Photoresponsive Materials

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Photo- and Thermoresponsive Supramolecular Assemblies: Reversible Photorelease of K^+ Ions and Constitutional Dynamics**

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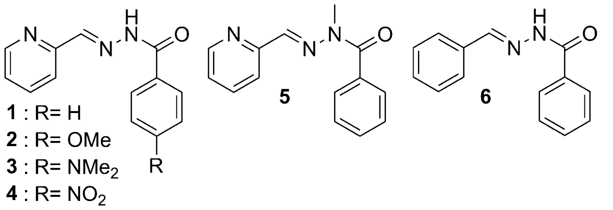
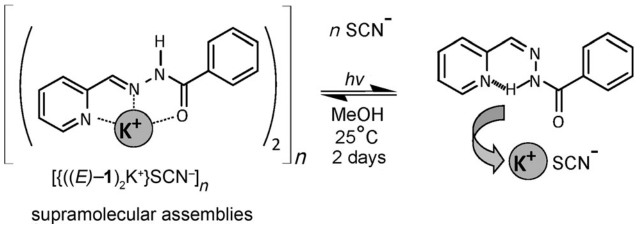
The stimulus-controlled self-assembly of long-range organized supramolecular entities is a topic of active investigation, in particular for its potential implementation in (photo-, thermo-) responsive soft-matter devices and materials.[1,2] On the other hand, materials containing reversible covalent bonds may undergo constitutional change by the incorporation or exchange of components, and may thus behave as dynamic materials.[3,4] The combination of these three features: supramolecular self-assembly, constitutional dynamics, and stimulus responsiveness, is especially attractive. We report herein such a case, in which supramolecular assemblies generated from complexes of dynamic ligand molecules may be dissociated by heating or irradiation with light, with the photorelease of a metal ion.

Previous studies by our research group[5] showed that acyl hydrazones, such as **1**–**4**, bind cations through the tridentate NNO binding site[6] and have the very attractive feature of being double dynamic entities capable of 1) configurational dynamics by *E*-to-*Z* photoisomerization stabilized by internal hydrogen bonding to the pyridine moiety[7] and 2) constitutional dynamics by component exchange involving the reversible acyl hydrazone bond.[3,4,8] With the system described herein, we explored both of these features. Crystalline supramolecular assemblies were generated reversibly by the binding of a cation by ligand **1** and its release by photoisomerization from (*E*)-**1** to (*Z*)-**1**, which cannot bind the cation (Scheme 1, Figure 1).





Scheme 1. Photoisomerization of ligand **1** from its (*E*)-**1** configuration in the complex units $[\{((E)\text{-}\mathbf{1})_2K^+\}SCN^-]$ that form the supramolecular crystalline assemblies to the (*Z*)-**1** isomer, with release of the potassium cation. Thermal back isomerization restores the metallosupramolecular assemblies.

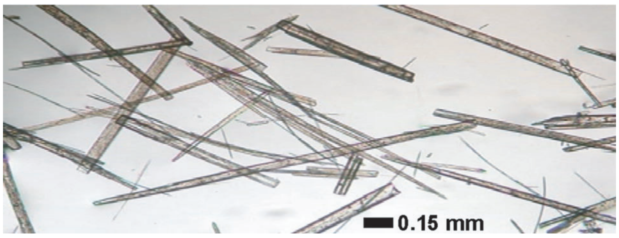


Figure 1. Observation of the solid-state fiberlike crystalline material $[\{((E)\text{-}\mathbf{1})_2K^+\}SCN^-]_n$ by optical microscopy.

Acyl hydrazone **1** was found to form a complex with KSCN with a binding constant of $24.8 \pm 4.6\,\text{M}^{-1}$ and 1:1 stoichiometry (from a Job plot; see Figure S1) in acetonitrile solution at 25 °C, as determined from ^{1}H NMR spectroscopic data (see Figures S2 and S3 in the Supporting Information). When the concentration of ligand **1** reached 70 mM in the presence of KSCN (35 mM) at 25 °C (in a thermostatic bath), a material composed of thin fiberlike objects (see Figure S4) was generated. Crystals suitable for X-ray diffraction analysis were obtained by the slow diffusion of diethyl ether into a solution of **1**–KSCN in acetonitrile. Determination of the solid-state molecular structure showed that the crystalline material is composed of assemblies of the complex $[\{((E)\text{-}\mathbf{1})_2K^+\}SCN^-]$, in which ligand **1** in its (*E*)-**1** form coordinates to the K^+ cation with 2:1 stoichiometry (Figure 2). These complexes stack on top of each other at a distance of 4.696 Å between two successive flat ligand molecules (or K^+ cations) to form a long channel of K^+ cations. The cations hold the assembly together by also interacting with the oxygen sites of the complexes above and below. The $K^+\cdots O$ distances are similar (2.90 Å) within a complex and between stacked

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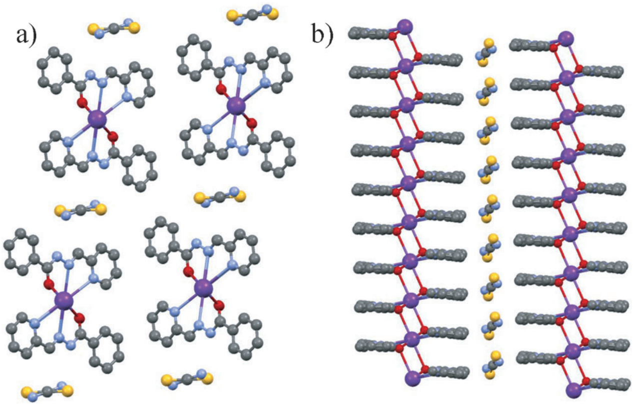


Figure 2. X-ray solid-state molecular structure of the crystalline metallosupramolecular assemblies formed by the complex $[\{((E)\text{-}\mathbf{1})_2K^+\}SCN^-]_n$: a) top view; b) side view showing the interaction between adjacent units in each stack of the complex. The SCN^- anions are disordered.[10]

complexes. The thiocyanate anions are disordered and occupy the space between two stacks by forming hydrogen bonds with the N−H group of **1** (average N···N,S distance: 3.275 Å). Only a 1:1 complex was detected in solution, probably as the result of an even weaker binding constant for the second ligand than for the first. Whereas the free ligand **1** is expected to adopt a W-type conformation, it undergoes conformational switching to the U form by rotation about the −NH−C(=O) amide bond on binding to the metal cation (see Scheme 1).[5,9] Crystals of **3**–KSCN assemblies were also obtained. The assemblies of **3**–KSCN had the same structure as that observed for assemblies of **1**–KSCN (see Figure S6).

To gain insight into the features that control this remarkable self-assembly process, we carried out a number of experiments. The yield for the formation of the assemblies was determined to be 64 % at 25 °C and 85 % at −10 °C for a solution of ligand **1** (100 mM) and KSCN (50 mM) in acetonitrile; 36 and 15 % of the ligand remained in solution, respectively. The failure of acyl hydrazones **5** and **6** to generate assemblies underlines the importance of both the pyridine moiety, which binds to K^+, and the hydrogen bond between the N−H group and the SCN^- anion. The assemblies formed selectively with potassium, rubidium, and ammonium cations, but not with sodium or cesium cations, although Na^+ also binds to **1** ($K_f = 33.0 \pm 4.1\,M^{-1}$ at 25 °C for NaSCN in acetonitrile). The absence of assembly formation with Na^+ may be related to its smaller size (with a radius of about 0.95 Å, compared to 1.33 Å for K^+), which makes it unable to bind to neighboring stacked ligands.

Assembly formation was found to depend on the geometry of the anions (50–200 mM solution). It occurred with linear triatomic anions (such as thiocyanate, azide, and cyanate) as well as with anions of tetrahedral geometry (such as perchlorate), but not with octahedral (such as hexafluorophosphate) or trigonal anions (such as acetate and benzoate). Moreover, anion selection occurred in the tetrahedral series: perchlorate gave assemblies, whereas triflate and methanesulfonate did not. A possible explanation rests in the space available between the two potassium complexes: it may be large enough to accommodate perchlorate but not triflate or methanesulfonate.

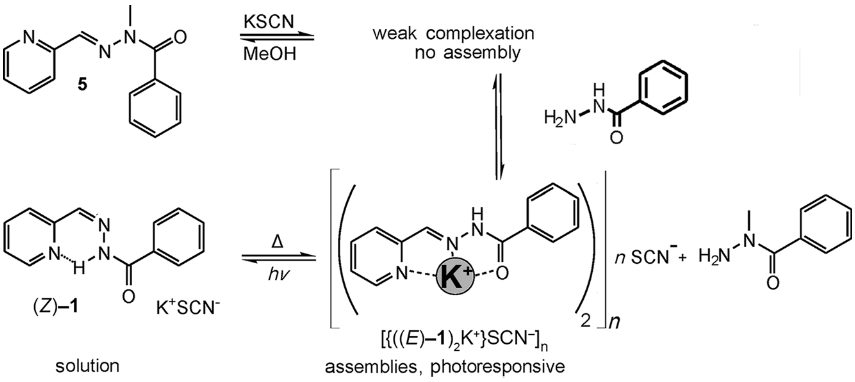
The combined selectivity towards both cations and anions is illustrated by experiments involving the successive addition of salts to a solution of **1**. Separately, tetrabutylammonium thiocyanate and potassium hexafluorophosphate did not yield assemblies, but did so when mixed together. Various combinations of salts were investigated for their ability to induce assembly formation (at different concentrations in acetonitrile as well as in methanol in a few cases; see Table S1). The results agree with the selectivities indicated above.

Heating of the solution containing the assemblies caused their disappearance and gave a clear solution at 50 and 65 °C, respectively, for 100 and 200 mM solutions of **1** in acetonitrile with KSCN (0.5 equiv; see Figure S8). The process is reversible: cooling of the solution regenerated the assemblies. The melting temperature of the assemblies also depended on the ligand and salt used (see the Supporting Information).

The crystalline assemblies described above were found to have interesting photochemical properties. Acyl hydrazones such as **1** underwent photoinduced *E*-to-*Z* conversion.[5] The $[\{((E)\text{-}\mathbf{1})_2K^+\}SCN^-]_n$ assemblies obtained in acetonitrile were found to disappear upon irradiation (1 h) with UV light (**1** absorbs at 300 nm), which led to the formation of (*Z*)-**1** in solution, as observed by ^{1}H NMR spectroscopy. Similar results were obtained in methanol (see the Supporting Information). In both solvents, the photoinduced (*E*)-**1**-to-(*Z*)-**1** configurational transformation of the ligand in the complex caused the concomitant release of K^+ ions into the solution (as (*Z*)-**1** cannot bind the cations) and the disappearance of the fiberlike assemblies (Figure 1). Thus, in acetonitrile, the total amount of cations in solution underwent a significant change from 36 % to the full amount of the added salt; the cations were in part free and in part complexed by nonisomerized ligand, according to the binding constant. Kinetic studies showed a slightly lower rate of *E*-to-*Z* isomerization in the solution containing the assemblies ($5.33 \times 10^{-2}\,min^{-1}$) than in the solution of **1** alone ($5.68 \times 10^{-2}\,min^{-1}$), probably owing to the stabilization of the *E* state by the binding of K^+ both in the assemblies and in solution in acetonitrile (see Figures S14 and S15). Moreover, in methanol, a solvent that disrupts hydrogen bonding, the crystalline assemblies were regenerated by the return from the metastable state (*Z*)-**1** to the stable state (*E*)-**1** after 2 days at room temperature (see Figure S16). The rate of the thermal back conversion from (*Z*)-**1** to (*E*)-**1** was faster in the presence of KSCN or potassium triflate (conditions under which no assembly occurs with triflate anions) than in the absence of potassium salts, which shows that the return transformation was somewhat accelerated by the formation of the weak complex in solution (see Figures S17–S19). Heating to 40 °C in the presence of KSCN (1 equiv) accelerated the *Z*-to-*E* return transformation by a factor of 6 (see Figure S20). Photoinduced dissociation of the assemblies also occurred in acetonitrile, but they were not reformed in 1 month at 25 °C owing to the higher stability of (*Z*)-**1** in this solvent.

Irradiation of the fiberlike material in the solid state and observation by optical microscopy revealed a change in their morphology from well-defined crystalline sticks to amorphous stains (see Figure S21). Thus, the complexes themselves in the crystalline material are photolabile.

The presence of a reversible C=N bond in compounds **1**–**6** allows for the exchange of molecular subunits by a transimination reaction[3,4,8] (Scheme 2) and thus for a dynamic constitutional modification in connection with the assembly process. When acyl hydrazone **5** and KSCN were mixed in methanol at 25 °C, no assemblies were formed. The addition of benzhydrazide to the solution induced a slow hydrazide exchange, which led to the formation of acyl hydrazone **1** (Figure 3). After 10 days, fiberlike assemblies appeared in solution, at the same rate as the exchange. Thus, covalent dynamics enabled the conversion of acyl hydrazone **5**, which cannot form assemblies, into **1**, which can. On irradiation of the mixture, the same behavior as described above was observed, with the disappearance of the crystalline assemblies as a result of (*E*)-**1**-to-(*Z*)-**1** photoconversion.



Scheme 2. Dynamic covalent exchange reaction between acyl hydrazone **5** and benzhydrazide to form (*E*)-**1** and its assemblies by the complexation of KSCN in methanol.

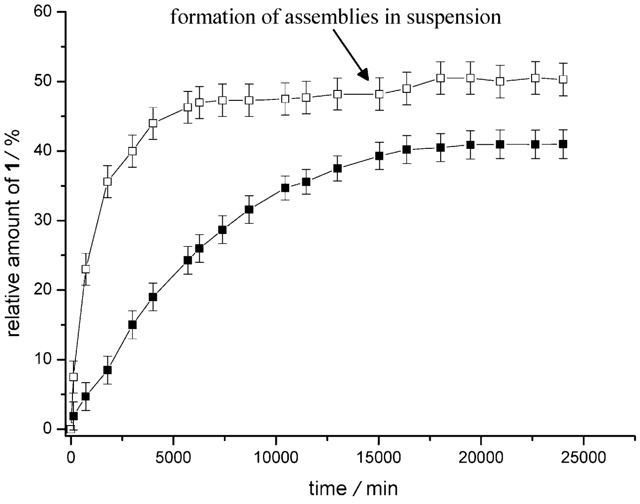


Figure 3. Ratio of the total amount of **1** formed (present as (*E*)-**1** + (*Z*)-**1** in solution and later as (*E*)-**1** in the assemblies) by dynamic covalent exchange between **5** (300 mM) and benzhydrazide (1 equiv) in the presence (□) and absence (■) of KSCN (1 equiv) in methanol with respect to the amount of **5**. After 15 000 min (10 days), the slope changes slightly as fiberlike crystalline objects appear.

The rate of exchange decreased by 30 % in the absence of KSCN (Figure 3) and increased by a factor of 6 and 10 with KSCN (5 equiv) and barium perchlorate (1 equiv; a stronger binder of ligand **5**), respectively. It remained unchanged in the presence of potassium triflate (1 equiv; conditions under which no crystalline assemblies are formed; see Figures S22–S26). After 17 days, the amount of **1** was 7 % larger in the presence of KSCN than in its absence. Thus, although the formation of a complex and its assembly induced rather weak exchange catalysis and component selection (relative to that observed for other systems),[3,4] constitutional dynamics enabled the generation of the entity able to form the supramolecular assemblies.

In conclusion, acyl hydrazones such as **1** underwent self-assembly into long-range organized fiberlike supramolecular entities on binding specific metal salts. The formation of the crystalline assemblies depended greatly on the charge and size of the cation as well as on the geometry of the anion. These assemblies displayed a reversible response to the physical stimuli heat and light. Heating of the solution led to their gradual dissolution, and they were regenerated upon simple cooling. Irradiation of the crystalline fiberlike assemblies induced configurational photoisomerization of the ligand from (*E*)-**1** to (*Z*)-**1** and caused their disappearance. The process is thermoreversible: the crystalline assemblies were regenerated over time by thermal return from the metastable state (*Z*)-**1** to the stable state (*E*)-**1**.

The system displayed photoinduced cation release. On photolysis of the crystalline metallosupramolecular assemblies, the release of the potassium cations, which are not bound by the photogenerated form (*Z*)-**1**, led to a significant increase in the cation concentration. This feature is of general interest, as it may be used to trigger a process that depends on an ionic threshold.[11] These effects hold for both the cations and the anions, which are also released on photodestruction of the assemblies. Acyl hydrazones such as **1** display double shape switching under the action of different, orthogonal effectors: a conformational W-to-U conversion on cation binding and a photoinduced configurational change from the *E* to the *Z* form. Finally, the metallosupramolecular crystalline assemblies behave as covalent dynamic materials, as they incorporate reversible covalent bonds, which allow for constitutional variation by component exchange under metal-ion catalysis. Thus, a compound unable to undergo assembly may be converted progressively into a compound capable of generating a self-assembled fiberlike material.

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