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Combined In Situ Illumination-NMR-UV/Vis Spectroscopy: A New Mechanistic Tool in Photochemistry

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Abstract: *Synthetic applications in photochemistry are booming. Despite great progress in the development of new reactions, mechanistic investigations are still challenging. Therefore, we present a fully automated in situ combination of NMR spectroscopy, UV/Vis spectroscopy, and illumination to allow simultaneous and time-resolved detection of paramagnetic and diamagnetic species. This optical fiber-based setup enables the first acquisition of combined UV/Vis and NMR spectra in photocatalysis, as demonstrated on a conPET process. Furthermore, the broad applicability of combined UVNMR spectroscopy for light-induced processes is demonstrated on a structural and quantitative analysis of a photoswitch, including rate modulation and stabilization of transient species by temperature variation. Owing to the flexibility regarding the NMR hardware, temperature, and light sources, we expect wide-ranging applications of this setup in various research fields.*

Photocatalysis is one of the booming fields in organic synthesis and has experienced a nearly exponential increase in publications of synthetic strategies and applications during the last decades.[1] Despite the high impact of new light-induced transformations on synthesis, detailed insights into photocatalytic mechanisms are still a real challenge. In photochemistry, ultrafast UV/Vis spectroscopy is so far the most commonly used method for detailed mechanistic studies, owing to its capability to detect the initial photoexcited states.[2] We and other groups have recently shown that NMR spectroscopy can provide essential mechanistic information on photochemical and photocatalytic processes, despite its insensitivity and poor time resolution,[3] by providing quantitative reaction profiles of reactants, products, and intermediates. Complementary to ultrafast UV/Vis, mechanistic features downstream from the initial photoexcitation, such as single- versus two-electron transfer processes,[3b] proton transfer pathways, or multiple concurrent reaction mechanisms, can be elucidated by NMR spectroscopy.[3a] Furthermore, owing to its high-resolution spectra, NMR spectroscopy provides detailed structural information about intermolecular interactions[4] and aggregation, revealing key information of activation or deactivation of substrates or catalysts in photocatalysis.[5]

However, besides the limited time resolution, NMR spectroscopy faces the additional challenge that single-electron transfer (SET) processes, which are typical for photocatalysis, cause an interplay of paramagnetic and diamagnetic species. Often, the lifetime of these paramagnetic radical intermediates is so short that they do not even affect the NMR spectra of the diamagnetic species. The information on these transient radicals can often be accessed only by photo-chemically induced dynamic nuclear polarization (photo-CIDNP) through their diamagnetic recombination and disproportionation products.[3b,6] In contrast, stable long-lived radicals can impose severe challenges to NMR spectroscopy. While in the case of several inorganic complexes or proteins paramagnetic NMR spectroscopy can be successfully applied,[7] it is usually not possible to detect paramagnetic states of small organic molecules, such as those used as photocatalysts in photochemistry. Furthermore, for the stable radical states of photocatalysts, chemical exchange often leads to severe line broadening even for the diamagnetic states.[3b]

Because consecutive photoinduced electron transfer (conPET) processes[8] (Figure 1) recently emerged as a hot topic to address the activation of strong bonds and higher redox potentials, detailed mechanistic investigations are highly demanded in the photocatalysis community. In conPET processes, long-lived radical anions (usually elusive to NMR spectroscopy) are the central key intermediates generated by PET utilizing a sacrificial electron donor **D**. A second photoexcitation of this radical anion leads to a photoexcited state with reduction potentials of up to -2.4 V.[8,9] This provides an elegant way to increase the scope for metal-free

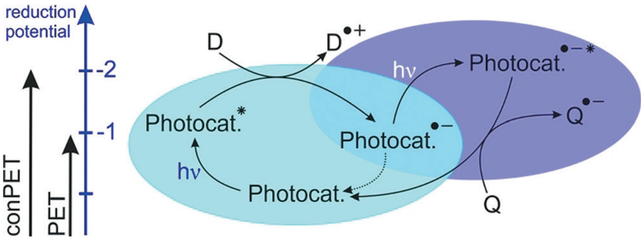

Figure 1. Schematic of a consecutive photoinduced electron transfer (conPET) process.[8c] D = sacrificial electron donor, Q = quenching substrate.

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photoredox catalysis under mild conditions using commercially available organic photocatalysts.

To extend the scope of high-resolution NMR spectroscopic investigations in photocatalysis with stable radicals, a combined NMR and UV/Vis spectroscopic tool would be ideal.[10] However, reaction profiles of photocatalytic processes featuring longer reaction times of up to several hours or even days impose severe challenges for separated setups. While separated setups can have matching experimental conditions such as temperature and concentration, an exact match of light absorption/intensity, which depend on the geometry and positioning of light source and reaction vessel as well as parameters such as convection/diffusion properties, is best realized by using an in situ combination.

In addition to photocatalysis, an in situ setup combining UV/Vis, NMR, and illumination would show a broad applicability in the field of photoswitches and molecular machines.[11] Herein, such a setup provides direct, quantitative correlations between absorbance and structure of switching states and can be used to track full conversion cycles.[12]

For static equilibria, Tolstoy et al. introduced an in situ combination of UV/Vis and high-resolution solution NMR spectroscopy (UVNMR) in 2009 to achieve absolute comparability of both methods.[13] However, this setup cannot be applied for dynamic, light-induced (photo) chemical processes because of the hampered diffusion caused by a reflector between bulk solution for NMR spectroscopy and an aliquot for UV/Vis spectroscopy. Furthermore, an additional light source for illumination is missing and the NMR probe has to be drilled to guide optical fibers to the tip of the NMR tube.

Therefore, in this paper we describe a fully automated triple combination of in situ illumination and UV/Vis and NMR spectroscopy. The potential of this setup is demonstrated by acquisition of combined UVNMR reaction profiles of a light-induced conPET process and a photoswitchable spiropyran.

Our new optical fiber-based UVNMR-illumination setup combines a UV/Vis-reflection dip probe (Avantes) with our in situ LED-illumination device[14] inside an NMR spectrometer (Figure 2 A). The optical fiber for illumination (with a sandblasted tip) and the reflection dip probe for UV/Vis measurements are placed together inside a coaxial quartz glass insert within an amberized NMR tube. The optical fiber for illumination and the reflection dip probe (Figure 2 B) were used for guiding the light of the LED illumination device and the deuterium-halogen (D-Hal)-lamp directly into the NMR tube and to detect the reflected light. A PTFE insert inside the NMR tube acts as reflector (Figure 2 B). Owing to an outer diameter of the coaxial quartz glass insert of 3 mm and an inner diameter of 4 mm of the outer NMR tube, an active layer of 1 mm is given in the range of the NMR radio frequency (RF) coils (Figure 2 B). To ensure homogeneity of the solution by diffusion, the distance between the tip of the insert and the PTFE reflector was set to approximately 1 mm (path length of approximately 2 mm). To adjust the path length, a customized screw cap was developed (Figure 2 C, for details see the Supporting Information), which connects the NMR tube and the insert tightly, so that even air-sensitive samples and (photo) reactions can be analyzed. The whole setup is portable, fully remote-controlled, and applicable to every conventional solution NMR spectrometer without any alteration. This allows for an extremely flexible application regarding the NMR setup (probe, field, temperature) adapted to the individual problems.

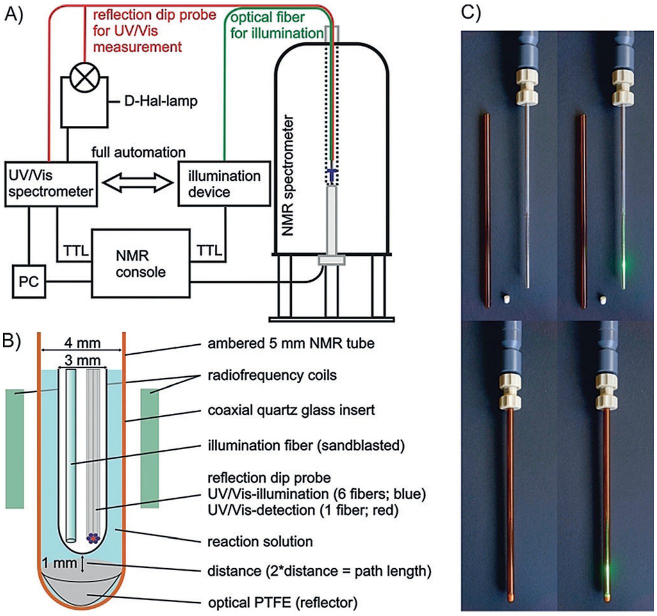

Figure 2. A) Schematic of UVNMR-illumination setup. B) Close-up of the illumination fiber and the reflection dip probe inside the NMR tube. C) Photos of the setup including the outer amberized NMR tube, PTFE reflector, screw cap, and coaxial insert with both optical fibers inside, (dis)assembled with/without light.

To enable combined, time-resolved UVNMR reaction profiles, an absolute time control of UV/Vis, NMR measurements, and illumination is required. Therefore, the NMR console was used as the central time control unit. It directly addresses the illumination device (LED transistor) and the UV/Vis spectrometer through TTL signals (Figure 2 A), implemented as events in modified NMR pulse sequences (see Supporting Information). For a UV/Vis measurement, the UV/Vis spectrometer forwards the TTL signal of the NMR console to a D-Hal-light source to control its shutter, that is, the emitted light hits the sample exclusively during the UV/Vis measurement.[15]

To demonstrate the power of our UVNMR-illumination setup combined in situ UV/Vis and NMR reaction profiles of a conPET process are presented. In this process, light (450 nm) transforms the photocatalyst *N*,*N*-bis(2,6-diisopropylphenyl)-perylene-3,4,9,10-bisdicarboximide (**PDI**) into the stable radical anion **PDI**$^{\cdot-}$ in presence of an electron donor **D** (in this case, NEt$_3$). A second photoexcitation of **PDI**$^{\cdot-}$ is proposed to allow for a reduction of aryl halides such as 4-bromo-benzaldehyde **Ald-Br** to the corresponding aryl **Ald** (Figures 1 and 3 A,B and the Supporting Information).[8a] In this reaction, **PDI** shows extreme line broadening effects in the NMR spectra (Figure 3 C). Even prior to illumination, all signals of **PDI** are significantly broadened most probably owing to an exchange with an electron donor acceptor complex between NEt$_3$ and **PDI** with the typical distance-

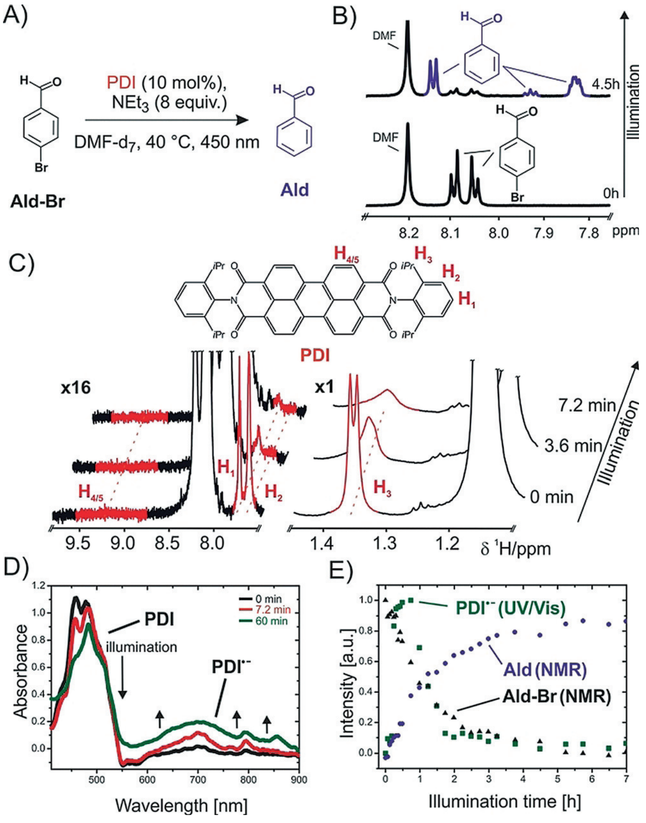

Figure 3. A) Photocatalytic reduction of 4-bromo-benzaldehyde **Ald-Br** to benzaldehyde **Ald** through a **PDI**-catalyzed conPET process.[8a] B) ^{1}H spectra of the reaction mixture, before and after illumination (450 nm) showing **Ald-Br** and **Ald** at 313 K in [D$_7$]DMF. C) Line broadening and vanishing of the **PDI** proton signals (red) upon illumination because of exchange with **PDI**$^{\cdot-}$. D) Conversion of **PDI** into **PDI**$^{\cdot-}$ monitored by in situ UV/Vis spectroscopy. E) Combined NMR and UV/Vis reaction profiles allow for in situ kinetic information of both paramagnetic (**PDI**$^{\cdot-}$) and diamagnetic reactants (**Ald-Br**, **Ald**) in photocatalysis.

dependent line broadening of radicals.[3b] The protons H_4 and H_5 (Figure 3C, see the Supporting Information) attached to the central perylene core nearly vanished, H_1 and H_2 are broadened, and even proton H_3 of the isopropyl group on **PDI** are slightly affected.[16] In contrast, without illumination the UV/Vis spectra show only small absorption bands of **PDI**$^{\cdot-}$ (Figure 3D; Supporting Information). This hints that in specific cases, NMR spectroscopy might be very sensitive for the detection of electron donor–acceptor complexes. Immediately after turning on the light, the NMR proton signals of the **PDI** core (H_4, H_5) vanish completely. The other NMR proton signals of **PDI** are only detectable for seconds or minutes. However, even in the case of detection within the first minutes, for example, of H_3, the severe line broadening prevents any reliable quantification of both diamagnetic photocatalyst and paramagnetic intermediate (Figure 3C).

UV/Vis spectroscopy shows its power for the detection of stable radicals. After a few minutes of illumination at 450 nm, the absorption maxima of **PDI**$^{\cdot-}$ (698 and 794 nm)[8a] rise, while the absorbance of **PDI** (455 and 482 nm) steadily decreases (Figure 3D). Besides its advantages in eliminating all previously described common issues associated with reaction conditions in separated setups, this study also reveals a general application of this combined UVNMR-illumination setup. In the case of UV/Vis detectable intermediates/reactants, a relative quantification over time by UV/Vis is feasible. Studies towards an absolute quantification are in progress.

Thus, the UV/Vis data provides important, time-resolved information about reactants invisible to NMR spectroscopy, enabling a semiquantitative reaction profile for the evolution of **PDI**$^{\cdot-}$. Complementary to the UV/Vis spectra, simultaneously recorded NMR spectra give full quantitative and structural insight into participating diamagnetic reactants and reaction/decomposition products (Figure 3E).[17]

With this in situ combination of NMR and UV/Vis spectroscopy and illumination, complete reaction profiles of the whole progress of a reaction including paramagnetic and diamagnetic species can be obtained and important interactions as well as structural details can be investigated. This enables totally new possibilities to elucidate reaction mechanisms in photocatalysis. Further studies about this controversial mechanism are in progress.

Photoswitches are another promising field of applications for the in situ combination of NMR and UV/Vis spectroscopy and illumination. In our previous study about photoswitchable spiropyrans, deviations between the quantitative data of UV/Vis and NMR spectroscopy were found, demonstrating the importance of identical light intensities and reaction vessels in separated setups.[18] To demonstrate the advantages of our UVNMR-illumination setup with only one illumination device and a common reaction vessel, a spectroscopic analysis of a similar photoswitchable spiropyran is presented. In this case, the colorless 1′,3′-dihydro-1′,3′,3′-trimethyl-6-nitrospiro[2*H*-1-benzo-pyran-2,2′-(2*H*)-indole] **1** can be switched to its open, purple, zwitterionic state **2** (Figure 4A) by irradiation with UV light (365 nm) inside the NMR spectrometer at 300 K in [D$_8$]THF.[11a] The in situ-recorded UV/Vis spectrum (Figure 4B) shows new absorption maxima at 533 and 575 nm with continuous illumination. Complementarily, the NMR spectrum (Figure 4C) gives immediate information about the quantity of the opened spiropyran **2** (21 % after 2 min). However, upon switching off the light, **2** vanishes within circa 24 s in the NMR spectrum ($\tau_{1/2}$ (300 K) = 17.4 s determined by UV/Vis spectroscopy), which prevents a detailed structural study by NMR spectroscopy at 300 K (Figure 4D and the Supporting Information).

By cooling the sample inside the NMR spectrometer to 180 K, without changing any other parameter of the setup, the thermal back-reaction rate was reduced significantly (Figure 4E and the Supporting Information). This enables more time-consuming NMR experiments to investigate both species without degradation products (see Supporting Information).

Structural information about the preferred configuration and conformation can be essential to understand different binding properties of the isomers of photo switchable molecules, for example, in biochemical applications.[19] Furthermore, the time-dependent conversion of different isomers can be tracked online by NMR and/or UV/Vis spectroscopy

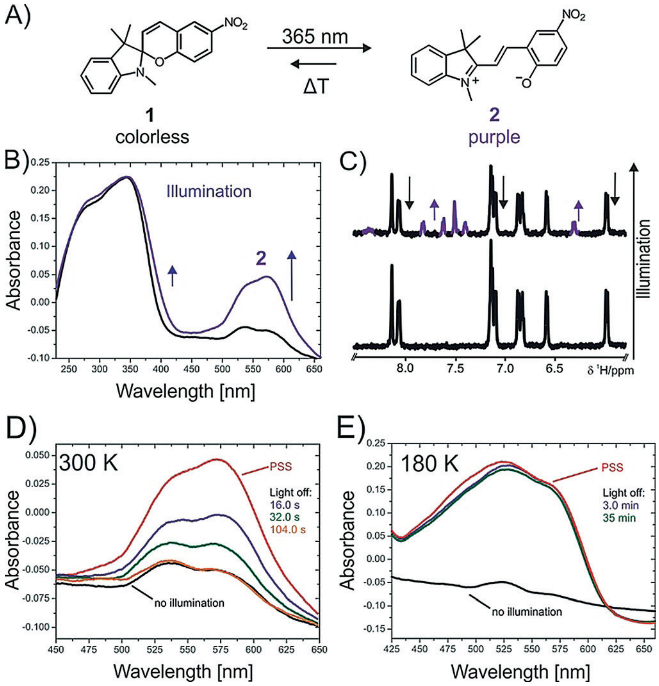

Figure 4. A) Equilibrium of spiropyran **1** and **2**. Upon excitation of **1** with a 365 nm LED, **1** switches into its open, colored form **2**. The photoswitch process can be detected by UV/Vis spectroscopy, while NMR spectroscopy unambiguously confirms the structure of the open form **2**. B) Absorption spectra under the influence of light (365 nm). C) Corresponding NMR spectra showing new signals of **2** after illumination at 300 K. D) UV/Vis spectra of the thermal back reaction of **2** to **1** at 300 K once the light is turned off. E) UV/Vis spectra of **2** at 180 K; the thermal back reaction is extremely slow, which enables a full investigation without the need of continuous illumination. PSS = photo stationary state.

to show the active species present during a reaction. In general the low-temperature applicability of the setup enables temperature-dependent rate modulation and stabilization to detect unstable intermediates by NMR and UV/Vis spectroscopy. In addition, combinations of UVNMR with advanced NMR techniques like DOSY to investigate aggregates or complexes are feasible.

To summarize, in this study we present a fully automated triple combination of in situ high-resolution NMR and UV/Vis spectroscopy and illumination in a new optical fiber-based setup. By merging two very important methods in the field of mechanistic investigations, it is now possible to monitor and quantify paramagnetic and diamagnetic species simultaneously and in a time-resolved manner during a light-induced photochemical transformation by NMR and UV/Vis spectroscopy. Besides the elimination of all common issues related to the use of separated systems, like concentration and temperature, the setup circumvents all deviations in terms of light intensity, reaction vessel, convection, and diffusion. Its applicability in a wide temperature range opens the opportunity to modulate the reaction rate of ongoing reactions or switching cycles to stabilize transient intermediates or conformers. Overall, the combined triple setup that includes high-resolution NMR and UV/Vis spectroscopy and illumination with different wavelengths will allow for detailed mechanistic and structural investigations in various research fields.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: conPET · NMR spectroscopy · photochemistry · photoswitches · UV/Vis spectroscopy

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