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Light-induced assembly and disassembly of polymers with Pd_nL_{2n}-type network junctions†

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Polymers containing Pd_nL_{2n} complexes as network junctions were obtained by reaction of poly(ethylene glycol)-linked N-donor ligands with Pd^{2+}. The addition of a metastable state photoacid renders the networks light sensitive, and gel–sol transitions can be achieved by irradiation with light. The inverse process, a light-induced sol–gel transition, was realized by using a molecularly defined Pd complex as an acid-sensitive reservoir for Pd^{2+}. Upon irradiation, Pd^{2+} ions are released, allowing the formation of an acid-resistant polymer network. Both the gel–sol and the sol–gel transitions are reversed in the dark.

Introduction

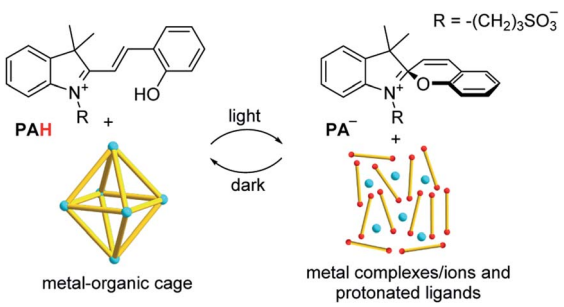
Polymer networks can be obtained by covalent interconnection of discrete metal–organic assemblies (macrocycles or cages) with organic linkers.[1,2] Two main synthetic strategies have been explored in this context: (a) the post-synthetic cross-linking of assemblies featuring reactive sites/groups in their periphery,[3–7] and (b) the utilization of polymer-linked ligands during the self-assembly process.[8–11] The incorporation of metal-based assemblies into polymer networks can lead to materials with interesting properties. For example, a hydrogel containing tetranuclear Fe cages was found to display sorption properties, which reflect the host–guest chemistry of the Fe cage.[8] Similarly, by cross-linking of porous Rh cages, it was possible to obtain materials with permanent porosity.[3] The utilization of cages as nodes in polymer networks is also interesting in terms of network topology, because cage junctions can act as highly connected nodes.[11] Another noteworthy feature of metal-based junctions is the fact that they can be altered or cleaved with appropriate stimuli.[8–10] Light is a particularly interesting stimulus, because it allows remote manipulation with high spatial and temporal control.[12] First studies about light-induced modifications of cage-containing polymer networks were recently published by Johnson and co-workers. They have shown that networks containing $Cu_{24}L_{24}$-type cages can be cleaved by photochemical reduction of the Cu(II) centers to Cu(I), resulting in a gel–sol transition.[9] The inverse process could be induced by re-oxidation with O_2. Furthermore, they have reported a system, where irradiation allows converting macrocyclic Pd_3L_6 junctions reversibly into $Pd_{24}L_{48}$ cage junctions.[10] The light sensitivity was achieved by using polymeric ligands containing photochromic dithienylethene groups. Below, we describe a new approach for rendering Pd-based polymer networks photosensitive. Importantly, our approach allows both the light-induced destruction of polymer networks and the light-induced formation of polymer networks without accumulation of 'chemical waste'.[13]

Results and discussion

The study described herein was inspired by our recent observation[14] that the assembly of certain metal–organic cages can be controlled with light if the merocyanine-based photoacid **PAH**[15] (Scheme 1) is added to the mixture.

Upon irradiation with blue light, **PAH** undergoes a ring-closure reaction, liberating a proton.[16] The increased acidity can lead to the disassembly of metal–organic cages if they contain acid-sensitive metal–ligand bonds. Importantly, cages containing more basic ligands display an increased susceptibility for an acid-induced cleavage.[17] In the dark, the process is reversed, and metal–ligand interactions are re-established.

In order to investigate if a photoacid can be used to control the assembly and disassembly of cage- and macrocycle-



Scheme 1 The photoacid **PAH** allows controlling the assembly of metal–organic cages.

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containing polymer networks, we have prepared the tetratopic N-donor ligands **L1–L4** (Scheme 2). All ligands feature a poly(ethylene glycol) spacer with an average molecular weight of M_n = 4600. The design of these ligands was inspired by work of Johnson and co-workers, who have used structural analogues of **L2** and **L3** for the assembly of networks with Pd_2L_4 and $Pd_{12}L_{24}$ cage junctions.[11b,c] Ligand **L1** features additional alkynyl spacers, which renders the terminal 3-pyridyl group less basic than the pyridyl groups of **L2** and **L3**. Ligand **L4**, on the other hand, shows more basic imidazolyl donor groups (for details, see the ESI†).

The geometry of the terminal pyridyl groups of **L1** favors the formation of Pd_2L_4-type metal–organic cages.[18] Upon mixing of $[Pd(CH_3CN)_4](BF_4)_2$ (1 equiv.) with **L1** (1 equiv.) in acetonitrile, an opaque gel was immediately obtained. The mixture was then tempered at 70 °C for 4 h to ensure the formation of a polymer network (**P1**) with intact Pd_2L_4 junctions. The gels **P2–P4** were prepared in an analogous fashion. Based on literature reports[19–21] and our own control experiments (see the ESI†), we expected the presence of Pd_2L_4 links with some $Pd_2L_3X_2$ defects[22,23] for **P2**, $Pd_{12}L_{24}$ cage junctions for **P3**, and a mixture of macrocyclic Pd_3L_6 and Pd_4L_8 junctions for **P4**.

The polymers **P1–P4** were characterized by NMR spectroscopy, scanning electron microscopy (SEM), and rheology measurements (for details, see ESI†). Selected data are depicted in Fig. 1. The ^{1}H magic angle spinning (MAS) NMR spectrum of **P1** shows six broad signals in the aromatic region, which are shifted downfield with respect to those of **L1** (Fig. 1a). It was possible to obtain a standard solution-based ^{1}H NMR spectrum of **P1** when the reaction between **L1** and $[Pd(CH_3CN)_4](BF_4)_2$ was performed under dilute conditions. The resulting spectrum was similar to what was obtained for the gel by MAS NMR. The SEM image of dried **P1** shows a three-dimensional cross-linked structure (Fig. 1b). Rheology measurements were used to assess the mechanical properties of **P1–P4**. The storage modulus (G') increases in the order **P2** < **P1** < **P3** < **P4**. Two factors are expected to contribute to the observed differences:

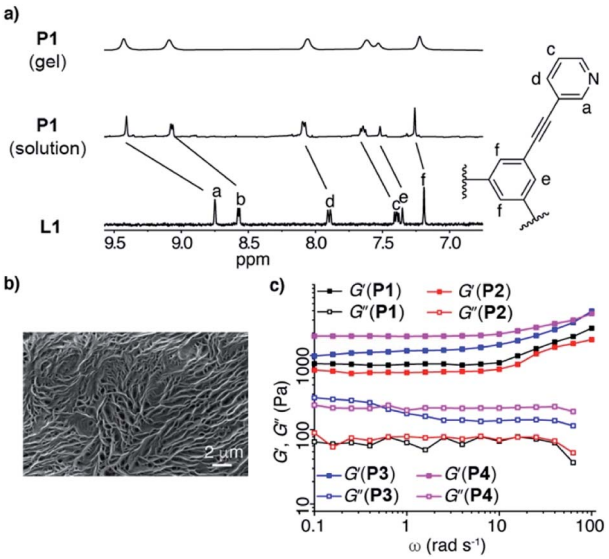
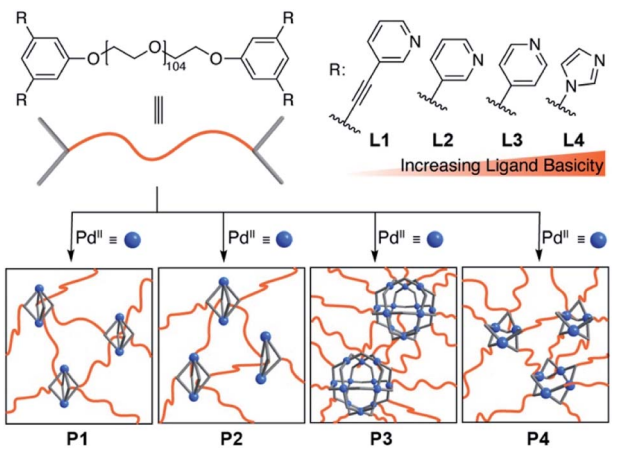


Fig. 1 (a) Aromatic region of the ^{1}H NMR spectra (400 MHz, CD_3CN) of **L1** (bottom), **P1** in dilute solution (middle), and ^{1}H MAS NMR spectrum of gel **P1** (top); (b) SEM image of **P1**; (c) rheology data for **P1–P4**.



Scheme 2 Polymers **P1–P4** with Pd_nL_{2n}-type network junctions are formed upon mixture of the N-donor ligands **L1–L4** with $[Pd(CH_3CN)_4](BF_4)_2$ in CH_3CN.

the cross-link density,[10,11] and the strength of the metal–ligand bond. The latter is related to the basicity of the ligands. An alternative measure for the donor strengths of a ligand is the Huynh Electronic Parameter (HEP).[24] We have determined the HEP parameter for close analogues of **L1–L4** (lacking the polymer linker), and the data confirmed that the relative donor capability of the ligands is in line with the ligand basicity (see the ESI†). The high G' value observed for **P4** is probably a reflection of the strong Pd–N bonds in the Pd_3L_6 and Pd_4L_8 assemblies. On the other hand, the donor strength of the ligand can be compensated by other factors (*e.g.* anion effects),[23] as evidenced by the higher G' value of **P1** when compared to what is found for **P2**.

The acid sensitivity of **P1–P4** was examined with trifluoroacetic acid (TFA). After addition of TFA (4 equiv. per N-donor group) and heating at 70 °C for 1 h, a gel–sol transition was observed for **P2–P4**, but not for **P1**. The higher acid resistance of **P1** is likely related to the low basicity of **L1**. Having established that acid-induced gel–sol transitions are possible, we subsequently performed test experiments with photoacid **PAH**. Unfortunately, **PAH** was not sufficiently soluble in CH_3CN to perform photoswitching experiments. Therefore, we have prepared the new photoacid **PAH′**(BF_4) featuring a neutral $-(CH_2)_2-OH$ side chain instead of the anionic $-(CH_2)_3-SO_3^-$ side chain of **PAH** (Fig. 2a). **PAH′**(BF_4) turned out to be soluble in CH_3CN.

An excess of **PAH′**(BF_4) was added to the respective gel (≥2 equiv. per donor group), and the mixture was homogenized by agitation with a vortex mixer. When the samples were irradiated with blue light (456 nm) for 1 h, we observed a similar behavior as for TFA additions: all gels were transformed to solutions except **P1**. The gel–sol transition could be reversed by heating the solutions in the dark for 2 h. The cycle was repeated another 4 times without noticeable difference in behavior.

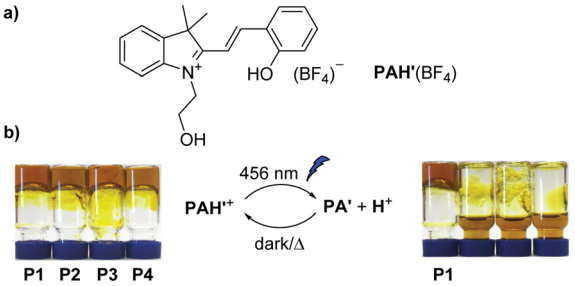


Fig. 2 (a) Structure of the photoacid **PAH′**(BF_4), and (b) reversible gel–sol transition of the polymer networks **P2**–**P4**. Polymer **P1** contains acid-resistant network junctions, and is therefore not affected by light.

The results obtained with **PAH′**(BF_4) showed that it is possible to use a photoacid for the light-triggered disassembly of polymers with Pd_nL_{2n} network junctions. Next, we set out to explore a more challenging task: the acid-induced assembly of Pd-based networks. In view of the good acid resistance of **P1**, we hypothesized that it might be possible to achieve the assembly of **P1** from **L1** and Pd^{2+} under acidic conditions. The prerequisite would be a source of Pd, which would liberate Pd^{2+} only under acidic conditions.

Previously, we had shown that metalloligand **L5** (Fig. 3) forms hexanuclear Pd complexes of the formula $[Pd_6(\mathbf{L5})_{12}]^{12+}$.[25] The two pyridyl groups of **L5** are highly basic, rendering the Pd assembly sensitive to acid.[14] Consequently, $[Pd_6(\mathbf{L5})_{12}]^{12+}$ represents a reservoir for Pd^{2+}, with metal ions being released under acidic conditions.

When a mixture of **L1** (1 equiv.), **L5** (2 equiv.) and $[Pd(CH_3CN)_4](BF_4)_2$ (1 equiv.) in CD_3CN was equilibrated at 70 °C for 3 h, a dark red solution was obtained. Inspection of this solution by NMR spectroscopy revealed the formation $[Pd_6(\mathbf{L5})_{12}]^{12+}$ along

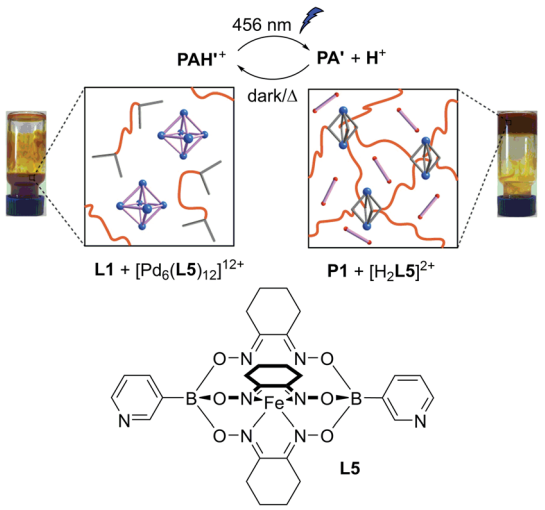


Fig. 3 Light-induced assembly of the Pd-based polymer network **P1** is achieved by irradiation of a mixture of **L1**, $[Pd_6(\mathbf{L5})_{12}]^{12+}$, and **PAH′**$(BF_4)$. The hexanuclear complex $[Pd_6(\mathbf{L5})_{12}]^{12+}$ acts as an acid-sensitive reservoir for Pd^{2+}, enabling the formation of **P1** under acidic conditions. The sol–gel transition can be reversed by heating the sample in the dark.

with 'free' polymer ligand **L1**. The preferential complexation of **L5** over **L1** can be explained by the higher donor strength of the former. When TFA (2 equiv. per total N-donor groups) was added, the mixture gradually converted to a gel when annealed at 70 °C for 2 h.

Next, we have performed a similar experiment using photoacid **PAH′**(BF_4) instead of TFA. After irradiation of the sample with blue light at 50 °C for 11 h, we observed the formation of a gel (Fig. 3). The network could be cleaved by keeping the sample in the dark at 70 °C for 7 h. A light induced sol–gel transition followed by a heat-induced gel–sol transition cycle could be repeated 4 times without noticeable difference.

Conclusions

To conclude, we have demonstrated that the photoacid **PAH′**(BF_4) can be used for the light-controlled assembly and disassembly of Pd-based polymers networks. Light-induced gel–sol transitions were achieved by using acid-sensitive Pd_nL_{2n} network junctions. For realizing the inverse process, the light-induced formation of a metallogel, we have employed a hexanuclear Pd cage as an acid-sensitive reservoir for Pd^{2+}. The relative basicity of the polymeric N-donor ligand is a key parameter for both processes, because the ligand basicity controls the acid-sensitivity of the polymer network. Another important factor is the pH range, which can be accessed with the photoacid. The metastable state acidity of **PAH′**(BF_4) is suited to cleave Pd–N bonds. In principle, it should be possible to use photoacids for the light-controlled cleavage of other types of metal–ligand assemblies. However, it might be necessary to use – or develop – photoacids with different properties in order to achieve a reversible cleavage of the respective metal–ligand bond. Investigations in this direction are ongoing in our laboratory.

Conflicts of interest

There are no conflicts to declare.

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