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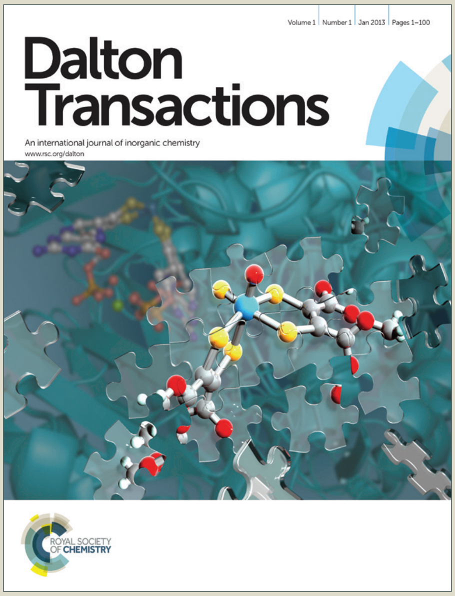

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ARTICLE

Light-responsive three-dimensional microstructures composed of azobenzene-based palladium complexes

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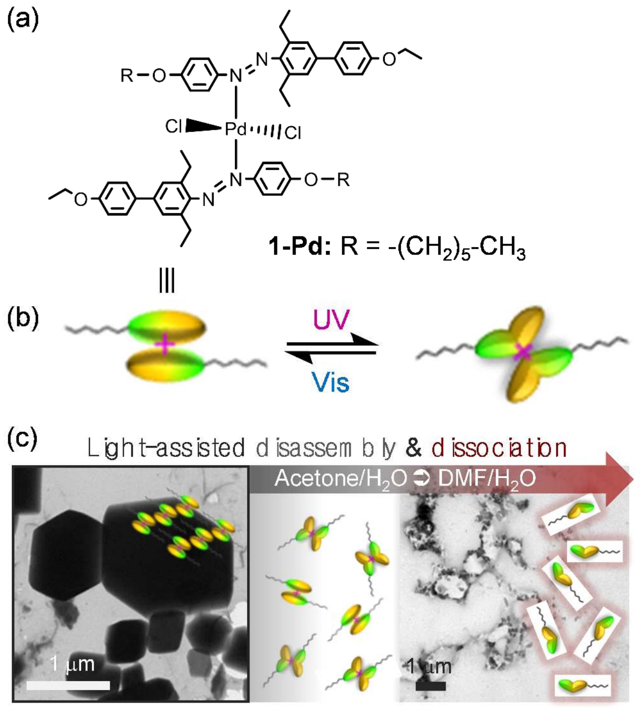
We describe not only fleeting assembly of photoisomerizable azobenzene-based palladium complexes into microstructured crystalline architectures but also their light-responsive functions. A transformation in the crystalline morphology from two-dimensional (2D) parallelogram-like sheets to three-dimensional (3D) cuboid- or rhombus-like structures was achieved by changing the solvent from tetrahydrofuran (THF) to acetone and N,N-dimethylformamide (DMF). The sizes of the structures, ranging from a few hundred nanometers to several hundred micrometers, were also modified by varying the complex concentration. In stark contrast to the very stable 2D sheets in the THF/H_2O suspensions, exposure of 3D structures in polar DMF/H_2O suspensions to ultraviolet (UV) light led to fast disassembly of the structures into isolated metal complexes and further dissociation of free azobenzene ligands from the complexes. In acetone/H_2O suspensions, interestingly, disassembly of 3D cuboid-like structures into isolated complex components occurred upon exposure to UV light without further dissociation of azobenzene ligands from the palladium complexes. Considering the photoisomerization ability of the azobenzene-based palladium complex in common organic solvents, the π-stacking interactions that support 3D structures are likely to be sufficiently weak that they might be broken by the UV-induced *trans*-to-*cis* isomerization in more polar solvent mixtures. As a consequence, disassembly proceeded under UV light irradiation. Moreover, the effect of solvent polarity on the UV-assisted dissociation (in DMF/H_2O) may be associated with the coordination ability of solvent molecules with the metal center.

Introduction

Transition metal complexes have received increasing attention due to their inherent optoelectronic, magnetic, electrochemical, and fluorescence characteristics as well as their ability to assemble into unique nano/microstructured architectures.[1-4] The self-assembled architectures–ranging from the nanometer scale to the micrometer scale–may exhibit unexpected physical and/or chemical properties depending on their morphology, size, and crystallinity.[3,4]

Metal complexes coordinated by photochromic azobenzene ligands may be promising light-responsive materials because they are expected to exhibit repeated molecular conformation changes with regard to the azobenzene ligands when isomerizing between the *trans* and *cis* states.[5] However, due to the influence of metal coordination on the isomerization behavior of azobenzene units, a rational molecular design is needed to improve the thermal stability of the two isomers. For instance, when azobenzene ligands react with a variety of transition metals, such as nickel(II), palladium(II), and platinum(II)[6], formation of two complexes, such as azobenzene-based mononuclear and dinuclear cyclometalated complexes, is possible. Abundant reports have demonstrated that a cyclometalation reaction preferentially happens through a lone pair of a nitrogen atom and an ortho carbon of a phenyl ring.[6,7] Accordingly, the *trans*-blocked azobenzene ligands in cyclometalated complexes do not undergo conventional *trans* ↔ *cis* photoisomerization in organic solvents. In contrast, even though mononuclear palladium complexes seem to show repeated light-triggered conformational changes with regard to their azobenzene units, only a few complexes formed through just one N:→M bond have been isolated so far.[8]

Our group recently succeeded in designing stable azobenzene-based mononuclear palladium complexes exhibiting good solubility in common organic solvents as well as repeated isomerization between the *trans* and *cis* states in response to the wavelength of light.[8e] The stability of transition metal complexes is significantly affected by a number of factors, such as coordination conditions including transition metal centers, the coordination ability and conformational flexibility of ligands, solvent polarity, and light.[8,9] Efforts to understand the photochemical/photophysical properties of these complexes in common organic solvents or aqueous media have frequently encountered instability problems (i.e., the facile dissociation of photochromic ligands from the complexes[8b]). Thus, both the rational design of stable metal complexes and their assembled nano/microstructures and the understanding of their functions remain formidable challenges.



Scheme 1 (a) Azobenzene-based mononuclear palladium complex, 1-Pd, adopting a trans square-planar structure. (b) Schematic representation of the reversible photoisomerization of an azobenzene-based palladium complex between the rod-shaped *trans* form and the pinwheel-shaped *cis* form. It is expected that the palladium centers would maintain the trans square-planar coordination geometry during photoisomerization. (c) Exposure of 3D microstructures to UV light leads to (i) disassembly of the structures into isolated 1-Pd components and (ii) further dissociation of free azobenzene ligands from the complex in acetone/H_2O and DMF/H_2O suspensions, respectively.

To gain a better understanding of the assembly of azobenzene-based metal complexes into diverse nano/microstructures and of their light-responsive functions, we chose photoisomerizable mononuclear palladium(II) complexes (1-Pd, see Scheme 1). During the course of our investigation, we discovered fleeting generation of two-dimensional (2D) and three-dimensional (3D) crystalline structures assembled from 1-Pd by changing the solvent used for dissolving 1-Pd from THF to more polar solvents, such as acetone and DMF. The sizes of structures, ranging from a few hundred nanometers to several hundred micrometers, were strongly dependent on the complex concentration. Moreover, in stark contrast to very stable 2D sheets, exposure of 3D microstructures in DMF/H_2O suspensions to UV light led to the facile dissociation of free azobenzene ligands from the complexes (Scheme 1c). On the other hand, disassembly of 3D aggregates into isolated metal complexes proceeded under UV light irradiation in acetone/H_2O suspensions without an appreciable release of azobenzene ligands into the surrounding medium.

Results and Discussion

Without the aid of any special capping or stabilizing agents,[10] microstructured architectures were produced by adding water to three types of 1-Pd solutions, in which 1-Pd was dissolved in THF, acetone, and DMF solutions, under gentle shaking conditions. The opaque suspensions were well dispersed without detectable precipitation during the absorption spectroscopy measurements. The transmission electron microscopy (TEM) images acquired for the THF/H_2O suspensions showed 2D structures,[11] whereas the acetone/H_2O and DMF/H_2O suspensions revealed 3D cuboid-like structures with a size of approximately 1 μm (Figures 1a-1c). The respective absorption spectra indicated not only an intense azobenzene-based π–π* absorption band, which was maximal in the 350-360 nm range, but also an evidently improved absorbance at wavelengths of approximately 600 nm and higher, demonstrating turbidity. Whereas for the DMF/H_2O suspension the π–π* band was similar to that acquired for the monomeric species in dilute DMF solution (Figure 1c and Table 1), the spectrum of the THF/H_2O suspension exhibited a weak shoulder near 350-390 nm together with a slight red-shift in the π–π* band from 352 nm to 355 nm. Such spectral changes are attributed to head-to-tail alignment between azobenzene chromophores, as expected from the X-ray crystallographic data.[8,12]

Our atomic force microscopy (AFM) image shows that the whole surface was rather uneven and contained a large number of small clusters with heights of approximately 1–4 nm, as shown in Figure 2. The clusters on the cuboid surface seem to merge with one another to grow larger if there were plenty of monomers and clusters in the mixed solvent systems. Indeed, depending on the initial concentration, the sizes of the 3D aggregates increased from a few hundred nanometers to several hundred micrometers (Figure 3). In particular, upon addition of only 0.3 mL of water to the 1-Pd acetone solution (3.0 mL), the

Table 1 Solvent property, UV-Vis absorption spectral data, crystalline structures assembled from 1-Pd, and their light-responsive behaviors

	1-Pd (azobenzene-based mononuclear palladium complex)					
	THF	THF/H_2O	acetone	acetone/H_2O	DMF	DMF/H_2O
polarity	5.7	–	10.4	–	13.7	–
λ_{max} (nm)	352	355	353	354	356	357
crystal morphology	–	2D parallelogram-like	–	3D cuboid- or rhombus-like	–	3D cuboid-like
size control	–	○	–	○	–	×
UV light	~40/60[a]	hardly influenced	dissociation of N:→Pd bond[a]	disassembly into isolated complex components (~40/60[a])	dissociation of N:→Pd bond	dissociation of N:→Pd bond

[a] *trans*/*cis* (%): Determined by UV-Vis absorption and ^{1}H NMR spectra at photostationary states of UV light.[8e]

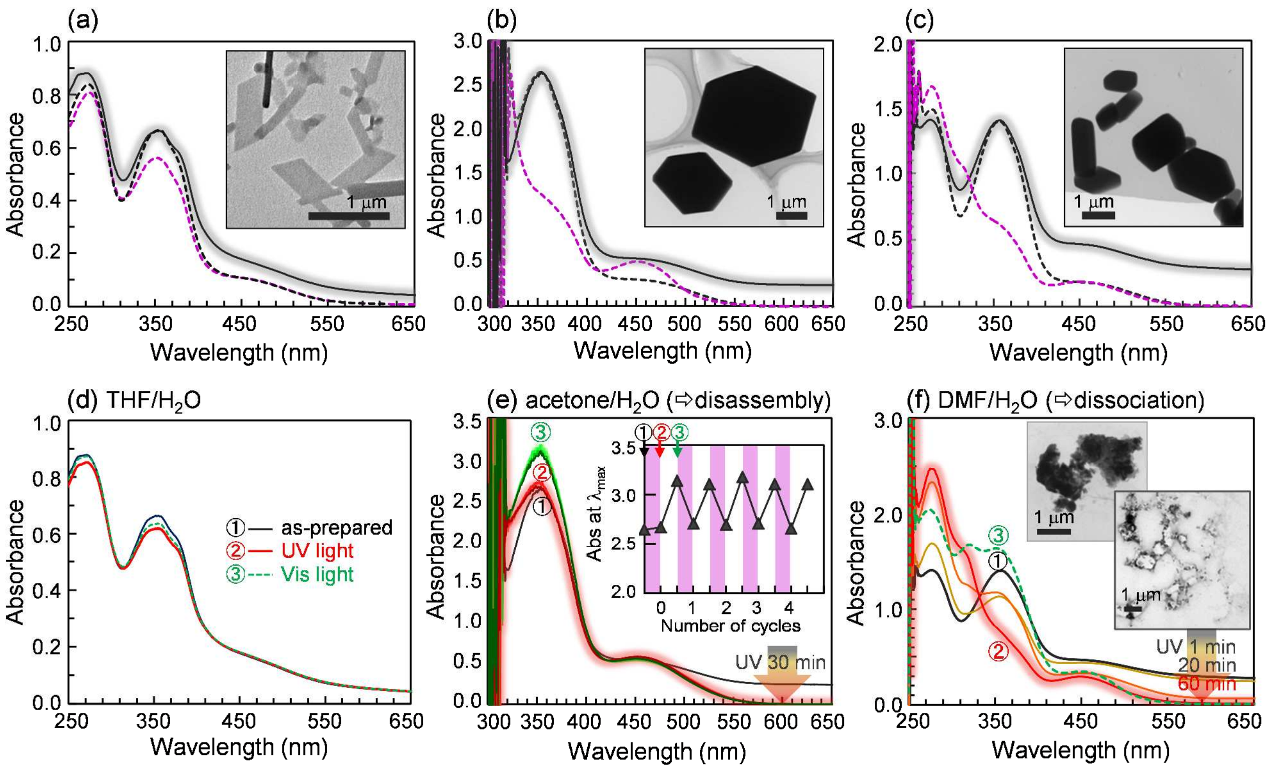


Fig. 1 Upper panel: UV-Vis absorption spectra and TEM images. Black solid lines: (a) 2.0 × 10^{-5} mol/L THF/H$_2$O (1/4, v/v), (b) 8.0 × 10^{-5} mol/L acetone/H$_2$O (4/1, v/v), and (c) 8.0 × 10^{-5} mol/L DMF/H$_2$O (5/1, v/v) suspensions. Black and violet dashed lines correspond to before (all *trans* 1-Pd) and after UV light irradiation of 1-Pd, respectively, in (a) THF, (b) acetone, and (c) DMF. The ratio of the *trans*-1-Pd and *cis*-1-Pd isomers in THF was estimated to be approximately 40/60 at the photostationary state of UV light, whereas UV-induced *trans*-to-*cis* isomerization was accompanied by dissociation of the weak N:→Pd in the complex in polar acetone and DMF (see Table 1).
Lower panel: Absorption spectral changes of 1-Pd suspensions after exposure to UV light and subsequent visible light. (d) 2.0 × 10^{-5} mol/L THF/H$_2$O (1/4, v/v), (e) 8.0 × 10^{-5} mol/L acetone/H$_2$O (4/1, v/v), and (f) 8.0 × 10^{-5} mol/L DMF/H$_2$O (5/1, v/v). Black, red, and green lines correspond to ① initial and after exposure to ② UV light and ③ subsequent visible irradiation, respectively. Inset in (e): Changes in absorbance at λ_{max} (354 nm) that were obtained after each photoswitching process. Inset TEM images in (f): After exposure of the DMF/H$_2$O suspension to UV light. We could observe largely disaggregated objects.

suspension (1.4 × 10^{-3} mol/L acetone/H$_2$O, 10/1 (v/v)) quickly turned opaque, and aggregates subsequently settled to the bottom of the quartz cuvettes. Optical microscopy (OM) images for the suspension exhibited strikingly large submillimeter-sized rhomboid-like structures (Figure 3d).

An X-ray diffraction (XRD) analysis in combination with the above AFM topographic and absorption spectral data helped us to understand the intermolecular interactions that govern the molecular assembly. The powder, 2D, and 3D structures show similar XRD patterns with three notable peaks at 10.55, 3.80 and 3.26 Å (Figure 4). First, given an intermetal distance of b = 11.66 Å (Pd$^{II}\cdots$Pd^{II})[8d] and a characteristic peak at 2θ = 8.37° (10.55 Å), the angle between adjacent layers in a head-to-tail fashion is expected to be approximately 65° in the 3D rhombus-like structures (see the inset of Figure 4). Second, a stronger peak at 3.80 Å, which is likely to arise from the π-stacked structures,[13] emerged in the spectrum obtained for 3D structures ($I_{3.80Å}/I_{3.26Å}$ = 5.40) when compared with the data for 2D sheets ($I_{3.80Å}/I_{3.26Å}$ = 2.75) and powder ($I_{3.80Å}/I_{3.26Å}$ = 1.10). Therefore, we conclude that the assembly of palladium complexes into 3D structures may occur through quite weak π-stacking interactions between biphenyl-substituted azobenzene ligands.

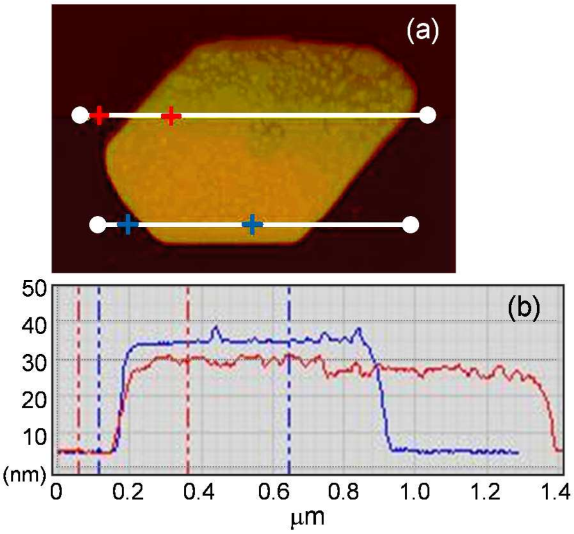


Fig. 2 (a) AFM image and (b) height profiles of 1-Pd cuboid-like structures (prepared from 3.9 × 10^{-5} mol/L acetone/H$_2$O (4/1, v/v)) on a mica substrate.

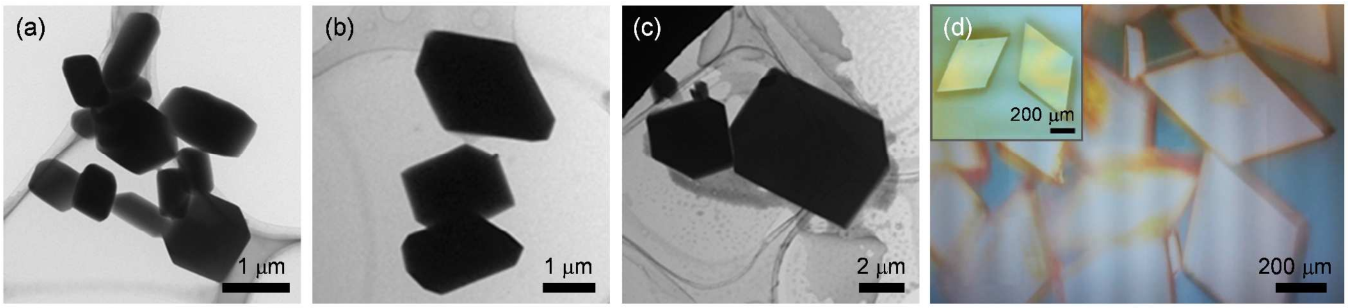


Fig. 3 (a)-(c) Unstained TEM and (d) OM images of 1-Pd 3D structures. The concentrations of the complex suspensions were (a) 3.9 × 10^{-5} mol/L acetone/H_2O (4/1, v/v), (b) 8.0 × 10^{-5} mol/L acetone/H_2O (4/1, v/v), (c) 1.7 × 10^{-4} mol/L acetone/H_2O (5/1, v/v), and (d) 1.4 × 10^{-3} mol/L acetone/H_2O (10/1, v/v).

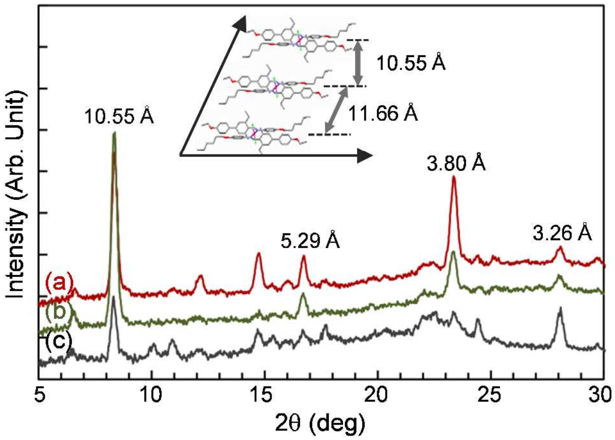


Fig. 4 XRD patterns of (a) 3D structures obtained from 1.4 × 10^{-3} mol/L acetone/H_2O (10/1, v/v), (b) 2D structures obtained from 1.1 × 10^{-3} mol/L THF/H_2O (5/4, v/v), and (c) powder.

To examine the molecular conformation changes of azobenzene-based palladium complexes and the resulting morphological transformation of aggregated structures, we prepared dilute suspensions of 1-Pd for UV-Vis absorption spectroscopy measurements. In sharp contrast to the stable 2D sheets, exposure of 3D aggregates produced from DMF/H_2O mixtures to UV light led to continuous reductions in the π–π* absorption band and the turbidity as the exposure time increased (Figure 1f). First, due to the quite modest π-stacking interactions, which are responsible for the generation of 3D aggregates, a molecular conformation change from the rod-shaped *trans*-form to the pinwheel-shaped *cis* form (Scheme 1b) could readily occur under UV light even in the crystalline state. Such UV-induced *trans*-to-*cis* isomerization of 1-Pd resulted in fast disassembly of 3D structures into isolated 1-Pd components, consequently producing the largely disaggregated objects (see the inset TEM images in Figure 1f). Second, the drastic change in the π–π* band was almost the same as that for the dilute DMF solution (Figures 1c and 1f) and it could be explained in terms of UV-assisted dissociation of the N:→Pd bond. That is, *trans*-to-*cis* isomerization of 1-Pd lowers the electron-donating ability of the nitrogen lone pair due to the electron-withdrawing nature of the azo group in the *cis*-azobenzene unit.[8e,14] As a consequence, weak interactions between azobenzene ligands and a palladium ion would facilitate the release of azobenzene ligands from the complexes in DMF.[8e] Moreover, a polar DMF solvent with a relatively strong coordination ability could boost the dissociation of the weak N:→Pd bond.[15]

Notably, exposure of 3D aggregates produced from the acetone/H_2O mixture to UV light gave rise to a slight increase in the π–π* absorption band as well as an obvious emergence of an n–π* band in the 450-460 nm range (Figure 1e). Simultaneously, the scattered light intensity was substantially reduced, and the suspension turned from opaque to transparent. Additional UV light irradiation for 20 min did not cause any marked spectral change, strongly indicating that the UV-exposed acetone/H_2O mixture reached a photostationary state. In other words, a large number of 3D aggregates were substantially disassembled into isolated 1-Pd components without an appreciable dissociation of the metal-ligand bond.

This last result encouraged us to confirm reverse *cis*-to-*trans* photoisomerization of 1-Pd by visible light irradiation in an acetone/H_2O mixture. Figure 1e shows that when the UV-exposed 1-Pd acetone/H_2O mixture was subsequently irradiated with visible light at 436 nm, the π–π* absorption band was further increased by approximately 20%, due to *cis*-to-*trans* isomerization. Repeated *trans* ↔ *cis* photoisomerization of the isolated components occurred by alternating irradiation with UV and visible light. We did not observe either an apparent increase in the scattered light intensity responsible for re-assembly into 3D structures under visible light irradiation or the undesirable dissociation of azobenzene ligands from 1-Pd under UV light irradiation, demonstrating that 1-Pd is stable in acetone/H_2O mixtures. Furthermore, addition of a small amount of water into the mixture solution resulted in the regeneration of aggregates.

Conclusions

A photoisomerizable azobenzene-based palladium complex crystallized into cuboid or rhombus-like structures by adding water to a 1-Pd acetone (or DMF) solution, whereas 2D parallelogram-like sheets were preferentially created in THF/H_2O mixed systems. TEM, AFM, XRD, and absorption spectroscopic results suggested that the 3D crystalline microstructured architectures were delicately supported through weak intermolecular π-stacking interactions. Solvent polarity was observed to significantly affect the light-responsive behavior of assembled aggregates composed of photoisomerizable azobenzene-based palladium complexes.

The light-responsive dynamic nature of transition metal complexes may find application in new types of sensors, chemical transporters, information storage, and luminescent devices.

Experimental

Acetone, tetrahydrofuran (THF), and N,N-dimethylformamide (DMF) of spectroscopic grade were used to dissolve 1-Pd. Each suspension was produced simply by adding water to the complex solution (filtered through a PTFE syringe filter prior to use) under gentle shaking conditions. The complex suspensions were exposed to UV light (365 nm, approximately 2 mW/cm^2, Supercure-204S, Tokina, combination of Toshiba color filters, UV-35+UV-D36A) to induce *trans*-to-*cis* isomerization or to visible light (436 nm, approximately 2 mW/cm^2, combination of Toshiba color filters, Y-43+V-44) to induce *cis*-to-*trans* isomerization. Transmission electron microscopy (TEM) and atomic force microscopy (AFM) samples were prepared by placing a drop of the complex suspension onto carbon-coated copper grids and freshly cleaved mica sheets, respectively. These samples were then dried under a nitrogen atmosphere. TEM was performed at 100 kV using a Hitachi H-7650 Zero A. We employed tapping-mode atomic force microscopy (AFM: Veeco Instruments Inc., AFM probes: NCH silicon pointprobe® tip, NanoWorld, Switzerland) to characterize the topographic morphology of the samples on the mica substrate. Optical microscopy (OM) images were obtained with an Olympus BX51 optical microscope using a few drops of complex suspension placed on a clean glass substrate. X-ray diffraction (XRD) patterns were measured with CuKα radiation on a Bruker D8 diffractometer. Absorption spectra were obtained using a Shimadzu UV-3100PC UV-VIS-NIR scanning spectrophotometer.

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A graphical contents entry

Light-responsive three-dimensional microstructures composed of azobenzene-based palladium complexes

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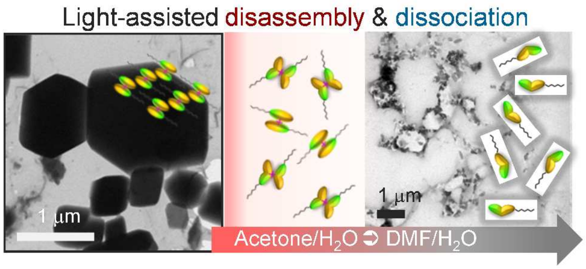

We describe not only fleeting assembly of photoisomerizable azobenzene-based palladium complexes into microstructured crystalline architectures but also their light-responsive functions.