

## EDGE ARTICLE

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## Introduction

Polymer networks can be obtained by covalent interconnection of discrete metal-organic assemblies (macrocycles or cages) with organic linkers.<sup>1,2</sup> 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,<sup>3–7</sup> and (b) the utilization of polymer-linked ligands during the self-assembly process.<sup>8–11</sup> 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.<sup>8</sup> Similarly, by cross-linking of porous Rh cages, it was possible to obtain materials with permanent porosity.<sup>3</sup> 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.<sup>11</sup> Another noteworthy feature of metal-based junctions is the fact that they can be altered or cleaved with appropriate stimuli.<sup>8–10</sup> Light is a particularly interesting stimulus, because it allows remote manipulation with high spatial and temporal control.<sup>12</sup> 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<sub>24</sub>L<sub>24</sub>-type cages can be cleaved by photochemical reduction of the Cu(II) centers to Cu(I), resulting in a gel-sol transition.<sup>9</sup> The inverse process could be induced by re-oxidation with O<sub>2</sub>. Furthermore, they have reported a system, where irradiation allows converting macrocyclic Pd<sub>3</sub>L<sub>6</sub> junctions reversibly into Pd<sub>24</sub>L<sub>48</sub> cage junctions.<sup>10</sup> The light sensitivity was achieved by using polymeric

Polymers containing Pd<sub>n</sub>L<sub>2n</sub> complexes as network junctions were obtained by reaction of poly(ethylene glycol)-linked N-donor ligands with Pd<sup>2+</sup>. 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<sup>2+</sup>. Upon irradiation, Pd<sup>2+</sup> 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.

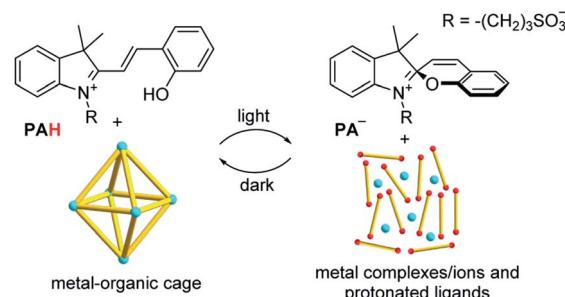
ligands containing photochromic dithienylethene groups. Below, we describe a new approach for rendering Pd-based polymer networks photosensitive. Importantly, our approach allows both the light-induced destruction of polymer networks and the light-induced formation of polymer networks without accumulation of 'chemical waste'.<sup>13</sup>

## Results and discussion

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

Upon irradiation with blue light, **PAH** undergoes a ring-closure reaction, liberating a proton.<sup>16</sup> 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.<sup>17</sup> 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  $\text{Pd}_2\text{L}_4$  and  $\text{Pd}_{12}\text{L}_{24}$  cage junctions.<sup>11b,c</sup> 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  $\text{Pd}_2\text{L}_4$ -type metal–organic cages.<sup>18</sup> Upon mixing of  $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$  (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  $\text{Pd}_2\text{L}_4$  junctions. The gels **P2–P4** were prepared in an analogous fashion. Based on literature reports<sup>19–21</sup> and our own control experiments (see the ESI†), we expected the presence of  $\text{Pd}_2\text{L}_4$  links with some  $\text{Pd}_2\text{L}_3\text{X}_2$  defects<sup>22,23</sup> for **P2**,  $\text{Pd}_{12}\text{L}_{24}$  cage junctions for **P3**, and a mixture of macrocyclic  $\text{Pd}_3\text{L}_6$  and  $\text{Pd}_4\text{L}_8$  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  $^1\text{H}$  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  $^1\text{H}$  NMR spectrum of **P1** when the reaction between **L1** and  $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$  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:

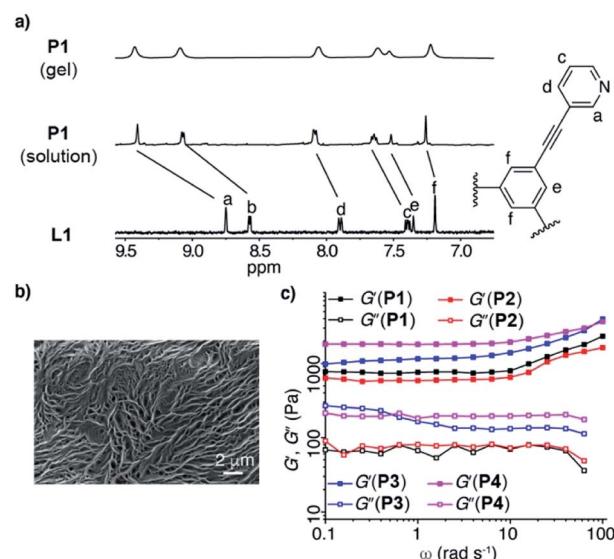
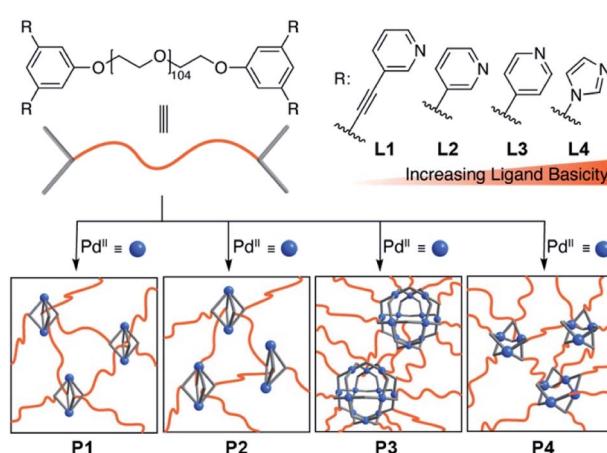


Fig. 1 (a) Aromatic region of the  $^1\text{H}$  NMR spectra (400 MHz,  $\text{CD}_3\text{CN}$ ) of **L1** (bottom), **P1** in dilute solution (middle), and  $^1\text{H}$  MAS NMR spectrum of gel **P1** (top); (b) SEM image of **P1**; (c) rheology data for **P1–P4**.

the cross-link density,<sup>10,11</sup> 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).<sup>24</sup> 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  $\text{Pd}-\text{N}$  bonds in the  $\text{Pd}_3\text{L}_6$  and  $\text{Pd}_4\text{L}_8$  assemblies. On the other hand, the donor strength of the ligand can be compensated by other factors (e.g. anion effects),<sup>23</sup> 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  $\text{CH}_3\text{CN}$  to perform photoswitching experiments. Therefore, we have prepared the new photoacid **PAH'( $\text{BF}_4$ )** featuring a neutral  $-(\text{CH}_2)_2-\text{OH}$  side chain instead of the anionic  $-(\text{CH}_2)_3-\text{SO}_3^-$  side chain of **PAH** (Fig. 2a). **PAH'( $\text{BF}_4$ )** turned out to be soluble in  $\text{CH}_3\text{CN}$ .

An excess of **PAH'( $\text{BF}_4$ )** was added to the respective gel ( $\geq 2$  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.



Scheme 2 Polymers **P1–P4** with  $\text{Pd}_n\text{L}_{2n}$ -type network junctions are formed upon mixture of the N-donor ligands **L1–L4** with  $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$  in  $\text{CH}_3\text{CN}$ .



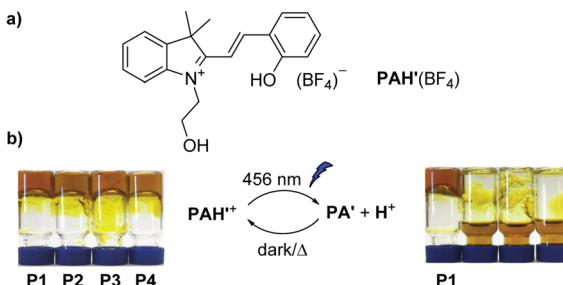


Fig. 2 (a) Structure of the photoacid **PAH'**(BF<sub>4</sub>), and (b) reversible gel-sol transition of the polymer networks P2–P4. Polymer P1 contains acid-resistant network junctions, and is therefore not affected by light.

The results obtained with **PAH'**(BF<sub>4</sub>) showed that it is possible to use a photoacid for the light-triggered disassembly of polymers with Pd<sub>n</sub>L<sub>2n</sub> 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<sup>2+</sup> under acidic conditions. The prerequisite would be a source of Pd, which would liberate Pd<sup>2+</sup> only under acidic conditions.

Previously, we had shown that metalloligand **L5** (Fig. 3) forms hexanuclear Pd complexes of the formula [Pd<sub>6</sub>(L5)<sub>12</sub>]<sup>12+</sup>.<sup>25</sup> The two pyridyl groups of **L5** are highly basic, rendering the Pd assembly sensitive to acid.<sup>14</sup> Consequently, [Pd<sub>6</sub>(L5)<sub>12</sub>]<sup>12+</sup> represents a reservoir for Pd<sup>2+</sup>, with metal ions being released under acidic conditions.

When a mixture of **L1** (1 equiv.), **L5** (2 equiv.) and [Pd(CH<sub>3</sub>CN)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> (1 equiv.) in CD<sub>3</sub>CN 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<sub>6</sub>(L5)<sub>12</sub>]<sup>12+</sup> along

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<sub>4</sub>) 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<sub>4</sub>) 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<sub>n</sub>L<sub>2n</sub> network junctions. For realizing the inverse process, the light-induced formation of a metallogele, we have employed a hexanuclear Pd cage as an acid-sensitive reservoir for Pd<sup>2+</sup>. 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<sub>4</sub>) 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.

## Acknowledgements

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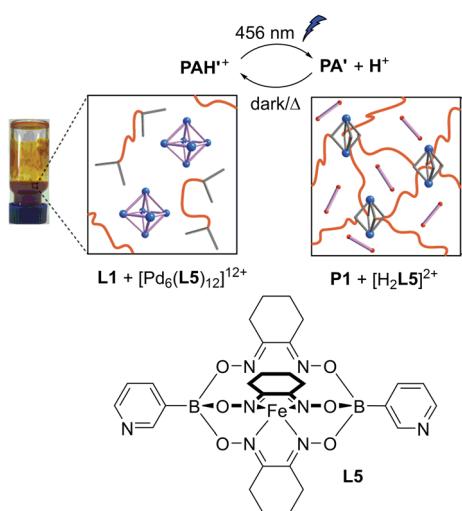


Fig. 3 Light-induced assembly of the Pd-based polymer network **P1** is achieved by irradiation of a mixture of **L1**, [Pd<sub>6</sub>(L5)<sub>12</sub>]<sup>12+</sup>, and **PAH'**(BF<sub>4</sub>). The hexanuclear complex [Pd<sub>6</sub>(L5)<sub>12</sub>]<sup>12+</sup> acts as an acid-sensitive reservoir for Pd<sup>2+</sup>, enabling the formation of **P1** under acidic conditions. The sol-gel transition can be reversed by heating the sample in the dark.



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