

Highlight Review

Light-switchable Metal-Organic Cages

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Sander J. Wezenberg studied chemistry at the University of Nijmegen where he carried out his Master's research in the group of Prof. Roeland Nolte. He then moved to Tarragona for his PhD studies in the field of supramolecular chemistry with Prof. Arjan Kleij at the Institute of Chemical Research of Catalonia. During this period he spent three months as a visiting researcher in the group of Prof. Joseph Hupp at Northwestern University. After receiving his PhD in 2011, he joined the group of Prof. François Diederich at ETH Zurich as a postdoctoral fellow. Two years later he moved to the University of Groningen to work with Prof. Ben Feringa and he was appointed Assistant Professor at the same university in 2017. He moved to Leiden University in 2019 to establish his independent research group. His main research interests are in the areas of anion binding, molecular switches, and self-assembled materials.

Abstract

The ability to control structure and function of metal-organic cages by external stimuli offers many possibilities. For example, preventing product inhibition in catalysis, releasing a drug at a specific site, or altering material properties. This Highlight Review describes the different strategies that have been developed to make light-responsive metal-organic cages able to undergo a structural change in response to a light stimulus and furthermore, major challenges and future perspectives are discussed.

Keywords: Metal-organic cages | Coordination cages | Molecular switches

Introduction

Metal-ligand interactions have been widely exploited to construct self-assembled macrocycles, polymers, cages, and frameworks, among others.^{1–8} Self-assembled metal-organic cages have attracted major attention for their well-defined inner void space and they have been applied in, for example, the stabilization of reactive species,^{9,10} catalysis,^{11–15} and they have been considered for drug delivery.^{16,17} In many cases stimulus-control of the cage structure is desired,^{18–20} for instance, to prevent product inhibition in catalysis or to release a loaded drug at a specific site. In this regard, the use of light is advantageous since it can be applied with high spatiotemporal precision without the production of waste. Nevertheless, the development of light-responsive cages has proven to be highly challenging and successful examples are rarely encountered in the literature.

In this Highlight Review, the aim is to provide a comprehensive overview of the strategies that have been developed so far to control the structure, and with that the function, of

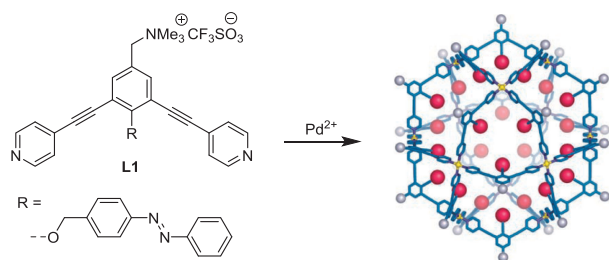
metal-organic cages using light. Other excellent review articles, in which examples of light-responsive metal-organic cages were included, have previously appeared (e.g. on stimuli-responsive metal-ligand assemblies^{18,19} and photoactive as well as photo-responsive host-guest systems^{21–24}). Herein, only cages that are able to undergo a structural modification in response to light are discussed and furthermore, the focus is on design principles and major challenges, rather than applications. Encapsulation of photoresponsive guests has also been investigated,^{21,22,25–27} but is not the subject of this review.

Before looking deeper into metal-organic cages, it should be mentioned that light-responsive metal-organic frameworks have been developed by incorporating photoswitchable linkers, primarily to control porosity and gas sorption.^{28,29} Preservation of framework integrity and unhindered switching are the main challenges in this case. In contrast, disassembly is desirable for certain applications of metal-organic cages and moreover, photoswitching may be facilitated by the reversibility of the metal-ligand interactions.

Achieving Light-responsiveness

Dangling Azobenzene Switches. The group of Fujita described various metal-organic cages consisting of 12 Pd ions and 24 bis-pyridyl bent bridging ligands.³⁰ In 2007, the same group described the use of ligand **L1** that was functionalized with azobenzene (Scheme 1).³¹ The complex was assembled in quantitative yield by combining the ligand with Pd(OSO₂CF₃)₂ in CD₃CN. In the assembled structure, the azobenzene moieties point inwards forming a dense array.

When the ligand alone was irradiated with 365 nm light, a photostationary state (PSS) containing the *trans* and *cis* isomer in a 33:67 ratio was obtained. Upon irradiation of the Pd₁₂(**L1**)₂₄ complex, however, the PSS ratio was reduced to 83:17 (*trans*/



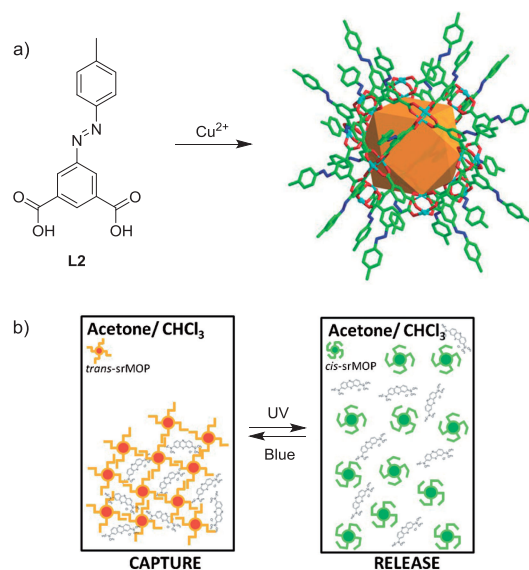
Scheme 1. Self-assembly of $\text{Pd}_{12}(\text{L1})_{24}$ complex. Adapted with permission from ref 31. Copyright 2007 Wiley-VCH.

cis). By control experiments with mixed ligand assemblies it was excluded that the decrease in PSS ratio is due to the dense packing of azobenzene molecules. Instead, it is most likely due to overlap of the Pd-pyridine metal-to-ligand charge transfer (MLCT) absorption band (300–370 nm) with the azobenzene excitation wavelength. Importantly, after irradiation with 436 nm light, a PSS ratio of 80:20 (*trans/cis*) was reached for both the ligand and the complex. Upon heating the complex, full *cis*-to-*trans* back conversion was achieved. Although the content of *cis*-azobenzene in the complex was thus not very high, full reversibility was demonstrated.

The *trans*-to-*cis* isomerization of azobenzene causes an increase in dipole moment and, in this case, reduces the hydrophobicity of the complex's interior. This feature was exploited for guest binding and release. The complex was shown to be able to encapsulate pyrene and 1-pyrenecarboxaldehyde in $\text{CD}_3\text{CN}/\text{D}_2\text{O}$ (1:1), driven by hydrophobic interaction. For the latter guest it was demonstrated that irradiation with UV light results in a weakening of the interaction, whereas the guest was fully taken up again after heating the solution.

Years later, the group of Zhao reported a metal-organic complex of which the organic linkers were also functionalized with azobenzene (Scheme 2a).³² The difference is that here the self-assembled structure was decorated on the exterior with the photoswitchable moieties. The isophthalic acid linker **L2** was combined with $\text{Cu}(\text{OAc})_2$ in *N,N*-dimethylacetamide and the $(\text{Cu}_2)_{12}(\text{L2})_{24}$ spherical complex precipitated by addition of MeOH. Ligand *trans*-to-*cis* isomerization was achieved by UV light irradiation in CHCl_3 and subsequent use of blue light resulted in back isomerization to the *trans* form. The PSS ratios were not determined for these processes.

Although the complex was soluble in CHCl_3 , it gradually precipitated and it could be redissolved by irradiation with UV light. Possible explanations for this redissolution are that π - π interactions between the $(\text{Cu}_2)_{12}(\text{L2})_{24}$ complexes are weakened upon *trans*-to-*cis* isomerization and that the larger dipole moment of *cis*-azobenzene enhances solubility in polar solvent. The difference in solubility was used for the entrapment and release of a methylene blue (MB) guest molecule (Scheme 2b). The MB concentration could be easily monitored by UV/Vis spectroscopy. In a mixed solvent system (5% acetone in CHCl_3) the *trans* complex was found to be insoluble, while the *cis* complex was highly soluble. A suspension of the *trans* complex was prepared under blue light irradiation in the presence of an excess of MB and non-captured MB was removed by centrifugal separation. When the soluble *cis* complex was generated by irradiation with UV light, the MB concentration in solution



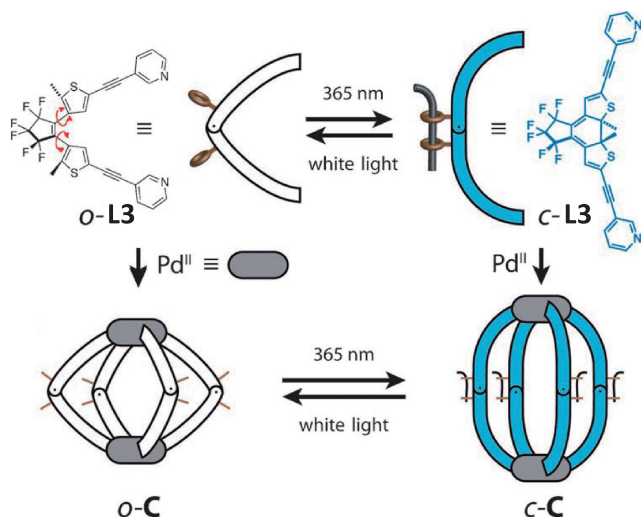
Scheme 2. (a) Assembly of $(\text{Cu}_2)_{12}(\text{L2})_{24}$ complex and (b) photoinduced guest capture and release. Adapted with permission from ref 32. Copyright 2014 Wiley-VCH.

increased. Remarkably, when the solution was subsequently irradiated with blue light, MB was almost fully taken up again.

In a subsequent study, the groups of Sun and Zhao addressed the issue of poor *trans*-to-*cis* isomerization in the solid state by incorporating the $(\text{Cu}_2)_{12}(\text{L2})_{24}$ complex into mesoporous silica (MS).³³ This incorporation was achieved by wet-impregnation with different loadings (10, 20, 40 wt %). For the 10 wt % composite, 365 nm irradiation of a solution in ethylene glycol afforded 92% of *cis* isomer, which is similar to that observed for the complex alone (95%). This isomerization process could be reversed by irradiation with 450 nm light.

Next, the adsorption properties of the composite and the bulk material were analyzed. Remarkably, the composite with the lowest loading exhibited a four-times larger decrease in the adsorption of propene (48.2%) than the bulk material (11.2%) upon 365 nm irradiation. It is suggested that in the *trans* state the copper sites are accessible for propene absorption, while in the *cis* state they are blocked, accounting for the difference. As for the composite *trans*-to-*cis* isomerization can occur freely, the change in absorption capacity is larger than for the bulk material.

Photoswitching Ligand Structure. In the designs above the cages are decorated with photoswitchable moieties in the interior or on the exterior. However, much larger changes in properties may be achieved by using molecular photoswitches as an integral part of the linkers. In a landmark paper from 2013,³⁴ the group of Clever described the $\text{Pd}_2(\text{L3})_4$ cage shown in Scheme 3, which contains dithienylethene (DTE) as the linker. The linker could be converted in high yield (in CD_3CN) from the open-ring (*o*) to the closed-ring (*c*) form by irradiation with UV light (365 nm), whereas the open-ring form could be fully regenerated using white light. The open-ring and closed-ring cages were obtained in quantitative yield by combining the respective ligand with $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ in CD_3CN . As for the ligand, these cages could be interconverted by UV and white light irradiation. Owing to the helical conformation of the open-ring form of the ligand, $\text{Pd}_2(\text{o-L3})_4$ exists as a mixture of



Scheme 3. Photoswitching of DTE ligand **L3** and the respective self-assembled cage. Reproduced with permission from ref 34. Copyright 2013 Wiley-VCH.

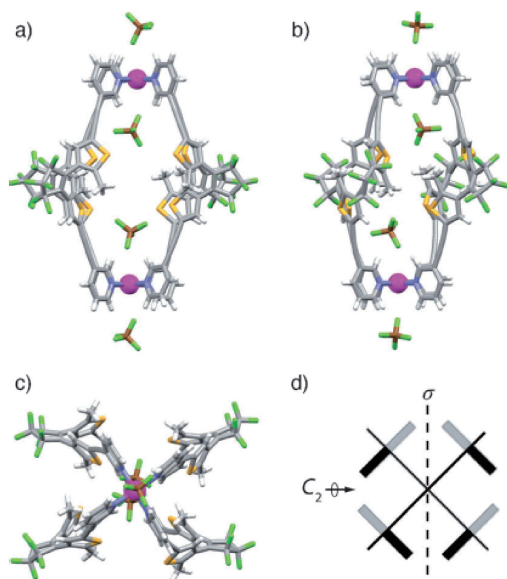


Figure 1. (a–c) Different views of the X-ray structure of *meso*-Pd₂(*o*-**L3**)₄ and (d) depiction of the stereochemical relationship. Color code: C gray, H white, N blue, B brown, F green, S yellow, Pd purple. Reproduced with permission from ref 34. Copyright 2013 Wiley-VCH.

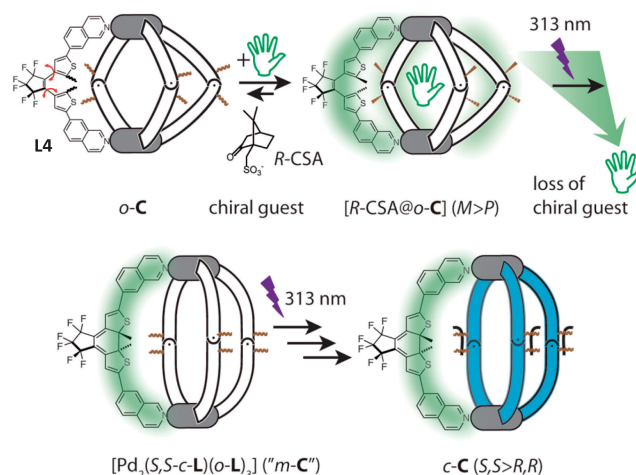
stereoisomers with similar energies as was derived from density functional theory (DFT) calculations. Interestingly, in the solid state, only the *meso*-isomer (*PPMM*) was observed (Figure 1). The closed-ring ligand is chiral and hence, Pd₂(*c*-**L3**)₄ also exists as a mixture of stereoisomers. Although de- and re-coordination of the pyridyl units to the Pd ions is slow (on the NMR timescale) it is possible for the open-ring cage stereoisomers to interconvert via C–C bond rotation in the DTE switch. In the closed-ring cage, this C–C bond rotation is no longer possible.

It was determined by DOSY NMR that the open-ring cage is smaller than the closed-ring cage. To this end, ¹H and ¹⁹F NMR

titrations were performed with a dodecafluorododecaborate anion ([B₁₂F₁₂]₂[−]) in CD₃CN. Intriguingly, the smaller opening cage displayed a much stronger affinity for this anion than the closed-ring cage (*K*_a = 3.2 × 10⁴ M^{−1} and *K*_a = 6.7 × 10² M^{−1}, respectively). Van 't Hoff analysis showed for both cages that binding is entropy-driven and hence, solvent release from the cage interior is suggested to be the driving force for binding. Furthermore, the stronger binding to the open cage is explained by the ability to adapt its structure to fit the guest (induced fit), which is not possible for the rigid closed-ring cage. Importantly, photoswitching was also possible in the presence of the guest.

Until recently, it remained unclear whether all DTEs can undergo the ring-closing process at the same time or if cages with open-ring and closed-ring ligands exist as intermediate stages. Clever and co-workers reported a crystal structure of mixed ligand cage Pd₂(*o*-**L3**)₂(*c*-**L3**)₂, revealing that cage interconversion is a stepwise process.³⁵ The crystals were grown over a period of six months from a solution of Pd₂(*o*-**L3**)₄ in CD₃CN, which was unintentionally exposed to sunlight. In the same report, three more ligands having different solubilizing chains were described. These solubilizing chains did not hinder cage assembly nor photoswitching. Furthermore, earlier NMR studies toward the binding of [B₁₂F₁₂]₂[−] to Pd₂(*o*-**L3**)₄ were corroborated by isothermal titration calorimetry (ITC), which afforded similar association constants (i.e. *K*_a = 4.6 × 10⁴ M^{−1} for the open-ring cage and *K*_a = 2.1 × 10³ M^{−1} for the closed-ring cage). Unfortunately, many other tested borates (e.g. [B₁₂Cl₁₂]₂[−], [B₁₂Br₁₂]₂[−]) did not show any sign of binding or only bound very weakly.

To address the same question, that is, if ring-closing occurs in an associated or stepwise manner, Clever and co-workers made use of supramolecular chirality transfer (Scheme 4).³⁶ Therefore, a cage with the extended ligand **L4** was prepared using the same procedure as before. The ligand could be interconverted between open-ring and closed-ring isomers using 313 nm and 617 nm light, respectively. The closed-ring cage was either synthesized using the respective ligand or it was accessed by irradiation of a solution of Pd₂(*o*-**L4**)₄. Again, only the *meso*-form of the open-ring cage was observed in the solid state, while



Scheme 4. Chirality induction by a chiral guest and subsequent enantiodifferentiation in the photochemical isomerization step. Reproduced with permission from ref 36. Copyright 2019 American Chemical Society.

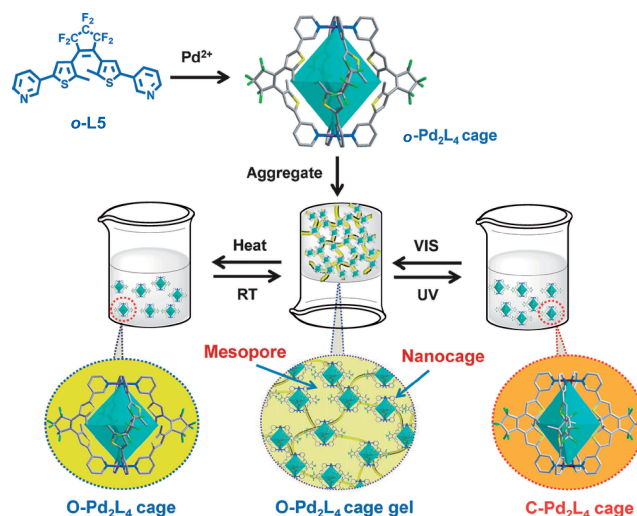
in solution the possible cage stereoisomers rapidly interconvert. Also the closed-ring cage exists as multiple stereoisomers, but in this case, enantiomers could be isolated as there is no rotation possible around the C-C bonds in the DTE switch.

In previous studies, the groups of van Esch and Feringa³⁷ as well as the group of Andréasson³⁸ demonstrated enantioselective DTE ring-closing in a chiral environment. In the study of Clever and co-workers it was shown that encapsulation of 1*S*- and 1*R*-camphor sulfonate (CSA) leads to chirality induction in the open-ring cage, as was evident from the appearance of strong Cotton effects in the circular dichroism (CD) spectrum. After irradiation of a solution of Pd₂(*o*-L4)₄ in CD₃CN, containing 1.5 equivalent of enantiopure CSA guest, a Cotton effect was preserved. This observation was attributed to enantioselective DTE ring-closing, which was confirmed by HPLC analysis of the DTE ligand L4 (after disassembly of the closed-ring cage) showing enantiomeric excess (ee). The maximum ee values, however, were only around 30% and based on this low degree of enantioenrichment, the authors assumed that the chiral guest is expelled from the cavity after the first ligand is ring-closed. This hypothesis was supported by showing that guest binding does not occur to mixed ligand cages.

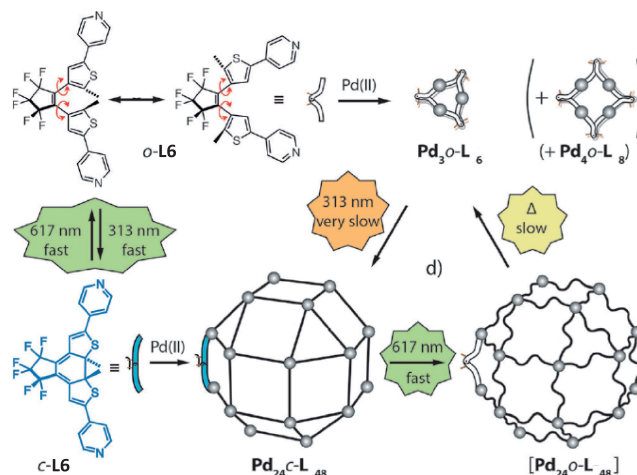
The groups of Zhang and Su used a similar DTE ligand (L5, Scheme 5) to prepare photoresponsive gels.³⁹ The open-ring ligand was combined with various metal salts, but only with Pd(NO₃)₂ gelation of DMSO took place. A gel was also obtained in a mixture of MeCN/DMSO, but no gelation was observed when using the closed-ring isomer. A combination of NMR spectroscopy and mass spectrometry revealed that the gel consists of Pd₂(L5)₄ cages. Irradiation of the gel with UV light resulted in a gel-to-solution transition and, when subsequently exposed to visible light, the gel reformed. It was found that only 15% photoconversion is needed for gel dissolution. The exact structure of the gel, however, is not yet fully understood and the authors do not rule out that a minor amount of coordination oligomer or polymer is formed and assists in the gelation process.

In the previous examples, the Pd₂L₄ cages underwent a change in structure but stayed intact over the course of the photoswitching process. For the *para*-substituted pyridyl donor ligand L6, however, Clever and co-workers observed a change in cage topology (Scheme 6).⁴⁰ The open-ring ligand L6 could be converted in 96% yield to the closed ring-isomer by 313 nm irradiation. Back isomerization was achieved in quantitative yield by 617 nm irradiation. When the open-ring ligand was combined with [Pd(CH₃CN)₄](BF₄)₂ in CD₃CN, a mixture of cyclic Pd₃(*o*-L6)₆ and Pd₄(*o*-L6)₈ complexes formed, whereas the closed-ring isomer gave a larger assembly under the same conditions. The hydrodynamic radius of this larger assembly was determined by DOSY NMR as 3.5 nm, which was assigned to a cuboctahedral Pd₂₄(*c*-L6)₄₈ complex. By light irradiation, the assembled structures could be interconverted, which requires de- and re-complexation of the pyridyl ligands. This process is much slower than the photochemical reaction and thus, irradiation leaves the system temporarily in an out-of-equilibrium state.

This change of topology was cleverly used by the group of Johnson to develop stimuli-responsive polymer networks in which the metal-organic cages function as crosslinks.⁴¹ They developed poly(ethylene glycol)-based ligand L7 having bis-pyridyl DTE termini (Scheme 7). Upon mixing the open-ring isomer with Pd(CH₃CN)₄(BF₄)₂ in CH₃CN a gel formed and



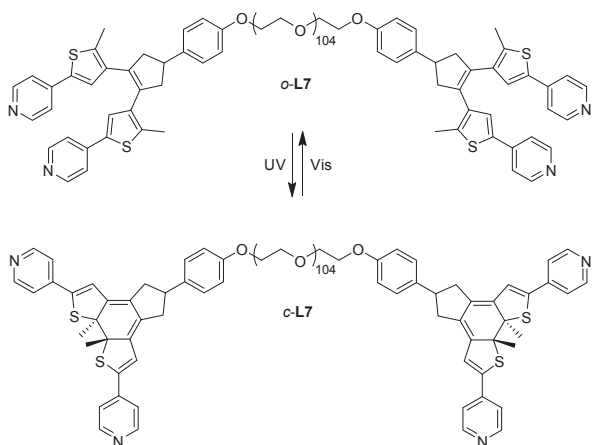
Scheme 5. Self-assembly and gelation process of Pd₂(L5)₄ cage. Reproduced with permission from ref 39. Copyright 2015 Wiley-VCH.



Scheme 6. Change of topology in DTE-based metal-organic cages. Reproduced with permission from ref 40. Copyright 2016 Wiley-VCH.

subsequent annealing was performed to allow equilibration of the network junctions. Irradiation of the gel with UV light led to a material with an almost double storage modulus (*G'*) and a slightly higher shear loss modulus (*G''*) and irradiation with green light led to recovery of the original gel properties. The change in elastic behavior was ascribed to the switching between Pd₃(*o*-L7)₆ rings and Pd₂₄(*c*-L7)₄₈ cuboctahedra, which alters the network topology.

DTE switches seem to be ideal for use as ligand scaffolds because they undergo a relatively small change in geometry upon isomerization and therefore, photoswitching is still allowed in the self-assembled state. Nevertheless, pyridyl analogs of azobenzene and overcrowded alkene have been used to successfully prepare light-responsive cages. For example, the group of Liu developed bis-(phenylazo)pyridine ligand L8, which self-assembled into an M₂L₄-type cage in the presence of [Pd(CH₃CN)₄](OTf)₂ in DMSO (Figure 2a).⁴² Upon irradiation



Scheme 7. Photoisomerization of poly(ethylene glycol)-based ligand **L7**.

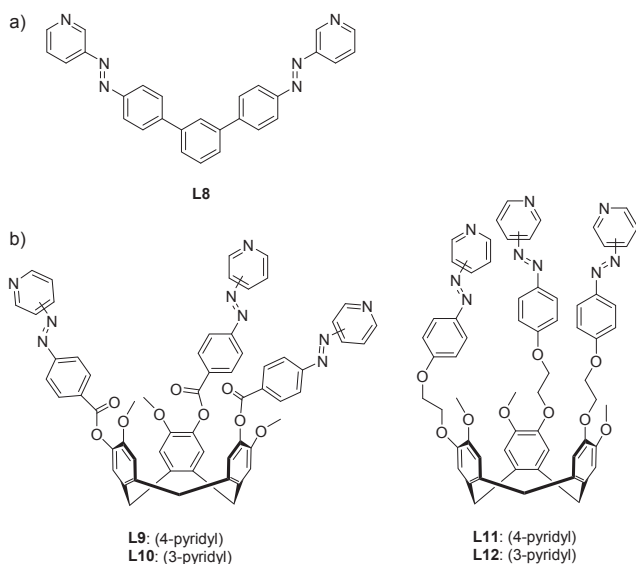
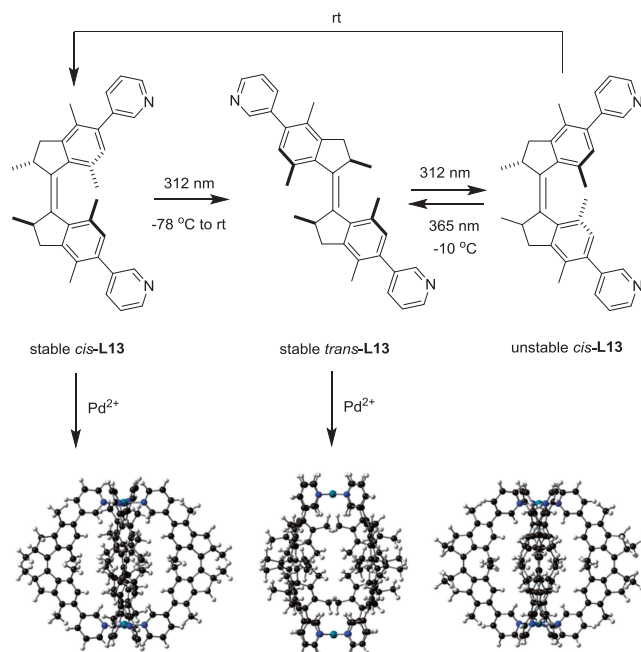


Figure 2. Azobenzene-containing ligands **L8–L12**.

with 365 nm light, a *trans*-to-*cis* isomerization was induced in the ligand and the reverse isomerization was achieved using 450 nm light. When the $\text{Pd}_2(\text{trans-L8})_4$ cage was irradiated with 365 nm light it disassembled and eventually the ligand precipitated. Nevertheless, irradiation with 450 nm light of the disassembled solution led to reassembly of the original cage.

In a different approach, the group of Hardie used tripodal cyclotriguaiacyclene derivatives that were functionalized with (phenylazo)pyridyl units (**L9–L12**, Figure 2b).⁴³ Irradiation of a solution of *trans*-**L10** in CD_2Cl_2 with 355 nm light resulted in a mixture of isomers with a *cis* content of about 76%. The reverse isomerization was induced with 450 nm light, although not in quantitative yield. The ligands **L11** and **L12** showed similar switching behavior, whereas **L9** was too insoluble for studying it further. Different M_3L_2 -type cages were prepared by combining these ligands with $\Delta, \Delta\text{-}[\text{Ir}(\text{C}^*\text{N})_2(\text{MeCN})_2](\text{PF}_6)$ in nitromethane. Irradiation of the cages at 365 nm in CH_2Cl_2 showed changes in the UV/Vis absorption spectra and the absence of an

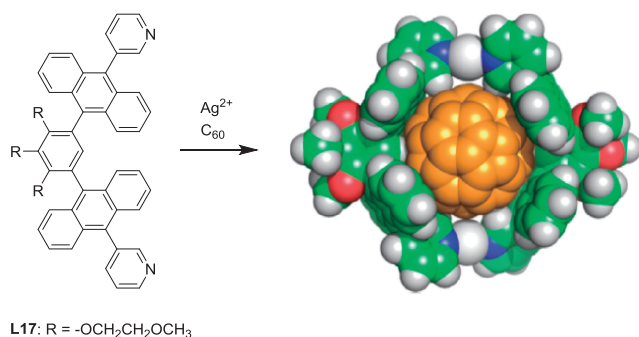


Scheme 8. Isomerization cycle of overcrowded alkene-based bis-pyridyl ligand **L13** and respective coordination cages.

isobestic point revealed that multiple cage isomers formed. Furthermore, conversion to the *cis* isomer was found to be less efficient than for the free ligand (16–40% *cis* content). Similar to the case of Fujita (*vide supra*),³¹ the lower *cis* ratio was attributed to overlap of the azobenzene absorption band with Ir(III)-based mixed CT bands. Importantly, the cages could be converted back to their initial *trans* form by using 450 nm light.

Wezenberg and Feringa recently described chiral overcrowded alkene-based bis-pyridyl ligand **L13**, which can be switched between three different states (Scheme 8).⁴⁴ Mixing of either the enantiopure stable (*S,S*)-*cis*-**L13** or the stable (*S,S*)-*trans*-**L13** with $\text{Pd}(\text{NO}_3)_2$ in CD_3CN led to formation of the respective $\text{Pd}_2(\text{L13})_4$ cages in quantitative yield. When the racemate was used instead, a similar ^1H NMR spectrum was obtained indicating chiral self-sorting behavior. Chiral self-sorting was confirmed by CD experiments and besides, DFT calculations revealed that the homochiral cages were lower in energy than possible heterochiral cages. Interestingly, both *cis* and *trans* cages were capable of binding a tosylate anion in a 1:1 fashion, however, without significant difference in binding strength ($K_a(\text{cis}) = 1.6 \times 10^3 \text{ M}^{-1}$ and $K_a(\text{trans}) = 1.8 \times 10^3 \text{ M}^{-1}$).

Starting from stable *cis*-**L13** (in CD_2Cl_2), unstable *trans*-**L13** could be generated using 312 nm irradiation at -78°C , which was then allowed to convert to the energetically more stable *trans*-**L13** isomer at room temperature via thermal helix inversion (THI).⁴⁵ Subsequent irradiation with 312 nm light affords unstable *cis*-**L13**, which undergoes THI when left at room temperature for several days to give stable *cis*-**L13**. For the cages, irradiation studies were performed in $\text{CD}_3\text{CN}/\text{CD}_2\text{Cl}_2$ and similar isomerization behavior as for the ligand was observed. However, when a solution $\text{Pd}_2(\text{unstable } \text{cis-L13})_4$, generated from $\text{Pd}_2(\text{stable } \text{trans-L13})_4$, was warmed to room temperature, the original stable *cis* cage did not reform but, instead, ill-defined complexes were observed. ^1H NMR analysis



Scheme 9. Assembly of Ag₂(L17)₂⊃C₆₀ complex. Adapted with permission from ref 46. Copyright 2013 American Chemical Society.

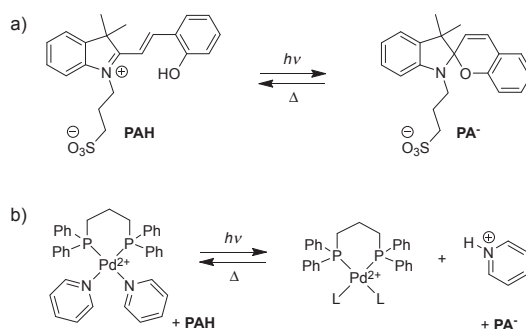
of the ligand after disassembly of the complexes upon addition of tetrabutylammonium glutarate followed by extraction showed a mixture of stable *trans*-L13 and stable *cis*-L13. The photochemical conversion from Pd₂(stable *trans*-L13)₄ to the Pd₂(unstable *cis*-L13)₄ is not quantitative and apparently, the remaining *trans* ligand hinders reformation of the original stable *cis* cage. Nevertheless, 365 nm irradiation of the unstable *cis* cage led to reversible formation of Pd₂(stable *trans*-L13)₄.

Alternative Strategies. The examples discussed so far are based on the attachment or integration of molecular photoswitches. As an alternative, the group of Yoshizawa employed photoinduced metal-ligand bond dissociation to develop a photoresponsive cage.⁴⁶ They used ligand L14, which had previously been shown to be capable of forming a Pd₂(L14)₄ cage tube (Scheme 9). When the same ligand was combined with AgNO₃ and fullerene (C₆₀) in CD₃CN, a Ag₂(L14)₂⊃C₆₀ complex was obtained. Silver ions are known to form stable metal-organic complexes, but bond dissociation occurs upon photoexcitation. By irradiation of the Ag₂(L14)₂⊃C₆₀ complex it disassembled and the C₆₀ guest was released, whereas the initial complex could be regenerated by addition of AgNO₃.

The group of Severin came up with an attractive approach in which the light-responsive unit is not in the cage itself, but is a photoacid that liberates a proton.⁴⁷ Consequently, a pyridyl ligand may be protonated leading to disassembly. Their photoacid (PAH) of choice was merocyanine, which ring-closes and releases a proton upon UV light irradiation (Scheme 10a). The resulting spiropyran form is metastable and hence, the merocyanine form is regenerated when irradiation is stopped. It was first demonstrated for a simple Pd complex (i.e. [Pd(dppp)(py)₂](OTf)₂) in an 8:2 CD₃CN/D₂O mixture, that the pyridyl ligand dissociates upon irradiation with 425 nm light as a result of protonation (Scheme 10b), which is reversible in the dark. Subsequently, following this unique concept, a large number of cage structures could be disassembled and re-assembled with a high switching efficiency (80%). Furthermore, it was shown for an octahedral M₆L₁₂-type cage that a borate guest molecule [B(*p*-C₆H₄F)₄]⁻ could be liberated and encapsulated again. The advantage of this approach is that the synthesis of new photoswitchable ligands is not needed.

Conclusion and Outlook

Several promising approaches toward the development of



Scheme 10. (a) Merocyanine/spiropyran interconversion and (b) pyridyl dissociation upon proton release by the photoacid (PAH).

light-responsive metal-organic cages have been discussed here, however, the total number of successful examples is limited. We can deduce that a number of factors have to be taken into account when designing light-responsive cages. For example, overlap of the excitation wavelength of the used molecular photoswitch with MLCT bands may reduce switching efficiency. Photoswitching could also be inhibited due to geometric constraints in the self-assembled cage. DTE switches seem to be highly suitable for use as ligand scaffolds in this regard, since their change in geometry upon isomerization is relatively small with respect to, for example, azobenzene and overcrowded alkene. Nevertheless, isomerization could still occur by de- and re-complexation of the ligand. Furthermore, what is highly important is that photoconversion is (nearly) quantitative since mixtures of ligand isomers could lead to ill-defined assemblies. A number of challenges thus have to be overcome, but the effort is worth it. Most light-responsive cages can pick up and release guest molecules on demand and, owing to this property, they hold promise for application in catalysis, separation technology, as well as drug delivery. Furthermore, changes in topology can be induced and this has been used to control material properties. Many more light-responsive metal-organic cages and applications are still to be explored and we look forward to new developments in this exciting and promising field.

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