Exploiting Coordination Isomerism for Controlled Self-Assembly

Nils Bäumer, Kalathil K. Kartha, Naveen Kumar Allampally, Shiki Yagai, Rodrigo Q. Albuquerque, and Gustavo Fernández*

Abstract: We exploited the inherent geometrical isomerism of a PtII complex as a new tool to control supramolecular assembly processes. UV irradiation and careful selection of solvent, temperature, and concentration leads to tunable coordination isomerism, which in turn allows fully reversible switching between two distinct aggregate species (1D fibers—2D lamellae) with different photoresponsive behavior. Our findings not only broaden the scope of coordination isomerism, but also open up exciting possibilities for the development of novel stimuli-responsive nanomaterials.

The occurrence of geometrical isomerism in coordination complexes, sometimes termed coordination isomerism, has been recognized for more than a century, and it is a commonly observed phenomenon in the photochemistry of square-planar complexes.[1,2] In particular, PtII compounds have been reported to undergo geometrical isomerization upon UV irradiation, leading to photostationary states whose isomer composition primarily depends on the choice of ligands and solvent.[2,3] To date, geometrical isomerization of PtII complexes has been exclusively investigated at the molecular level, for instance to obtain otherwise inaccessible coordination compounds,[4] rotors,[5] and photoactivated catalysts.[6]

In an attempt to broaden the scope of coordination isomerism, we reasoned that the inherently different geometry of cis and trans PtII complexes might be exploited as a new method to control self-assembly processes. Based on the versatility of metal coordination in providing multiple directional interactions, this strategy would complement the existing arsenal of tools in stimuli-responsive materials[7] and living supramolecular polymerization.[8]

In order to facilitate geometrical isomerism in PtII complexes, the use of small and/or conformationally unrestricted coordinating ligands appears to be a prerequisite.[9,10] Otherwise, steric repulsion between cis-coordinated ligands, along with the stronger aggregation propensity of the more preorganized trans species, will preferentially stabilize the trans form, which can inhibit isomerization,[11] or even induce photodecomposition.[12]

While screening our library of ligands, we noticed that the inclusion of an azobenzene moiety in the molecular design enhances the conformational freedom of the system,[13,14] which might allow a good balance between isomerization and aggregation. Additionally, complexation with PtII inactivates the azobenzene moiety to light irradiation so it will not influence the coordination isomerism through additional isomerization possibilities.[15,16] On this basis, we designed a new PtIICl2 complex (C1), with L being a 4-phenylazo-pyridyl-based ligand featuring peripheral amide groups and dodecylxoy side chains[13,14] (Scheme 1; for synthesis and characterization, see the Supporting Information). This rational choice of ligand, solubilizing groups, and hydrogen-bonding units enables simultaneous control over coordination isomerism and self-assembly for the first time. UV irradiation and appropriate choice of solvent, temperature, and concentration allows fully reversible switching in the aggregate morphology (1D—2D) and represents an innovative strategy towards stimuli-responsive self-assembled materials.

The self-assembly behavior of C1, synthesized as a pure trans form, was initially probed in methylcyclohexane (MCH) using variable-temperature (VT) UV/Vis studies at 2 x 10−3 M. These experiments showed only negligible absorption changes when monomer solutions where cooled from 363 K to 293 K (Figure 1a). However, further cooling to 273 K causes a marked red shift in the absorption maximum from 406 nm to 418 nm along with an isosbestic point at 401 nm and a concurrent hyperchromism (Figure 1a). These spectral changes, which are independent of the cooling rate (see Figure 1a and Figure S6), can be attributed to the aggregation of C1. Notably, the corresponding plots of absorption versus temperature monitored at different wavelengths show a rather unusual two-step curve (Figure 1a inset and Figure S7); a smooth regime between 363 K and around 293 K followed by a sharp transition below a critical elongation temperature (Tc ≈ 293 K) that is characteristic of a nucleated supramolecular polymerization (for thermodynamic analysis, see Figure S8 and Table S1). The initial transition, which cannot be fitted to any of the existing thermodynamic models for supramolecular polymerization, suggests a pre-nucleation event involving conformational changes of the azobenzene.
group(s), such as planarization, at higher temperatures. VT dynamic light scattering (DLS) studies at temperatures above the $T_c$ showed no significant changes in the correlation and size distribution functions (Figure S9), thus validating our hypothesis. Further cooling to 283 K (below the $T_c$) does initiate the self-assembly of $C_1$, as evident by the marked increase in the particle size (Figure S9). Atomic force microscopy (AFM) on highly-oriented pyrolytic graphite (HOPG) revealed the absence of assemblies above 293 K (Figure S10). At the $T_c$, short rods with a uniform height of 2–3 nm and a length of 40–70 nm are observed (Figure 1b and Figure S11), which further grow longitudinally into fibers with lengths between 60 and 700 nm (average length ($l_{ave}$) = 261 ± 73 nm) when the temperature is decreased to 273 K (Figure 1c, and Figures S12, S13). Combined 1D and 2D NMR studies, both in CDCl$_3$ and MCH-d$_{14}$ (Figures S14–S17), demonstrate a slipped molecular packing stabilized by aromatic and N–H···Cl interactions.[11b,13] This proposed arrangement is in agreement with the packing observed in the crystal state for structurally related model compound $C_2$ with shorter ethoxy chains, which exhibits N–H···Cl, C(aromatic)–H···Cl and aromatic interactions (Figure 1d and Figure S18).

After detailed self-assembly studies of $C_1$, we confirmed that the azobenzene moieties are indeed inactive under UV irradiation when coordinated to Pt$^{II}$ (Figure S19–S25).[15] In a recent example, Shionoya and co-workers[5] elegantly showed that discrete Pt$^{II}$-centred azaphosphatriptycene molecular gears efficiently undergo coordination isomerism under irradiation in appropriate solvents. Polar solvents favour efficient trans-to-cis conversion due to preferential stabilization of the dipole moment of the cis form.[3,5] On a similar basis, we tested whether coordination isomerism is also possible for our system ($C_1$). To our satisfaction, a new set

---

**Scheme 1.** Molecular structures of $C_1$ and $C_2$, and a cartoon representation of the supramolecular assembly of $C_1$ triggered by coordination isomerism.

---

**Figure 1.** a) VT UV/Vis spectra of $C_1$ (MCH, 2 × 10$^{-7}$ M, 363 K–273 K; 1 K min$^{-1}$). Inset: plot of absorbance versus T extracted from VT UV/Vis ($\lambda$ = 450 nm). b, c) AFM height images recorded upon spin-coating a 5 × 10$^{-7}$ M solution of $C_1$ in MCH on HOPG at 293 K (b) and 273 K (c). d) Packing of $C_2$, derived from X-ray crystal analysis.
of signals corresponding to cis-C1 are observed over time in the 1H NMR spectra when solutions of trans-C1 are kept under ambient conditions in moderately polar solvents such as CDCl3 and CD2Cl2 (Figure 2). A similar trend is observed when a concentrated solution of trans-C1 in CDCl3 (20 mM) is diluted to 1 mM (Figure S26). For both time- and concentration-dependent 1H NMR experiments in CDCl3, a maximum of 33% cis-C1 is obtained at equilibrium. The ratio of cis-C1 can be further increased to 40% in more polar solvents such as DMSO using high temperatures (Figure S27). However, the strong hydrophobicity of C1 due to the presence of long alkyl chains results in rapid precipitation even when using these harsh conditions, which precludes further analysis in polar media. Nevertheless, using the same experimental protocol for less hydrophobic C1 allowed us to achieve a maximum cis ratio of 73% (Figure S28). Decreasing the solvent polarity by using CD2Cl2 leads to a reduction in the maximum amount of formed cis-C1 (10%), whereas no traces of cis-C1 were observed in nonpolar solvents such as MCH-d8 and TCE-d4 (c = 1 × 10−3 M, Figure 2 and Figures S29, S30). This behavior can be rationalized by comparing the relative stability of both isomers using DFT calculations (Figure S31). Thus, while polar and dilute solutions stabilize cis-C1, high concentration and solvents of low polarity favor the trans form, a phenomenon that appears to be reinforced by aggregation. Accordingly, we expect that only trans-C1 has the appropriate geometry to promote aggregation, rendering the distorted cis form as a dormant species. Interestingly, the reverse cis-to-trans isomerization of C1 can be readily achieved by UV irradiation, irrespective of the solvent polarity (CDCl3, 33% to 16% and DCM-d2, 10% to 2%; Figure 2 and Figure S32). The absence of the free ligand in solution during this transition is indicative of a twisting mechanism as the most probable isomerization pathway.15 Even though UV irradiation does not fully back-isomerize the system, a complete recovery of trans-C1 is possible by re-

![Figure 2](image-url)
(\text{ave} = 69.5 \pm 15.6 \text{ nm}) but slightly larger widths (between 20 and 60 nm), which is a product of bundling of the rods already observed at higher temperature (Figure 3d and Figure S44). This behavior can be rationalized by the simulations, since the alkyl chains surrounding the aromatic core of the stacks potentially offer lateral van der Waals binding sites. This effect, together with the restriction in the degrees of freedom of the stacks containing the distorted \textit{cis} isomer compared to the fibers formed by the pure \textit{trans} isomer, is expected to facilitate the bundling of the rods.

Ultimately, we validated the reversibility of the system through full recovery of the \textit{trans} form. To this end, the lamellar aggregates from the \textit{cis} + \textit{trans} mixture were heated to the monomer state (363 K) and subsequently irradiated with UV light in order to back-isomerize the \textit{cis} isomers present (ca. 33\%) to the \textit{trans} form. Cooling the resultant hot solution led to the same aggregation pathway as the freshly prepared \textit{trans}-\text{C}_1 in MCH (\text{c} = 2 \times 10^{-4} \text{ M}, Figure S47). This indicates a nearly quantitative recovery of the \textit{trans} form, as demonstrated by the observation of short fibers by AFM imaging (Figure S48).

In conclusion, we have described a new Pt\textsuperscript{II} complex (\text{C}_1) that undergoes both geometrical isomerism and supramolecular polymerization under controlled experimental conditions. While nonpolar media (MCH) induce the formation of thin 1D fibers of pure \textit{trans}-\text{C}_1, the use of more polar solvents (CHCl\textsubscript{3}) to prepare the aggregate solution enables the formation of the distorted \textit{cis} isomer and leads to attenuated growth into small 2D lamellae. Current work in our lab aims at optimizing the efficiency of coordination isomerism with the ultimate goal of controlling the size of supramolecular assemblies.

**Acknowledgements**

N.B., G.F., and K.K.K. acknowledge the European Commission (ERC-StG-2016 SUPRACOP-715923) for funding.

**Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** coordination isomerism · photoresponsive behavior · self-assembly · supramolecular polymers · \( \pi \)-conjugated systems

**How to cite:** Angew. Chem. Int. Ed. 2019, 58, 15626–15630  
Angew. Chem. 2019, 131, 15772–15776

---

[1] I. Lifschitz, W. Froentjes, Z. Anorg. Allg. Chem. 1935, 224, 173.
[2] “Rearrangements in Ground and Excited States”. P. de Mayo, Organic Chemistry: A Series of Monographs, Vol. 3, Elsevier Science, Burlington, 1980.
[3] P. Haake, T. A. Hylton, J. Am. Chem. Soc. 1962, 84, 3774.
[4] S. H. Mastin, P. Haake, J. Chem. Soc. D 1970, 202.
[5] H. Ube, Y. Yasuda, H. Sato, M. Shionoya, Nat. Commun. 2017, 8, 14296.
[6] V. N. Svecak, D. A. de Vekki, N. K. Skvortsov, Russ. J. Appl. Chem. 2001, 74, 921.
Recent examples of seeded supramolecular polymerization:

[7] a) S. Yagai, Y. Kitamoto, S. Datta, B. Adhikari, Acc. Chem. Res. 2019, 52, 1325; b) Monographs in Supramolecular Chemistry (Ed.: R. G. Weiss), Royal Society of Chemistry, Cambridge, 2018; c) A. Sorrenti, J. Leira-Iglesias, A. J. Markvoort, T. F. A. de Greef, T. M. Hermans, Chem. Soc. Rev. 2017, 46, 5476; d) M. Kathan, S. Hecht, Chem. Soc. Rev. 2017, 46, 5536; e) Y. Kim, H. Li, Y. He, X. Chen, X. Ma, M. Lee, Nat. Nanotechnol. 2017, 12, 551; f) M. Yamauchi, T. Ohba, T. Karatsu, S. Yagai, Nat. Commun. 2015, 8, 8936; g) S. S. Babu, V. K. Praveen, A. Ajayaghosh, Chem. Rev. 2014, 114, 1973; h) Z. Chi, X. Zhang, B. Xu, X. Zhou, C. Ma, Y. Zhang, S. Liu, J. Xu, Chem. Soc. Rev. 2012, 41, 3878; i) T. Aida, E. W. Meijer, S. I. Stupp, Science 2012, 335, 813; j) A. Gopal, M. Hifsdheen, S. Furumi, M. Takeuchi, A. Ajayaghosh, Angew. Chem. Int. Ed. 2012, 51, 10505; Angew. Chem. 2012, 124, 10657.

[8] Recent examples of seeded supramolecular polymerization:

a) A. Jain, S. Dhiman, A. Dhayani, P. K. Vemula, S. J. George, Nat. Commun. 2019, 10, 450; b) S. Ogi, K. Matsumoto, S. Yamaguchi, Angew. Chem. Int. Ed. 2018, 57, 2339; Angew. Chem. 2018, 130, 2363; c) T. Fukui, T. Uchihashi, N. Sasaki, H. Watanabe, M. Takeuchi, K. Sugiyasu, Angew. Chem. Int. Ed. 2018, 57, 15465; Angew. Chem. 2018, 130, 15691; d) E. E. Greciano, B. Matarranz, L. Sánchez, Angew. Chem. Int. Ed. 2018, 57, 4697; Angew. Chem. 2018, 130, 4787; e) Q. Wan, W.-P. To, C. Yang, C.-M. Che, Angew. Chem. Int. Ed. 2018, 57, 3089; Angew. Chem. 2018, 130, 3143; f) G. Ghosh, S. Ghosh, Chem. Commun. 2018, 54, 5720; g) W. Wagner, M. Wehner, V. Stepanenko, S. Ogi, F. Würthner, Angew. Chem. Int. Ed. 2017, 56, 16008; Angew. Chem. 2017, 129, 16224; h) K. Zhang, M. C.-L. Yeung, S. Y.-L. Leung, V. W.-W. Yam, Proc. Natl. Acad. Sci. USA 2017, 114, 11844; i) A. Aliprandi, M. Mauro, L. De Cola, Nat. Chem. 2016, 8, 10; j) R. D. Mukhopadhyay, A. Ajayaghosh, Science 2015, 349, 241; k) J. Kang, D. Miyajima, T. Mori, Y. Inoue, Y. Itoh, T. Aida, Science 2015, 347, 646.

[9] a) D. Cornacchia, R. Z. Pellicani, F. P. Intini, C. Pacífico, G. Natile, Inorg. Chem. 2009, 48, 10800; b) D. Cornacchia, L. Cerasino, C. Pacífico, G. Natile, Eur. J. Inorg. Chem. 2008, 1822; c) F. Bolutta, M. Gléria, V. Balzani, J. Phys. Chem. 1972, 76, 3934.