiched between phenolate and benzoate planes in “chair” form. Strong hydrogen bonds are formed between the phenolic oxygen atoms of **255** and the piperazine guest.

In 2011, Rebek and co-workers synthesized photoswitchable cavitands **977** and **978** (see Scheme 19) bearing the azo moiety as one of the walls [415]. The thermal- and photoisomerization behaviors of azo cavitands **977** and **978** were





Scheme 6 Structures of crown ethers with one azo group on its periphery



Scheme 6 (continued)

**Table 6** Azo crown ethers in Scheme 6

Compound	References	Compound	References	Compound	References	Compound	References
183	[111]	206	[112]	229	[108]	252	[113]
184	[111]	207	[114]	230	[115]	253	[108]
185	[111]	208	[114]	231	[115]	254	[116]
186	[111]	209	[114]	232	[117]	255	[116, 117]
187	[100]	210	[118]	233	[119]	256	[120]
188	[121, 122]	211	[123]	234	[119]	257	[124, 125]
189	[121, 122]	212	[123]	235	[101]	258	[126]
190	[52, 122]	213	[123]	236	[101]	259	[126]
191	[52]	214	[101]	237	[127]	260	[126]
192	[127]	215	[101]	238	[128]	261	[126]
193	[127]	216	[101]	239	[128]	262	[126]
194	[127]	217	[115, 129–131]	240	[128]	263	[126]
195	[54, 55]	218	[129–132]	241	[133]	264	[126]
196	[134]	219	[135]	242	[136, 137]	265	[126]
197	[138]	220	[139]	243	[136, 137]	266	[126]
198	[138]	221	[54, 140]	244	[113]	267	[126]
199	[138]	222	[141]	245	[113]	268	[126]
200	[112]	223	[141]	246	[113]	269	[126]
201	[112]	224	[54, 117, 140, 142–146]	247	[113]	270	[147, 148]
202	[101, 112, 134]	225	[54]	248	[137]	271	[149]
203	[112]	226	[54]	249	[137]	272	[117]
204	[112]	227	[108]	250	[137]		
205	[112]	228	[108]	251	[113]		

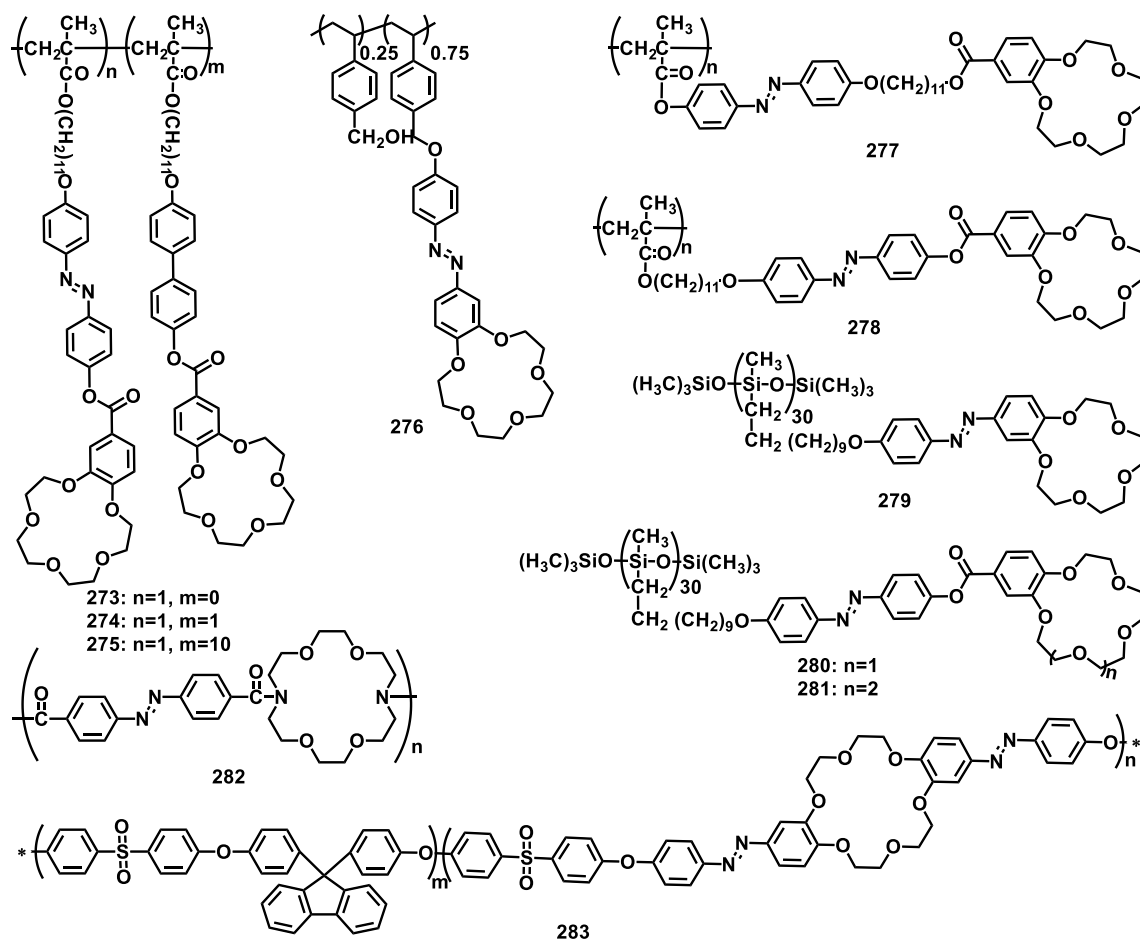
analyzed in  $d_{12}$ -mesitylene (Fig. 8). *Trans*–*cis* photo-isomerization is achieved by illuminating with 365 nm light for 15 min to reach a photostationary state. *Cis*–*trans* conversion can be achieved by heating to 164 °C for 5 min or irradiating with light longer than 450 nm for 20 min. *Trans*–*cis* and *cis*–*trans* cycles can be repeated 5 times without degradation of the system. Both the *trans*-isomers of **977** and **978** are able to bind neutral adamantane guests. The binding behaviors of *trans* azo cavitanes **977** and **978** were studied in  $d_{12}$ -mesitylene. The highest values of stability constants were observed for 1-adamantanecarbonitrile and 2-adamantanone, which can interact with the amide on the upper rim of cavitanes. The complexation of adamantane guests can be light-controlled for **978**, but not for **977** without tert-butyl substitution. This striking contrast is because the bound guest is replaced with an introverted tert-butyl.

In 2016, Scherman and co-workers described the synthesis and photo-responsive binding properties of macrocycle **1220** containing bis(imidazolium)-azobenzene motifs (Fig. 9) [553]. NMR analysis revealed macrocycle **1220** existed as all-*trans* stereoisomer in a freshly prepared trideuterioacetonitrile solution. Isomerization products generated

by irradiating UV light were a mixture of stereoisomers *E,E*-**1220** (18%), *E,Z*-**1220** (38%) and *Z,Z*-**1220** (44%). Visible light illumination causes the photostationary state *E,E*-**1220** as the main isomer. Stereoisomer *E,E*-**1220** could complex with 4,4'-dipyridyl-*N,N'*-dioxide (4DPDO), 4-phenylpyridine *N*-oxide and biphenyl-4,4'-dicarboxylate. Irradiation of the complex with UV light induced the *trans*- to *cis*-isomerization of the azo groups, resulting in the 4DPDO guest release from the cavity. Further exposure of the mixture to visible light reverts the guest encapsulation into the macrocycle cavity.

### Self-assembly

In 2008, Liu et al. used click chemistry to covalently connect the host and guest in threaded  $\beta$ -CD-based azobenzene complexes (Fig. 10) [172]. Azobenzene substituted with propargyl alcohol was coupled to azide functionalized  $\beta$ -CD, forming different isomers depending on the reaction conditions. The hydrothermal 1,3-cycloaddition led to self-locked isomer **334a** (see Scheme 10), whereas Cu(I) catalyzed click chemistry gave the self-unlocked



**Scheme 7** Structures of azo crown ethers linked with polymers

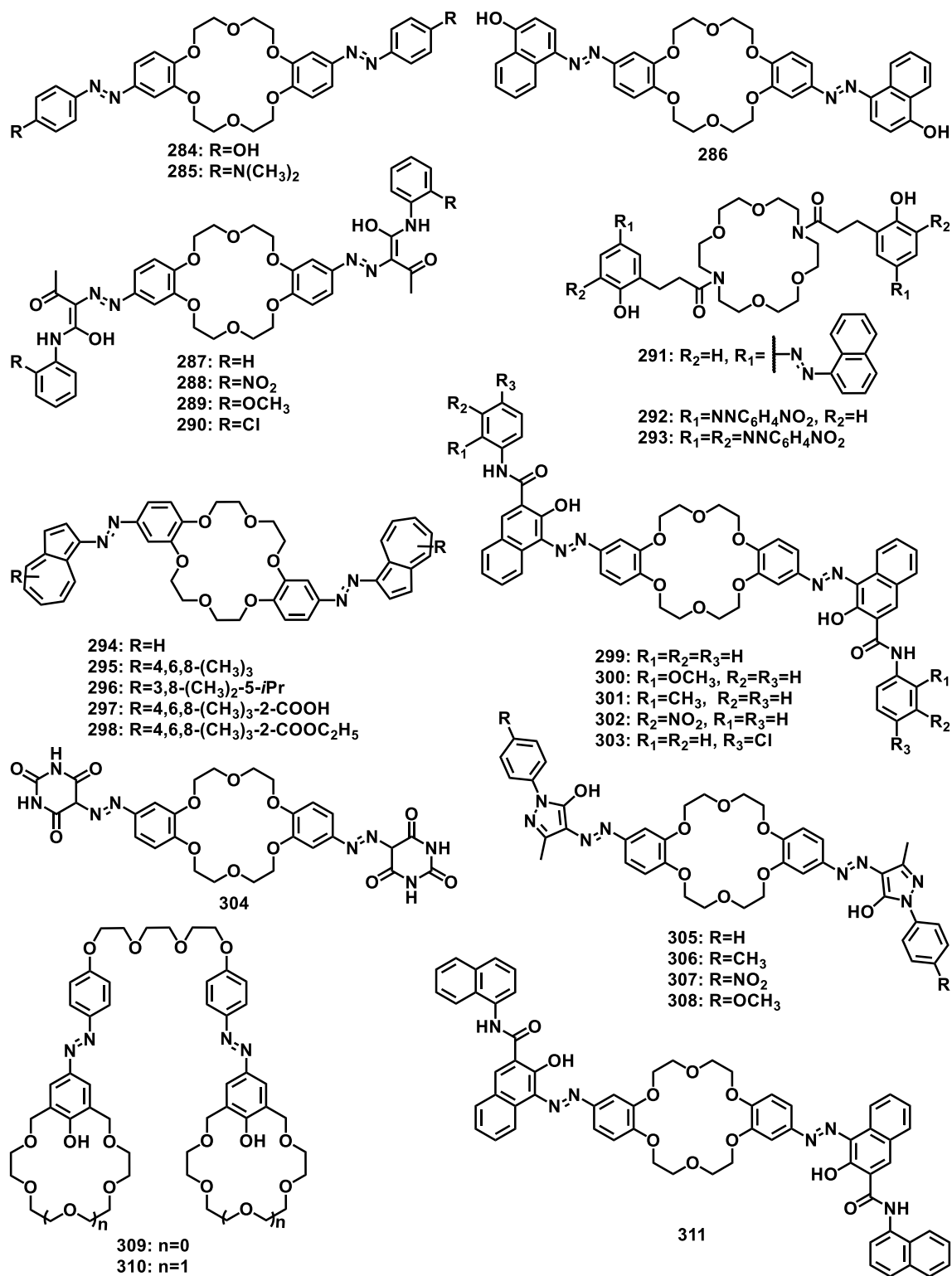
**Table 7** Azo crown ethers in Scheme 7

Compound	References	Compound	References	Compound	References	Compound	References
273	[150]	276	[118]	279	[151]	282	[152]
274	[150]	277	[153]	280	[133]	283	[154]
275	[150]	278	[153]	281	[151]		

isomer **334b**. A possible mechanism for the synthesis of **334a** involved the primary formation of the inclusion complex of  $\beta$ -CD with azobenzene, and the subsequent reaction between the azido group of  $\beta$ -CD with the ethynyl group of azobenzene. In aqueous solution and in solid state, **334a** formed dimer capsule, in which the azobenzene moieties were included by both its own cavity and the cavity of the second  $\beta$ -CD, as demonstrated by ROESY-NMR and solid state structure. In DMSO, however,  $^1\text{H}$  NMR spectroscopy shows that **334a** existed as the monomeric self-locked conformer, which could be

regarded as a new type of [1] rotaxane without a stopper. In water–DMSO mixture, **334b** assembled to linear oligomeric supramolecule, as demonstrated by high resolution TEM and FTICR-MS. The above study shows that the spatial arrangement factor can be of great importance for the self-assembling morphology.

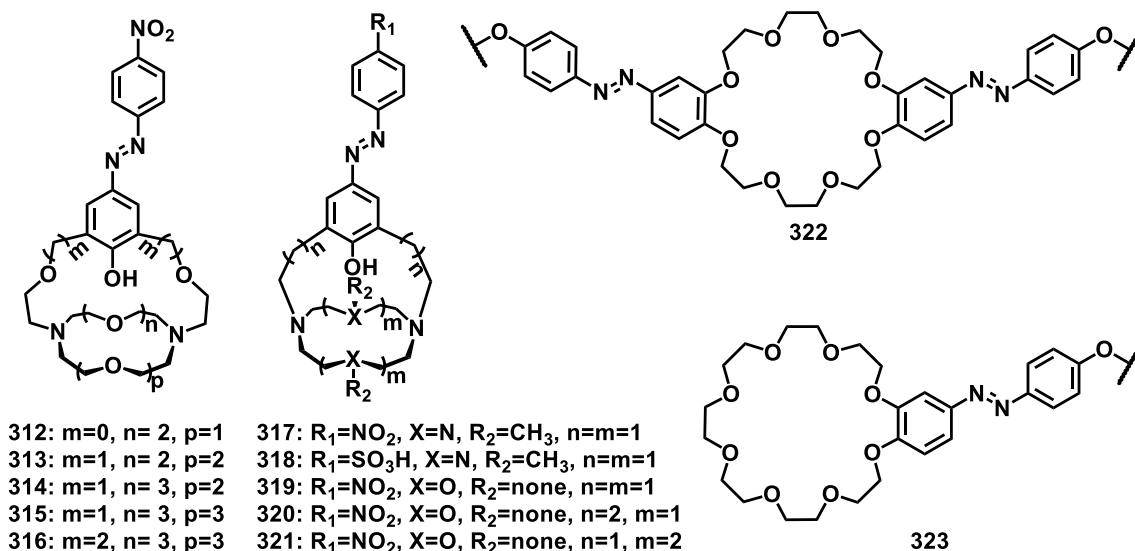
In 2015, the same group reported the photo-controlled nanotube–nanoparticle conversion for the assembly of an amphiphilic porphyrin derivative and azobenzene-bridged bis(permethyl- $\beta$ -CDs) **365** (see Scheme 11 and Fig. 11) [207]. The porphyrin derivative could form aggregates



Scheme 8 Structures of crown ethers with two azo groups on its periphery

**Table 8** Azo crown ethers in Scheme 8

Compound	References	Compound	References	Compound	References	Compound	References
284	[154, 155]	291	[127]	298	[126]	305	[156, 157]
285	[158]	292	[127]	299	[156, 157]	306	[156]
286	[155]	293	[127]	300	[156]	307	[156]
287	[157]	294	[126]	301	[156]	308	[156]
288	[156]	295	[126]	302	[156]	309	[108]
289	[156]	296	[126]	303	[156]	310	[108]
290	[156]	297	[126]	304	[156]	311	[156]

**Scheme 9** Structures of crown ethers with azo groups in complex ring**Table 9** Azo crown ethers in Scheme 9

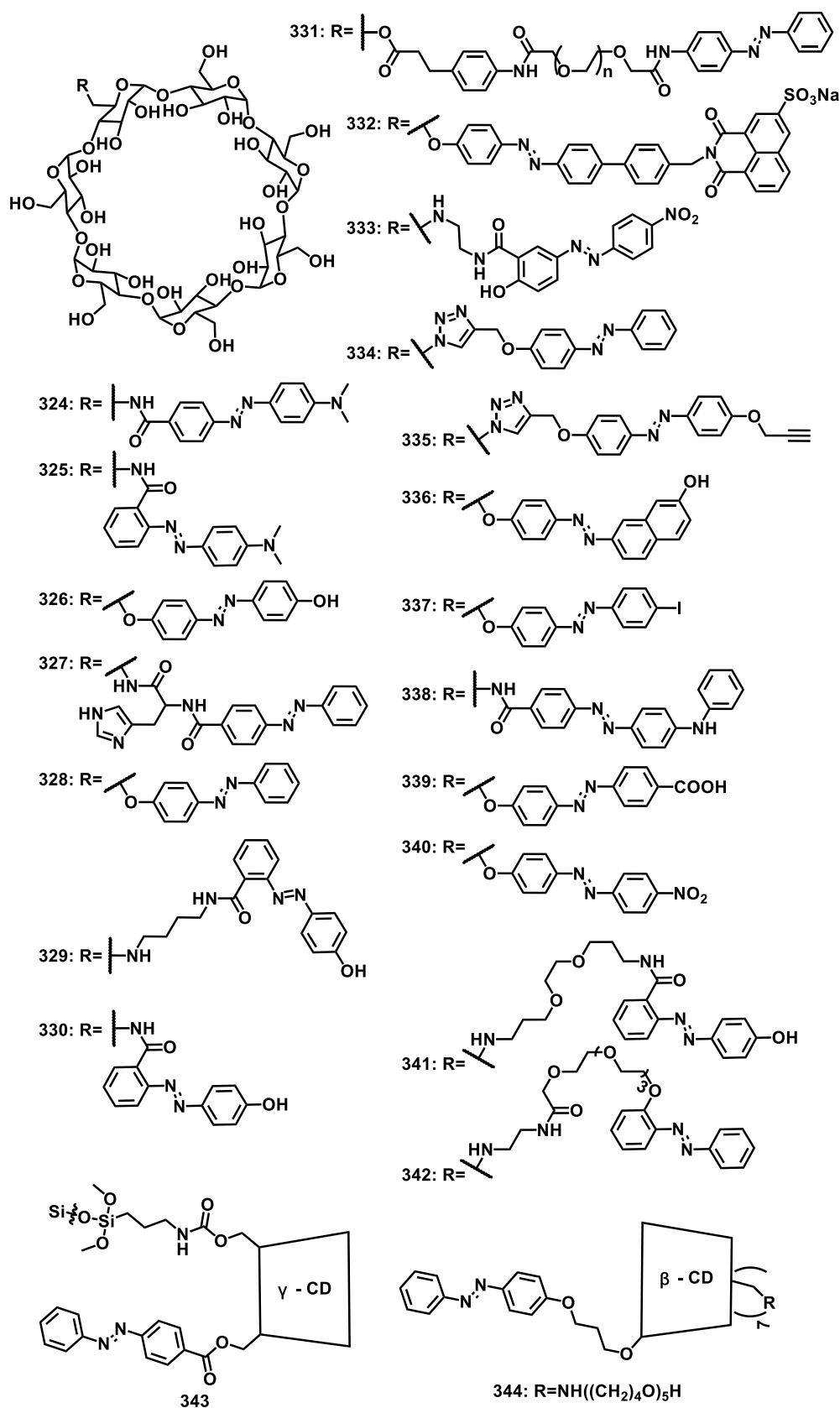
Compound	References	Compound	References	Compound	References	Compound	References
312	[141]	315	[141]	318	[159]	321	[160]
313	[141]	316	[141]	319	[160, 161]	322	[162]
314	[141]	317	[159]	320	[160]	323	[163]

with an average hydrodynamic diameter about 180 nm. Upon addition of *trans*-**365** in solution of the porphyrin derivative, the morphology of the aggregate transformed to secondary assembly nanotubes, which is revealed by TEM images. The average inner and outer diameters of the nanotubes were about 45 and 61 nm with a wall thickness of about 8 nm. Upon photoisomerization the nanotubes reversibly changed to nanospheres with the average diameter of 180–220 nm.

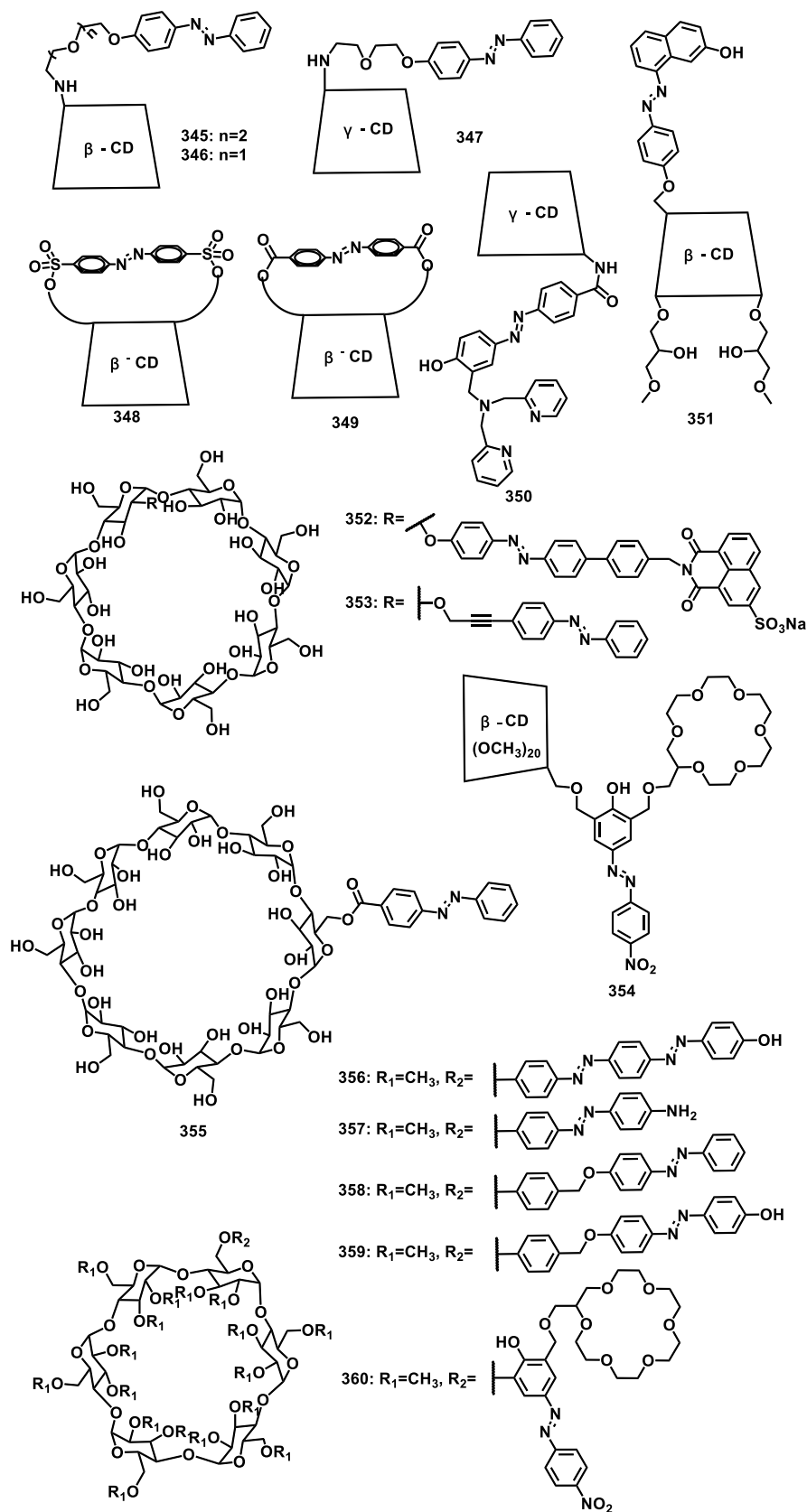
In 2013, Aseyev and co-workers synthesized polymer **443** (see Scheme 15) with azo calix[4]arene in the main chain that was substituted with tetraethylene glycol monomethyl

ether chains [254]. The poly(azo calix[4]arenes) exhibited lower critical solution temperature behavior in aqueous solution and upper critical solution temperature behavior in alcohols. In alcohols, the phase transition temperature of the polymers decreases proportionally with increasing the *cis* content by irradiating with 365 nm light. The cloud point can be modulated by irradiation or thermal relaxation depending on the *trans/cis* ratio of the azobenzene groups. The 365 nm light assisted writing on solutions of the polymer in alcohols can be realized (Fig. 12).

In 2016, Ballester and co-workers developed a heterodimeric capsule containing an azobenzene-appended calix[4]



Scheme 10 Structures of azo cyclodextrins with one host unit

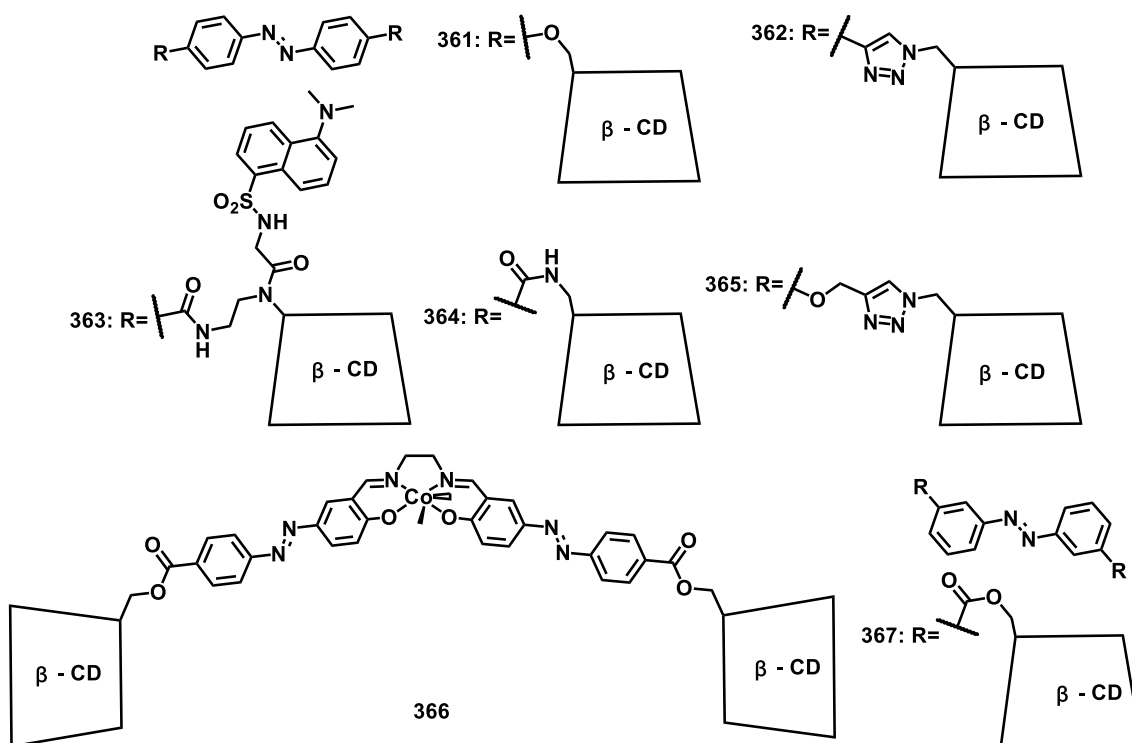


Scheme 10 (continued)

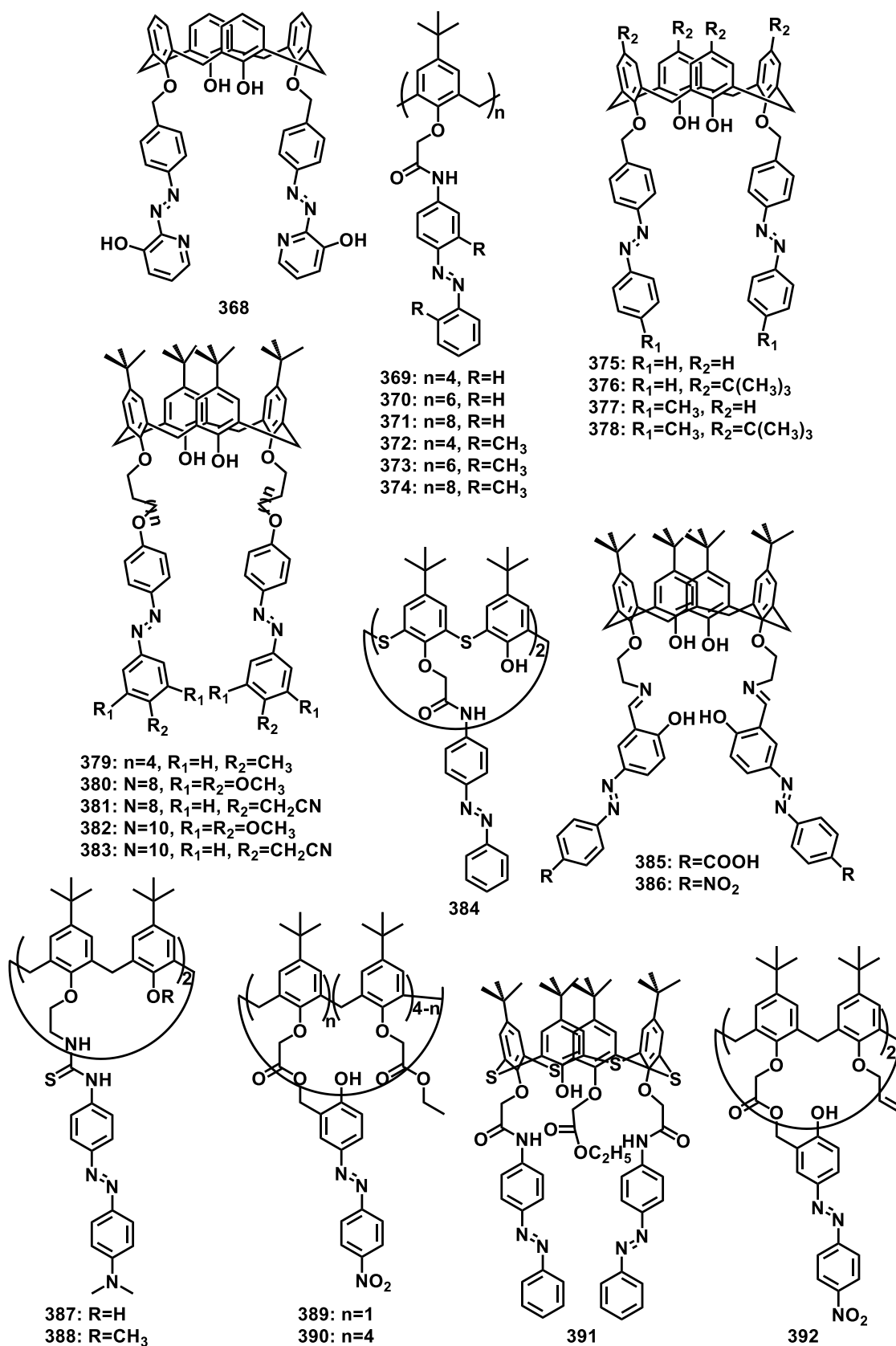


**Table 10** Azo cyclodextrins in Scheme 10

Compound	References	Compound	References	Compound	References	Compound	References
324	[165–170]	334	[171, 172]	344	[173]	354	[148]
325	[165, 166, 168, 169]	335	[171]	345	[174]	355	[175]
326	[171]	336	[176]	346	[177]	356	[178]
327	[179]	337	[180]	347	[181]	357	[182]
328	[171, 180, 183]	338	[170]	348	[184]	358	[185]
329	[186, 187]	339	[188]	349	[189–193]	359	[185]
330	[186, 187]	340	[183]	350	[194]	360	[147, 148]
331	[195]	341	[187]	351	[196]		
332	[180, 197, 198]	342	[199]	352	[198]		
333	[169, 200]	343	[201, 202]	353	[203]		

**Scheme 11** Structures of azo cyclodextrins with more than one host unit**Table 11** Azo cyclodextrins in Scheme 11

Compound	References	Compound	References	Compound	References	Compound	References
361	[171, 204, 205]	363	[206]	365	[171, 207, 208]	367	[209]
362	[210]	364	[211]	366	[212]		



Scheme 12 Structures of azo calixarenes (part 1)

**Table 12** Azo calixarenes in Scheme 12

Compound	References	Compound	References	Compound	References	Compound	References
<b>368</b>	[215]	<b>375</b>	[216]	<b>382</b>	[217]	<b>389</b>	[218]
<b>369</b>	[219]	<b>376</b>	[216]	<b>383</b>	[217]	<b>390</b>	[218, 220]
<b>370</b>	[219]	<b>377</b>	[216]	<b>384</b>	[221]	<b>391</b>	[221]
<b>371</b>	[219]	<b>378</b>	[216]	<b>385</b>	[222]	<b>392</b>	[218]
<b>372</b>	[219]	<b>379</b>	[223]	<b>386</b>	[224]		
<b>373</b>	[219]	<b>380</b>	[217]	<b>387</b>	[225]		
<b>374</b>	[219]	<b>381</b>	[217]	<b>388</b>	[226]		

arene **638** (see Scheme 18) and a tetraurea calix[4]pyrrole without azobenzene **638a** in the presence of polar guests [289]. In the presence of trimethylphosphine oxide guest, irradiating the heterodimeric capsule results in the formation of all-*cis*-**638-638a** capsule, indicating photo-isomerization in only half of capsule is not sufficient to cause the disassembly of the capsule. In a more complicated system, in which both trimethylphosphine oxide and bis-(*N*-oxide *N,N,N',N'*-tetramethylamino)hexane existed, two capsules, **638-638a** and **638a-638a**, are formed at the same time and the equilibrium between them can be modulated by light.

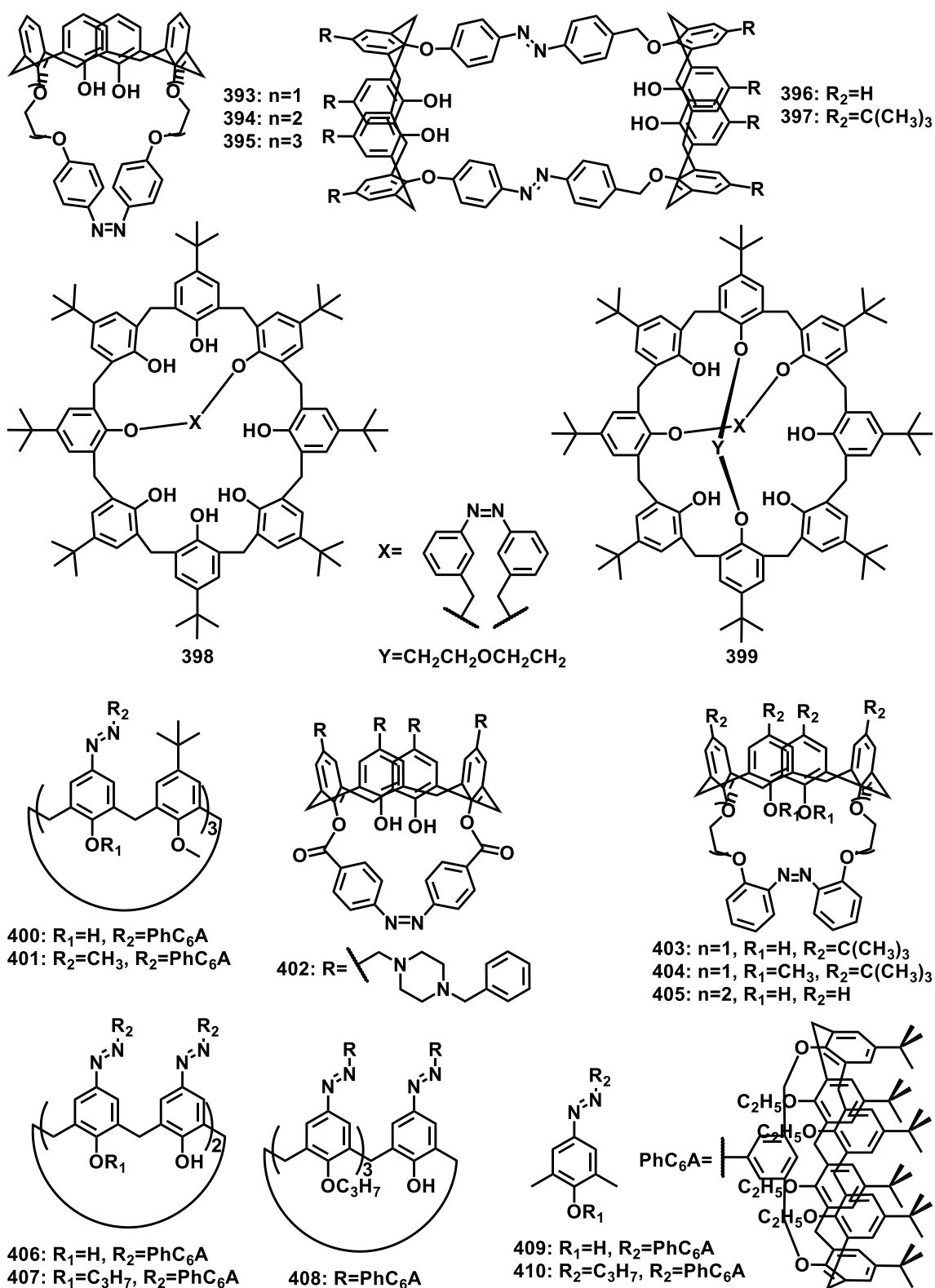
In 2014, the same group further developed a tetraurea aryl extended calix[4]pyrrole **1007** (see Scheme 20) with four azobenzene groups at the upper rim [437]. By encapsulating 4,4'-bipyridine bis-*N,N'*-oxide as a template, **1007** assembles into a hydrogen-bonded dimeric capsule (Fig. 13). The capsule can be detected by <sup>1</sup>H NMR spectroscopy in solution only when all azobenzene units are in *trans* forms. The capsule disintegrates when irradiated with 400 nm light and reassembles after *cis*-to-*trans* relaxation in the dark. They further presented photo-responsive homodimeric and heterodimeric capsules using two novel calix[4]pyrrole [433]. This study may be further developed to photo-responsive drug delivery if can operate in aqueous media.

In 2008, Gin and co-workers prepared a shape-switchable metallacycle **1259** (see Scheme 27) bearing azobenzene units via coordination-driven self-assembly [572]. The Pt containing metallacycle forms mesogen at room temperature in a thermotropic columnar liquid crystal (LC) phase, which was swollen in polar solvents (dioxane, diglyme, and ethylene glycol) to further form a lyotropic LC phase (Fig. 14). For the lyotropic LC state of unpolymerised **1259**, irradiation with 375 nm light resulted in conversion to the *cis*-isomer, accomplished by phase transition from a liquid crystalline phase to an isotropic phase. However, cross-linking the lyotropic LC assembly led to a nanostructured polymer network, preventing disruption of the LC order when photoconversion to the *cis*-isomers upon UV irradiation. The material may be useful to drug-delivery or controlled nano-filtration applications.

In 2011, Norikane et al. developed photo-responsive liquid crystallines based on azobenzenophanes **1021** and **1022** (see Scheme 21 and Fig. 15) [481]. The self-assembling material can be switched by light. In the liquid crystalline state, dimer **1021** behaves as a rod-like molecule exhibiting smectic phases, while the disk-like trimer **1022** forms columnar phases. These materials exhibit isothermal phase transition from liquid crystalline to isotropic state upon UV light irradiation because of shape change of the molecules. The liquid crystalline phase forms again upon heating the isotropic phase at 120 °C for 10 s. Such photo-responsive materials could be useful in applications to photolithography and photo-responsive adhesives.

In 2009, Wang and co-workers integrated four azobenzene units in the backbone of azobenzenophane **1015** (see Scheme 21) by connecting through intermediate carbazole groups [474]. Although **1015** does not form an extended 2D network on its own, self-assembled monolayers of host-guest networks were observed by mixing it with 1,3,5-tris(10-carboxydecyloxy)-benzene (TCDB) on a highly ordered pyrolytic graphite surface. Depending on the mixing ratio of TCDB and the macrocycle, the TCDB network captures either a monomer or a dimer of **1015**. The structures of the networks dependent on the isomers of **1015** can be distinguished by scanning tunneling microscopy, which revealed that all the azo groups are in the *trans* form (t,t,t,t). Upon irradiation of the monolayer by 366 nm light, azobenzene units of the macrocycle partially isomerize and give rise to different isomers including *trans-trans-trans-cis* (t,t,t,c) and *trans-cis-trans-cis* (t,c,t,c) isomers (Fig. 16).

In 2013, Wegner and Reuter reported an azobenzene macrocycle **1223** (see Scheme 25) displaying the light-controlled switchable  $\pi$ -stacking (Fig. 17) [482]. **1223** can form 3D networks through significant  $\pi$ -stacking interactions. Light-controlled sol-gel transition of **1223** could be observed only in aromatic solvents, because they are incorporated inside the 3D  $\pi$ -stacking network. These results suggested that



Scheme 13 Structures of azo calixarenes (part 2)

**Table 13** Azo calixarenes in Scheme 13

Compound	References	Compound	References	Compound	References	Compound	References
<b>393</b>	[227]	<b>398</b>	[228]	<b>403</b>	[229–232]	<b>408</b>	[233]
<b>394</b>	[227]	<b>399</b>	[228]	<b>404</b>	[229, 230]	<b>409</b>	[233, 234]
<b>395</b>	[227]	<b>400</b>	[233]	<b>405</b>	[235]	<b>410</b>	[233]
<b>396</b>	[216]	<b>401</b>	[233]	<b>406</b>	[233]		
<b>397</b>	[216]	<b>402</b>	[236]	<b>407</b>	[233]		

**1223** might be useful for building up materials for small molecules controlled release by light stimulation.

In 2017, Xie et al. synthesized a carbohydrate-based macrocyclic azobenzene **1272** (see Scheme 27) using one-pot *O*-alkylation mediated macrocyclization approach [574]. **1272** exhibits reversible photo-isomerization between *trans*- and *cis*-isomers upon irradiation of light with different wavelengths. Moreover, thermal stability of the *cis*-isomer ( $t_{1/2}$  = 51 days) is better than of the acyclic analogue ( $t_{1/2}$  = 19 days). Circular dichroism study revealed the chirality transfer from the sugar unit to azobenzene, which adopts preferentially P-helicity for both *trans*- and *cis*-isomers. In cyclohexane and ethanol, **1272** can form organogels, which are responsive to temperature, light and mechanical force (Fig. 18). Furthermore, **1272** displays a helical transition behavior during gelation that can be modulated by changing temperature.

## Application

Based on the exploration of recognition, self-assembly and other properties, the chemistry of azo macrocycles gives rise to several applications. Here, we highlight a few of them containing selective sensing and imaging, photocontrolled supramolecular catalysis, molecular machine, and so on.

### Azo isomerization mechanism

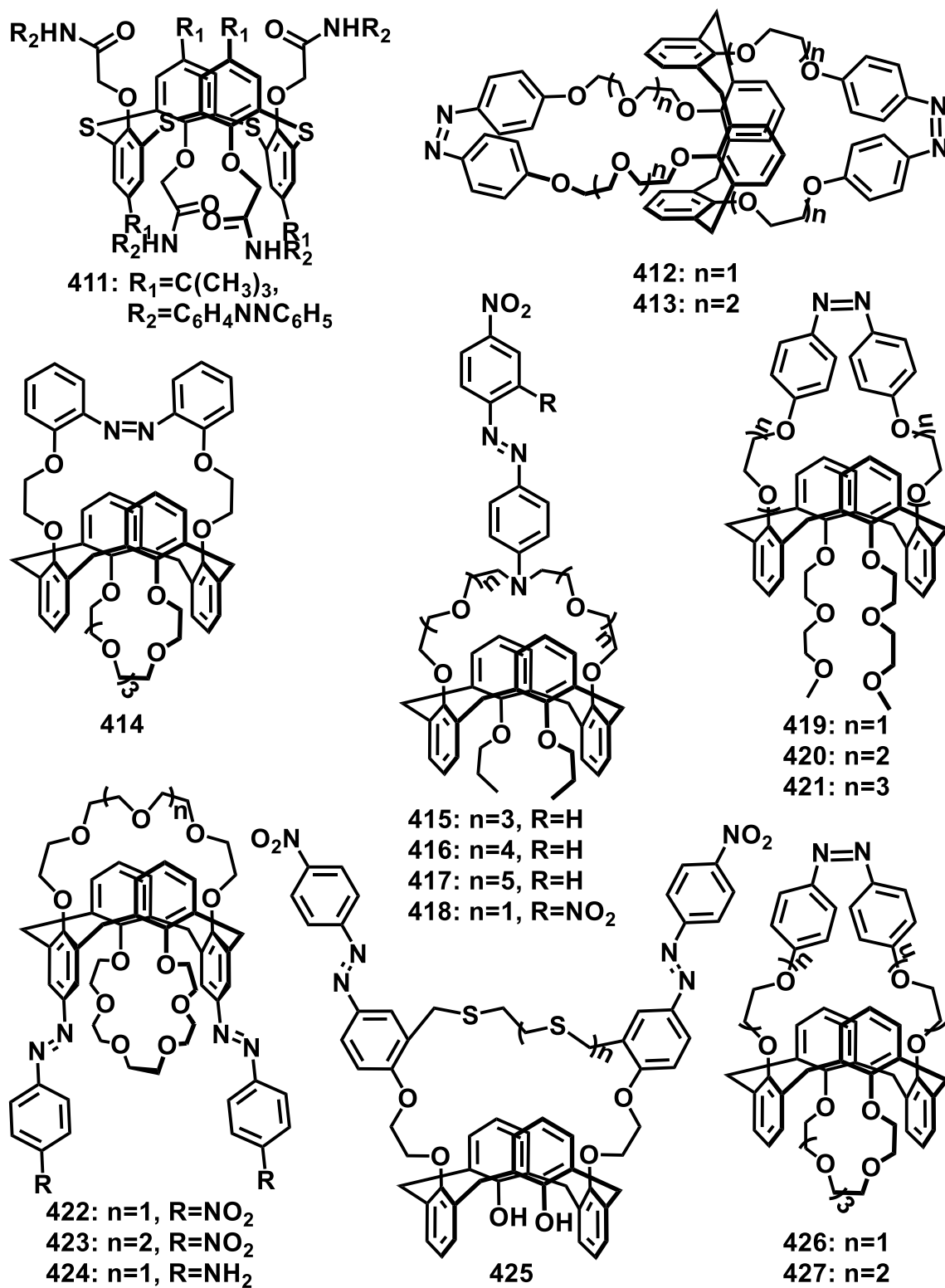
In 1982, Rau and Lueddecke synthesized two azobenzophanes **1049** and **1069** (see Scheme 21) for application in studying *trans*–*cis*-isomerization mechanism of azobenzenes [484]. For the photoisomerization, two different pathways have been proposed: a rotation around the N–N double bond and a direct inversion of the orientation of one of the phenyl rings. For the two macrocycles, inversion was the only possible isomerization pathway because of the steric hindrance. The quantum yield of the *trans*–*cis*-isomerization was 0.24 for  $n$ – $\pi^*$  excitation of **1049**, which is similar to that of azobenzene (0.23). This indicates that the *trans*–*cis*-isomerization of azobenzene under  $n$ – $\pi^*$  excitation is through an inversion mechanism.

## Sensing and imaging

Although some works involved in sensing have been described in the section of recognition, we herein discuss sensing for works closer to practical application. In 1992, Kumar and co-workers reported a small-cavity cryptand phenol **319** (see Scheme 9) which could be applied for the colorimetric determination of lithium in blood serum without sample pretreatment or solvent extraction [161]. The compound **319** exhibits a greater than 4000:1 selectivity for lithium over sodium due to rigid configuration of a well-preorganized binding site for lithium complexation. The standard curve for lithium is linear up to 3.5 mM and contains the therapeutic range. Serum was diluted 40 times for the measurement and the obtained results for serum spiked with lithium correlated well with flame photometry measurements.

In 2010, Lang and co-workers developed a pH sensor **549** (see Scheme 18) based on azo calix[4]arene bearing four carboxyl groups [319]. The crystal structure obtained in DMF solution revealed that **549** adopt a flattened cone conformation. Moreover, the aqueous solution of **549** displayed distinct color change responding to pH in the range of 1–13, which is broad than most of pH sensing compounds (Fig. 19). The color change is reversible, suggested that **549** may have a potential application as a good pH sensor.

Peoples are interested in concentrations of biological molecules, not only in tissue and body fluid but also in single cell level, in which fluorescence imaging is highly on demand. In 2016, Yilmaz and co-workers developed anthracene and pyrene appended azo calix[4]arene **666** and **667** (see Scheme 18) and applied **666** in fluorescence imaging of  $\text{Cu}^{2+}$  in living cells [355]. The azo calix[4]arenes shown selective complexation to  $\text{Cu}^{2+}$  over other metal ions, which is revealed by UV–Vis and fluorescence spectroscopies. The binding constants are calculated as  $2.34 \times 10^3$  and  $7.51 \times 10^3 \text{ M}^{-1}$  for **666** and **667**, respectively. Once incubated with **666** containing medium following  $\text{Cu}^{2+}$  treatment, the tested SW-620 cells showed obvious fluorescence (Fig. 20).



Scheme 14 Structures of azo calixarenes (part 3)

**Table 14** Azo calixarenes in Scheme 14

Compound	References	Compound	References	Compound	References	Compound	References
<b>411</b>	[221, 237]	<b>416</b>	[238]	<b>421</b>	[227]	<b>426</b>	[235, 239, 240]
<b>412</b>	[227]	<b>417</b>	[238]	<b>422</b>	[241]	<b>427</b>	[235]
<b>413</b>	[227]	<b>418</b>	[242]	<b>423</b>	[241]		
<b>414</b>	[240]	<b>419</b>	[227]	<b>424</b>	[241]		
<b>415</b>	[238]	<b>420</b>	[227]	<b>425</b>	[243]		

## Devices

In 1992, Tamaoki et al. synthesized and studied the isomerizations of azobenzenophane **1013** (see Scheme 21) in polycarbonate films through spectrophotometry [462]. The efficiency of photoisomerization of **1013** is dependent on the light intensity both in solution and on polymer film. This unique feature can be applied in the construction of photochromic memory with non-destructive read-out property (Fig. 21). The memory was written and read-out by exposure to 366 nm light at 5 mW cm<sup>-2</sup> and 20 μW cm<sup>-2</sup>, respectively. The memory can be initialized by irradiating with light of wavelength longer than 450 nm.

In 2006, Rouis et al. elaborated organic diodes based on sandwiching azo calix[4]arene layers between indium-thin oxide and Al contacts [282]. Optical and electrical properties of these devices were studied by current–voltage characteristics and electrical impedance spectroscopy in a wide frequency range. These materials displayed characteristic of semiconductors with energy band gaps in the range of 1.7–3 eV and the electrical characteristics follow a space charge limited conduction behavior. Authors also determined and fitted the relaxation frequencies of the hopping charge carriers.

## Photocontrolled supramolecular catalysis

In 2003, Cacciapaglia et al. devised a photoswitchable supramolecular catalyst based on Ba<sup>2+</sup> complex of azo bis(benzo-18-crown-6) ether **176** (see Scheme 5) to photocontrol the rate for ethanolysis of 4-carboxyacetanilides in basic solution (Fig. 22) [109]. Efficient ethanolysis requires the cooperation of two metal centers: one to bind the carboxylate group, and the other to deliver the alkoxide to the amide. The *trans*-azobenzene spacer is too extended to allow for

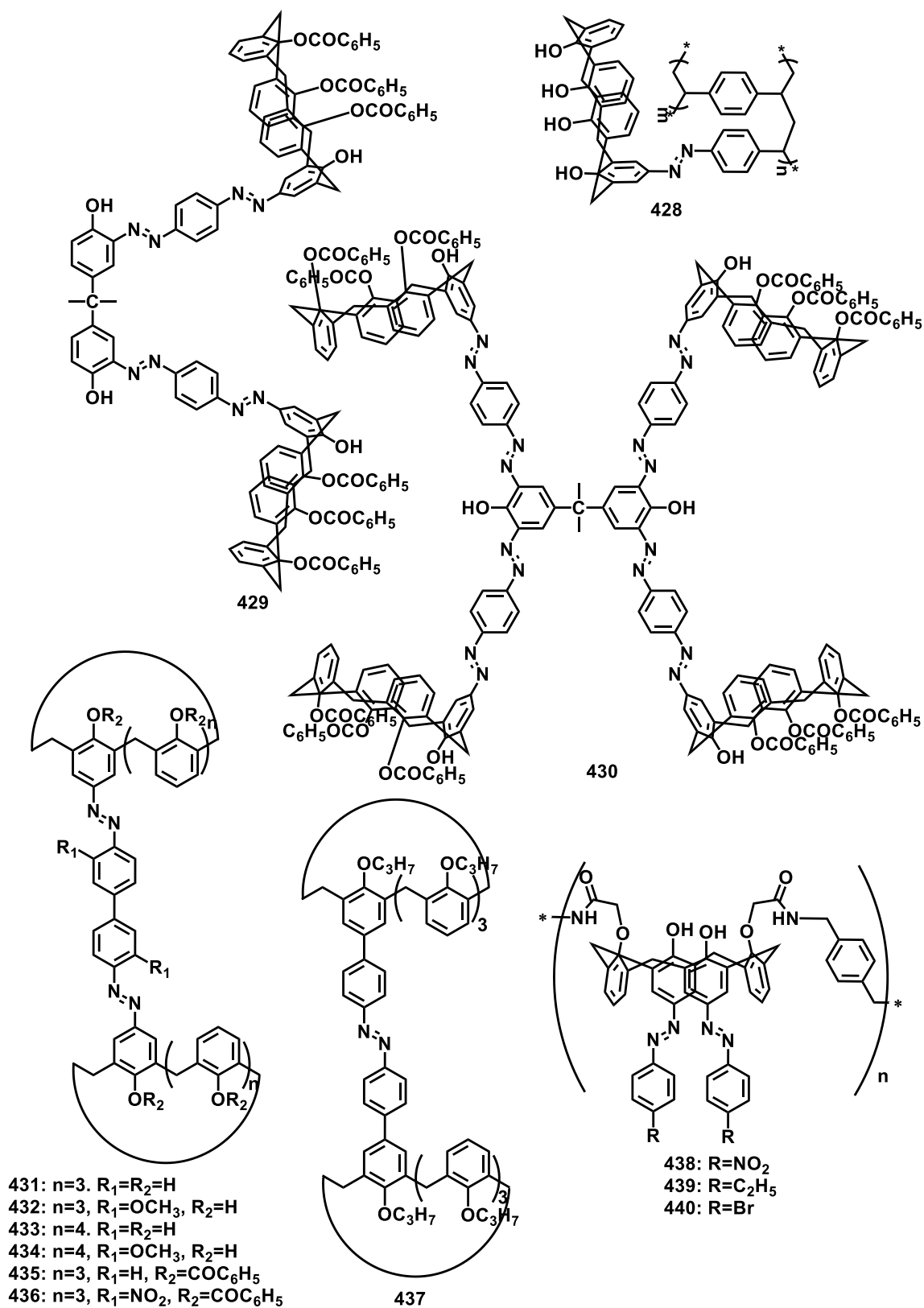
proper two-point binding and *cis*-**176** is efficient catalyst ( $k_{cis}/k_{trans}$  up to 5), which is confirmed by molecular models. The catalytic activity could be reversibility switched in situ between ‘faster’ and ‘slower’ for several times by alternating exposure to UV or visible light.

## Molecular machine

In 2006, Aida and co-workers achieved the coupling of several molecular motions in a light-powered system (Fig. 23) [507]. A photoresponsive host contain an azobenzene unit, a ferrocene unit as pivot, and two porphyrin units as binding sites. The host complexes with 4,4'-biisoquinoline guest with high binding constant. In the formed complex, the change in molecular shape on photoisomerization of the azobenzene is transmitted via rotation of ferrocene and ultimately induced the rotary motion in the guest. The author confirmed the motion by studying the chirality of the guest through circular dichroism spectra. The original state can be regenerated through irradiation with visible light. The system convert light energy into significant motion and larger system that could address remote control of molecular motion might be developed through similar strategy.

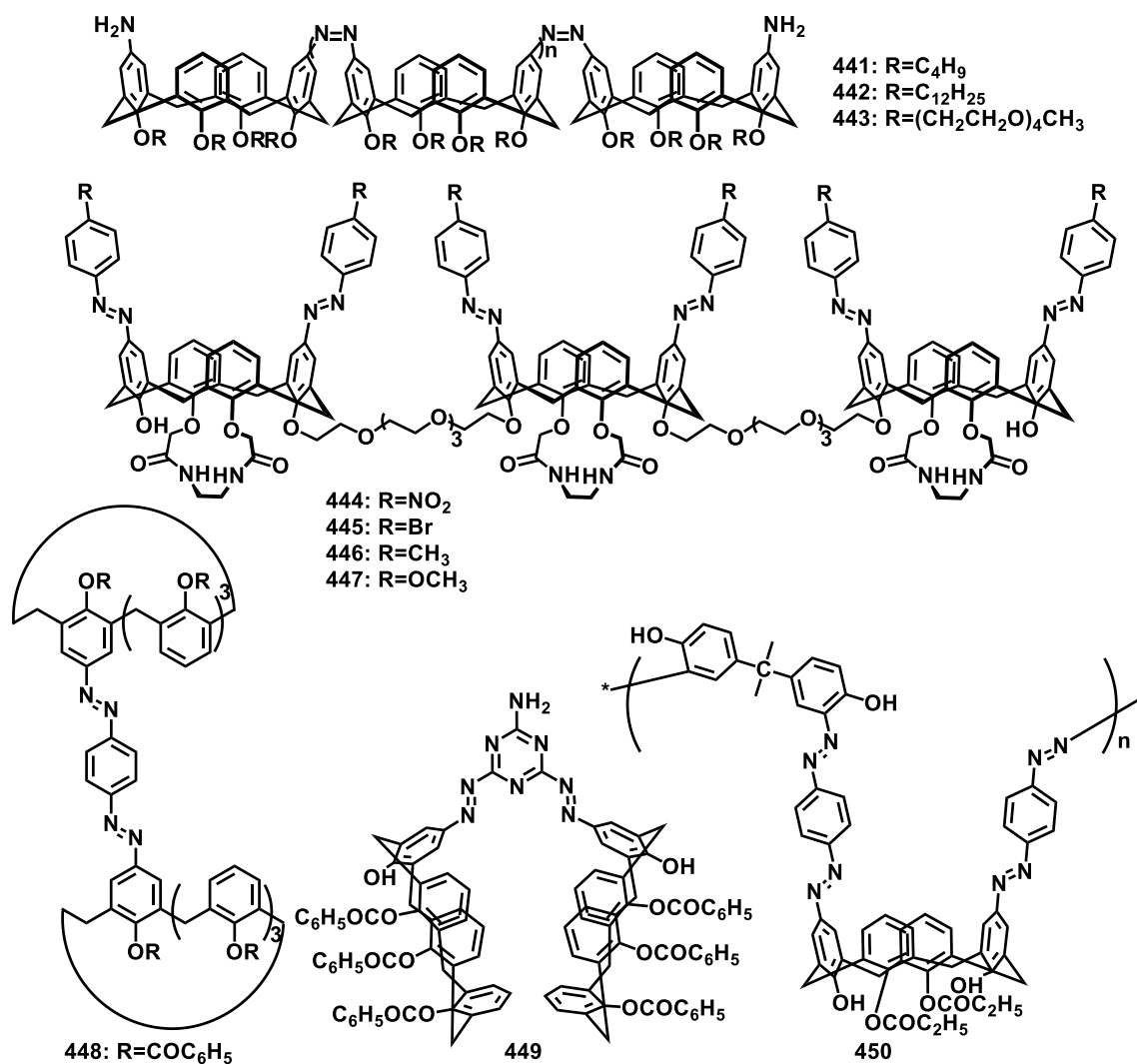
## Others

In 2010, Haberhauer and Kallweit described the unidirectional photoisomerization process of in an azobenzene bearing macrocycle **1267** (Fig. 24) [575]. *Trans*- to *cis*-isomerization of azobenzene generates two enantiomeric *cis*-isomers with P or M chirality, respectively. For most of azobenzene derivatives the two enantiomeric isomers are energy equal and are in fast racemization. It is possible to switch the azobenzene unit unidirectionally by linking a chiral clamp. The irradiation with light of the achiral



Scheme 15 Structures of azo calixarenes (part 4)

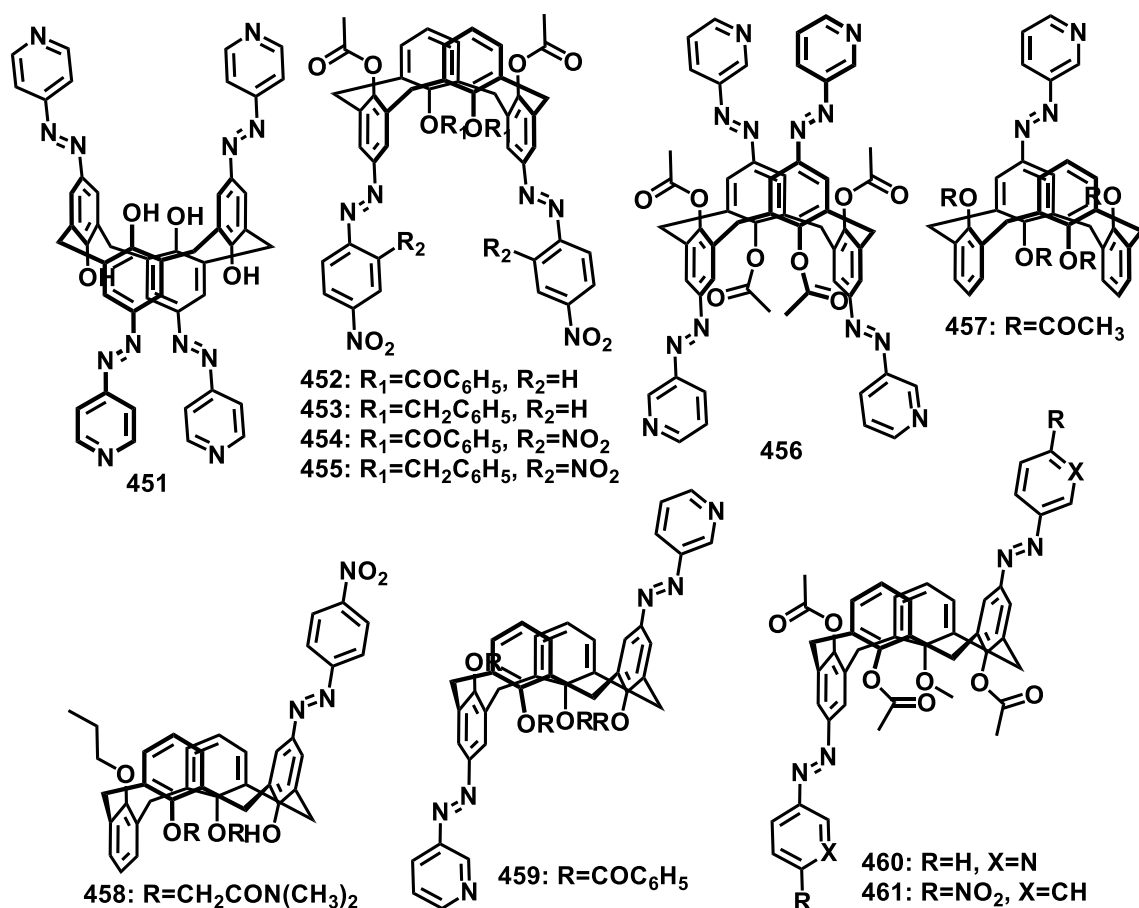




Scheme 15 (continued)

**Table 15** Azo calixarenes in Scheme 15

Compound	References	Compound	References	Compound	References	Compound	References
428	[244]	434	[245]	440	[246]	446	[247]
429	[248]	435	[249]	441	[250, 251]	447	[247]
430	[252]	436	[249]	442	[250, 251]	448	[249]
431	[245]	437	[253]	443	[254]	449	[255]
432	[245]	438	[246]	444	[247]	450	[248]
433	[245]	439	[246]	445	[247]		



Scheme 16 Structures of azo calixarenes (part 5)

Table 16 Azo calixarenes in Scheme 16

Compound	References	Compound	References	Compound	References	Compound	References
451	[256]	454	[257]	457	[257]	460	[257]
452	[257]	455	[257]	458	[258]	461	[257]
453	[257]	456	[257]	459	[257]		

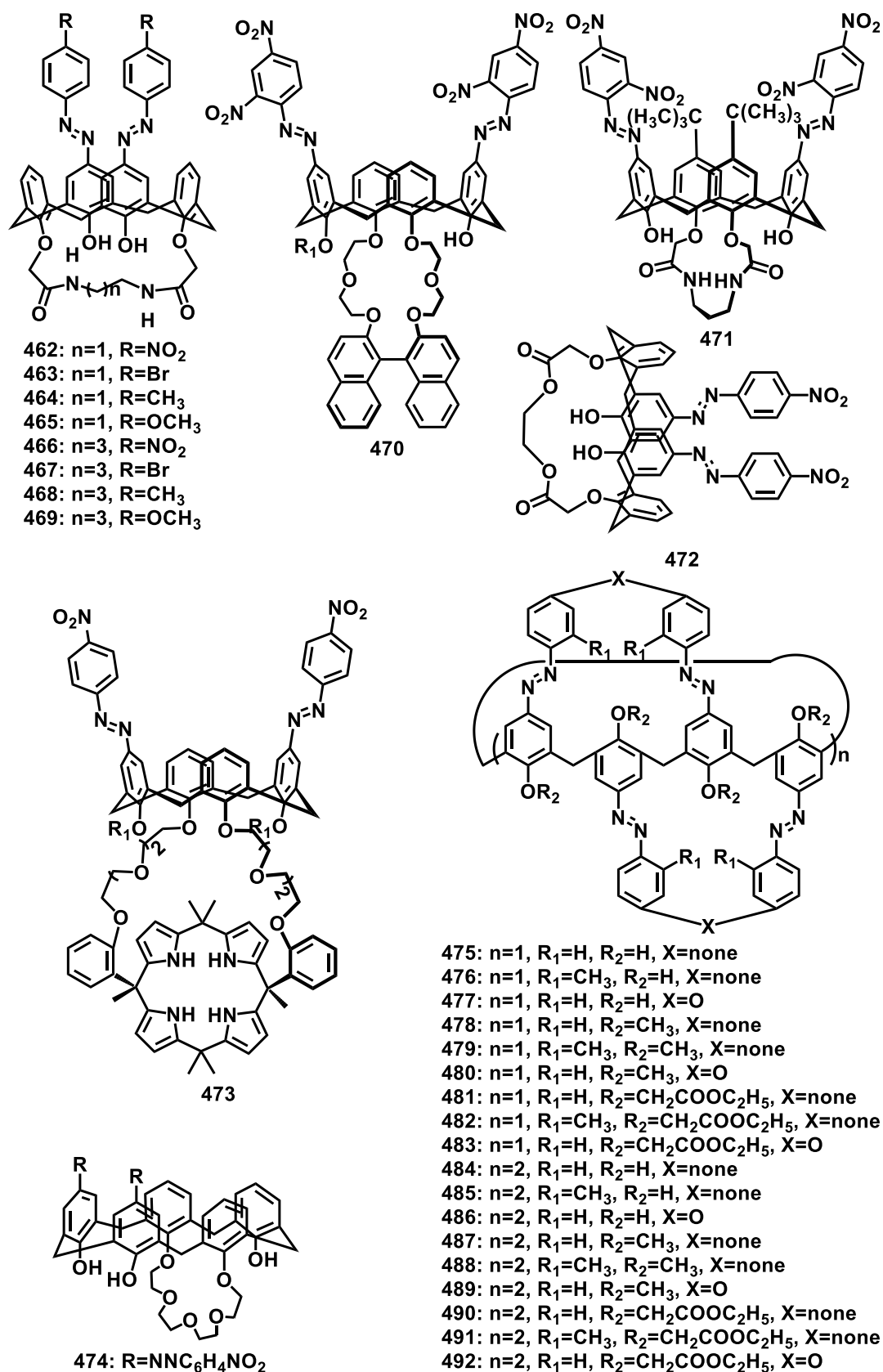
*trans*-isomer of **1267** gives rise to the *cis*-isomer with P helicity. The quantum mechanical computation revealed that the *cis*-(P) isomer of **1267** is much more stable than the *cis*-(M) isomer.

In 2013, Deligöz and co-workers synthesized four azo calix[4]arene dyes for the application in dyeing fibers, including cotton, wool, acetate, polyether and polyamine [322]. Both perspiration fastness and water fastness of fibers dyed by these compounds are good. Furthermore, thermogravimetric analysis revealed that these dyes are all stable

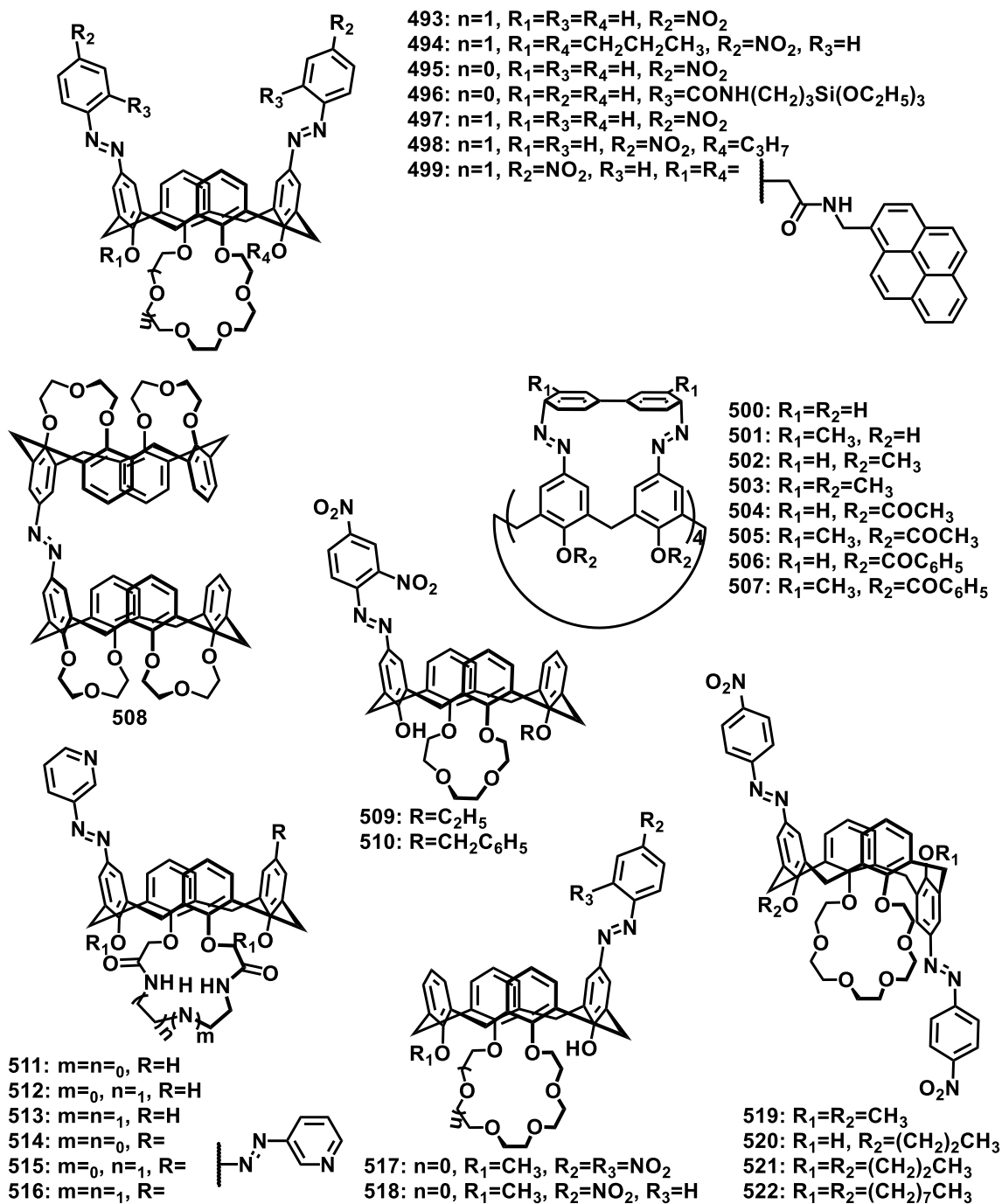
up to 245 °C, which can be effectively used in most kind of inks. It is worth mentioning that the tautomerization of these macrocycles need to be considered in the future.

## Summary

Introducing azo groups into macrocycles can endow them with more intriguing chemical and physical properties, such as efficient recognition, guest induced color change



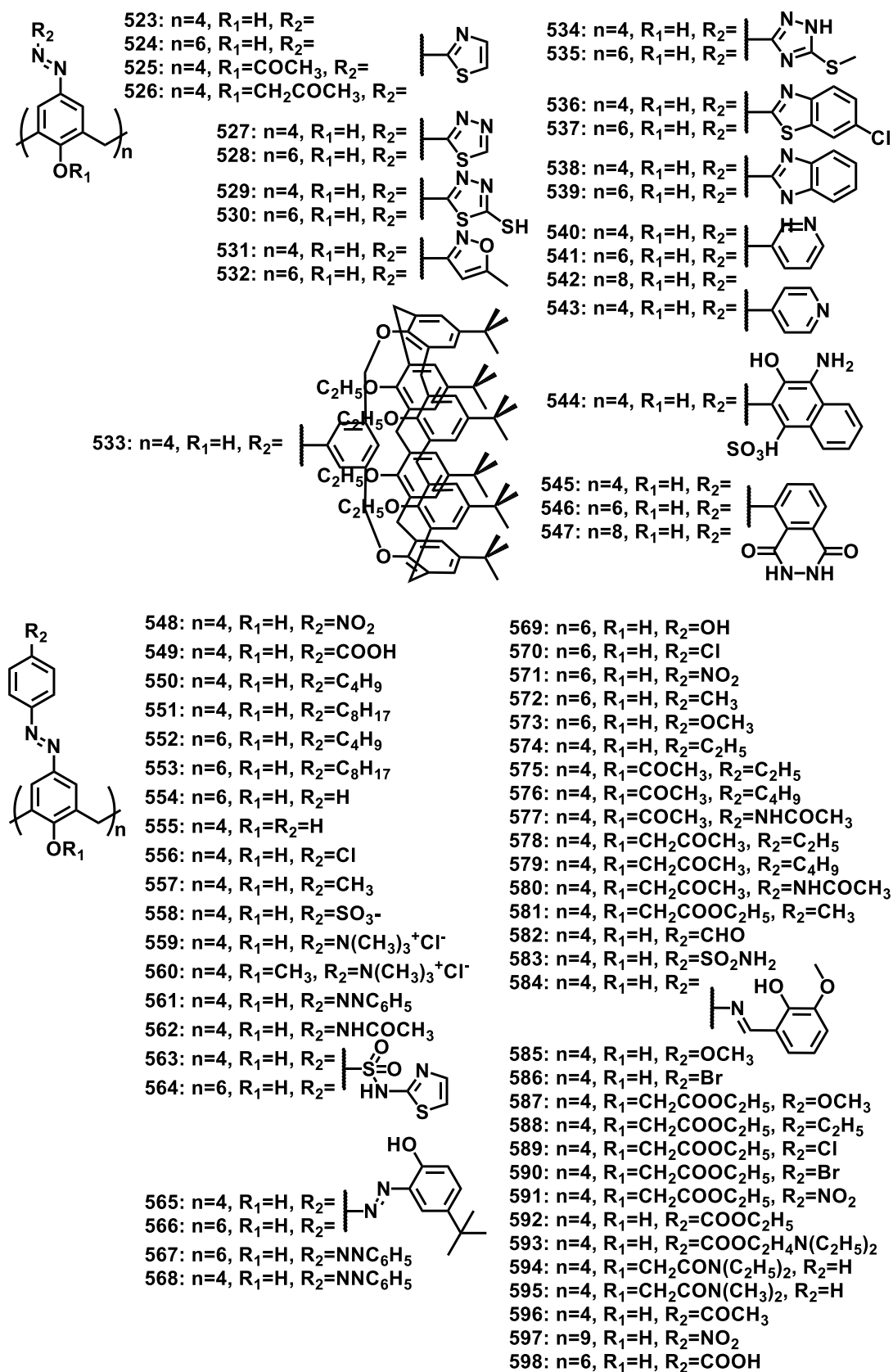
Scheme 17 Structures of azo calixarenes (part 6)



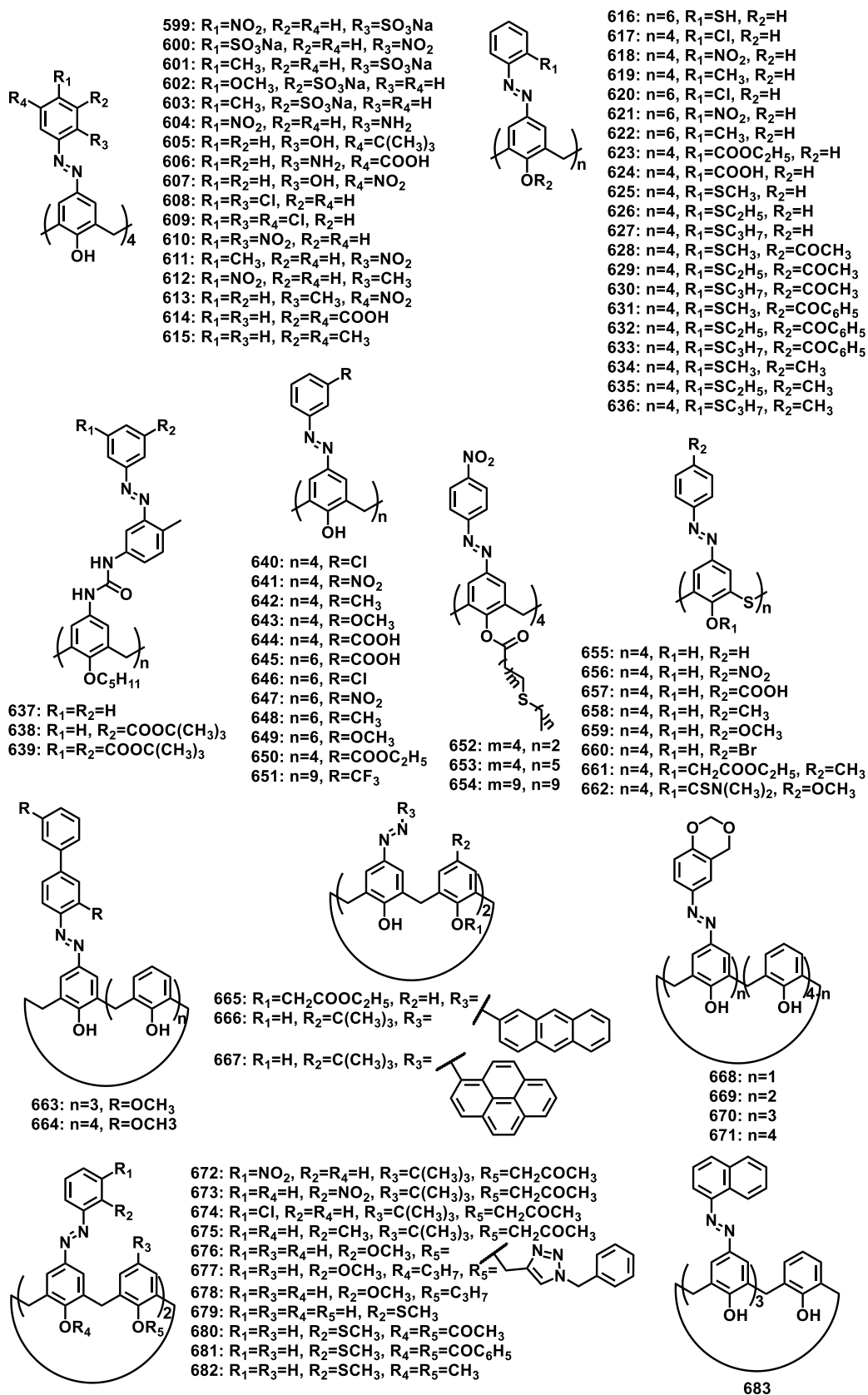
Scheme 17 (continued)

**Table 17** Azo calixarenes in Scheme 17

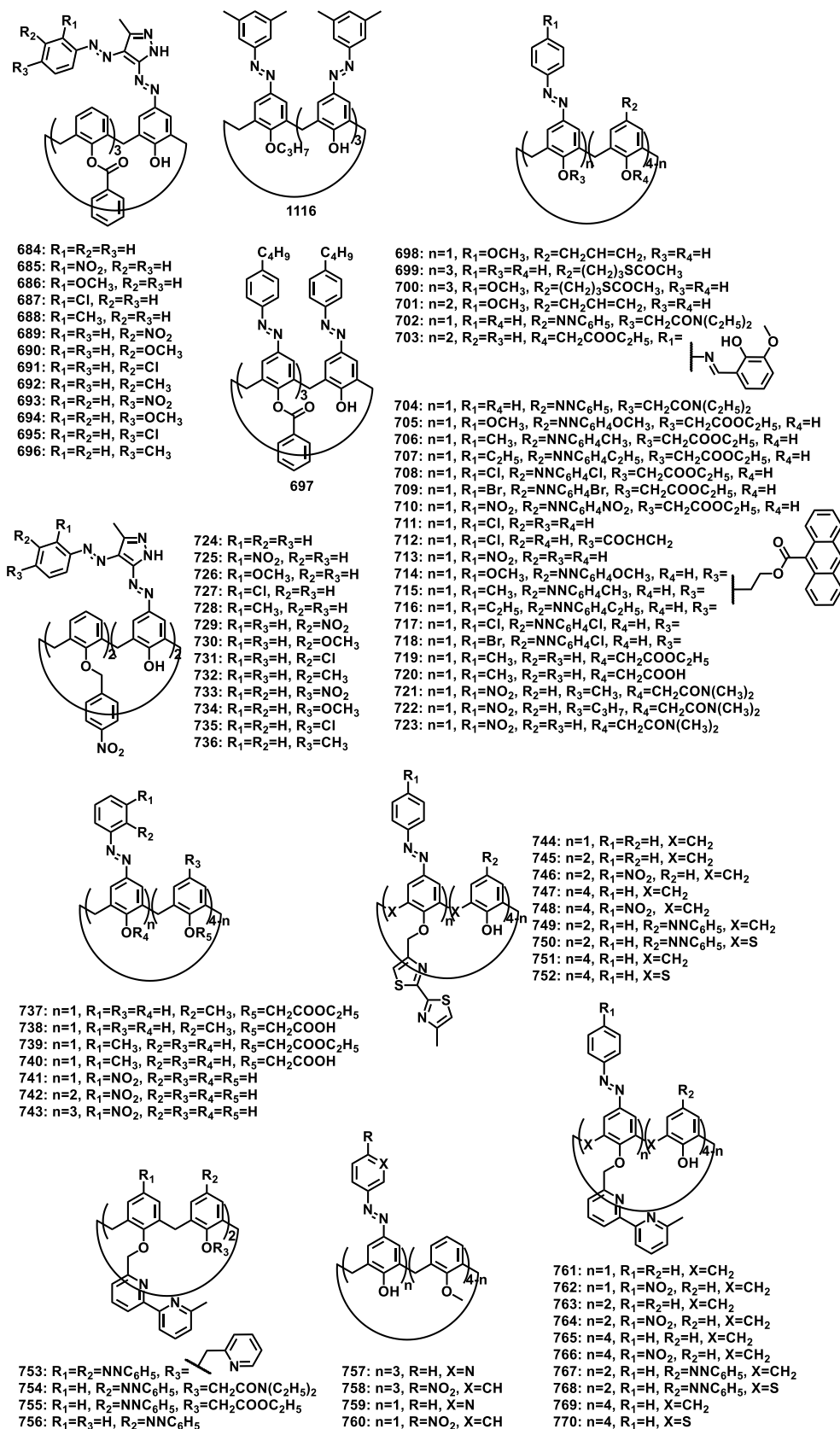
Compound	References	Compound	References	Compound	References	Compound	References
462	[247]	478	[259]	494	[260]	510	[261]
463	[247]	479	[259]	495	[262]	511	[263]
464	[247]	480	[259]	496	[262]	512	[263]
465	[247]	481	[259]	497	[226]	513	[263]
466	[247]	482	[259]	498	[233, 234]	514	[263]
467	[247]	483	[259]	499	[264]	515	[263]
468	[247]	484	[265]	500	[266]	516	[263]
469	[247]	485	[265]	501	[266]	517	[120]
470	[225]	486	[265]	502	[266]	518	[120]
471	[267]	487	[265]	503	[266]	519	[260]
472	[268]	488	[265]	504	[266]	520	[260]
473	[269]	489	[265]	505	[266]	521	[260]
474	[270]	490	[265]	506	[266]	522	[260]
475	[259]	491	[265]	507	[266]		
476	[259]	492	[265]	508	[253, 271]		
477	[259]	493	[234, 272]	509	[261]		



Scheme 18 Structures of azo calixarenes (part 7)

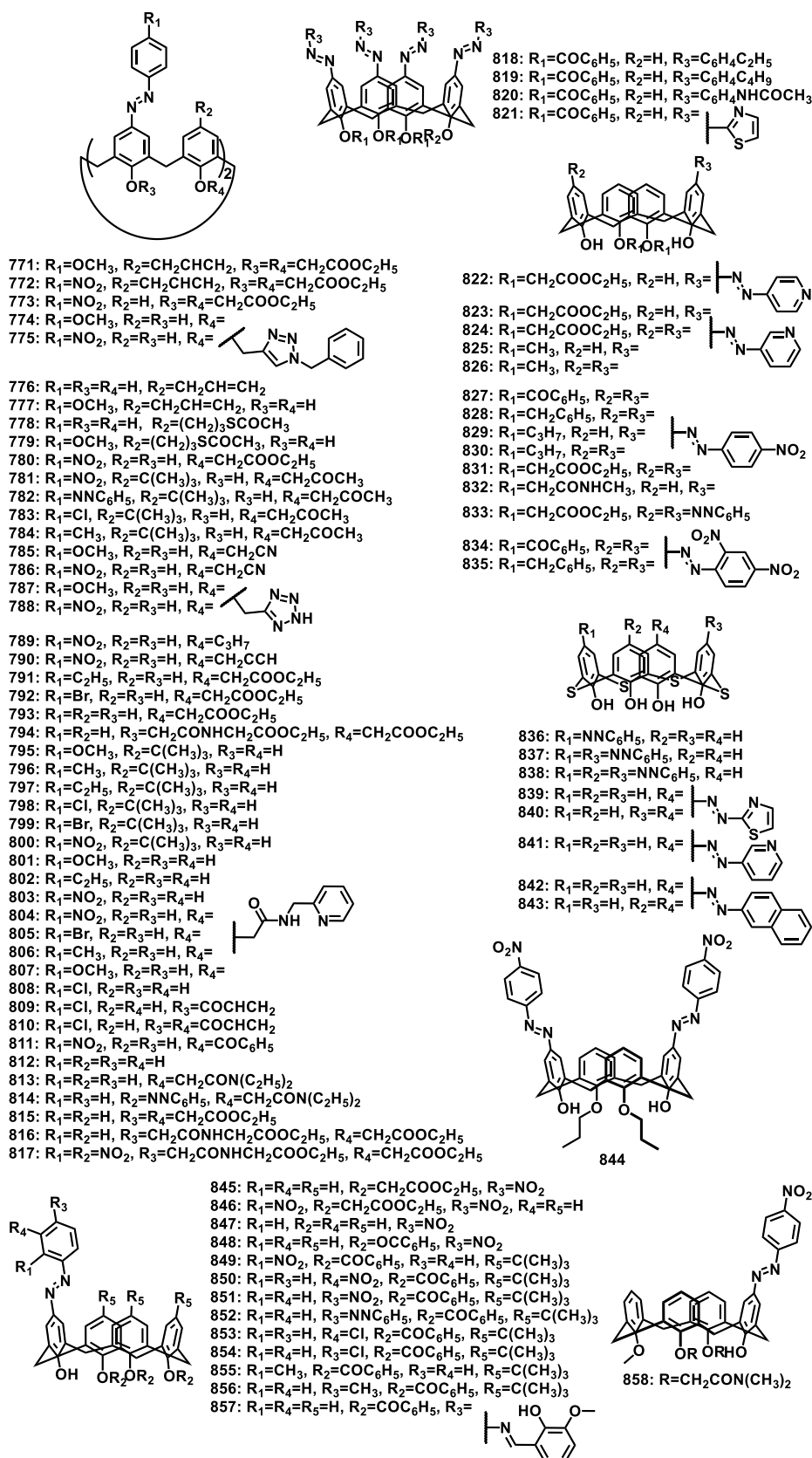


Scheme 18 (continued)

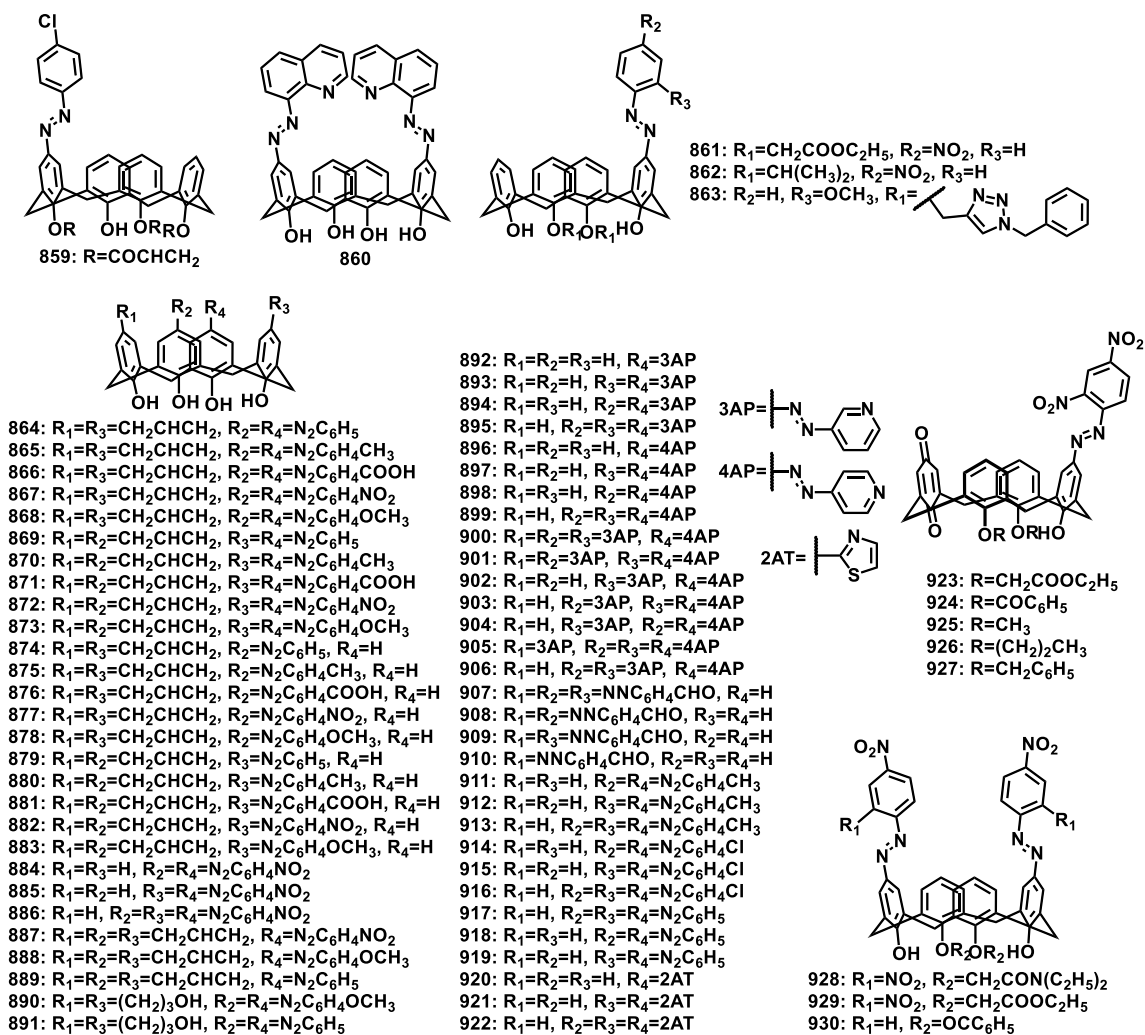


Scheme 18 (continued)





Scheme 18 (continued)



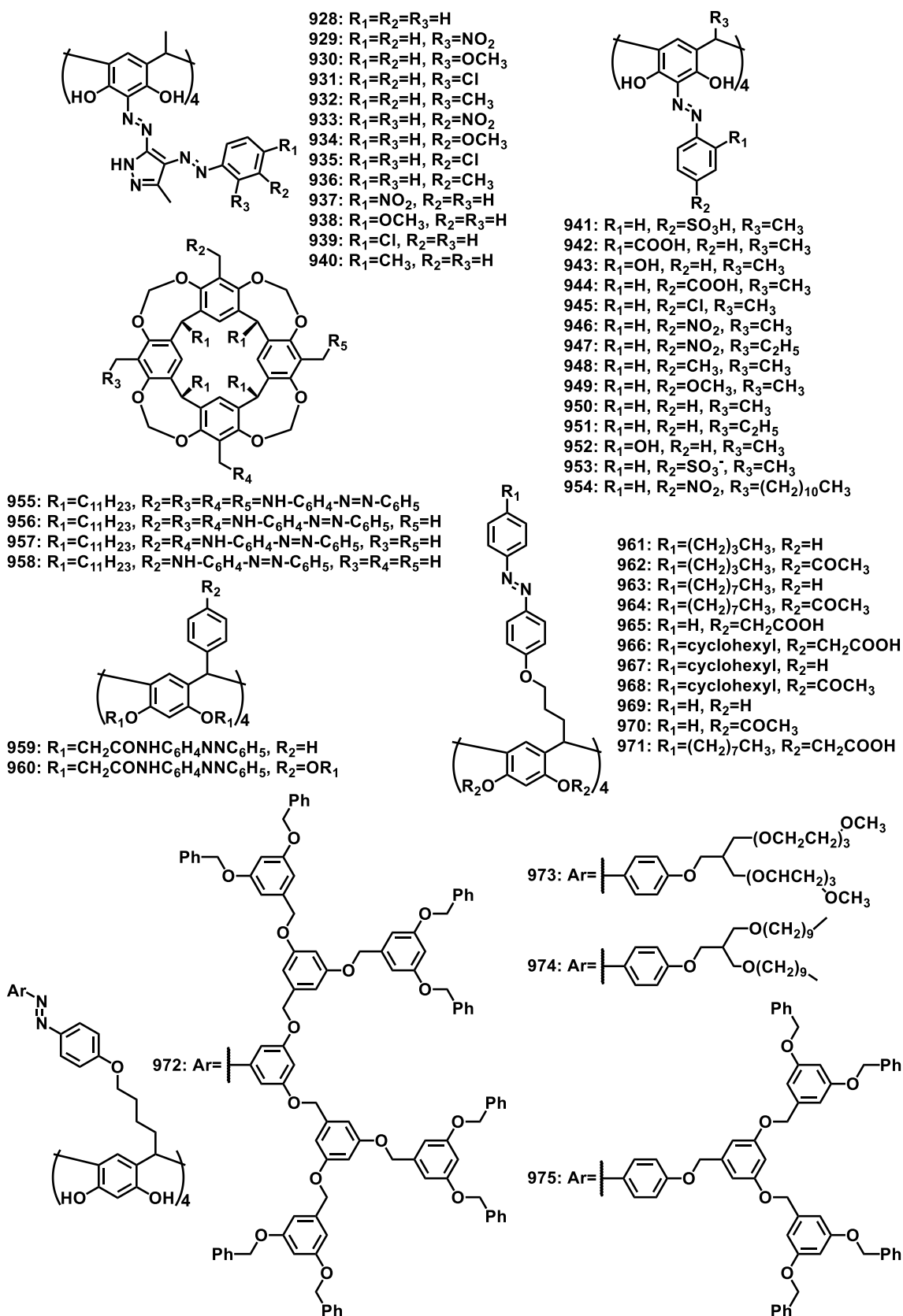
Scheme 18 (continued)

**Table 18** Azo calixarenes in Scheme 18

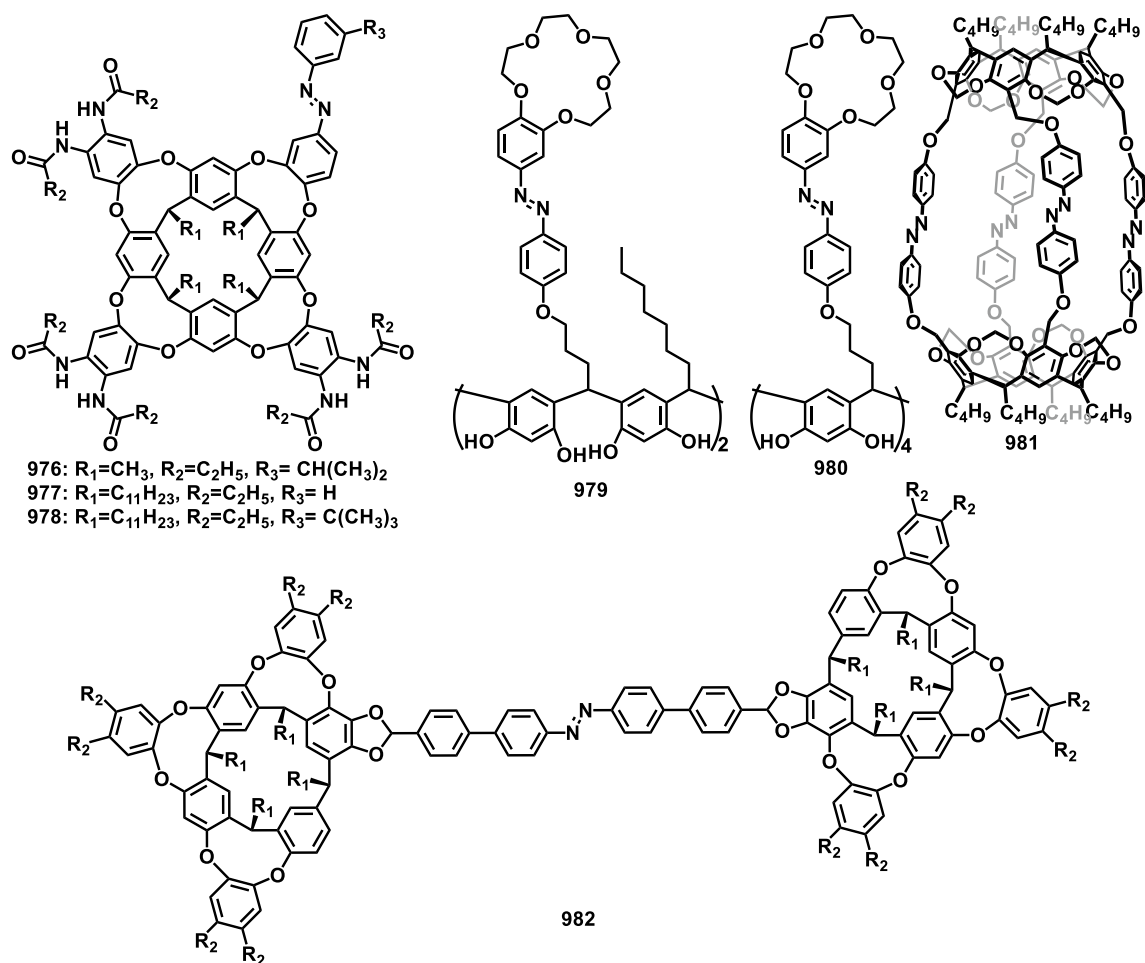
Compound	References	Compound	References	Compound	References	Compound	References
523	[273, 274]	625	[275]	727	[276]	829	[268]
524	[277, 278]	626	[275]	728	[276]	830	[268]
525	[279, 280]	627	[275]	729	[276]	831	[268]
526	[279, 280]	628	[275]	730	[276]	832	[268]
527	[281]	629	[275]	731	[276]	833	[282, 283]
528	[284, 285]	630	[275]	732	[276]	834	[257]
529	[281]	631	[275]	733	[276]	835	[257]
530	[284, 285]	632	[275]	734	[276]	836	[286]
531	[281]	633	[275]	735	[276]	837	[286]
532	[284, 285]	634	[275]	736	[276]	838	[286]
533	[233]	635	[275]	737	[287]	839	[286]
534	[281]	636	[275]	738	[287]	840	[286]
535	[284, 285]	637	[288]	739	[287]	841	[286]
536	[281]	638	[288, 289]	740	[287]	842	[286]
537	[284, 285]	639	[288]	741	[290]	843	[286]
538	[281, 291]	640	[292]	742	[290]	844	[260]
539	[284, 285]	641	[290, 292]	743	[290]	845	[293]
540	[257, 294]	642	[292]	744	[295]	846	[296]
541	[294]	643	[292]	745	[295]	847	[296]
542	[294]	644	[297]	746	[295]	848	[298]
543	[273, 294]	645	[299]	747	[295]	849	[300]
544	[301]	646	[302]	748	[295]	850	[300]
545	[303]	647	[302]	749	[304]	851	[300]
546	[303]	648	[302]	750	[304]	852	[300]
547	[303]	649	[302]	751	[304]	853	[300]
548	[290, 292, 305–311]	650	[312]	752	[304]	854	[300]
549	[313–323]	651	[324]	753	[325]	855	[300]
550	[315, 326]	652	[282, 327, 328]	754	[325]	856	[300]
551	[315]	653	[282, 327, 329–331]	755	[325]	857	[332]
552	[274, 277]	654	[327]	756	[325]	858	[258]
553	[333]	655	[286, 304, 334, 335]	757	[257]	859	[336]
554	[302, 337]	656	[286, 334]	758	[257]	860	[338, 339]
555	[290, 293, 340, 341]	657	[286, 342]	759	[257]	861	[343]
556	[292, 311]	658	[342]	760	[257]	862	[344]
557	[290, 292]	659	[342, 345]	761	[346]	863	[347]
558	[317, 322, 348]	660	[342]	762	[346]	864	[285, 349]
559	[306]	661	[350]	763	[346]	865	[349]
560	[306]	662	[345]	764	[346]	866	[349]
561	[351, 352]	663	[245]	765	[346]	867	[349]
562	[351, 353]	664	[245]	766	[346]	868	[349]
563	[274, 351]	665	[354]	767	[304]	869	[349]
564	[277]	666	[355]	768	[304]	870	[349]
565	[356]	667	[355]	769	[304]	871	[349]
566	[274, 277, 356]	668	[357]	770	[304]	872	[349]
567	[274, 277]	669	[357]	771	[285]	873	[349]
568	[353]	670	[357]	772	[285]	874	[349]
569	[274, 277]	671	[357]	773	[282, 329–331]	875	[349]
570	[302]	672	[300, 358–360]	774	[347, 361–363]	876	[349]
571	[302]	673	[300, 358–360]	775	[362]	877	[349]
572	[302]	674	[300, 358–360]	776	[364]	878	[349]
573	[302]	675	[300, 358–360]	777	[364]	879	[349]
574	[279, 280, 365, 366]	676	[347]	778	[364]	880	[349]
575	[279, 280]	677	[347]	779	[364]	881	[349]

**Table 18** (continued)

Compound	References	Compound	References	Compound	References	Compound	References
576	[279, 280]	678	[347]	780	[246, 329, 343, 367–370]	882	[349]
577	[279, 280]	679	[275]	781	[300, 359, 360]	883	[349]
578	[279, 280]	680	[275]	782	[300, 359, 360]	884	[290, 298, 308, 310, 311]
579	[279, 280]	681	[275]	783	[300, 359, 360]	885	[308, 310, 311]
580	[279, 280]	682	[275]	784	[300, 359, 360]	886	[308, 310, 311]
581	[350, 371]	683	[372]	785	[363]	887	[284, 285]
582	[373]	684	[374]	786	[363]	888	[284, 285]
583	[322]	685	[374]	787	[363]	889	[284, 285]
584	[332]	686	[374]	788	[363]	890	[284, 285]
585	[365, 366]	687	[374]	789	[234, 272, 343]	891	[284, 285]
586	[365, 366]	688	[374]	790	[362]	892	[257, 294]
587	[371]	689	[374]	791	[246]	893	[257, 294]
588	[371]	690	[374]	792	[246]	894	[257, 294]
589	[371]	691	[374]	793	[328, 329, 375]	895	[257, 294]
590	[371]	692	[374]	794	[376]	896	[294]
591	[371]	693	[374]	795	[377–380]	897	[294]
592	[312, 381]	694	[374]	796	[378]	898	[294]
593	[312]	695	[374]	797	[378]	899	[294]
594	[340, 341]	696	[374]	798	[378]	900	[294]
595	[340]	697	[382]	799	[378]	901	[294]
596	[383]	698	[364]	800	[378]	902	[294]
597	[324]	699	[364]	801	[377, 379]	903	[294]
598	[117]	700	[364]	802	[377, 379]	904	[294]
599	[384]	701	[364]	803	[377, 379]	905	[294]
600	[384]	702	[385]	804	[247]	906	[294]
601	[384]	703	[332]	805	[247]	907	[373]
602	[384]	704	[340, 386]	806	[247]	908	[373]
603	[384]	705	[365, 387]	807	[247]	909	[373]
604	[384]	706	[365, 387]	808	[336]	910	[373]
605	[301]	707	[365, 387]	809	[336]	911	[290, 311]
606	[301]	708	[365, 387]	810	[388]	912	[290, 311]
607	[301]	709	[365, 387]	811	[388]	913	[290, 311]
608	[348]	710	[387]	812	[340]	914	[311]
609	[348]	711	[336]	813	[340]	915	[311]
610	[348]	712	[336]	814	[340]	916	[311]
611	[348]	713	[388]	815	[329]	917	[290]
612	[348]	714	[366]	816	[329]	918	[290]
613	[348]	715	[366]	817	[329]	919	[290]
614	[322]	716	[366]	818	[279, 280]	920	[273]
615	[233]	717	[366]	819	[279, 280]	921	[273]
616	[274, 277]	718	[366]	820	[279, 280]	922	[273]
617	[292]	719	[287]	821	[279, 280]	923	[389]
618	[292]	720	[287]	822	[257]	924	[389]
619	[292]	721	[390]	823	[257]	925	[389]
620	[302]	722	[390]	824	[257]	926	[389]
621	[302]	723	[258]	825	[257]	927	[389]
622	[302]	724	[276]	826	[257]	928	[391]
623	[392–398]	725	[276]	827	[257]	929	[391]
624	[392, 394, 396, 397]	726	[276]	828	[257]	930	[298]



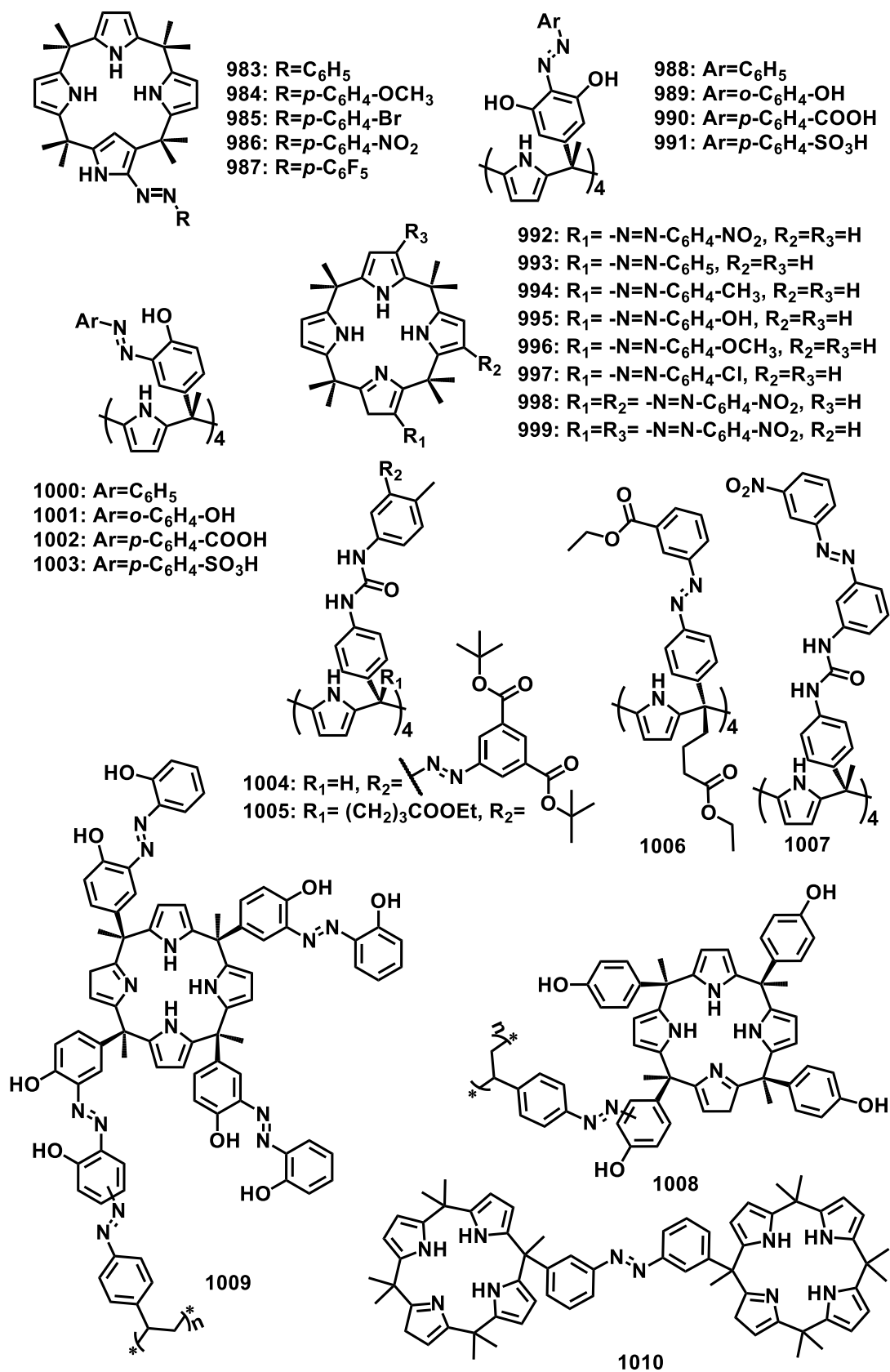
Scheme 19 Structures of azo resorcinarenes



Scheme 19 (continued)

**Table 19** Azo resorcinarenes in Scheme 19

Compound	References	Compound	References	Compound	References	Compound	References
928	[401]	942	[402]	956	[403]	970	[404]
929	[401]	943	[402]	957	[403]	971	[405]
930	[401]	944	[402, 406]	958	[403]	972	[407]
931	[401]	945	[408]	959	[219]	973	[407]
932	[401]	946	[408, 409]	960	[219]	974	[407]
933	[401]	947	[409]	961	[404, 410–413]	975	[407]
934	[401]	948	[408]	962	[404]	976	[414]
935	[401]	949	[408]	963	[404]	977	[415]
936	[401]	950	[408, 409]	964	[404]	978	[415]
937	[401]	951	[409]	965	[411–413]	979	[416]
938	[401]	952	[408]	966	[411–413]	980	[416]
939	[401]	953	[417]	967	[404, 411]	981	[418]
940	[401]	954	[419–422]	968	[404]	982	[423]
941	[402]	955	[403]	969	[404, 411]		

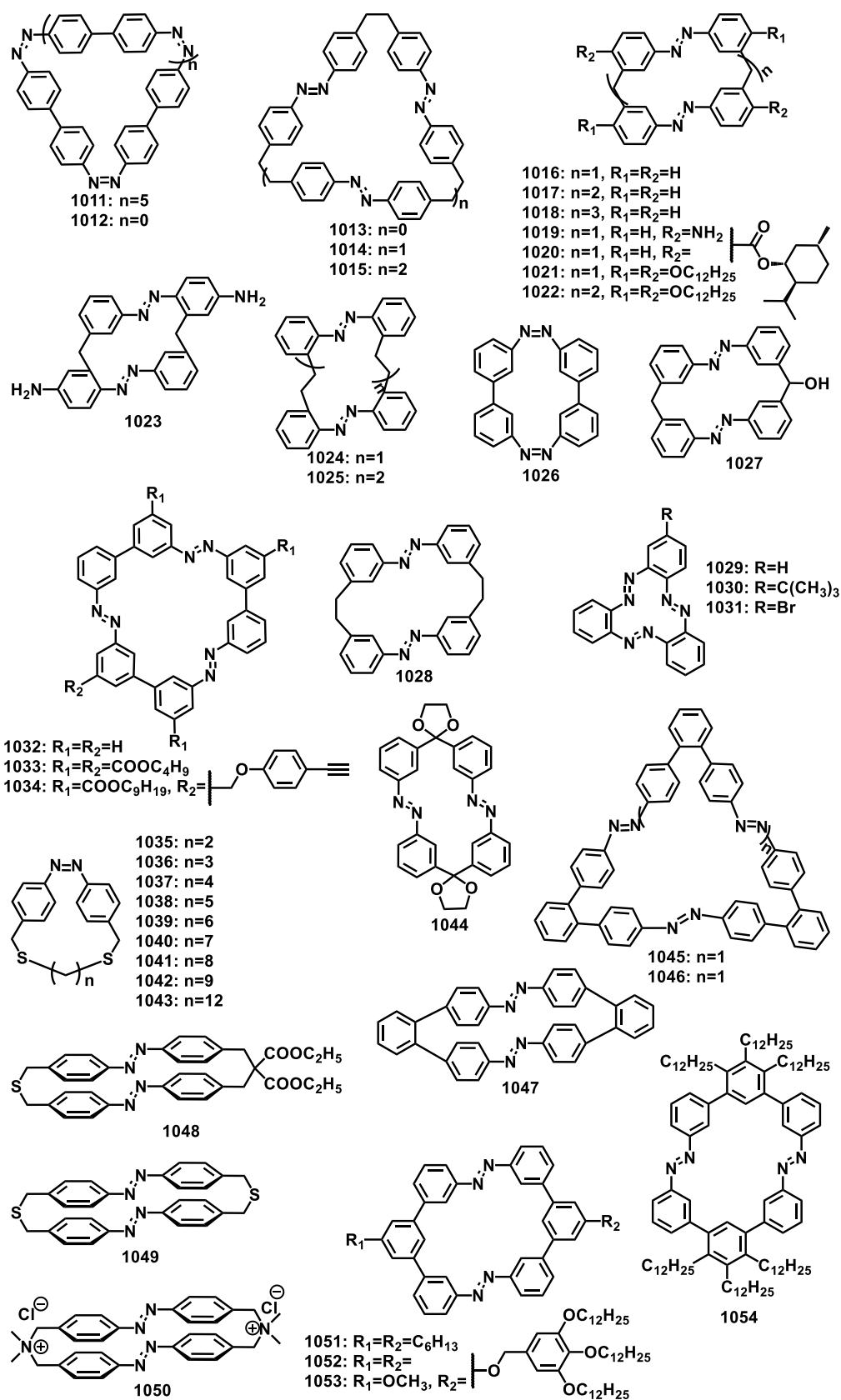


Scheme 20 Structures of azo calixpyrroles

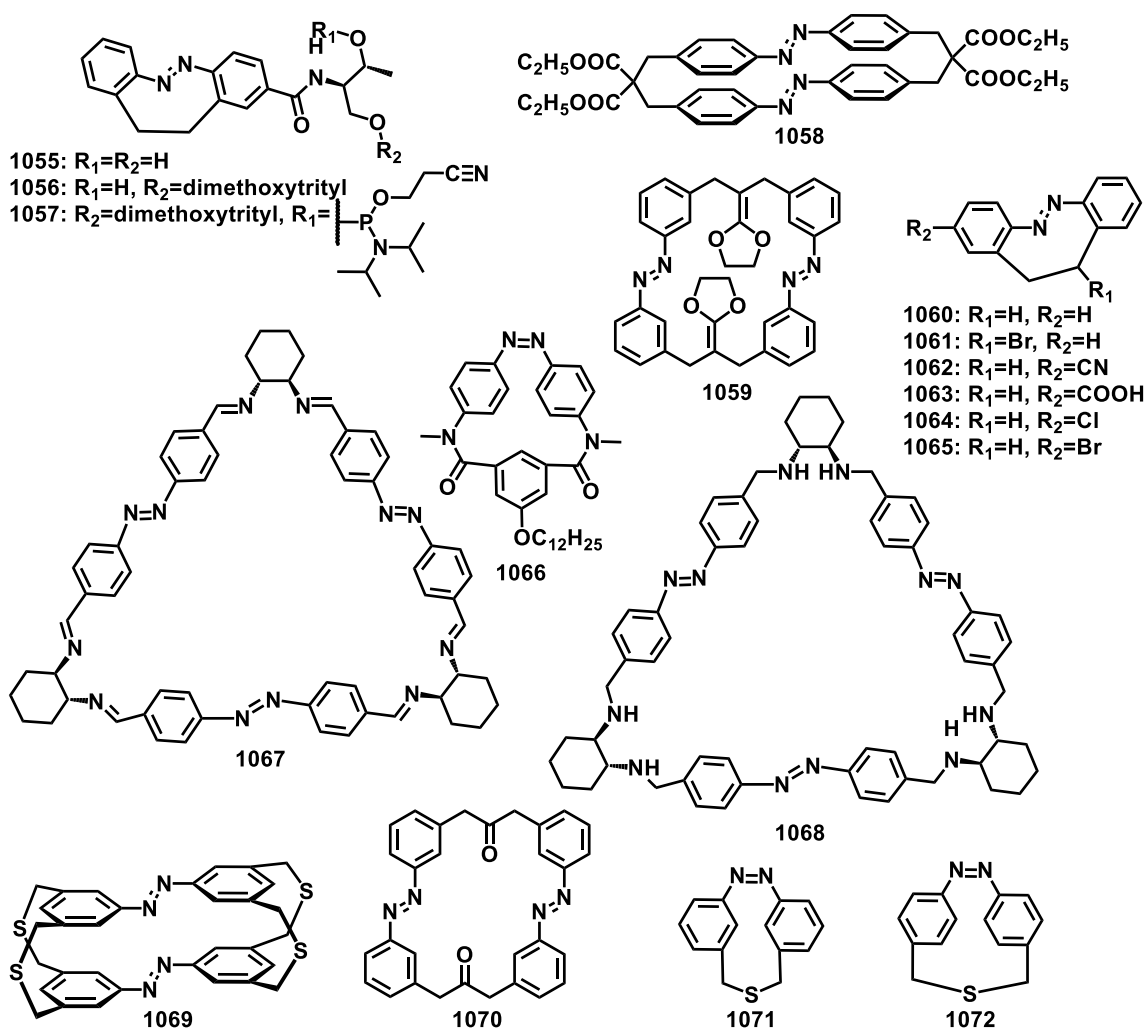
**Table 20** Azo calixpyrroles in Scheme 20

Compound	References	Compound	References	Compound	References	Compound	References
983	[429]	990	[430, 431]	997	[432]	1004	[433]
984	[429]	991	[430, 431]	998	[434]	1005	[433]
985	[429]	992	[432, 434, 435]	999	[434]	1006	[436]
986	[429, 434, 435]	993	[432]	1000	[430, 431]	1007	[437]
987	[429]	994	[432]	1001	[430, 431]	1008	[438]
988	[430, 431]	995	[432]	1002	[430, 431]	1009	[438]
989	[430, 431]	996	[432]	1003	[430, 431]	1010	[439]





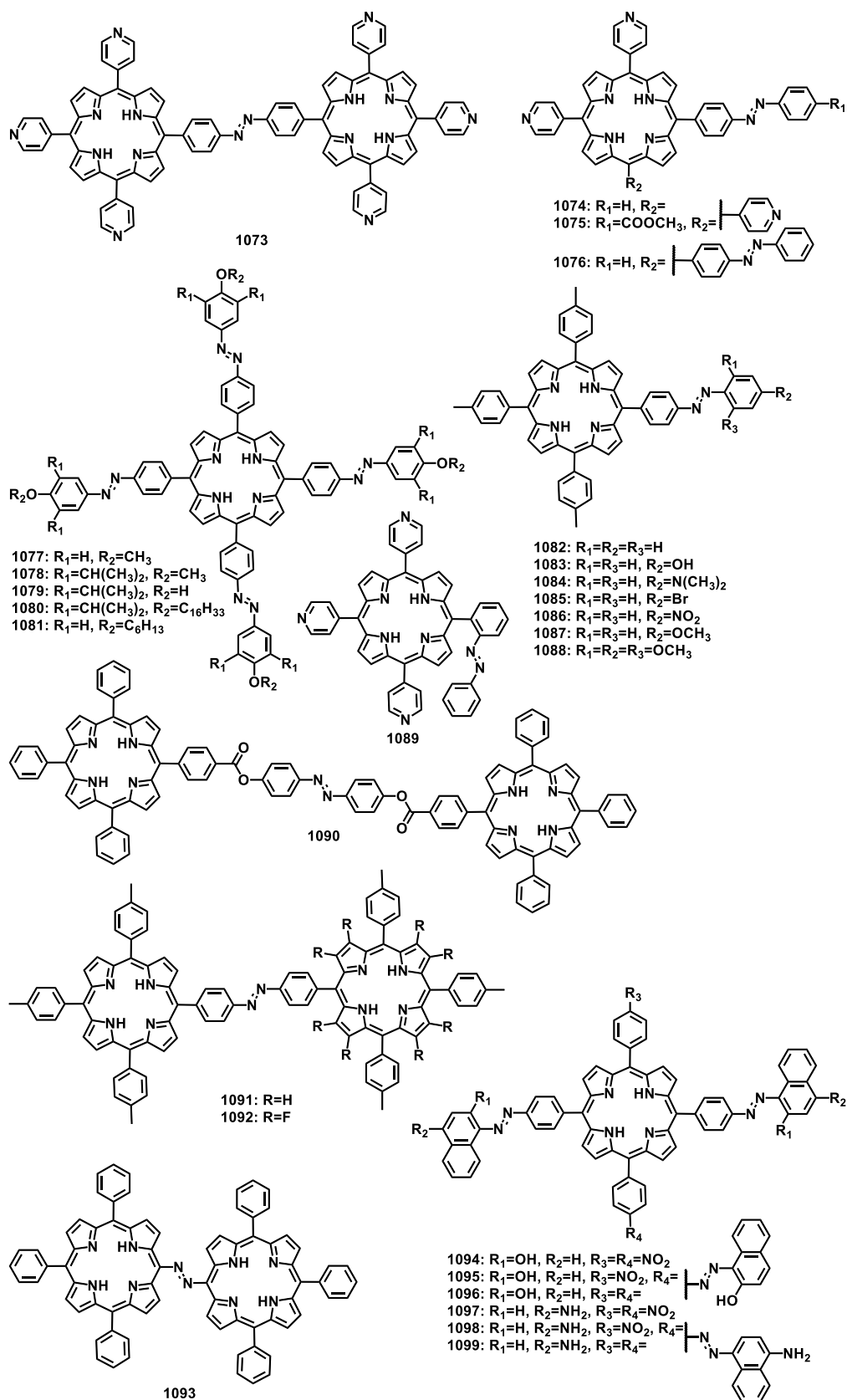
Scheme 21 Structures of azobenzophanes



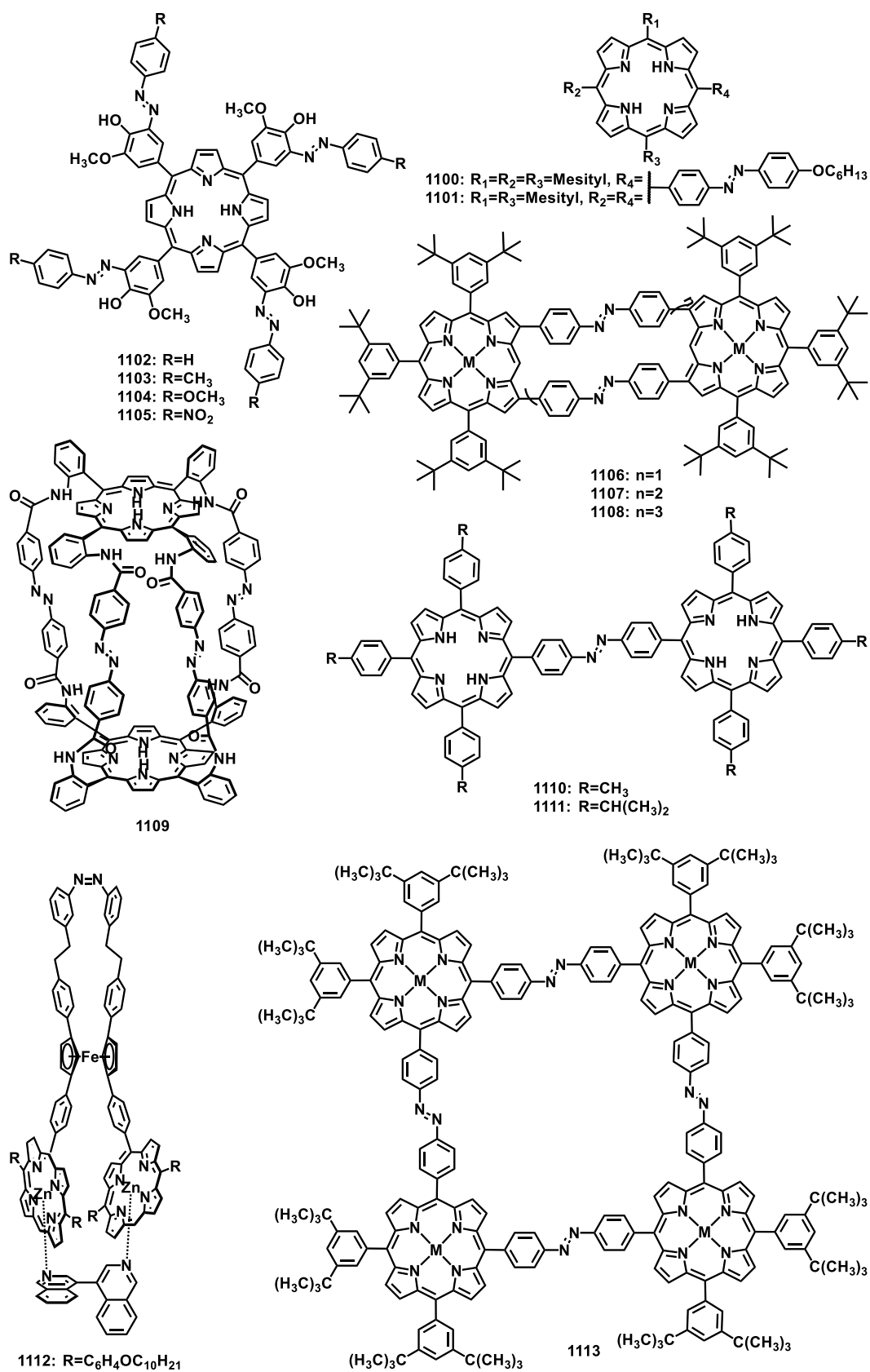
Scheme 21 (continued)

Table 21 Azobenzenophanes in Scheme 21

Compound	References	Compound	References	Compound	References	Compound	References
1011	[440]	1027	[441]	1043	[442]	1059	[443]
1012	[444]	1028	[441]	1044	[441]	1060	[445–459]
1013	[446, 460–462]	1029	[463–466]	1045	[467]	1061	[445]
1014	[446, 460, 461, 467–471]	1030	[464]	1046	[467]	1062	[472, 473]
1015	[460, 461, 474]	1031	[464]	1047	[462, 467, 475]	1063	[472, 473]
1016	[476, 477]	1032	[465]	1048	[441, 478, 479]	1064	[472]
1017	[480, 481]	1033	[482]	1049	[441, 475, 478, 483–488]	1065	[472, 473]
1018	[480]	1034	[482]	1050	[489]	1066	[490]
1019	[491]	1035	[442]	1051	[492]	1067	[493]
1020	[491]	1036	[494]	1052	[492]	1068	[493]
1021	[481, 495]	1037	[442]	1053	[492]	1069	[483, 484, 486]
1022	[481]	1038	[442]	1054	[492]	1070	[443]
1023	[496]	1039	[442]	1055	[472, 473]	1071	[497]
1024	[446, 496]	1040	[442]	1056	[473]	1072	[497]
1025	[446]	1041	[442]	1057	[473]		
1026	[441, 498]	1042	[442]	1058	[479]		



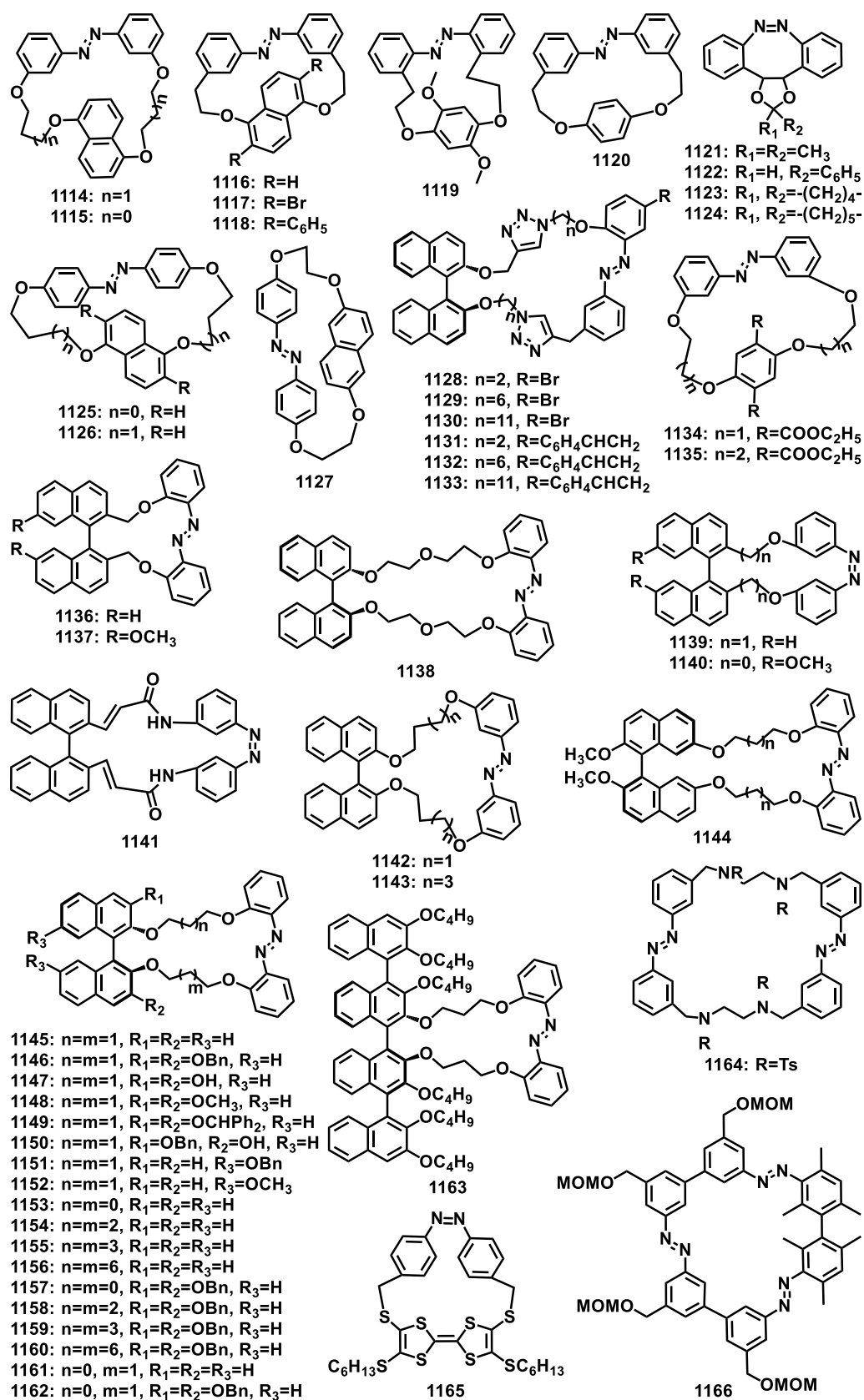
Scheme 22 Structures of azo porphyrins



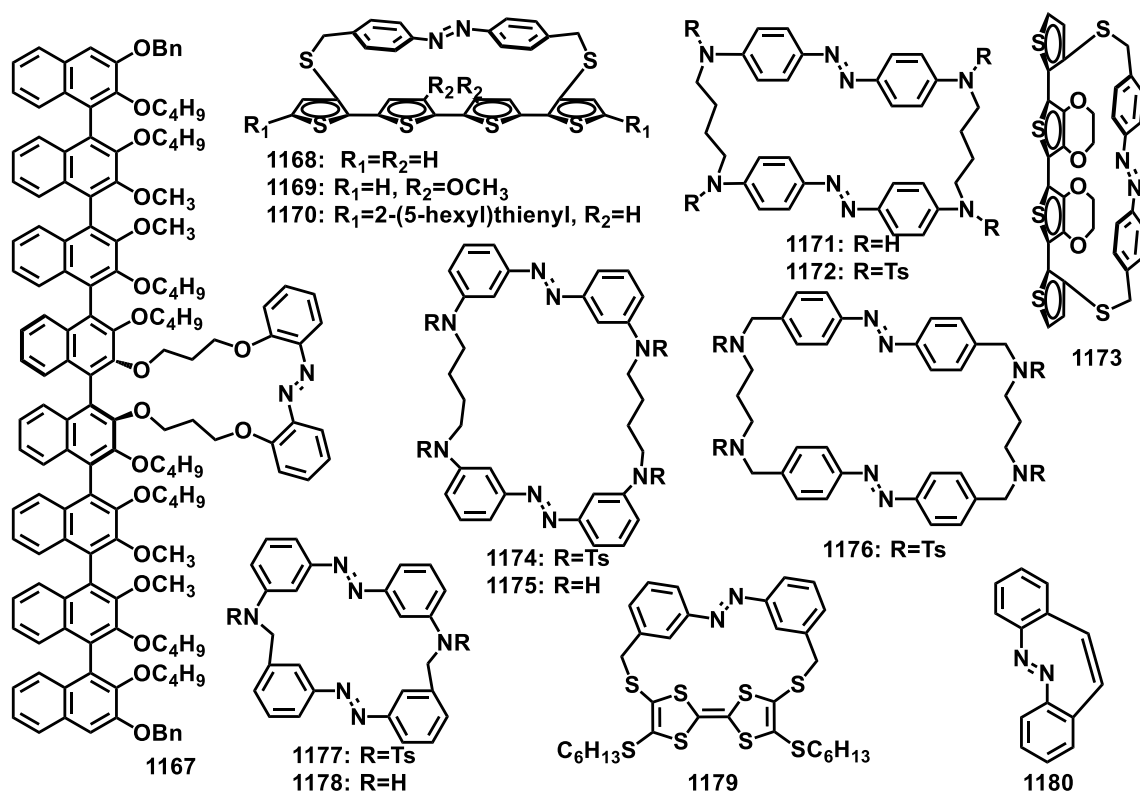
Scheme 22 (continued)

**Table 22** Azo porphyrins in Scheme 22

Compound	References	Compound	References	Compound	References	Compound	References
<b>1073</b>	[499]	<b>1084</b>	[500]	<b>1095</b>	[501]	<b>1106</b>	[502]
<b>1074</b>	[499]	<b>1085</b>	[500]	<b>1096</b>	[501]	<b>1107</b>	[502]
<b>1075</b>	[499]	<b>1086</b>	[500]	<b>1097</b>	[501]	<b>1108</b>	[502]
<b>1076</b>	[499]	<b>1087</b>	[500]	<b>1098</b>	[501]	<b>1109</b>	[503]
<b>1077</b>	[504]	<b>1088</b>	[500]	<b>1099</b>	[501]	<b>1110</b>	[489]
<b>1078</b>	[504]	<b>1089</b>	[499]	<b>1100</b>	[505]	<b>1111</b>	[489]
<b>1079</b>	[504]	<b>1090</b>	[506]	<b>1101</b>	[505]	<b>1112</b>	[507, 508]
<b>1080</b>	[504]	<b>1091</b>	[509]	<b>1102</b>	[510]	<b>1113</b>	[502]
<b>1081</b>	[505]	<b>1092</b>	[509]	<b>1103</b>	[510]		
<b>1082</b>	[500]	<b>1093</b>	[511]	<b>1104</b>	[510]		
<b>1083</b>	[500]	<b>1094</b>	[501]	<b>1105</b>	[510]		



Scheme 23 Structures of other azo macrocycles (part 1)

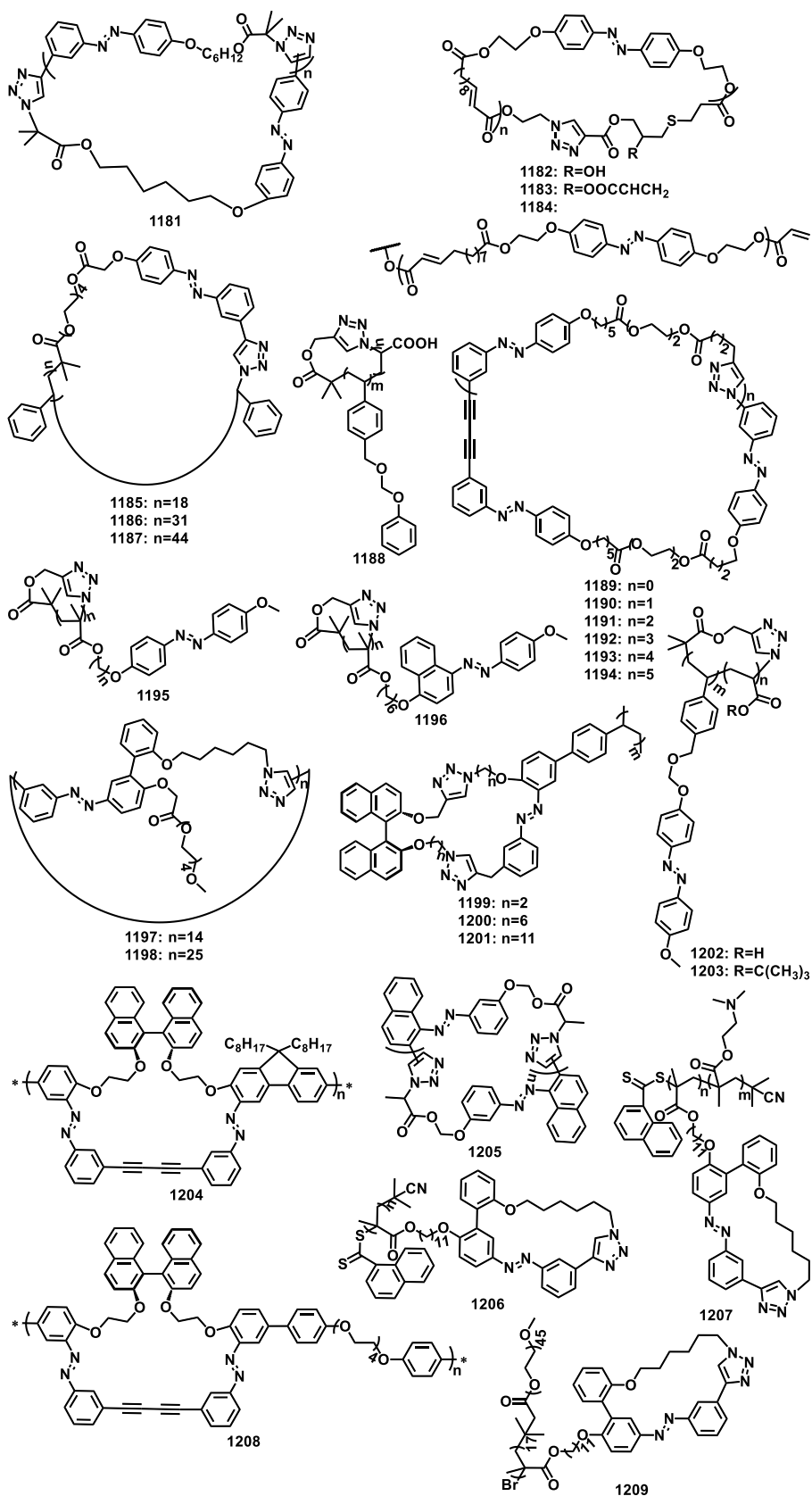


Scheme 23 (continued)

Table 23 Other azo macrocycles in Scheme 23

Compound	References	Compound	References	Compound	References	Compound	References
1114	[512]	1131	[513]	1148	[514–516]	1165	[517]
1115	[518]	1132	[513]	1149	[514–516]	1166	[519]
1116	[520, 521]	1133	[513]	1150	[514–516]	1167	[516]
1117	[522–524]	1134	[522]	1151	[514, 516]	1168	[525]
1118	[522]	1135	[522]	1152	[514]	1169	[525]
1119	[522]	1136	[526]	1153	[526–528]	1170	[525]
1120	[521]	1137	[526]	1154	[527]	1171	[529]
1121	[530]	1138	[531]	1155	[527]	1172	[529]
1122	[530]	1139	[526]	1156	[527]	1173	[525]
1123	[530]	1140	[526]	1157	[527, 528]	1174	[529]
1124	[530]	1141	[532]	1158	[527]	1175	[529]
1125	[518]	1142	[516]	1159	[527]	1176	[529]
1126	[518]	1143	[516]	1160	[527]	1177	[529]
1127	[518]	1144	[516]	1161	[528]	1178	[529]
1128	[513]	1145	[533, 534]	1162	[528]	1179	[517]
1129	[513]	1146	[514, 515]	1163	[516]	1180	[445]
1130	[513]	1147	[514, 516]	1164	[529]		

**Scheme 24** Structures of other azo macrocycles (part 2)

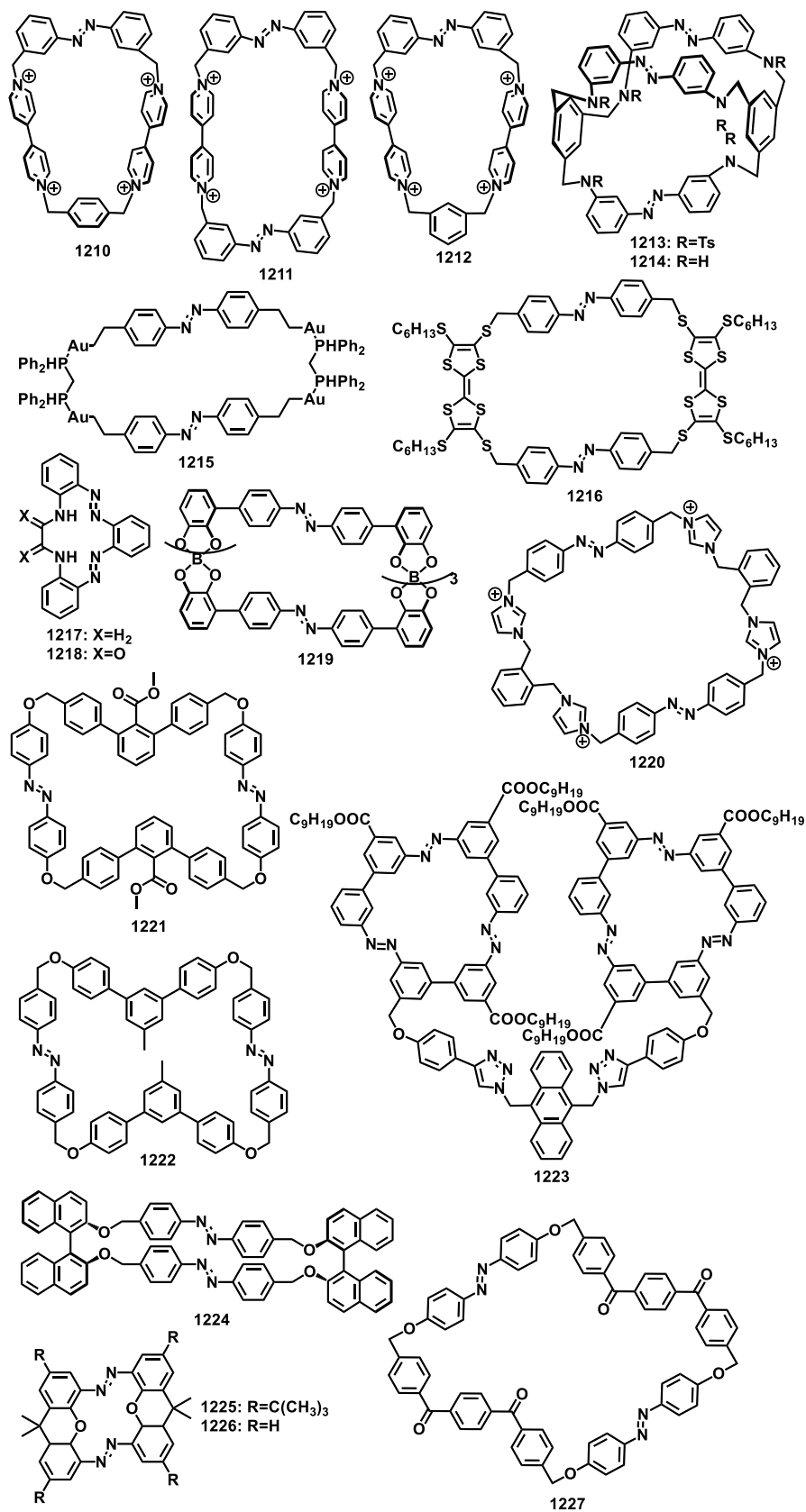




**Table 24** Other azo macrocycles in Scheme 24

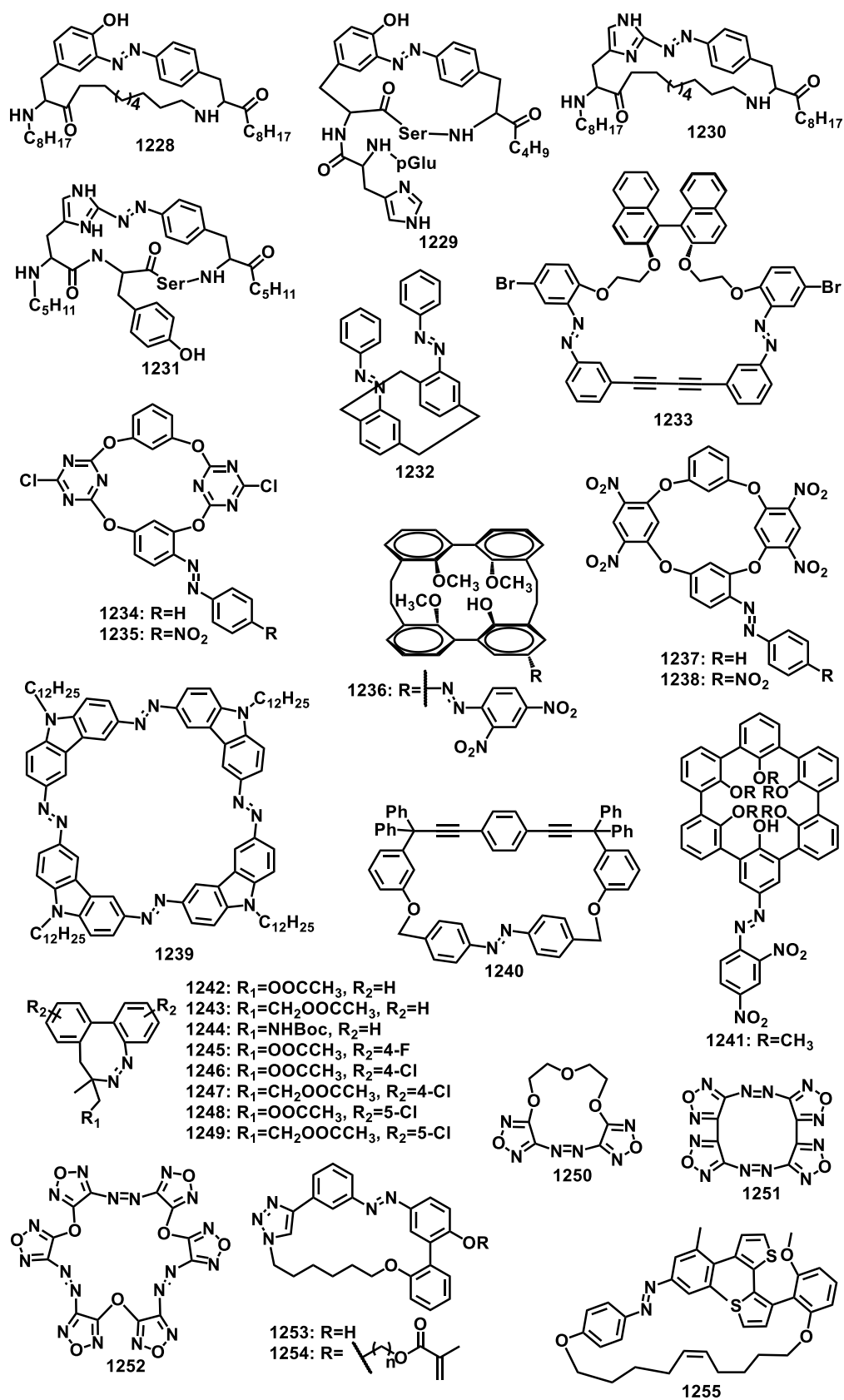
Compound	References	Compound	References	Compound	References	Compound	References
<b>1181</b>	[535]	<b>1189</b>	[536]	<b>1197</b>	[537]	<b>1205</b>	[538]
<b>1182</b>	[539]	<b>1190</b>	[536]	<b>1198</b>	[537]	<b>1206</b>	[540, 541]
<b>1183</b>	[539]	<b>1191</b>	[536]	<b>1199</b>	[513]	<b>1207</b>	[542]
<b>1184</b>	[539]	<b>1192</b>	[536]	<b>1200</b>	[513]	<b>1208</b>	[543]
<b>1185</b>	[544]	<b>1193</b>	[536]	<b>1201</b>	[513]	<b>1209</b>	[545]
<b>1186</b>	[544]	<b>1194</b>	[536]	<b>1202</b>	[546]		
<b>1187</b>	[544]	<b>1195</b>	[547]	<b>1203</b>	[546]		
<b>1188</b>	[548]	<b>1196</b>	[549]	<b>1204</b>	[543]		

**Scheme 25** Structures of other azo macrocycles (part 3)



**Table 25** Other azo macrocycles in Scheme 25

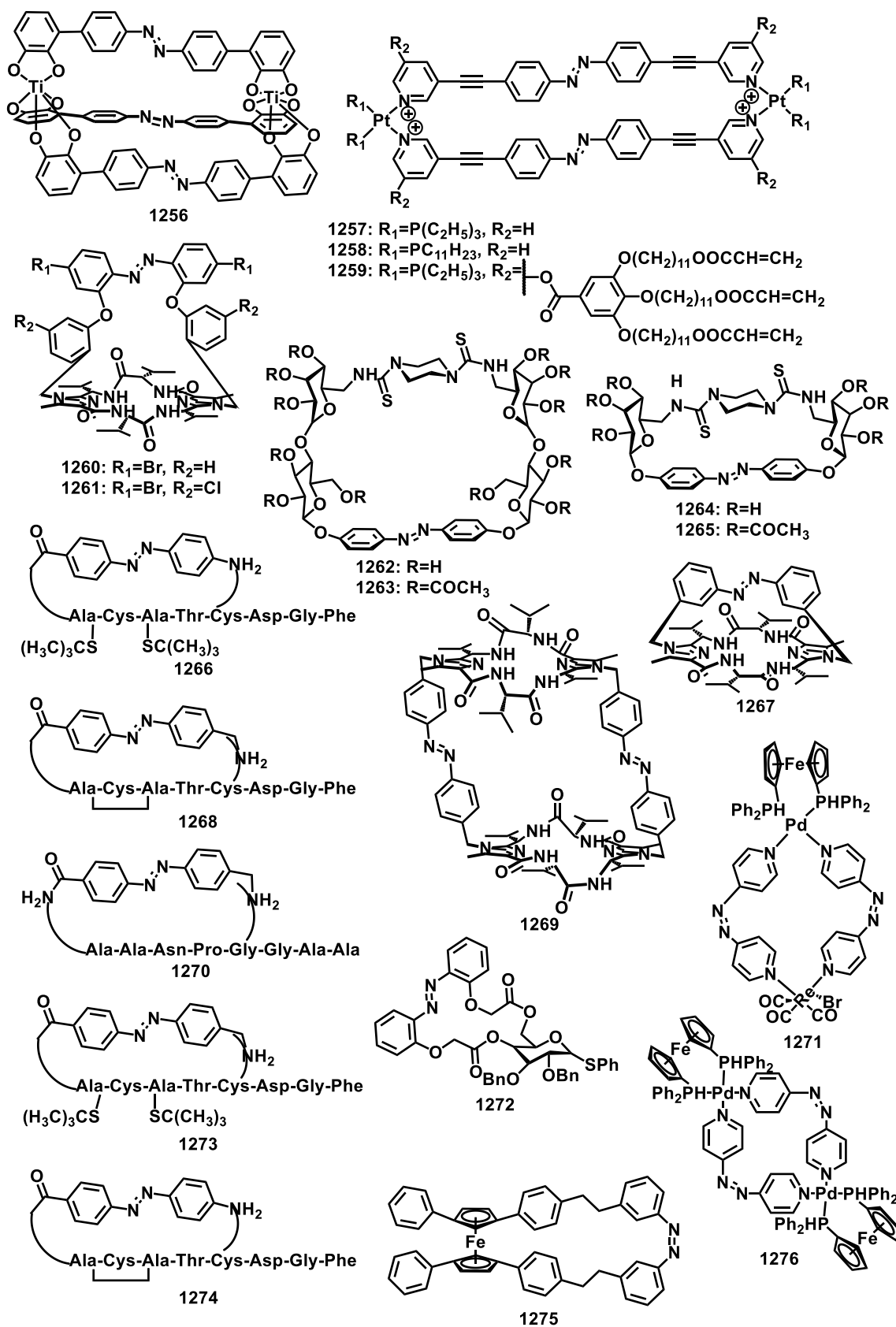
Compound	References	Compound	References	Compound	References	Compound	References
<b>1210</b>	[550, 551]	<b>1215</b>	[552]	<b>1220</b>	[553]	<b>1225</b>	[554]
<b>1211</b>	[550, 551]	<b>1216</b>	[517]	<b>1221</b>	[555]	<b>1226</b>	[475]
<b>1212</b>	[551]	<b>1217</b>	[556]	<b>1222</b>	[555]	<b>1227</b>	[555]
<b>1213</b>	[529]	<b>1218</b>	[556]	<b>1223</b>	[482]		
<b>1214</b>	[529]	<b>1219</b>	[557]	<b>1224</b>	[555]		



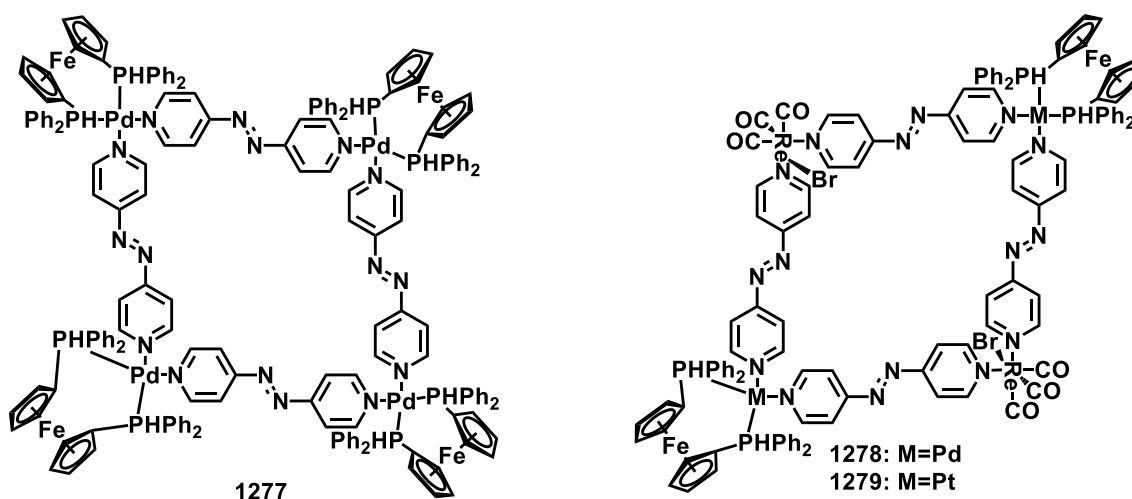
Scheme 26 Structures of other azo macrocycles (part 4)

**Table 26** Other azo macrocycles in Scheme 26

Compound	References	Compound	References	Compound	References	Compound	References
1228	[476]	1235	[558]	1242	[559]	1249	[559]
1229	[476]	1236	[117, 494, 560]	1243	[559]	1250	[561]
1230	[476]	1237	[558]	1244	[559]	1251	[561]
1231	[476]	1238	[558]	1245	[559]	1252	[561]
1232	[521]	1239	[562]	1246	[559]	1253	[540]
1233	[543]	1240	[563]	1247	[559]	1254	[540]
1234	[558]	1241	[494]	1248	[559]	1255	[564]



Scheme 27 Structures of other azo macrocycles (part 5)



Scheme 27 (continued)

Table 27 Other azo macrocycles in Scheme 27

Compound	References	Compound	References	Compound	References	Compound	References
1256	[557]	1262	[524]	1268	[565]	1274	[565]
1257	[566]	1263	[524]	1269	[567]	1275	[508, 568, 569]
1258	[566]	1264	[522–524]	1270	[570]	1276	[571]
1259	[572]	1265	[524]	1271	[571]	1277	[571]
1260	[573]	1266	[565]	1272	[574]	1278	[571]
1261	[573]	1267	[575]	1273	[565]	1279	[571]

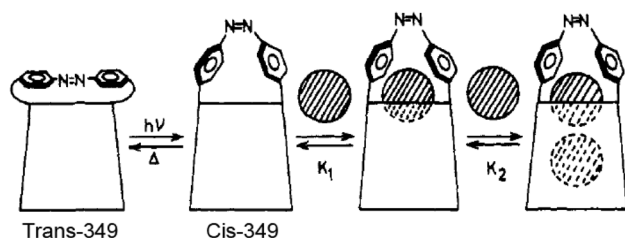
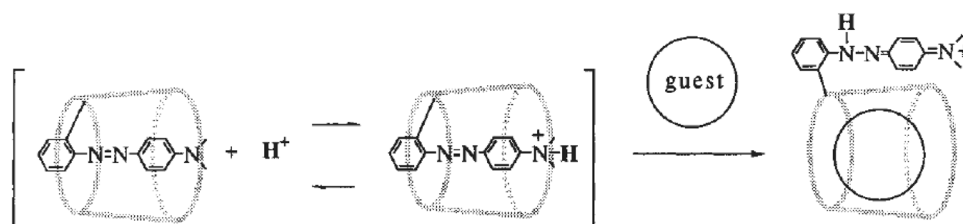


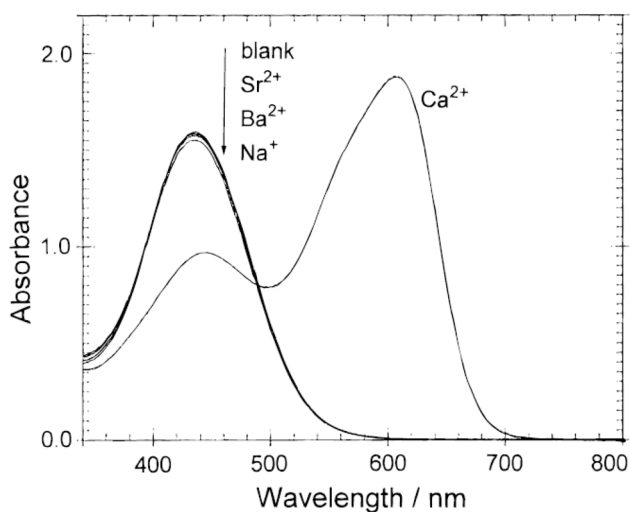
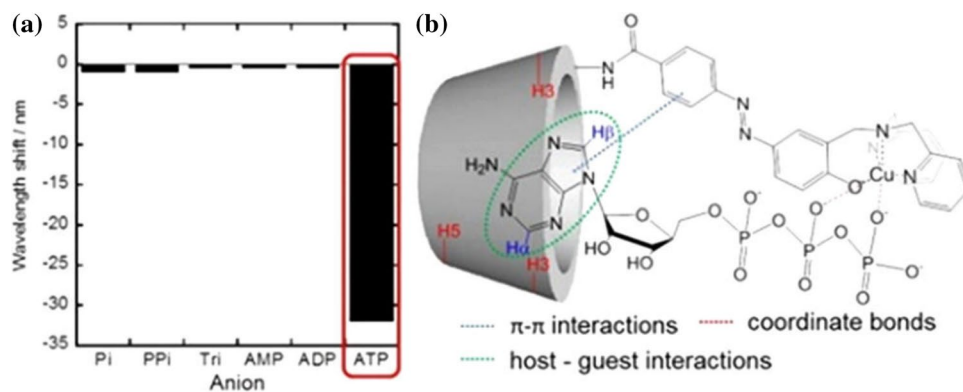
Fig. 1 Illustration of isomerization and complexation with guest of 349. Reproduced with permission from Ref. [191]. Copyright 1979 from American Chemical Society

for optical sensing, and photo-response. In this review, we first comprehensively summarized the structures of various macrocycles containing azo group. Most of popular macrocycles have many azo-modified derivatives, especially for crown ether and calixarene, due to the convenient synthesis of azo compounds and the facile modification of these macrocyclic scaffolds.

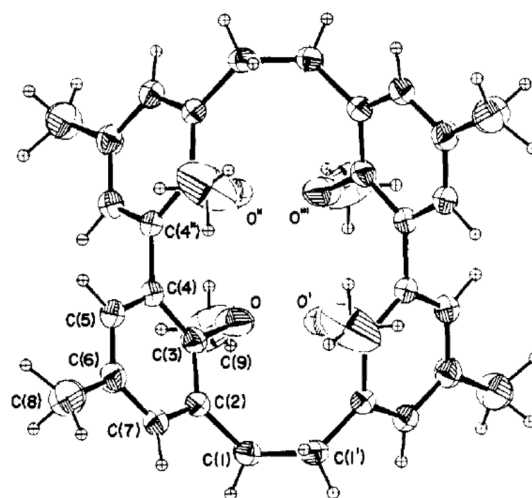
Fig. 2 Illustration of the guest-induced conformational change of 325 that causes the color change. Reproduced with permission from Ref. [165]. Copyright 1992 from Nature Publishing Group



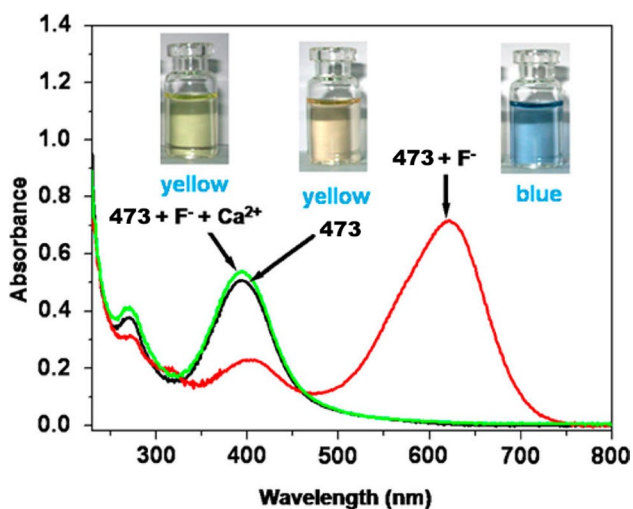
**Fig. 3** **a** Selective sensing to ATP by **Cu-350** in the presence of phosphoric acid derivatives. **b** Suggested structure of **Cu-350/ATP** complex. Reproduced with permission from Ref. [194]. Copyright 2017 from American Chemical Society



**Fig. 4** UV absorption spectra of **928** upon extraction with aqueous metal chloride solution. Reproduced with permission from [391]. Copyright 1998 from American Chemical Society



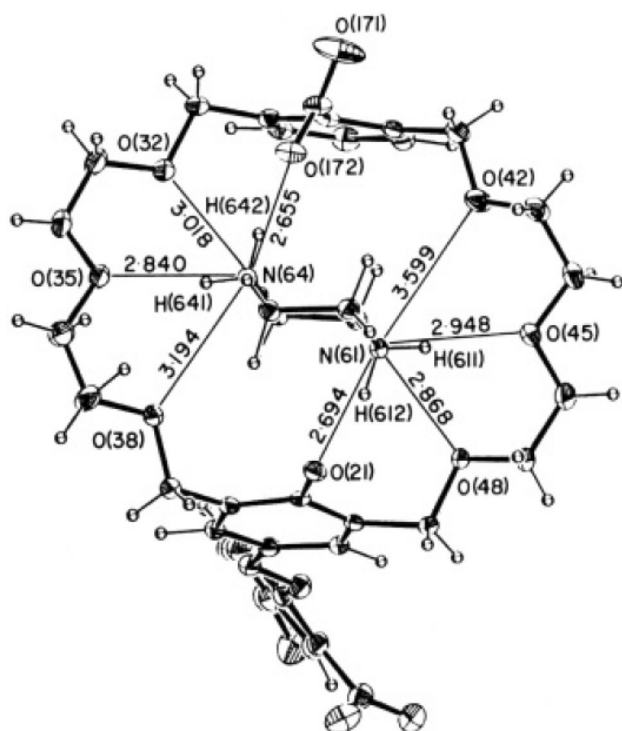
**Fig. 6** Molecular structure of **1236a** shown by the ORTEP drawing. Reproduced with permission from Ref. [560]. Copyright 1985 from American Chemical Society



**Fig. 5** F<sup>-</sup> coordination by **473** and displacement by Ca(NO<sub>3</sub>)<sub>2</sub>. Reproduced with permission from Ref. [269]. Copyright 2011 from American Chemical Society

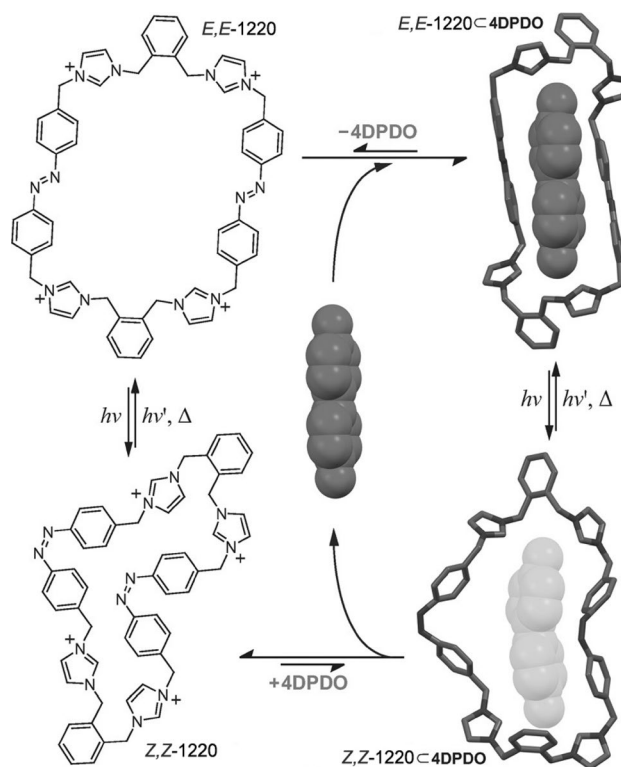
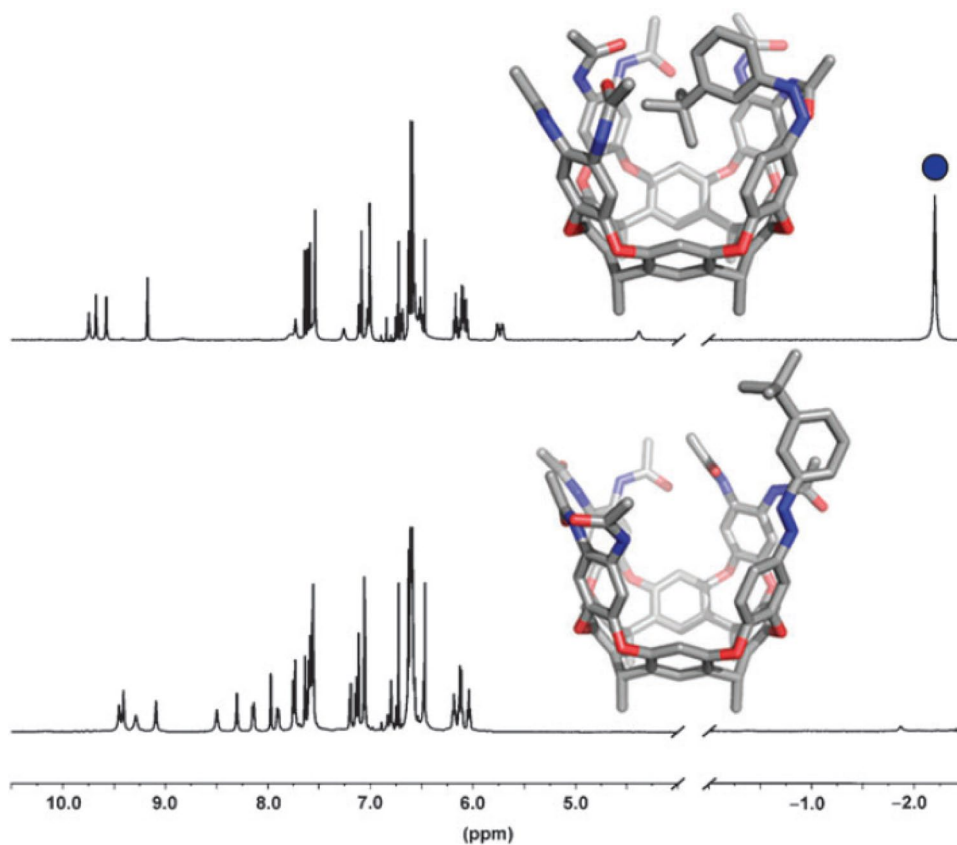
Furthermore, we reviewed several representative examples of these azo macrocycles for molecular recognition, self-assembly and application to give readers an impression of their properties and research status. In general, most works about azo macrocycles focused on their syntheses and (photo-responsive) model guest recognition. We listed > 1200 azo macrocyclic molecules but rarely found the works about application, and even self-assembly.





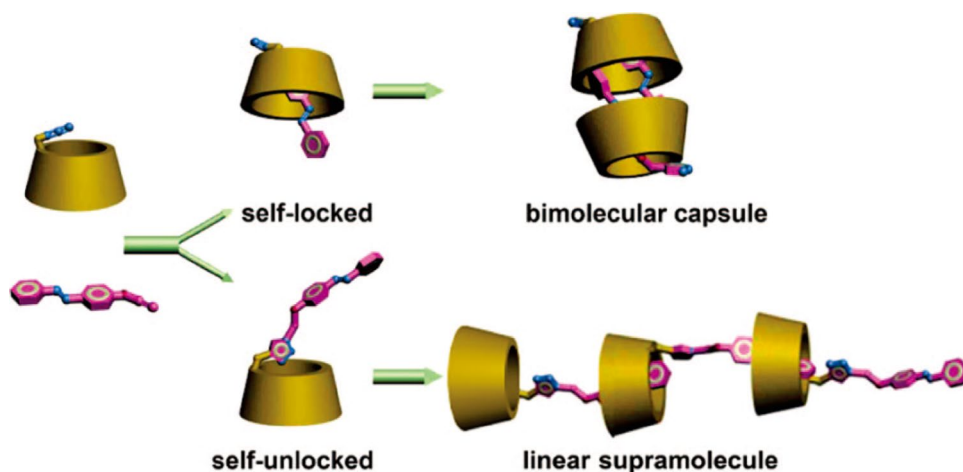
**Fig. 7** An ORTEP drawing of the molecular structure of the 255-piperazine complex. Reproduced with permission from Ref. [116]. Copyright 1988 from American Chemical Society

**Fig. 8**  $^1\text{H}$  NMR spectra in  $d_{12}$ -mesitylene showing *trans*-**978** (bottom) and self-contained *cis*-**978** (top). The inverted tert-butyl signal is marked by a blue circle. Reproduced with permission from Ref. [415]. Copyright 2011 from Royal Society of Chemistry. (Color figure online)

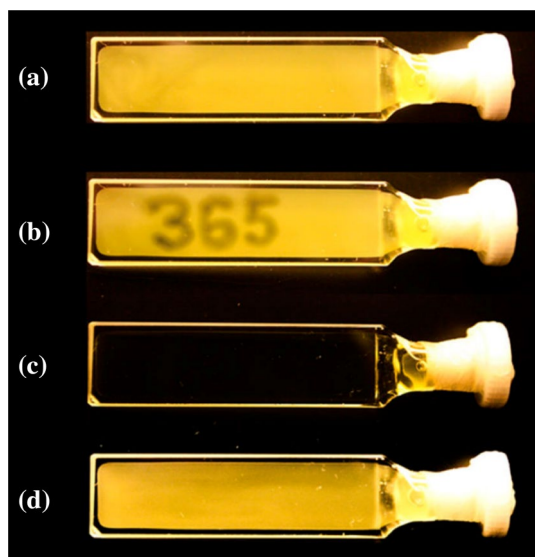
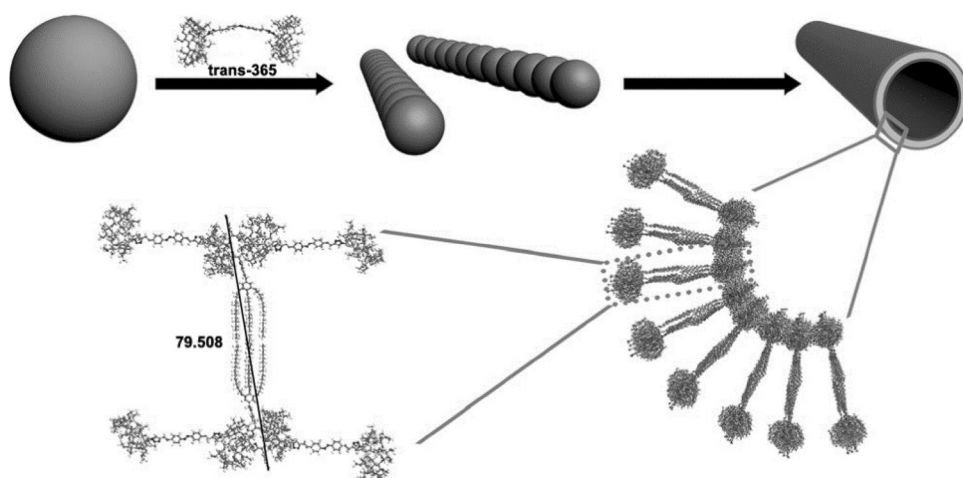


**Fig. 9** Schematic representation of the photo-controlled catch and release of 4DPDO by **1220**. Reproduced with permission from Ref. [553]. Copyright 2016 from Wiley-VCH Verlag GmbH & Co. KGaA

**Fig. 10** Deduced self-assembly structures of **334a** (top) and **334b** (bottom). Reproduced with permission from Ref. [172]. Copyright 2008 from American Chemical Society



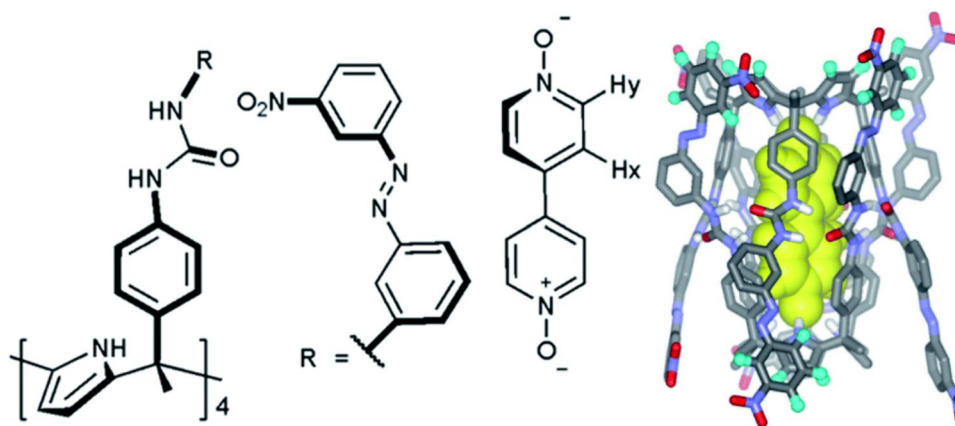
**Fig. 11** Illustration of the secondary assembly of amphiphilic porphyrin derivative mediated by *trans*-**365**. Reproduced with permission from Ref. [207]. Copyright 2015 from Wiley-VCH Verlag GmbH & Co. KGaA



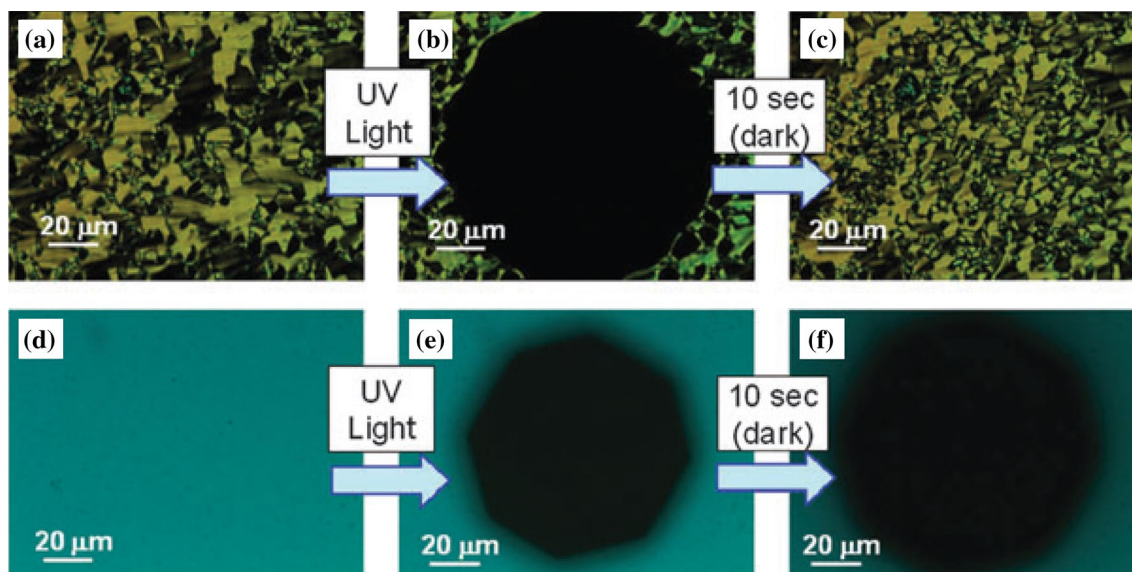
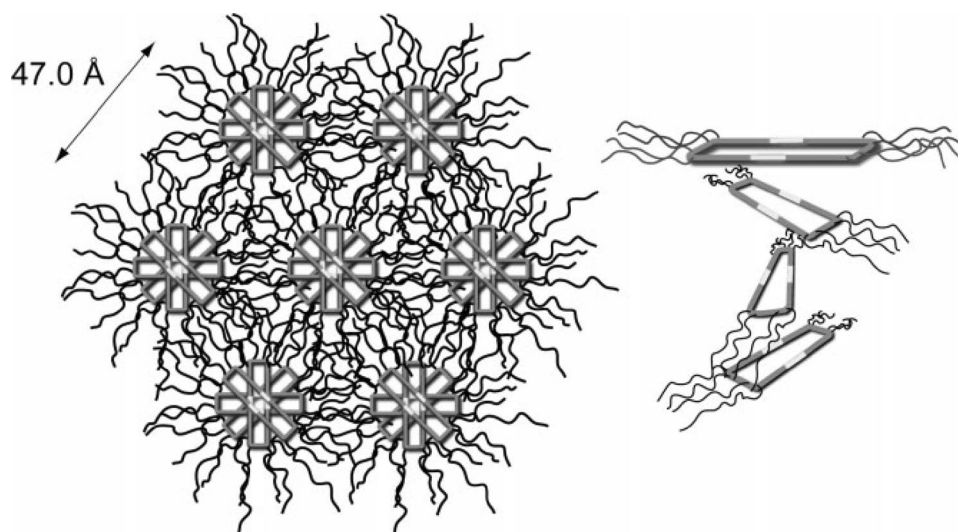
**Fig. 12** Photographs of poly(azo calix[4]arenes) **443** in ethanol: **a** at 20 °C before irradiation; **b** after photoassisted writing at 20 °C; **c** at 40 °C and **d** at 20 °C after thermal relaxation. Reproduced with permission from Ref. [254]. Copyright 2013 from American Chemical Society

In our opinion, the supramolecular chemistry and application of azo macrocycles are still in their infancy and will develop flourishingly in the future since both azo compounds and macrocycles have high status in various fields. The breakthrough relies on finding methods to use both properties of azo compounds, such as photo- and redox-response, fast internal conversion and color, and unique supramolecular chemistry of each macrocycle. We have a vision that azo macrocycles will have more fascinating application in fields of diagnosis and therapy, molecular machine, liquid crystal and nonlinear optics. Its biomedical application, for

**Fig. 13** Structures of arylex-tended tetraurea calix[4]pyrrole and bis-pyridine-*N*-oxide (left) and energy minimized structure of the capsular assembly (right). Reproduced with permission from [437]. Copyright 2014 from Royal Society of Chemistry



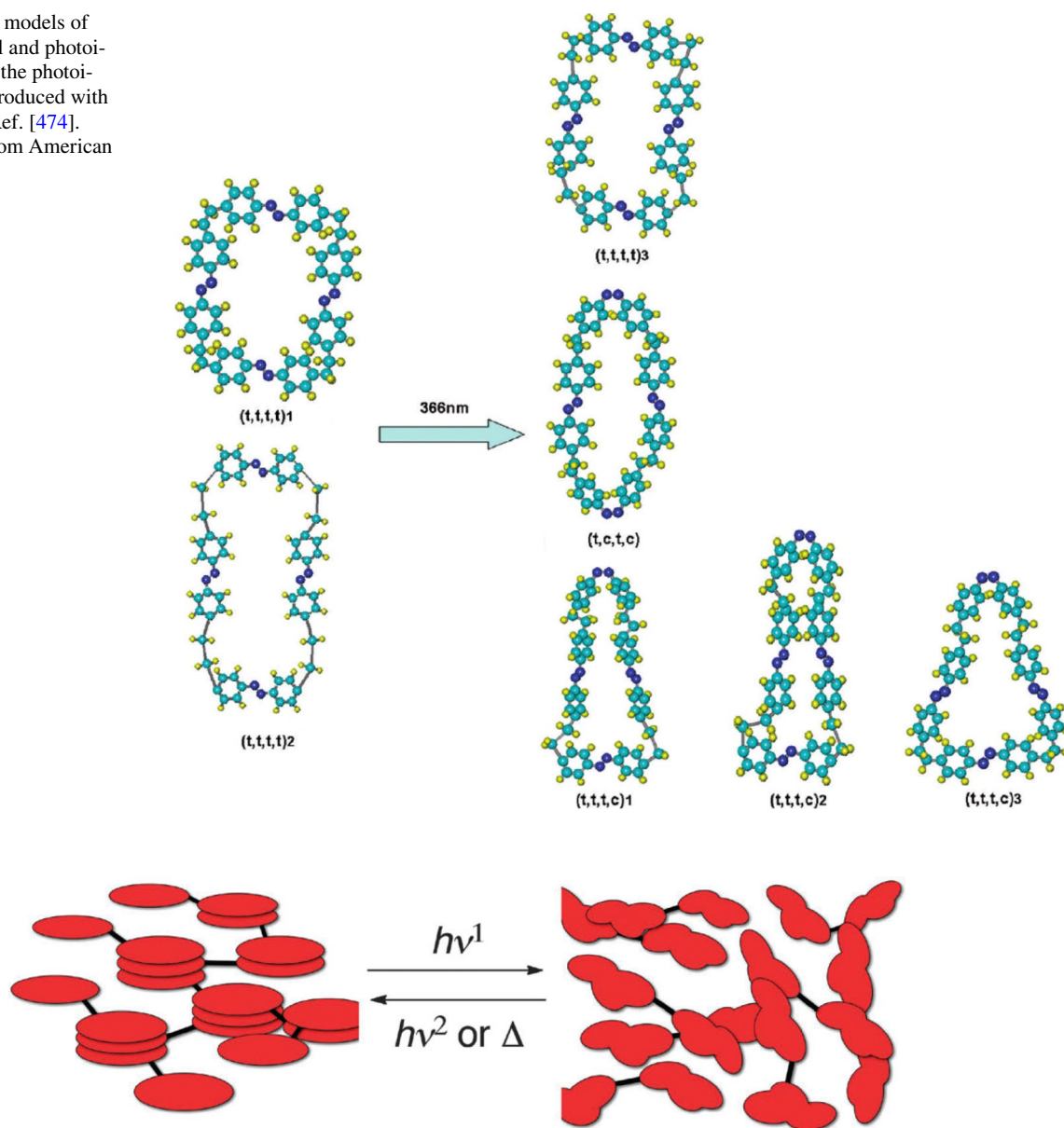
**Fig. 14** Proposed, idealized model of the thermotropic columnar hexagonal LC phase of **1259** (left). Addition of polar solvent serves to swell this phase (right). Reproduced with permission from Ref. [572]. Copyright 2008 from Wiley-VCH Verlag GmbH & Co. KGaA



**Fig. 15** Polarizing optical photomicrographs of **1021** at 120 °C (a–c) and **1022** at 25 °C (d–f) before 365 nm light UV irradiation (a, d), during irradiation for 5 s (b, e) and 10 s after ceasing the irradiation (c, f). The initial states are SmC (a) and columnar (d) phases. The

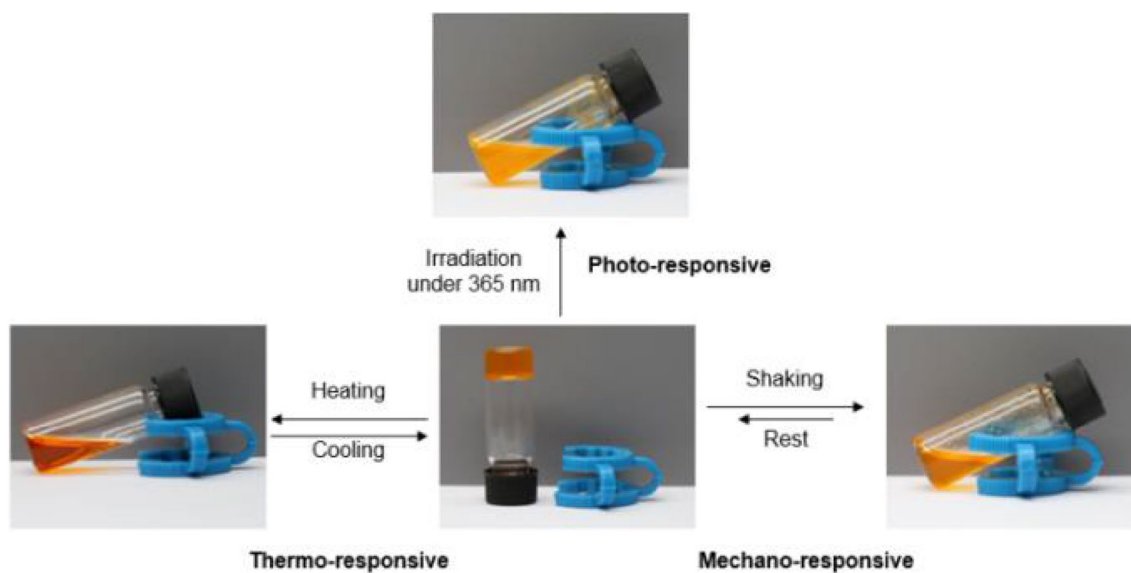
dark area in (b–f) corresponds to an isotropic phase. Reproduced with permission from Ref. [481]. Copyright 2011 from Royal Society of Chemistry

**Fig. 16** Molecular models of the conformational and photoisomers of **1015** in the photoisomerization. Reproduced with permission from Ref. [474]. Copyright 2009 from American Chemical Society



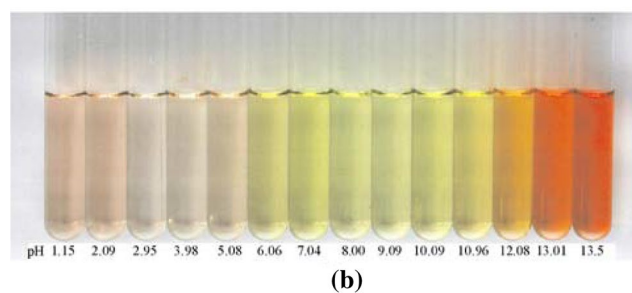
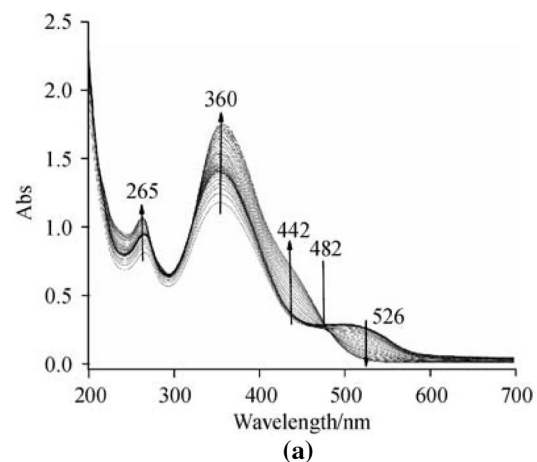
**Fig. 17** Schematic representation of 3D-networks dimeric switchable azobenzene macrocycle **1223**. In the all-*E* conformation linked p-stacks are formed (left). Irradiation induces isomerization to a mix-

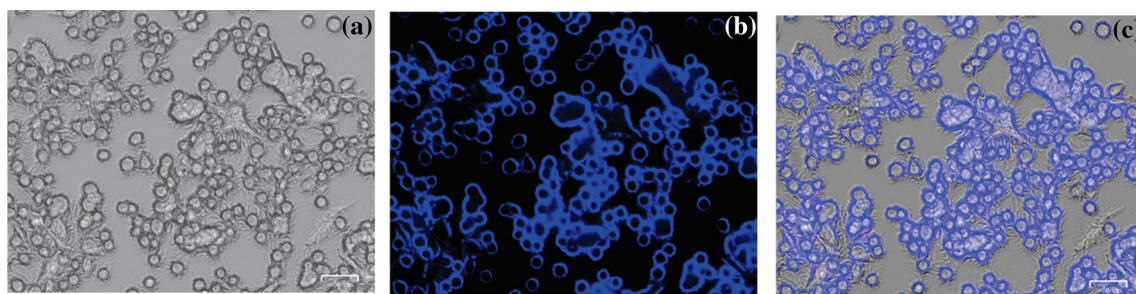
ture of *Z*-isomers all deviating from planarity, which impedes the supramolecular interaction (right). Reproduced with permission from Ref. [482]. Copyright 2013 from Royal Society of Chemistry



**Fig. 18** Pictures showing the multi stimuli-responsive behavior of gel of **1272** in cyclohexane. Reproduced with permission from Ref. [574]. Copyright 2017 from Wiley-VCH Verlag GmbH & Co. KGaA

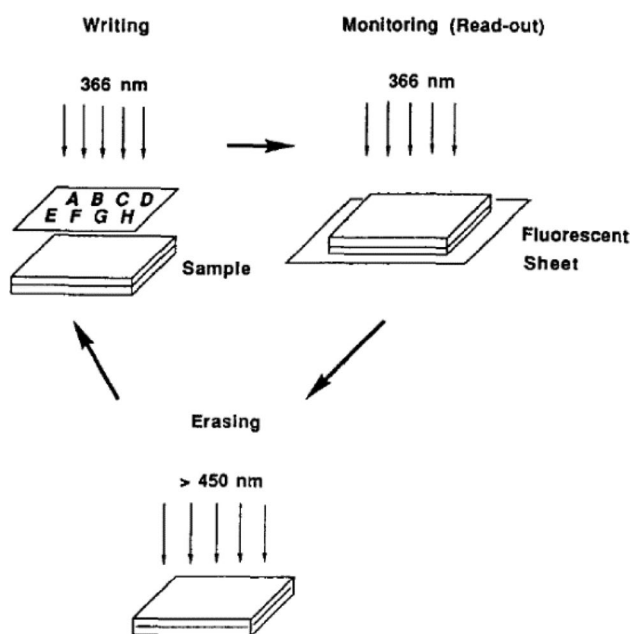
**Fig. 19 a** UV–Vis spectra of **549** titrated with a dilute NaOH solution. **b** Color changes corresponding to different pH values. Reproduced with permission from Ref. [319]. Copyright 2010 from Wiley-VCH Verlag GmbH & Co. KGaA. (Color figure online)





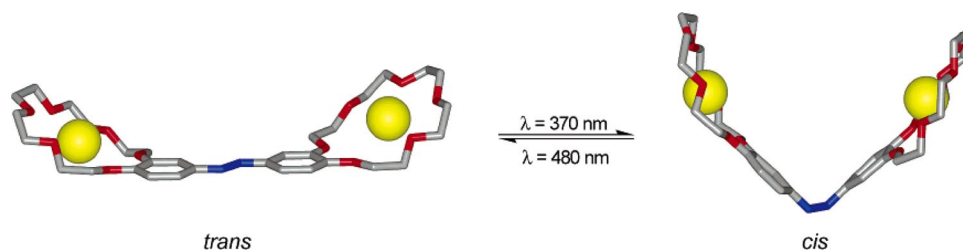
**Fig. 20** Fluorescence image and their corresponding bright-field transmission images. **a** Control cells (only cells without  $\text{Cu}^{2+}$  or ligand **666**); **b** fluorescence image of SW-620 cells after treatment

with  $\text{Cu}^{2+}$  and ligand **666**; **c** merge view of bright field and fluorescence images. Reproduced with permission from Ref. [355]. Copyright 2016 from Elsevier

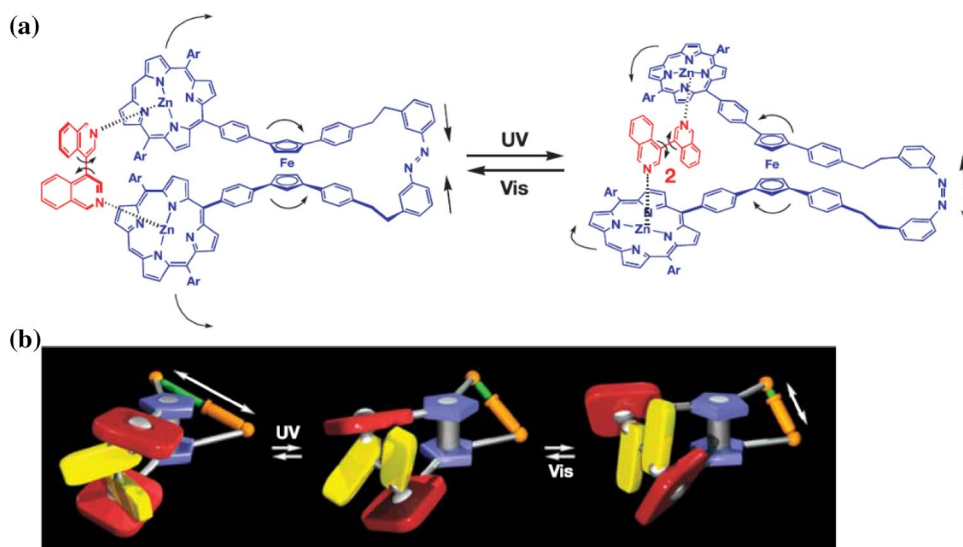


**Fig. 21** Procedures for writing, monitoring and erasing of memories. Reprinted from Ref. [462]. Copyright 1992 with permission from Elsevier

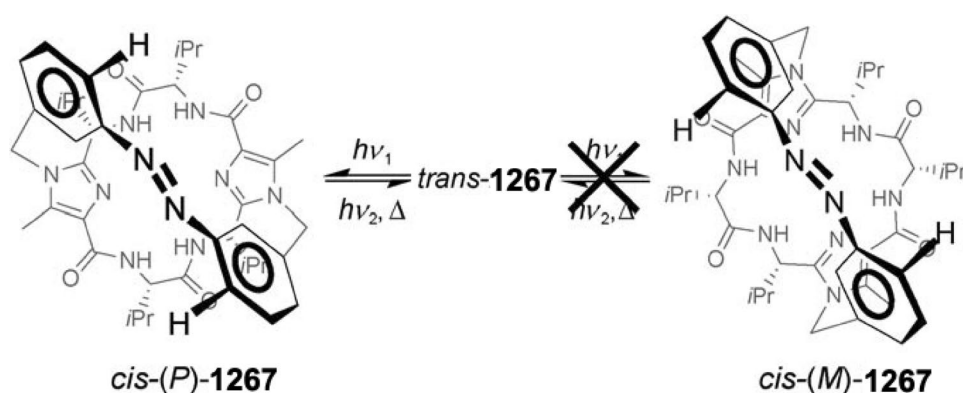
**Fig. 22** Computer-generated structures of interswitchable *trans* and *cis* forms of **176-2**[ $\text{Ba}^{2+}$ ]. Reproduced with permission from Ref. [109]. Copyright 2003 from American Chemical Society



**Fig. 23** Design and concept of light-powered molecular pedal. Reproduced with permission from Ref. [507]. Copyright 2006 from Nature Publishing Group



**Fig. 24** Unidirectional switching of the cyclic azo macrocycle **1267**. Reproduced with permission from Ref. [575]. Copyright 2010 from Wiley-VCH Verlag GmbH & Co. KGaA



example, tumor-selective imaging and targeting drug delivery based on hypoxia-responsive azo macrocycle, is of our particular interest in the near future.

**Acknowledgements** This work was supported by NSFC (21672112), the Fundamental Research Funds for the Central Universities and Program of Tianjin Young Talents, which are gratefully acknowledged.

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