Light-driven charging of a molecular Cu(I) complex for storage of photoredox equivalents and discharging in the dark

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The diurnal day/night cycle presently is a great challenge for the harvest of solar energy rendering suitable energy storage schemes inevitable. In the described experiments a Cu(I) 4*H*-imidazolate complex is efficiently photoreduced in the presence of a sacrificial donor. The obtained two-electron reduced species is stored for more than 14 hours in the dark. In a dark reaction, the stored photoredox equivalents can be transferred to an electron acceptor while the starting Cu(I) complex is almost completely regained. Repetition of the photoreduction/reoxidation revealed a photoreduction efficiency of 72% after four cycles.

Keywords: Solar energy conversion, day/night cycle, copper complex, photoredox equivalents, energy storage.

Turning solar energy into chemical reactivity is a long-standing goal of scientific endeavours and a desirable ambition for an ever-growing mankind.[1] The insatiable and constant hunger for energy urges us to cope with the diurnal day/night cycle, thus demanding solar energy storage solutions. Besides photoelectrochemical schemes[2], several solid state material based approaches have been proposed to harvest light in form of excited electrons and to store these photoredox equivalents until consumption in dark processes. Most examples for photoelectron storage are metal oxides[3], such as TiO_2-WO_3, TiO_2-Cu_2O or La_2NiO_4 as well as carbon nitrites[3,4]. We here report on the first *molecular* example for the storage of photoredox equivalents by a Cu(I) 4*H*-imidazolate complex with storage times in the range of 14 hours (Figure *1*).

Photoactive copper complexes are regarded as a viable alternative for rare metal complexes, such as those based on ruthenium.[5–7] Neutral Cu(I) 4*H*-imidazolate complexes[8,9] (*cf.* Figure *1*) are relatively new among Cu(I) coordination compounds[10] and bring in the necessary prerequisites for the harvesting of solar light and intermolecular photoredox reactions, such as a broad and intense visible absorption peaking at about 510 nm, sufficiently long excited state lifetimes around 100 ns and two-electron reducibility.[8,9] The Cu(I) centre enables the long-lived excited state due to the population of excited triplet states as well as the broad visible absorption by virtue of metal to ligand charge transfer bands.[8,9] The 4*H*-imidazolate ligand serves as the electron storage, as it represents a Wurster-type[11] two-electron redox system.[8,9,12–17]

The discovery, described in this contribution, represents an alternative approach to materials-based storage schemes, which combines photosensitizer and storage medium in one molecular entity. This allows for the tailoring of its properties by chemical modifications.

Results

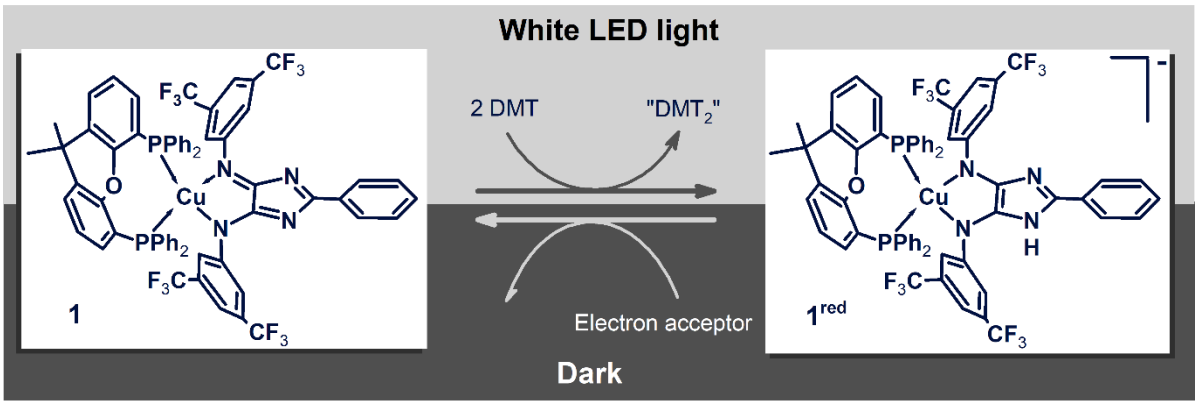

Figure 1. Presentation of the photoreduction of the Cu(I) 4*H*-imidazolate complex **1** to the respective two-electron photoreduced species **1**^{red} (proposed structure) and electron transfer to an acceptor in a dark process.

Photoreduction of complex **1** to **1**^{red} was achieved by irradiation with white LED-light in the presence of the sacrificial electron donor *N*,*N*-dimethylamino-*p*-toluidine (DMT)[18,19] (Figure 1, see SI for experimental details). As presented in Figure *2*A-B irradiation in presence of the electron donor leads to a dramatic decrease of the visible absorption bands (photobleach) due to the formation of the two-electron reduced species (leuco-form[17,20]). It seems likely, that the reduction of the complexes proceeds via consecutive one-electron transfer steps. However, the spectral signature of the one-electron reduced species[17] was not observed in these experiments, most probably due their fast consumption during the process.

After irradiation of **1** for about 8 hours in the presence of DMT, the absorption band has decreased to 0.6% of its absorbance prior to irradiation, representing a photoreduction efficiency better than 99%. Due to high initial absorbance the spectrum prior to irradiation was taken in a 1 mm cuvette and multiplied with a factor of ten to match with the spectra taken during irradiation, which were all taken in a 10 mm cuvette under strict inert conditions. Control experiments in the dark with a reaction solution that contained all components did not show spectral changes over a period of about 20 hours, underpinning the light-dependence of the described process (see SI, Figures S7).

After irradiation the solution of the photoreduced complex **1**^{red} was kept in the dark for about 14 hours during which only a marginal increase of the absorption band was observed from 0.6% to 2.1% of the initial absorbance (Figure 2C). The slight increase of the absorption is probably due to trace amounts of air dissolved in the Teflon stirring bar or due to an electron back-transfer from the photoreduced complex **1**^{red} to the photooxidized DMT. Altogether, the

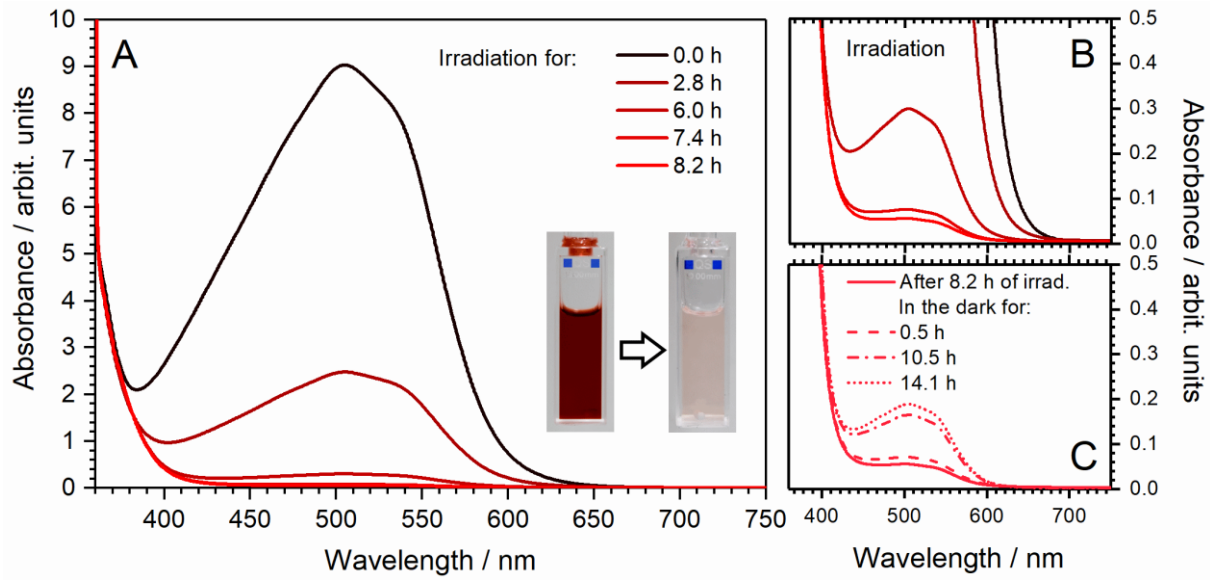

Figure 2. **A** - decrease of the absorption band of **1** during irradiation in the presence of DMT. The spectrum at 0 h was obtained from a measurement in a 1 mm cuvette multiplied by a factor of ten. The other spectra were obtained in a 10 mm cuvette. The photos of the cuvette document the dramatic photobleach of the reaction mixture prior to and after irradiation. **B** – Zoom-in into the low absorbance region reached during irradiation. **C** – Stability of the absorbance of **1**^{red} in the dark. For comparison the absorbance scale of **C** and **B** are identical.

photoreduced complex shows a remarkable long-term stability. This long-term stability allows to harvest photoredox equivalents in a light reaction, store them and to make them available in a dark reaction (*vide infra*).

Methyl viologen (MV^{2+}) was chosen as a model electron acceptor due to the characteristic absorption bands of its one-electron reduced form ($MV^{\bullet+}$).[21] In the dark, one drop of a

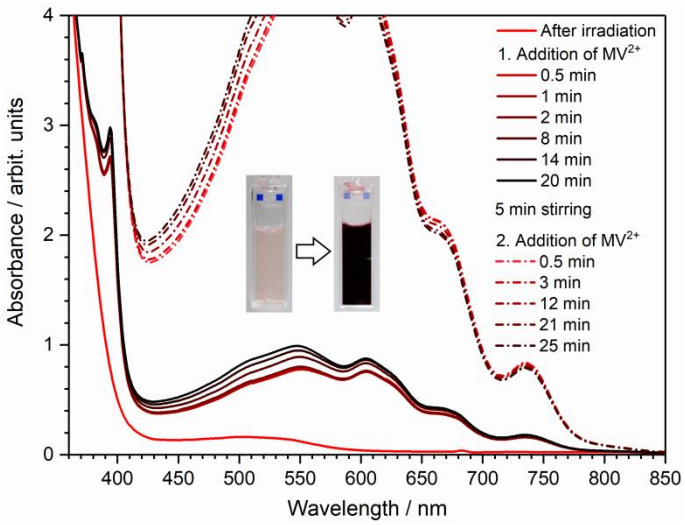

Figure 3. Re-appearance of the absorption band of **1** together with the absorption bands of the $MV^{\bullet+}$ radical cation[21] at 398 nm, 608 nm, 664 nm and 735 nm, as a result of the addition of MV^{2+}. Due to reaching the detector limits, the spectral representation was cut at an absorbance of 4. The photographs show the recoloration of the solution with a mix of **1** and $MV^{\bullet+}$ colours.

solution of MV^{2+} in acetonitrile was added to the solution of the photoreduced complex. Immediately, the characteristic absorption bands of $MV^{\bullet+}$ appeared at 398 nm, 608 nm, 664 nm and 735 nm together with the absorption band of the neutral complex **1** at about 500 nm (Figure *3*). This observation demonstrates the transfer of photoredox equivalents from the photoreduced complex $\mathbf{1}^{red}$ to the substrate MV^{2+} in a dark reaction. Control experiments with MV^{2+} and DMT in acetonitrile did not furnish any detectable amounts of $MV^{\bullet+}$ neither in the dark nor under irradiation for 20 hours with white LED-light. Addition of a second drop of the MV^{2+} solution led to a second increase in the absorption bands of both the reoxidised, neutral **1** and the $MV^{\bullet+}$ bands. Due to the strong absorbance of both species, **1** and $MV^{\bullet+}$, exceeding the detector limits, no further MV^{2+} was added. However, already 65% of the initial absorbance have been gained in this experiment but a more elaborate experimental setup is necessary to follow the reoxidation completely, which we are working on. From the absorption spectra given in Figure 3 and Figure S19 it becomes apparent, that the concentration of $MV^{\bullet+}$ is slowly decreasing while the concentration of **1** is increasing. This concentration increase (**1**) / concentration decrease ($MV^{\bullet+}$) points to a second reduction of $MV^{\bullet+}$ to MV^0, the latter having very low absorbance in the visible part of the spectrum.[21] The reduction $MV^{\bullet+}/MV^0$ (-1.26 V *vs*. Fc/Fc^+)[21] is thermodynamically feasible with **1**, which has reduction potentials of **1** / $\mathbf{1}^-$ (–1.63 V) and $\mathbf{1}^-$ / $\mathbf{1}^{red}$ (–2.13 V) *vs.* Fc/Fc^+ (see SI).

Molecular oxygen may also serve as electron acceptor and readily reoxidises the photoreduced complex $\mathbf{1}^{red}$. Exposure of the solution of $\mathbf{1}^{red}$ to air immediately led to a recoloration due to the formation of **1** (cf. Figure *1* and Figure S8). The reoxidation ceased after about 30 minutes with a total recovery of the initial absorbance of about 90 %. The reoxidation by molecular oxygen form air was used to study the cycling stability of the photoreduction / reoxidation cycle as presented in Figure 4. In a similar experiment as described above, **1** was irradiated for about 8 hours with white LED-light in the presence of DMT leading to the described photoreduction to $\mathbf{1}^{red}$, *i.e.* accumulation of photoredox equivalents. These photoredox equivalents could then be transferred to molecular oxygen. After the thorough removal of the remaining air in the solution of **1** the photoreduction / reoxidation cycle was repeated for a total of four cycles (*cf.* Figure 4 and Figures S11-S18). The time course of the photoreduction / reoxidation cycles was followed by UV-Vis absorption spectroscopy and the accumulated as well as transferred charge was calculated from the absorption data taking two electrons per photoreduced complex $\mathbf{1}^{red}$ into account. In this experiment a charge accumulation of 83% was obtained in the first and second cycle, which corresponds to 57 mAs or $2.9 \cdot 10^{-7}$ mol of $\mathbf{1}^{red}$. In the third and fourth cycle the charge accumulation efficiency was 72%, *i.e.* 49 mAs or $2.6 \cdot 10^{-7}$ mol of $\mathbf{1}^{red}$. As described above, under strictly inert conditions a photoreduction efficiency of more than 99% can be achieved. The observed drop of the photoreduction efficiency in the third and fourth

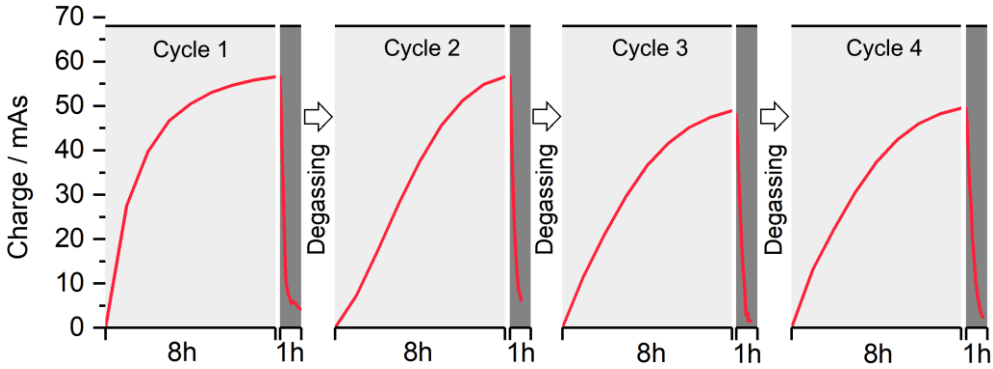

Figure 4 Presentation of the photoreduction / reoxidation cycles of **1** in the presence of DMT, *i.e.* the accumulation of photoredox equivalents in a light-driven process (light grey) consumption of photoredox equivalents by molecular oxygen from air in a dark process (dark grey). The theoretical maximum charge accumulated upon complete photoreduction in this experiment is at 68 mAs (horizontal black line).

cycle as well as the decreased photoreduction rate, as is apparent from Figure 4, is probably due to the formation of water as the product of molecular oxygen reduction and possible side reactions connected with that.

Control experiments with the ligand in the presence of DMT resulted in a decrease of the ligand absorption band to about 51% of the initial absorbance over 89 hours (see SI Figure S9). The aerobic reoxidation ceased at 78 % of the initial absorbance. These observations indicate, that the ligand represents the electron storage medium, albeit only the Cu(I) complex provides sufficiently long excited state lifetimes for effective photoreduction. The diminished reversibility by aerobic reoxidation suggests, that side reactions may play a significant role, which have been effectively supressed in case of the Cu(I) complex.

Discussion

The presented results demonstrate the light-induced storage of photoredox equivalents on a molecular species, *i.e.* copper(I) 4*H*-imidazolate complexes. To the best of our knowledge, this is the first example of that kind allowing to charge a molecular species with the power of visible light and to store the charge over more than half a day until utilisation in a dark reaction. In the present case, photosensitiser and energy storage medium are one molecular entity that is based on a Cu(I) centre and an organic two-electron redox system[11,16,22–25]. It is noteworthy, that, among 4*H*-imidazolate complexes, so far, only Cu(I) 4*H*-imidazolates have been found to possess sufficient excited state lifetimes for photoreduction of about 100 ns.[8] Their Ru(II) counterparts only have lifetimes in the hundred picosecond range[14] but are still able to take up multiple electrons by electrochemical pathways[14,26–28]. Based on the reports by Beckert and coworkers[17], at the current state, we anticipate the formation of a Cu(I) 1*H*-imidazolate complex (**1**^{red}) upon photoreduction of **1** as given in Figure *1*,. Structural and

spectroscopic characterisation of **1**^{red} is currently underway, to gain a deeper understanding of the observed photoreduction and reoxidation processes.

It is interesting, to compare the reported photoredox equivalent storage system with redox flow batteries, as both systems are solution based and Wurster-type redox systems are investigated as well as redox active components in redox flow batteries (*e.g.* quinones).[23] From the reported experiments (*vide supra*) an approximate storage capacity of 117 As/L can be deduced which ranges about three orders of magnitude below current redox flow batteries.[23] However, one has to consider that molar concentrations are used in redox flow batteries but concentrations below 1 mM have been used in the here described experiments. Anticipating similar charging and discharging behaviour also at molar concentrations, the reported system may cope with redox flow battery systems gaining its energy directly from sunlight.

Besides the storage of photoredox equivalents, the described observations have implications for photoredox processes. The first implication is a buffering or relay effect[29]. Let us consider a photoredox reaction where the photosensitizer reduces a substrate after being reductively quenched by a sacrificial donor.[30] In response to an intermittent decline of substrate concentration in a photoredox process, the described storage abilities would allow for the buffering of idle photoredox equivalents until consumption by regained substrate concentration and thus mitigate damage to the photosensitizer. A second aspect is particularly connected with the Cu(I) 4*H*-imidazolate complexes examined above, that is the formation of the leuco-form upon photoreduction (reversible bleaching effect). The low absorbance of the photoreduced Cu(I) 4*H*-imidazolate complexes in the visible spectrum represents a negative feedback loop to the (temporary) absence of substrate in a photoredox process under continuous illumination and thus a potential means to mitigate photodamage.

Conclusions

A molecular Cu(I) 4*H*-imidazolate complex is described for the efficient harvesting and storage of light energy in the form of photoredox equivalents on time scales relevant to cope with the diurnal day/night cycle. Photoredox equivalents are generated by a two-electron photoreduction on the Cu(I) complex, which is accompanied by a significant decrease of the visible absorption band of the Cu(I) complex. The starting Cu(I) complex is efficiently regained upon transfer of the stored photoredox equivalents to the electron acceptors methyl viologen and molecular oxygen in a dark reaction and after a storage period of more than 14 hours. Four cycles of photoreduction and reoxidation have been investigated and underscore the reversibility of the system. Conceptually, a broad applicability of the outlined molecular

storage of photoredox equivalents is anticipated such as in solar energy conversion and storage schemes as well as photocatalysis.

Methods

Irradiation experiments Each experiment was done in duplicate with the preparation of the test sample and a reference sample. The reference sample was kept in the dark while all experimental manipulations were done with the test sample. The preparation of the samples was done under low light conditions and strictly under nitrogen or argon atmosphere using standard Schlenk-technique. Degassing of the samples was achieved by a freeze-pump-thaw triple cycle. The samples were either prepared in 5 ml vials sealed with a septum cap or in a quartz cuvette with 1 mm or 10 mm optical path length equipped with a vacuum tight stopcock. The 1 mm cuvettes were purged twice with degassed, anhydrous acetonitrile under inert atmosphere to remove residual air from the quartz surface. The sample solutions were prepared in anhydrous acetonitrile with final concentrations between $2 \cdot 10^{-4}$ mol/l to $6 \cdot 10^{-4}$ mol/l for the copper complexes and $2 \cdot 10^{-1}$ mol/l of DMT. The test sample was irradiated with an LED white light source (ChiliTec GmbH, Germany, 6 W, 4200 K) with an irradiance of 20 mW/cm^2.

Charge transfer experiments with methyl viologen For the reduction of methyl viologen hexafluorophosphate (MV^{2+} $2\,PF_6^-$), a solution of the oxidizing agent in anhydrous acetonitrile was prepared ($2.5 \cdot 10^{-2}$ mol/l) and degassed with a freeze-pump-thaw triple cycle. One drop of solution was added via syringe to the stirred solution of the photobleached **1**^{red} in the cuvette under nitrogen atmosphere. UV-Vis absorption spectra were taken subsequently until the development of the $MV^{\bullet+}$ bands ceased.

Cyclisation experiments For the cyclisation experiment, the reaction solution was prepared as given above albeit with a final concentration of **1** of $6 \cdot 10^{-5}$ mol/l in anhydrous acetonitrile in a 10 mm cuvette. The absorbance was followed by UV/Vis spectroscopy during irradiation and stopped when the absorbance change plateaued. For the reoxidation the cuvette was opened and strirred while the recoloration was followed by UV/Vis spectroscopy until the absorbance change started plateauing. Subsequently the solution was carefully degassed by freeze-pump-thaw triple cycle and the next cycle comprising of irradiation and reoxidation was started.

For further information see SI.

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Acknowledgements

The authors gratefully acknowledge the help of Peter Mons with the implementation of the spectroscopic investigations. Rainer Beckert is gratefully acknowledged for the provision of the 4*H*-imidazole ligand.

Author contributions

N.H. prepared and characterized the complex. M.S. N.H. and F.W. carried out the photoreduction and reoxidation experiments. M.S. and N.H. interpreted the data. B.D. gave critical input to data interpretation and the discussion. M.S. directed the work and wrote the manuscript.

Competing interests

The authors declare no competing interests.