VIP Photoswitches Very Important Paper

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Light-Controlled Interconversion between a Self-Assembled Triangle and a Rhombicuboctahedral Sphere

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Dedicated to Professor Herbert W. Roesky on the occasion of his 80th birthday

Abstract: *Stimuli-responsive structural reorganizations play an important role in biological processes, often in combination with kinetic control scenarios. In supramolecular mimics of such systems, light has been established as the perfect external trigger. Here, we report on the light-driven structural rearrangement of a small, self-assembled Pd_3L_6 ring based on photochromic dithienylethene (DTE) ligands into a rhombicuboctahedral $Pd_{24}L_{48}$ sphere measuring about 6.4 nm across. When the wavelength is changed, this interconversion can be fully reversed, as confirmed by NMR and UV/Vis spectroscopy as well as mass spectrometry. The sphere was visualized by AFM, TEM, and GISAXS measurements. Due to dissimilarities in the photoswitch conformations, the interconversion rates between the two assemblies are drastically different in the two directions.*

The control of self-assembled architectures by external stimuli has received a great deal of attention in the last years. Most reported examples rely on either the addition of small molecules, the application of an electrochemical potential, or the irradiation with light.[1] With regard to metal–organic rings and cages,[2] a number of examples have been reported in recent years including multiresponsive lanterns,[3] concentration-dependent structural interconversions,[4] cation-responsive gelation of rotaxane-ring hybrids,[5] and chloride-[6] or proton-triggered[7] release of molecular cargo. Photochemical inputs have previously been used to affect the structure[8] and guest uptake[9] of light-switchable rings, the control over the gelation of nanocages,[10] the physical properties of self-assembled spheres possessing exohedral[11,12] or endohedral[13] azobenzene attachments, and in reporter-coupled release systems.[14]

A careful supramolecular design makes it possible to adjust for the effect of the external stimulus with respect to the extent of the system's answer. For example, we have recently shown that halide ions can be used as triggers to modulate a cage's affinity for neutral guests by inducing slight conformational changes.[15] In a related system, however, the same trigger was found to cause a two-step structural reorganization between three entirely different architectures.[16]

A similar variation in the intensity of the effect of an external stimulus can also be achieved with light. Previously, we reported a light-switchable $[Pd_2\mathbf{L^1}_4]$ coordination cage based on four photochromic dithienylethene (DTE)[17] ligands $\mathbf{L^1}$ whose two interconvertible photoisomers render the cage either flexible or rigid, thus stimulating the uptake or release of anionic guests, respectively (Figure 1 a).[18] Herein, based on the same DTE backbone, we report a system that is capable of complete structural reorganization,[19] accompanied by a change in nuclearity, upon irradiation with light. All self-assembled compounds discussed in this work are composed of square-planar Pd^{II} ions and a variable number of bismonodentate pyridyl ligands $\mathbf{L^2}$ possessing a light-switchable DTE backbone carrying two *para*-substituted pyridyl donors (Figure 1 b). This compound has been previously used in the context of some light-responsive systems.[20] The use of this ligand in the preparation of self-assembled structures, however, has not yet been reported, with the exception of a nonfluorinated variant that was incorporated into photochromic metal–organic frameworks.[21,22] Modulation of color and

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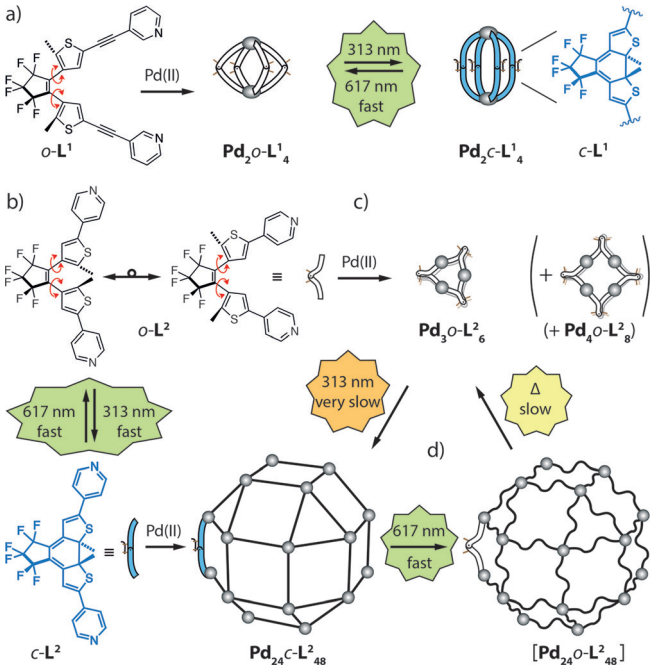

Figure 1. Self-assembly, structural conversion, and comparison of photoswitching kinetics of a) the previously reported ligand $\mathbf{L^1}$ and the isomeric cages $Pd_2(o\text{-}\mathbf{L^1})_4$ and $Pd_2(c\text{-}\mathbf{L^1})_4$ and b) the new ligand $\mathbf{L^2}$ giving c) the self-assembled ring $Pd_3(o\text{-}\mathbf{L^2})_6$ and d) the rhombicuboctahedral sphere $Pd_{24}(c\text{-}\mathbf{L^2})_{48}$.

electronic conjugation form the basis for most applications of the DTE photoswitch. Conformational differences between the photoisomers, however, have only scarcely been exploited.[17a,23]

As depicted in Figure 1b, the open-ring photoisomer of ligand $o\text{-}\mathbf{L^2}$ features two single bonds between the central cyclopentene ring and thiophene substituents that allow the ligand to adopt several conformations close in energy. Combining ligand $o\text{-}\mathbf{L^2}$ with $[Pd(CH_3CN)_4](BF_4)_2$ in a 2:1 ratio in CD_3CN followed by heating for 1 h at 70 °C resulted in a mixture of two highly symmetric products as evidenced by NMR spectroscopy (Figure 2a).[24] The ESI mass spectrum clearly confirmed the formation of a mixture of three- and four-membered-ring products $[Pd_3(o\text{-}\mathbf{L^2})_6](BF_4)_6$ and $[Pd_4(o\text{-}\mathbf{L^2})_8](BF_4)_8$ (Figure 3a).[25] Diffusion-ordered NMR spectroscopy (DOSY) further supported the formation of a 3:1 mixture of two assemblies with hydrodynamic radii of 1.34 nm and 1.52 nm, respectively (Figure 2b and the Supporting Information). When $Pd(NO_3)_2{\cdot}H_2O$ was used as the metal source, only the three-ring was formed according to the ^{1}H NMR spectrum and ESI mass spectrometry (Supporting Information). We suspect anion-template effects to be responsible for the control over the size of the assembled rings.[26] Unfortunately, irradiation of the nitrate-based ring led to the formation of precipitates. Therefore, the following experiments were carried out using the 3:1 mixture of $Pd_3(o\text{-}\mathbf{L^2})_6$ and $Pd_4(o\text{-}\mathbf{L^2})_8$ with tetrafluoroborate as the counter anion. Figure 4a shows a DFT-optimized structure of the three-ring. The calculation readily converged on a C_3-symmetric structure in which one thiophene of each ligand points its methyl substituent towards the outer rim whereas the other arms' methyl groups occupy the inside of the sidewalls. Since only one set of NMR signals was observed for the corresponding protons, we postulate a fast flipping between two energetically degenerate enantiomeric forms, as supported by semiempiric PM6 calculations and VT NMR experiments (Supporting Information).

The pale yellowish free ligand $o\text{-}\mathbf{L^2}$ was converted within 5 min into the intensely blue-colored closed-ring photoisomer $c\text{-}\mathbf{L^2}$ by irradiation at $\lambda = 313$ nm (in MeCN, yield > 96 %). The reverse isomerization proceeded quantitatively by irradiation at $\lambda = 617$ nm (Figure 2a).

Subsequently, we studied the palladium-mediated self-assembly of the closed-ring photoisomer $c\text{-}\mathbf{L^2}$. Heating a 2:1 mixture of $c\text{-}\mathbf{L^2}$ and $[Pd(CH_3CN)_4](BF_4)_2$ in CD_3CN gave rise to a downfield shift of all aromatic proton signals accompanied by strong signal broadening (Figure 2a). The ^{1}H DOSY spectrum showed a single set of signals assigned to a huge supramolecule with a hydrodynamic radius of about 3.5 nm (Figure 2b). In accordance with Fujita's recent studies regarding the size dependence of large self-assembled spheres on the angular relationship between the two donor atom lone pairs of rigid bis-monodentate ligands, we postulate the formation of a large rhombicuboctahedral sphere of the formula $Pd_{24}(c\text{-}\mathbf{L^2})_{48}$ (Figure 1d).[27]

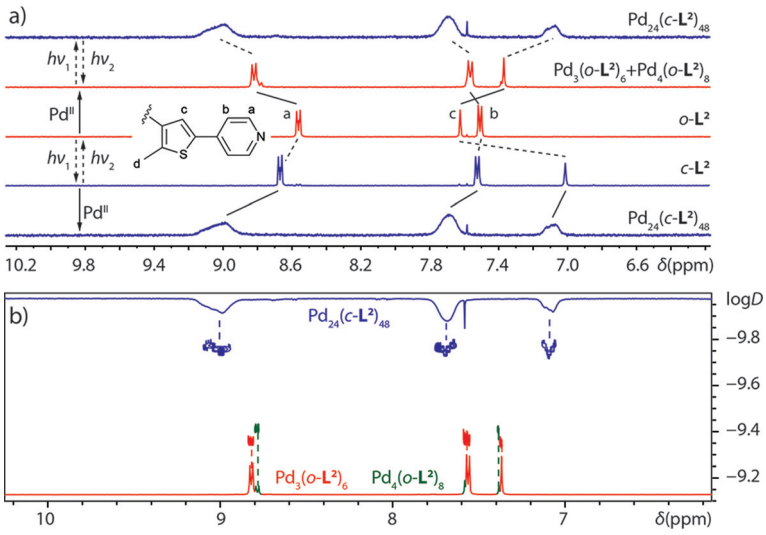

Figure 2. a) ^{1}H NMR spectra (300 MHz, CD_3CN, 300 K) of ligands $o\text{-}\mathbf{L^2}$ and $c\text{-}\mathbf{L^2}$ and the BF_4^- salts of the self-assembled rings $Pd_3(o\text{-}\mathbf{L^2})_6$ (including some $Pd_4(o\text{-}\mathbf{L^2})_8$) and sphere $Pd_{24}(c\text{-}\mathbf{L^2})_{48}$. b) Superposition of ^{1}H DOSY spectra of $Pd_3(o\text{-}\mathbf{L^2})_6$, $Pd_4(o\text{-}\mathbf{L^2})_8$, and $Pd_{24}(c\text{-}\mathbf{L^2})_{48}$ (400 MHz, CD_3CN, 296 K).

With a value of 138.2° (DFT EDF2/6-31G*), the bend angle in ligand $c\text{-}\mathbf{L^2}$ is considerable larger than the threshold of 130–134° that decides between the formation of a smaller $Pd_{12}\mathbf{L}_{24}$ or larger $Pd_{24}\mathbf{L}_{48}$ sphere (Figure 5c and Supporting Information). A geometry-optimized model of the rhombi-

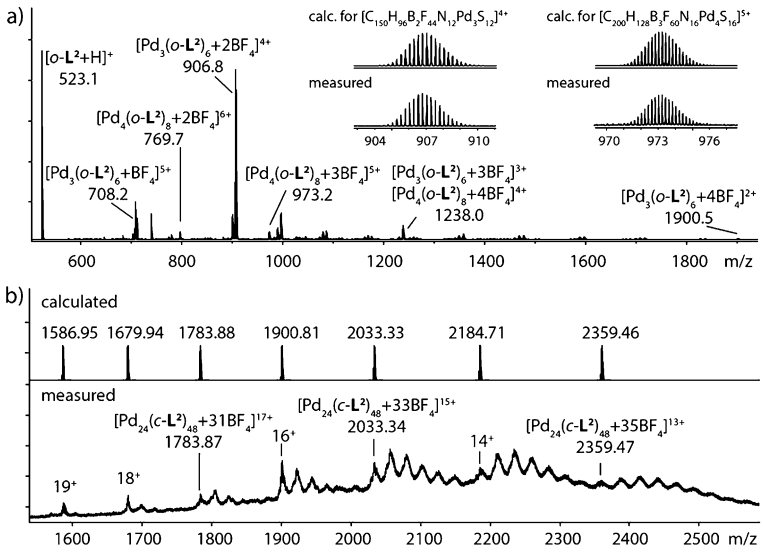

Figure 3. a) ESI mass spectrum of rings $Pd_3(o\text{-}\mathbf{L}^2)_6$ and $Pd_4(o\text{-}\mathbf{L}^2)_8$. The inset shows the simulated and observed isotopic pattern of $[Pd_3(o\text{-}\mathbf{L}^2)_6+2BF_4]^{4+}$ and $[Pd_4(o\text{-}\mathbf{L}^2)_8+3BF_4]^{5+}$ b) Cold-spray ionization (CSI) mass spectrum of sphere $Pd_{24}(c\text{-}\mathbf{L}^2)_{48}$ with BF_4^- counter anions. The positions of the measured peaks with charges between +19 and +13 are assigned and marked with the simulated peak positions.

cuboctahedral $Pd_{24}(c\text{-}\mathbf{L}^2)_{48}$ cage (Figure 4b) gave a radius of 3.2 nm, which corresponded well to the value of 3.5 nm obtained from the ^{1}H DOSY experiment. Due to symmetry considerations, the species $Pd_{12}(c\text{-}\mathbf{L}^2)_{24}$ and $Pd_{24}(c\text{-}\mathbf{L}^2)_{48}$ should also be distinguishable by their number of ^{1}H NMR signals.[28] Since ligand $c\text{-}\mathbf{L}^2$ is chiral (and racemic) and the as-synthesized $Pd_{24}(c\text{-}\mathbf{L}^2)_{48}$ sample is a mixture of hundreds of stereoisomers, the NMR spectra suffered from intense signal broadening. Resolution of the racemic ligands by chiral HPLC and assembly of homochiral cages delivered NMR spectra which indeed showed a signal splitting assignable to the $Pd_{24}(c\text{-}\mathbf{L}^2)_{48}$ sphere (Supporting Information). In addition, a cryospray ionization mass spectrometry (CSI-MS) measurement of the self-assembled compound in MeCN at −40 °C clearly revealed the anticipated stoichiometry for the large $Pd_{24}(c\text{-}\mathbf{L}^2)_{48}$ sphere. As depicted in Figure 3b, signals corresponding to the cage cation including between 29 and 35 BF_4^- counter anions could be unambiguously identified.

Despite numerous attempts, we were not able to obtain X-ray-quality crystals of the $Pd_{24}(c\text{-}\mathbf{L}^2)_{48}$ sphere due to the pronounced sensitivity of the deep-blue photochromic $Pd_{24}(c\text{-}\mathbf{L}^2)_{48}$ compound to daylight. We were, however, successful in visualizing the $Pd_{24}(c\text{-}\mathbf{L}^2)_{48}$ particles by a transmission electron microscopy (TEM) measurement, which revealed both the size (6–7 nm) and spherical shape of individual cages upon deposition of a MeCN solution of complex $[Pd_{24}(c\text{-}\mathbf{L}^2)_{48}](BF_4)_{48}$ onto carbon-coated copper grids (Figure 4d).[29] Furthermore, we obtained atomic force microscopy (AFM) images of $Pd_{24}(c\text{-}\mathbf{L}^2)_{48}$ deposited on a freshly cleaved graphite surface which showed particles with a height of 6.8 ± 0.5 nm above the surface consistent with the anticipated diameter (Figure 4c). In addition, a grazing-incidence small-angle X-ray scattering (GISAXS) experiment was performed using a silicon substrate. According to Guinier's approximation, a particle size of around 5.8 nm was obtained, which is closer to the expected diameter of the $Pd_{24}(c\text{-}\mathbf{L}^2)_{48}$ sphere (6.4 nm) than that of the smaller $Pd_{12}(c\text{-}\mathbf{L}^2)_{24}$ cage (4.8 nm) (Supporting Information).

Next, we compared the kinetics of the photoconversion between the free ligands $\mathbf{L}^1$ and $\mathbf{L}^2$ and their palladium-mediated self-assemblies $Pd_2(o\text{-}\mathbf{L}^1)_4$, $Pd_2(c\text{-}\mathbf{L}^1)_4$, $Pd_3(o\text{-}\mathbf{L}^2)_6$, and $Pd_{24}(c\text{-}\mathbf{L}^2)_{48}$, using identical wavelengths from the same light source (Figure 1).

An interesting difference in the behavior of the $\mathbf{L}^1$ and $\mathbf{L}^2$ systems was observed: Solutions of both free ligands were found to switch back and forth within minutes (Figure 5a,b, denoted as "fast" in Figure 1). Whereas both of the $Pd_2(\mathbf{L}^1)_4$ cage photoisomers could also be interconverted in a similar time frame (and the same is true for the photoreaction carried out with the large sphere $Pd_{24}(c\text{-}\mathbf{L}^2)_{48}$), a drastically different switching rate

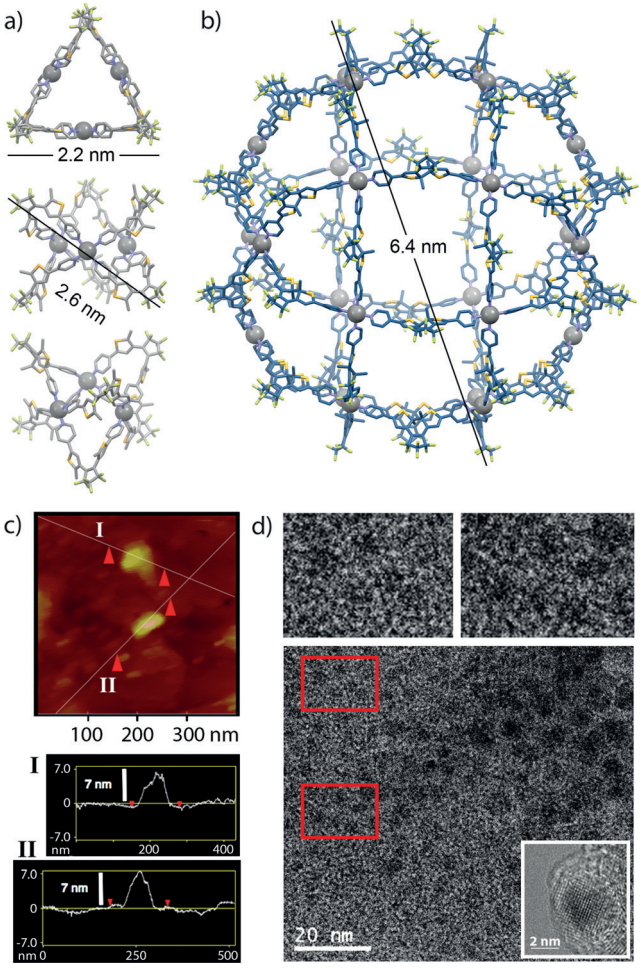

Figure 4. a) Perspective views of the DFT-optimized structure calculated for the three-ring compound $Pd_3(o\text{-}\mathbf{L}^2)_6$. b) Semiempirical (PM6) geometry-optimized molecular model of $Pd_{24}(c\text{-}\mathbf{L}^2)_{48}$. c) AFM-based measurement of the diameter of the $Pd_{24}(c\text{-}\mathbf{L}^2)_{48}$ spheres. d) TEM images of $Pd_{24}(c\text{-}\mathbf{L}^2)_{48}$ spheres (inset: sintered Pd^0 nanoparticle after prolonged irradiation with electrons).

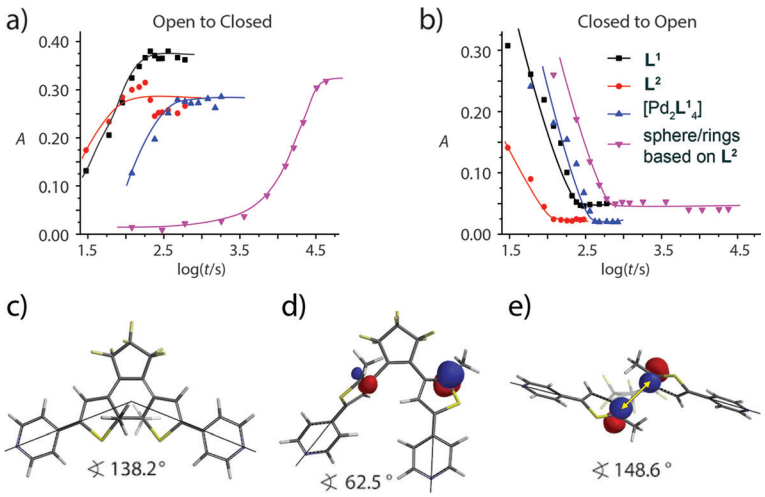

Figure 5. Kinetics of the photoconversions of a) open-form ligands and cages irradiated with $\lambda = 313$ nm light, and b) closed-form ligands and cages upon irradiation with $\lambda = 617$ nm light. c) Geometry-optimized structure of closed-form ligand *c*-**L²**. d) Conformation of ligand *o*-**L²** as a part of ring $Pd_3(o\text{-}\mathbf{L^2})_6$ and e) in the free state. The frontier orbitals whose constructive overlap is required for the photocyclization are indicated. The donor-atom angles are printed under the structures.

was observed when the ring assembly $Pd_3(o\text{-}\mathbf{L^2})_6$ was irradiated (Figure 1 d and 5a). This observation can be explained by the different conformations that the open-form photoswitch is able to adopt in the discussed architectures. Photoexcitation leads to the desired ring-closure/opening by a Woodward–Hoffmann-allowed antarafacial, conrotatory 6-electron electrocyclic reaction (Figure 5 e) from the so-called anti-parallel conformation, only.[17a] All photoisomers of the discussed ligands and self-assemblies can adopt this conformation, except for the ligands in the rings $Pd_3(o\text{-}\mathbf{L^2})_6$ and $Pd_4(o\text{-}\mathbf{L^2})_8$. Here, the backbones of the photoswitches adopt a highly twisted conformation and are unable to undergo photocyclization due to unfavorable orbital overlap (Figure 5 d). Therefore, only the minute amounts of free *o*-**L²** that are present in the equilibrium mixture of the $Pd_3(o\text{-}\mathbf{L^2})_6$ and $Pd_4(o\text{-}\mathbf{L^2})_8$ rings are able to undergo photocyclization. Under gradual but very slow shifting of the dynamic equilibrium, the latter reaction delivers the closed-form ligand *c*-**L²** that subsequently reacts with Pd^{II} cations to the $Pd_{24}(c\text{-}\mathbf{L^2})_{48}$ spheres, a process that was measured to take approximately 15 h to reach complete photocyclization and formation of the large spheres.

It is worth noting that also the reverse reaction of the large sphere to the small three- and four-rings requires de- and recomplexation of the ligands to the palladium cations. In this case, however, the initial photoreaction is quickly finished to give a tentative open-form sphere $Pd_{24}(o\text{-}\mathbf{L^2})_{48}$, thereby driving the system out of equilibrium. Since this species does not represent the thermodynamic minimum, it subsequently disintegrates to yield the entropically favored small ring assemblies. The latter process is temperature dependent and could be monitored by DOSY NMR spectroscopy (Supporting Information).

Stimuli-responsive structural reorganization processes play an important role in natural systems such as microtubule growth, the action of chaperones, and the assembly of viral capsids. Light has been established as the perfect external trigger to control dynamic supramolecular architectures. We believe that the herein demonstrated combination of the fatigue-resistant, high-fidelity DTE photoswitch with the robust Pd(pyridine)$_4$ coordination motif will significantly contribute to the development of a next generation of artificial self-assembled systems that joins light-triggered elements with a variety of other functionalities. As such, the control over structural rearrangements promises to spur progress in the fields of molecular machinery, supramolecular catalysis, nanomedicine, and molecular electronics.

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