

RESEARCH ARTICLE

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Cite this: *Inorg. Chem. Front.*, 2021, **8**, 5195Gating the photoactivity of azobenzene-type ligands trapped within a dynamic system of an M_4L_6 tetrahedral cage, an M_2L_2 metallocycle and mononuclear ML_n complexes†Piotr Cecot,^{†a,b} Anna Walczak,^{†a,b} Grzegorz Markiewicz^{†b} and Artur R. Stefankiewicz^{†a,b}

Complexation of transition metal ions by a doubly chelating bis(diimine)-type ligand incorporating a photoresponsive azobenzene linker yielded two types of structurally distinct metallocyclic architectures, an $[M_4L_6]^{8+}$ tetrahedral cage and an $[M_2L_2]^{4+}$ metallocycle. In solution, these complexes are open for reversible interconversions between each other by varying the $M:L$ ratio, or switching into a dynamic library of $[M(L'/L'')]_n^{2+}$ mononuclear species upon addition of a competing monoamine. While the unbound ligand presents the reversible photoactivity of the azo bond, its complexes are photochemically inert, due to the inherent topology of these assemblies resulting from the restrictions of coordinate bond formation.

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Introduction

Multistimuli-induced reversibility of chemical bonds is a key challenge of modern chemistry.^{1–5} When achieved, one can gain control over the global topology, physicochemical properties and ultimately potential functions of dynamic assembly, for instance, in catalysis to prevent product inhibition or in medicine to release an active compound at a specific site. Structural switching can be achieved by changing the proportion of the added reagents *e.g.* metal ions and/or *via* external stimuli, *e.g.* temperature or light.^{6–9} The controlled modulation of more than two dynamic bonds (molecular and/or supramolecular) within a single system remains challenging and is limited to only a few examples.^{10–14} Azobenzene derivatives are a well-known class of photoactive compounds that can undergo reversible isomerization upon light irradiation and/or thermal activation. This property has been used for the creation of many advanced photoswitchable systems.¹⁵ The structural and topological control can as well be achieved through component exchange and/or metal-ion coordination, and one of

the most useful units for this is the 2-pyridine-imine *N,N*-chelating center. It owes its popularity to the reversibility of coordinate and imine bonds¹⁶ as well as the convenient synthesis of highly complex metallocyclic structures.^{17–19}

Several principles for designing appropriate ligands for multi-walled coordination cages were proposed by, *inter alia*, the Raymond,²⁰ Fujita, Ballester, Stang, Clever and Nitschke groups.^{21–24} The structure of these complexes is subject to the influence of several factors, including ligand shape, host-guest interactions, external environment, and the metal-ion:ligand ratio.^{25–31} Thus, depending on the degree of freedom of rotation around the bonds and their stability, one can completely change the structures or adjust their topology to adapt to the guest molecule or other environmental stimuli.

In earlier work, we presented a photochemical study of acyclic azobenzene-substituted metal ion complexes.³² Although the coordination indeed affected the *trans* → *cis* conversions, the complexes obtained retained the partial photoactivity of the azo bonds, since these were present in unconstrained arms of the ligands. Recently,³³ the retention of photosensitivity was also shown for a Pd_2L_4 type complex based on a bis(pyridylazo)terphenyl ligand. Gated photochromism is much less common but can be achieved in several ways,^{34,35} including, *inter alia*, the complexation process. Yamamura *et al.* found that the formation of both macromonocyclic and macrobicyclic complexes of B(III) and Ti(IV), respectively, with catecholate co-ligands led to a complete loss of photosensitivity and locking of the ligand azo unit in its *trans* configuration. The opposite case was found with terpyridine units in place of cate-

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cholates, where the *cis* form of the ligand was locked in the mononuclear Fe(II) complex.^{36,37} To the best of our knowledge no dynamic photochromic system, in which the photosensitivity of the azo bond can be locked by coordination within an M_2L_2 metallocycle, an M_4L_6 tetrahedral cage and a library of ML_2/ML_3 complexes, has been reported.

Herein, we describe the dynamic system of structurally distinct metallosupramolecular assemblies of acyclic and cyclic topologies formed between transition metal ions (Zn^{2+} , Fe^{2+} , and Cd^{2+}) and mono- and doubly-chelating azobenzene ligands. In solution, these species are labile, allowing reversible switching between them driven by the changes of the $M:L$ ratio and/or *via* transimination of the ligands upon addition of competitive amines. While the ligand itself exhibits the typical photochemical activity of azobenzene units, its complexes present gated photochromism upon irradiation, due to the coordination driven locking of the azo bonds within the rigid metallosupramolecular structures.

Results and discussion

Synthesis

Ligand *trans*-L was synthesized by the condensation of commercially available pyridine-2-carbaldehyde and *trans*-4,4'-diaminoazobenzene, following a previously reported procedure (Scheme 1, see the ESI† for details).³² As expected, the ligand was isolated in its thermodynamically favoured pure *trans*-azo form, as confirmed by 1H NMR spectroscopy (*vide infra*). To a suspension of *trans*-L in acetonitrile, solutions of Zn^{2+} , Cd^{2+} or Fe^{2+} salts were added, yielding two structurally different complexes, depending on the metal:ligand ratio. $[M_4L_6]^{8+}$ tetrahedral cages were obtained when *trans*-L was mixed with Zn^{2+} and Fe^{2+} salts in a 2 : 3 ratio, while a 1 : 1 ratio yielded $[M_2L_2]^{4+}$

metallocycles for Zn^{2+} and Cd^{2+} salts (Scheme 1, see the ESI† for details).

Solid state study

Slow vapor diffusion of Et_2O into an acetonitrile solution of $[Zn_4L_6](ClO_4)_8$ yielded orange crystals, which were characterized by single-crystal X-ray diffraction. The structural determination showed that it crystallizes in the tetragonal space group $P4_2/n$ with the cation as the S_4 isomer ($\Delta\Delta\Delta\Delta$ or $\Lambda\Lambda\Delta\Delta$), composed of four equivalent Zn^{2+} cations coordinated by six *trans*-L molecules (Scheme 1 and Fig. S26a†). Unfortunately, the crystals diffracted weakly, especially in high-angle regions; therefore, the structure was optimized using DFT b3lyp/6-31g (d) computation to locate the missing electron densities (Fig. S26b, see the ESI† for optimization details). The same crystallization technique with the material obtained from the reaction in a 1 : 1 stoichiometry yielded single crystals of the metallocycle $[Cd_2L_2](ClO_4)_4$ (Fig. S26c†). The complex crystallizes in the triclinic space group $P\bar{1}$. Each of the two Cd(II) centres is coordinated by two pyridine-imine units and two ClO_4^- counterions, which complement both the coordination sphere and the charge of the central Cd^{2+} cation.

Solution study

After characterization in the solid state, we focused our studies on solutions to establish the stability of the complexes obtained and to perform photochemical measurements. The 1H NMR spectra of the ligand *trans*-L, $[Zn_4L_6](NTf_2)_8$, and $[Zn_2L_2](NTf_2)_4$ are shown in Fig. 1. In solution, the ligand exists exclusively as the *trans*-azo isomer, as evidenced by a single set of resonances, with the most indicative being the single imine proton resonance at 8.67 ppm (ref. 38) (*cis*-L form was found upon photoisomerization – *vide infra*). The ligand



Scheme 1 a) Synthesis of *trans*-L and its $[M_4L_6](anion)_8$ and $[M_2L_2](anion)_4$ complexes, followed by reversible interconversion between $[M_4L_6]^{8+}$ and $[M_2L_2]^{4+}$ complexes and their switching into a dynamic library of mononuclear $[M(L'/L'')]_n^{2+}$ species upon transimination of the ligand *trans*-L with 4-aminoazobenzene. Counterions are omitted for clarity; transimination schemes for a (b) tetrahedral cage and (c) metallocycle.





Fig. 2 ^1H NMR spectra (600 MHz) of (a) ligand *trans*-L in CDCl_3 before (red) and after irradiation (yellow); signals of *cis*-L marked in magenta. (b) $[\text{Zn}_4\text{L}_6](\text{NTf}_2)_8$ cage in CD_3CN before (red) and after irradiation (yellow). (c) Conversion of the $[\text{Zn}_4\text{L}_6](\text{NTf}_2)_8$ cage in CD_3CN into a library of $[\text{M}(\text{L}'/\text{L}'')_3]^{2+}$ species after addition of 4-aminoazobenzene (for full titration spectra, see Fig. S22†). (d) $[\text{Zn}_2\text{L}_2](\text{NTf}_2)_4$ metallocycle in CD_3CN before (red) and after irradiation (yellow). (e) Conversion of the $[\text{Zn}_2\text{L}_2](\text{NTf}_2)_4$ metallocycle in CD_3CN into a library of $[\text{M}(\text{L}'/\text{L}'')_2]^{2+}$ species after addition of 4-aminoazobenzene (for full titration spectra, see Fig. S23 and S24†).

10^{-3} s^{-1} and $t_{1/2} = 288 \text{ s}$ at 333 K (Fig. S34a and 34b†). Both photochemical and thermal reactions were found to be fully reversible in irradiation/heating cycles (Fig. S30 and S31†).

In contrast to our previous study,³² where the photoactive moieties were placed in the outer coordination sphere, the azobenzene units of both the $[\text{M}_4\text{L}_6]^{8+}$ cage and the $[\text{M}_2\text{L}_2]^{4+}$ metallocycle are tied up within the cyclic and rigid coordination structures. Taking into account that the *trans* \rightarrow *cis* isomerization of the azo bond leads to a significant shortening of the L molecule, and a subsequent change in the angle between two chelating centres, photoisomerization of the bound ligand in the complexes would be expected to lead to rearrangement into species of quite different topology. Indeed, in the past irradiation has been shown to lead to complete dissociation of a metallocage species derived from a ligand incorporating two diazo units linking simple pyridine donors.³³

The absorption spectra of both $[\text{Zn}_4\text{L}_6](\text{NTf}_2)_8$ and $[\text{Zn}_2\text{L}_2](\text{NTf}_2)_4$ show similar profiles to that of the *trans*-L spectrum, with λ_{max} values at 362 and 372 nm, respectively. Irradiation of their solutions under identical conditions to those found to isomerize *trans*-L, gave, however, unexpected results. Namely, both cage and metallocycle showed high resistance to photoisomerization, yielding only <10% conversions in the photo-stationary state achieved after prolonged photoirradiation (Fig. S28 and S29†). Given that the measurements were made on very dilute solutions (required for absorption spectroscopy), and the formation of both $[\text{Zn}_4\text{L}_6]^{8+}$ and $[\text{Zn}_2\text{L}_2]^{4+}$ complexes is

reversible, it was concluded that the observed conversions most likely originated from the released *trans*-L molecules, not from the complexes. Indeed, when the irradiated samples of $[\text{Zn}_4\text{L}_6]^{8+}$ and $[\text{Zn}_2\text{L}_2]^{4+}$ were heated to induce a backward *cis* \rightarrow *trans* conversion, an abnormal release of *trans*-L was observed. In contrast to the isolated L, the first-order backward isomerisation is affected by the disassembly processes so the conversion exceeds 100% of *trans*-L (Fig. S34c and 34d†).

To omit the problem with the partial disassembly, we followed the isomerization by ^1H NMR spectroscopy, which allows the use of higher concentrations and observation of all species in the solution. As shown in Fig. 2b, UV irradiation of the $[\text{Zn}_4\text{L}_6](\text{NTf}_2)_8$ cage does not lead to any observable changes. All resonances remain unchanged, proving that the cage is photochemically stable, in terms of azo bond photoisomerization. Similar results were obtained for $[\text{Zn}_2\text{L}_2](\text{NTf}_2)_4$ (Fig. 2d), proving that the metallocyclic structure is also photochemically locked. Having the photoactive ligand L, and its photochemically inert complexes, we decided to check if it is possible to introduce the *cis*-L into assemblies prior to the complexation. However, when the mixture of *trans/cis*-L was treated with Zn^{2+} salt we observed a gradual decrease in the absorbance, without indicative red/blue shifts for the selective formation of metallosupramolecular assemblies. Coordination also does not stimulate the reverse isomerization of the azo unit, even when the mixture with an excess of a metal salt is allowed to stand for 24 h for a spontaneous *cis* \rightarrow *trans* backward conversion (Fig. S32†).

Transimination

Having the photoinactive cyclic complexes, we decided to examine whether they could be converted into acyclic products *via* the transimination reaction and thus possibly modulate the photosensitivity of the azo units. Addition of the competing 4-aminoazobenzene into a solution of $[\text{Zn}_4\text{L}_6](\text{NTf}_2)_8$ in CD_3CN yielded, through a transimination reaction, a library of mononuclear $[\text{M}(\text{L}'/\text{L}'')_3]^{2+}$ octahedral complexes bearing azobenzene units (Scheme 1 and Fig. 2c). Similar changes were observed for the $[\text{Zn}_2\text{L}_2](\text{NTf}_2)_4$ metallocycle, which was also converted into a library of mononuclear complexes, although due to the limited number of ligands formed, the reaction yielded $[\text{M}(\text{L}'/\text{L}'')_2]^{2+}$ species (Scheme 1 and Fig. 2e). Our previous work³² has shown that the mononuclear $[\text{ML}_n]^{i+}$ complexes bearing azobenzene moieties retain some partial photoactivity of the azobenzene unit despite the metal ion complexation. However, when the dynamic libraries of $[\text{M}(\text{L}'/\text{L}'')_3]^{2+}$ and $[\text{M}(\text{L}'/\text{L}'')_2]^{2+}$ complexes were subjected to UV radiation, we did not observe a significant increase in their photoactivity (*trans* \rightarrow *cis* conversions were found to be about 10% for both libraries; Fig. S33†).

Conclusions

In conclusion, a new dynamic metallosupramolecular system consisting of photoactive ligands and transition metal ions in



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