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

Andreas Seegerer*, Philipp Nitschke*, and Ruth M. Gschwind*

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1. Setup

1.1 General Information

The setup presented in this publication was developed and optimized on a Bruker Avance III HD 600 (600.13 MHz) with a fluorine selective TBI F probe and Topspin 3.2. However this setup is applicable to any other modern NMR spectrometer with a 5 mm gradient probe head (as shown in section 1.3) and the related software. All components of the UVNMR-illumination device were commercially available if not otherwise indicated. Customized parts are labeled with the corresponding article number of the vendor. In the following sections the setup is shown in three parts: the electronic setup outside the NMR spectrometer, the spectroscopy setup inside the NMR spectrometer and the corresponding pulse sequences and settings for a fully automated acquisition.

1.2 Electronic setup

The setup for simultaneous UV/Vis and NMR measurements under the influence of light from an external light source required a simple combination of mostly commercially available components (Figure S1). For the acquisition of NMR data an NMR spectrometer (here a Bruker Avance III HD 600; Bruker; Billerica, Massachusetts; USA) and a compatible NMR console (here: Avance III HD) is required. For fully automated measurements of UV/VIS and NMR spectra as shown in this publication two free Real-time Clock Pulse (RCP) outputs of the Intelligent Pulse Sequence Operator (IPSO) unit or the former Time Control Unit (TCU) are needed. These outputs can be found in all Bruker NMR consoles which are equipped with a TCU3 unit or newer versions of it. Unfortunately we do not have any information if the setup is also working fully automated with other NMR consoles since this setup was developed exclusively on Bruker machines and we did not have access to NMR consoles of different brands. However we do not see any problems to transfer the setup if the required RCP outputs are available. Manually triggered UVNMR experiments are possible with every setup.

The NMR console represents the central control unit of our device. Via the RCP outputs it is cable-connected to a commercially available UV/Vis spectrometer (Avaspec-ULS-2048-RS-USB2; Avantes; Apeldoorn, Netherlands) and an LED illumination device. This LED illumination device was already developed in our working group. The corresponding highpower LEDs (365 nm and 450 nm) which were used in this publication were purchased by Lumitronix (Cree XT-E, royal blue, 500 mW, 68332) and Laser Components (LEUVA66X00RV00, 365 nm, 2.06 W). However any other commercially available LED can be used in this setup.

Due to the connection to the NMR console both components the LED illumination device as well as the UV/Vis spectrometer can be controlled fully automated by modified pulse programs via TTL signals [see section 1.4]. The UV/Vis spectrometer itself is further connected to a D-Hal-lamp (Avalight-DH-S-Ba; Avantes; Apeldoorn, Netherlands) by a customized Y-cable purchased by Avantes. Due to this connection between the UV/Vis spectrometer and the D-Hal-lamp the TTL signals from the NMR console can directly trigger an UV/Vis measurement and can open and close the internal shutter inside the D-Hal-lamp. This direct control of the shutter was an essential point in the development of our setup. If the shutter is opened outside the acquisition [ms] of an UV/Vis spectrum the light of the D-Hal-lamp (200-2500 nm) reaches unhampered the sample which can cause deviations in the results e.g. due to photodegradation by hard UV irradiation.

The NMR console and the UV/Vis spectrometer are furthermore connected to a PC with the corresponding software Bruker Topspin 3.2 (NMR) and Avasoft 8.6full (UV/VIS; Avantes; Apeldoorn, Netherlands). All measurements, UV/VIS as well as NMR are controlled by modified pulse programs in Topspin (see section 1.4).

To transfer the emitted light of the LED light source and the D-Hal-lamp into the sample inside the spectrometer and to read out the UV/Vis data with the UV/VIS spectrometer, all three components were connected to optical fibers which are guided into the NMR tube inside the NMR spectrometer (see following section).
Figure S1. Schematic overview of all electronic and spectroscopic components of the UV/NMR-illumination setup including their wiring.
1.3 Spectroscopy setup

For measuring UV/Vis and NMR spectra under the influence of LED light inside a NMR spectrometer it was necessary to design a new device which was placed inside a standard 5 mm NMR tube. To make the setup applicable for any conventional NMR user, it was essential to us that no alteration of the NMR spectrometer and/or the NMR probe was required as it was described in a former publication about UVNMR combinations.\(^2,3\) Therefore a combination of different optical fibers was developed which was guided directly from the top of the NMR spectrometer into the NMR tube (Figure S1).

The LED light source (see section 1.2) is connected to a commercially available optical fiber with an outer diameter of 1000 µm (BFH48-1000high; Thorlabs). This illumination fiber is guided directly into the NMR sample (Figure S2A). To ensure a homogeneous illumination of the sample inside the NMR tube, the tip of the optical fiber was uncovered and roughened by sandblasting in the range of the NMR receiver coils. This setup for the illumination of NMR samples inside an NMR spectrometer was already described in an earlier publication of our working group.\(^1\)

The D-Hal-lamp and the UV/Vis spectrometer are connected to a bundle of 7 optical fibers with an outer diameter of 100 µm each purchased by Avantes (FCR-7UV200). In the 230 mm long tip of this bundle the 7 optical fibers are arranged radial symmetrically (Figure S2B). The tip has outer diameter of 1000 µm. The 6 outer fibers (Figure S2B, blue) are connected to the D-Hal-lamp, the central fiber (red) is connected to the UV/Vis spectrometer (changing the connection of the 6 outer fibers to the UV/Vis spectrometer instead to the D-Hal-lamp diminished the detected absorbance intensity). This “UV/Vis fiber” is also guided directly into the NMR tube inside the NMR spectrometer.

Here, the outer NMR tube is a standard thin wall tube with an outer diameter of 5 mm. To diminish the influence of light from the outside commercially available ambered tubes were used. To guide and to center the optical fibers (described above) inside the outer NMR tube a coaxial quartz glass insert (Norell NI5CCI-B-QTZ) with an outer diameter of 3 mm in the range of the stem was added. By nature natural quartz glass is transparent (90-95%) to light >210 nm which ensures the applicability of the setup even in the UV region.

On the bottom end of the tube a customized insert made of optical PTFE (RESTAN; www.image-engineering.de) was put in place to reflect the light of the optical fibers which were connected to the D-Hal-lamp. The reflected light is afterwards detected by the central fiber (red) to give a UV/Vis spectrum of the solution inside the tube (Figure S2B).

Optical PTFE is a diffuse reflector and it is known to have a very high chemical and thermal resistance and can be shaped very easily. Furthermore the material is UV persistent and reflects more than 98% of incoming light in a range between 380-1700 nm. Due to its high thermal expansion coefficient it was necessary to test if the PTFE insert breaks the tube at higher temperatures. Therefore several “stress tests” with abrupt temperature changes were made. According to these tests our setup is at least applicable for a temperature range between 180-323 K. Outside this range no tests were made.
To control the required pathlength for the UV/Vis measurements a new screw cap was developed (Figure S3). Depending on the concentration and the extinction coefficient according to the Lambert-Beer-law a particular distance between the PTFE reflector and the tip of the coaxial insert can be set to give an optimal UV/Vis spectrum. The screw cap is placed on the top of the outer ambered NMR tube and tightened by a customized union nut. Through a 4 mm channel inside the screw cap the quartz glass insert can be introduced into the NMR tube and can be fixed at a particular height by a second union nut. Furthermore it is used to place the stem of the coaxial insert perfectly inside the range of the radiofrequency (rf) coils of the NMR spectrometer. This is essential to achieve a good shimming quality in the NMR experiments and to get good results.

For quantification, we highly recommend to use the NMR results due to slight deviations in the distance settings between blank and sample. However, during the reaction the distance stays constant enabling a relative quantification of ratios by UV/Vis.

Since photochemical reactions and compounds are often influenced by the presence of oxygen two O-rings were added to make the screw cap air tight. Due to this enhancement, reactions under inert conditions are now open for investigation (as shown in the recent PDI study in the manuscript). First tests showed an exclusion of air for at least 7 days.

**Figure S2.** A) Depiction of all NMR tube related components B) Detailed setup of the UV/Vis related parameters.
To link the optical fibers with the top end of the coaxial quartz glass insert a second screw able connector was developed. Similar to the airtight screw cap described before also here a union nut and an O-ring was used to connect the coaxial insert with a plastic tube in which both optical fibers were fastened. The tube is furthermore used to stabilize the whole setup and to inject it more easily into the NMR spectrometer.

**Figure S3.** Detailed depiction of the airtight screw cap.
1.4 Automation and modification of pulse sequences

As described in section 1.2 an automated measurement of UV/Vis spectra and LED illumination is achieved by a direct connection of the UV/Vis spectrometer and the LED transistor to the NMR console (Bruker Avance III HD). They are cable (BNC) connected via two RCP outputs of the T-Controller located in the Intelligent Pulse Sequence Organizer (IPSO; here IPSO 19") unit, which synchronizes all acquisition related processes.

However to run a combined UV/Vis and NMR experiment under the influence of the external LED light source which is exclusively controlled by the NMR console, modified NMR pulse sequences are required. In general the IPSO unit provides a variety of RCP outputs, whereas most of them have a preset function. The free RCP outputs can be programmed by the user adding special events to the standard pulse sequence. The outputs work on Transistor-transistor-logic (TTL) and are active low by default. By applying certain commands in the pulse program they can be switched from active low to inactive high and back.

Here, the free RCP outputs 28 and 29 were chosen to connect the LED light source and the UV/Vis spectrometer/D-Hal-lamp to the NMR console. According to the Bruker user manual, the following command syntaxes to control the devices were added to the pulse program.

\[ \text{d11 setnmr3}^{\wedge}28 \] and \[ \text{d11 setnmr3}|28 \] turn the LED off and on

\[ \text{d11 setnmr3}^{\wedge}29 \] and \[ \text{d11 setnmr3}|29 \] close/open the shutter of the UV/Vis spectrometer and initiate a measurement

(The minimum switching time d11 is given at 25 ns. Note: d11 can also be replaced by a fixed value (e.g. 1s))

To control the UV/Vis spectrometer with these commands, it was necessary to enable the external trigger mode in the related UV/Vis spectrometer software (Avasoft 8.6full).

Figure S4 schematically shows the resulting pulse sequence of a combined UVNMR illumination experiment. Here, the UV/Vis measurement is conducted prior to the NMR measurement under LED illumination. First the LED is turned off, then the shutter inside the D-Hal-lamp opens and the UV/Vis spectrometer initiates a measurement. After the UV/Vis measurement is completed the shutter is closed and the LED is turned on again. Then the common acquisition cycle starts (here: 1D \(^1\)H spectrum), resulting in one UV/Vis spectrum and one NMR spectrum for this experiment. The delay \(d_{UV/Vis}\) is of special interest here. This delay represents the integration time of the UV/Vis measurement (see Avasoft) and is acquired from the manual measurement of the blank sample prior to the actual experiment and has to be adjusted for every new sample.

For every measurement with this UV/NMR-illumination-setup a blank measurement under the same conditions was made previously to set the parameters for the UV/Vis and NMR measurements.
Figure S4. Modified pulse sequence of our combined UVMRR illumination experiment. A series of switching 5V TTL pulses of the T-Controller of the IPSO Unit directly control the UV/Vis spectrometer and the transistor of the illumination LED.

The corresponding pulse program to the pulse sequence shown in Figure S4 is:

```
;zg30_UV_light (based on zg30)
;avance-version (07/04/03)
;1D sequence
;using 30 degree flip angle
;performing one UV/Vis experiment before AQ cycle
;continous illumination during the whole experiment
;
;%CLASS=HighRes
;%DIM=1D
;%TYPE=
;%SUBTYPE=
;%COMMENT=

#include <Avance.incl>
```
Supporting Information

"acqt0=p1*0.66/3.1416"

1 ze
1m setnmr3^28 ;turn off illumination
d11 setnmr3|29 ;open shutter start UV/Vis experiment
1m setnmr3^29 ;close shutter
1m setnmr3|28 ;turn on illumination
2 30m
d1
p1*0.33 ph1
go=2 ph31
d21
30m mc #0 to 2 F0(zd)
exit

ph1=0 2 2 0 1 3 3 1
ph31=0 2 2 0 1 3 3 1

:pl1 : f1 channel - power level for pulse (default)
:p1 : f1 channel - 90 degree high power pulse
:d1 : relaxation delay; 1-5 * T1
:d11: set d11 according to the blank measurement in the UV/Vis spectrum
:d21: delay between experiments
:NS: 1 * n, total number of scans: NS * TD0

:$/ld: zg30,v 1.9 2007/04/11 13:34:31 ber Exp $

:d11: set d11 according to the integration time of the blank measurement in the UV/Vis spectrum.
For most measurements the d11 was determined to be around 400 ms.

The delay of one millisecond (1 m) for the events (setnmr3^28; setnmr3^29; setnmr3|28) ensures that the light emission of the LED is definitely zero to avoid interferences with the UV/Vis measurement. [1]

In principle the command series for the UV/Vis measurement can be put anywhere in the pulse program e.g. before, after or during acquisition. Furthermore the command order can be changed at will if needed e.g. for experiments requiring light pulses instead of continuous illumination.

Since in our case the standby output level of the RCP used for the connection to the UV/Vis spectrometer and the D-Hal-lamp was high (~5 V) the shutter of the D-Hal-lamp was opened after every NMR experiment. To avoid the influence of the emitted light to the sample a customized TTL inverter between the NMR console and the UV/Vis spectrometer was added to set the standby TTL level low (~0 V).

1.5 Comparison of reaction rates – conventional LED illumination setup vs. new combined LED UV/Vis illumination setup

To check for possible disadvantages of our new UVNMR-illumination setup we conducted a study about the illumination capabilities compared to our old illumination setup.[1] Figure S5 shows a schematic top view of our current illumination setup A) and our new UVNMR-illumination setup B) in the NMR tube. Our new systems have two major differences compared to our established illumination setup. First, instead of one fiber the glass insert is now filled with two fibers, the illumination fiber and the UV/Vis fiber. As the UV/Vis fiber is not transparent to light in horizontal axis this could lead to a ‘dark area’ (Figure S5B) in the sample which is not reached by the light emitted from the illumination fiber resulting in a hampered reaction rate. Secondly, two fibers require a bigger quartz glass insert (3 mm outer diameter), which in return reduces the layer thickness of the sample from 2 to 1 mm. This could lead to a faster reaction rate if the emitted light is not strong enough to thoroughly penetrate the whole sample in the old illumination setup. Either way, the differences of both setups are so pronounced when it comes to illumination that a comparison seems mandatory.

**Figure S5.** Schematic top view of the two LED illumination setups. A) Depiction of the old, conventional illumination setup with a layer thickness of 2 mm for the sample B) new combined UVNMR-illumination setup with a layer thickness of 1 mm for the sample. Due to the incorporation of the second UV/Vis fiber the issue of an unlit, dark area arises.

As a test reaction for the comparison of reaction rates the photocatalytic oxidation of 4-methylbenzyl alcohol (MBA) with riboflavin tetraacetate (RFTA) was chosen (Figure S6). This reaction was already thoroughly investigated in our working group and does not require the exclusion of oxygen.[4] Hence a stock solution can be prepared for all samples which greatly improves the comparability of all measurements.
Supporting Information

**Materials:** The solvents D$_2$O and CD$_3$CN were purchased from Deutero GmbH and Sigma Aldrich. 4-Methoxybenzylalcohol was purchased from Sigma Aldrich and was used without further purification. The photocatalyst Riboflavin tetraacetate (RFTA) was synthesized according to the reported procedures.$^{[4,5]}$

**Sample preparation:** The NMR samples were prepared in pairs as a 1 mL solution of D$_2$O/CD$_3$CN (1:1) containing 2 mM riboflavin tetraacetate (RFTA) and 20 mM 4-methoxybenzyl alcohol (MBA). The solution was then split and filled into two ambered NMR tubes, each containing 350 µL of the stock solution. Afterwards the tubes were connected to their illumination setup by inserting the respective glass insert (2 mm outer diameter for conventional; 3 mm outer diameter for the new quartz glass insert) and sealing everything airtight.

**In situ NMR measurements:** NMR experiments were conducted on a Bruker Avance 500 spectrometer with a 5 mm QXI probe. The resulting NMR spectra were processed and evaluated with Bruker Topspin 3.2. The samples were illuminated by a Cree XT-E royal blue high power LED with a center wavelength of 450 nm and 500 mW optical output power (Lumitronix, Cree XT-E, 68332). The light was guided directly into the sample with the help of an optical fiber as described previously.$^{[1]}$ After a first $^1$H spectrum in the dark, all following spectra were recorded under continuous illumination. There was no need to record alternating illuminated and dark spectra since it was already shown that no signal is distorted by Photo-CIDNP effects in D$_2$O/CD$_3$CN. The kinetics were derived from the integrals of the $^1$H aldehyde signal of 4-methoxybenzyl aldehyde (MBAld) since it does not overlap with other signals (Figure S7A). The integral of the $^1$H MBAld signal was referenced to the aromatic protons of the starting material 4-methoxybenzyl alcohol (MBA).

**Discussion:** Figure S7A shows that MBAld is generated under continuous blue light illumination. The MBAld aldehyde signal does not overlap with any other signal and is hence suitable for integration. Figure S7B depicts the integral area of the MBAld aldehyde signal 1 under illumination over time for the two compared setups. Whereas the black kinetic corresponds to the conventional illumination setup containing only the illumination fiber and the smaller inlet (2 mm) and the red kinetic belongs to the new setup incorporating the illumination and UV/Vis fiber in a bigger inlet (3 mm). The reaction profiles clearly reveal that there is no significant difference between the two setups. One might even argue that the newer setup has a slightly higher reaction rate. This could be due to the smaller layer of thickness compared to the old setup (1 mm vs. 2 mm) which allows for a more potent illumination of the sample. But it could also be because of slight differences in the sandblasted fiber tips of the illumination fiber since every fiber tip is crafted individually. In summary, our new setup shows no significant variations in reaction rate compared to our old illumination setup, which implies that the ‘dark area’ (Figure S5B) caused by the UV/Vis fiber has no notable impact on the reaction rate or at least is canceled out by fast diffusion or by the thinner layer of solution allowing for a better illumination.

![Figure S6](image-url). Photocatalytic oxidation of MBA is used as a test reaction for the comparison of reaction rates between the two illumination setups, shown in Figure S5.

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**Figure S6.** Photocatalytic oxidation of MBA is used as a test reaction for the comparison of reaction rates between the two illumination setups, shown in Figure S5.
Figure S7. A) Photocatalytic generation of 4-methoxybenzyl aldehyde over time; the $^1$H aldehyde signal 1 at 10.24 ppm poses a suitable signal for integration as it does not overlap with other signals. B) Reaction profile of the $^1$H aldehyde signal 1 at 10.24 ppm for the two illumination setups: Conventional illumination fiber (black) and UV/Vis fiber + illumination fiber (red).
2. Summary of conPET processes and investigations of the photoreduction of aryl halides with PDI as photocatalyst

2.1 Summary of conPET processes

Recently, König et al. introduced the consecutive photoinduced electron transfer (conPET) process to achieve higher redox potentials. Here aryl radicals can be obtained from aryl halides utilizing the excited states of stable radical anions (Photocat•) (Figure S8). These stable radical anions are generated via a classical photoinduced electron transfer (PET) process with the help of a sacrificial electron donor (D; e.g. NEt3, DIPEA). In conPET processes organic dyes (Photocat•; e.g. N,N-bis(2,6-diisopropylphenyl)-perylene-3,4,9,10-bisdicarboximide (PDI), Rhodamine-6G and 9,10-Dicyanoanthracene) are used as photocatalysts as they form stable colored radicals under inert atmosphere. Upon a second photoexcitation these stable radicals (Photocat•) are proposed to form a further excited state (Photocat••), which is able to transfer an electron to aryl halides resulting in an aryl radical precursor (Q•). After fragmentation this precursor can be trapped by various additives to yield the desired product.

The first conPET process published in 2014 reported the photoreduction of aryl halides with blue light (455 nm) irradiation utilizing N,N-bis(2,6-diisopropylphenyl)-perylene-3,4,9,10-bisdicarboximide (PDI) as a photocatalyst. The general reaction conditions are illustrated in Figure S9.

In the proposed and controversially discussed reaction mechanism (Figure S10), an initial photoexcitation of PDI with blue light (455 nm) yields the excited PDI•, which gets reductively quenched by the sacrificial electron donor NEt3 to yield PDI•• and NEt3•+. The stable PDI•• radical anion is proposed to be excited by a second photon (455 nm) to give PDI•••. This photoexcited state is
supposed to be able to reduce the given substrate (Ald-Br) resulting in an aryl radical precursor (Ald-Br•) and ground state PDI. Ald-Br• then fragments into Br• and the neutral radical Ald•, which can abstract a proton from either NEt₃⁺ or the solvent (e.g. DMF) to give the final product Ald. If the proton was abstracted from NEt₃ it will lead to a cationic imine species, which immediately reacts with water in solution to give diethylamine (DEA) and acetaldehyde.

Figure S10. Catalytic mechanism of the first conPET process with PDI as proposed by König et al.[8]

2.2 Investigations of the photoreduction of aryl halides with PDI as photocatalyst

2.2.1 General information

Materials:

The solvents DMSO-d₆ and DMF-d₇ were purchased from Deutero GmbH. Both solvents were dried over 4 Å molecular sieves and deoxygenated via Freeze-Pump-thaw prior to use. N,N'-Bis(2,6-diisopropylphenyl)-3,4,9,10-perylene-tetracarboxylic-diyimide (PDI) was purchased from TCI chemicals and used without further purification. 4-bromo-benzaldehyde (Ald-Br) and triethylamine (NEt₃) were purchased from Merck. NEt₃ was dried over 4 Å molecular sieves prior to use and 4-bromo-benzaldehyde (Ald-Br) was used without further purification.

Combined UVNMR-illumination reaction profiles

All measurements were conducted on a Bruker Avance III HD 600 (600.13 MHz) spectrometer with a fluorine selective TBIF probe in combination with our new UVNMR-illumination device described in section 1. The samples were illuminated by a Cree XT-E royal blue high power LED (Lumitronix, 450 nm; 500 mW, 68332).

If not otherwise indicated, measurements were conducted at 313 K in 300 µL solutions of DMF-d₇ or DMSO-d₆ containing 1 mM (0.1 eq.) N,N-bis(2,6-diisopropylphenyl)-perylene-3,4,9,10-bis(dicarboximide) (PDI), 10 mM (1 eq.) 4-bromo-benzaldehyde (Ald-Br) and 80 mM (8 eq.) triethylamine (NEt₃).

Preparation blank:
Supporting Information

Ald-Br and NEt₃ were dissolved in DMF-d⁷ in an NMR tube under inert conditions. The quartz glass insert was added and the sample was sealed airtight with the customized screw cap (see setup).

Blank measurement:

The blank measurement was conducted prior to the combined reaction kinetic. The sample was injected into the NMR spectrometer to reach a temperature of 313 K. Then a blank UV/Vis spectrum was recorded. The resulting integration time given by the UV/Vis spectrometer determined the d₁₁ delay in the NMR pulse program (section 1.4), which was necessary for later automation. An NMR spectrum was also taken as quality control, which ensured correct sample preparation.

Preparation sample:

Under argon atmosphere the required amount of PDI was added to the blank sample. The quartz glass insert was inserted and the sample was sealed with our customized screw cap. To dissolve the PDI completely the sample was sonicated.

Oxygen-test:

Prior to the kinetic investigations an oxygen-test sequence was conducted for every new sample to exclude the presence of oxygen. Therefore, the prepared sample was put into the NMR spectrometer to reach a temperature of 313 K. All PDI signals start to broaden once illumination starts. If oxygen is present in the reaction solution the PDI signals sharpen again once the light is turned off. This behavior can be exploited as a simple test to verify successful deoxygenation. Three single scan NMR spectra are measured in total. The first one before any illumination took place. The second one after an illumination time of 1.0 s and the third one two minutes after the illumination. As 1.0 s of illumination is already enough to induce the line broadening, the PDI signals are broader in spectrum two. If oxygen is present the PDI signals in spectrum three are sharp again, if deoxygenation was successful then spectrum two and three are identical.

Sample measurement:

For all NMR measurements the delay d₁₁ in the pulse program was set to the required integration time determined in the blank UV/Vis measurement. The reaction profiles were generated by alternately recording non illuminated and illuminated ¹H NMR spectra. This ensured that no signal intensities were distorted by possible photo-CiDNP effects.⁴ One UV/Vis spectrum was automatically recorded prior to every NMR measurement (dark and light). After a first spectrum without illumination a row of ¹H spectra was collected alternating between illuminated and unilluminated proton spectra. Only spectra without illumination were used to generate reaction profiles. The NMR kinetics are derived from the aromatic proton integrals of Ald-Br and Ald (Signal 3, Figure S11) and referenced to the respective signal in the first spectrum without illumination. Assignments were made by evaluating standard sets of 1D and 2D NMR spectra. The chemical shifts were referenced to the solvent signals (DMF-d⁷). The UV/Vis kinetics are derived from the absorption maximum of the radical anion of PDI at 798 nm (see manuscript). Its intensity is referenced semi-quantitatively to its own maximum absorbance (=1.0). Referencing the radical anion to the ground state PDI was not possible because of the donor-acceptor complex of PDI and NEt₃.
Supporting Information

Figure S11. Numeration of PDI, Ald-Br, Ald, NEt$_3$ and DEA used for the assignment and further characterization.

2.2.2 Assignments of starting materials, catalyst and products

Assignments were made by evaluating standard sets of 1D and 2D NMR spectra. Figure S12 shows the $^1$H proton spectrum with an illustration of all reaction components before illumination under reaction conditions (PDI 1 mM, Ald-Br 10 mM, NEt$_3$ 80 mM, deoxygenated in DMF-d$_7$ at 313 K) before illumination.

Figure S12. Full $^1$H proton NMR spectrum of the reaction mixture at 313 K in DMF-d$_7$ before illumination. The reaction components PDI (1 mM), Ald-Br (10 mM) and TEA (80 mM) are illustrated.

Figure S13 depicts the assignments for the most prominent reaction components. As described in the manuscript all PDI signals are significantly broadened even prior to illumination with respect to their distance to the perylene core probably because of an acceptor-donor complex with NEt$_3$. Especially the PDI proton signals 4 and 5 are broadened so much that they are only detectable as one broad signal just above the noise level (Figure S14). Hence the chemical shift for the PDI protons 4 and 5 can only be given in a chemical shift range from 9.7 to 8.6 ppm. The methine proton of the isopropyl group of PDI was not assignable as it is covered by the DMF signal at 2.92 ppm and is hence not
discussed further. The remaining PDI proton signals could be readily assigned. The other reaction components (Ald-Br, Ald, NEt₃ and DEA) also can be assigned in a straightforward manner. The amine proton of DEA is not assignable probably due to exchange line broadening with the residual water in solution. The reaction product Ald is partially deuterated (ratio 1:2 H/D), since the reaction is carried out in fully deuterated DMF which can also act as a proton source besides NEt₃.

**Figure S13.** Assignment of PDI, Ald-Br, Ald, TEA and DEA in DMF-d₇. ¹H chemical shifts are highlighted blue and referenced to DMF (8.03 ppm). For the isopropyl groups only one chemical shift for the methyl groups is given because the methine proton is completely covered by the DMF solvent signal at 2.92 ppm.

**Figure S14.** Excerpt of the ¹H proton spectrum region of the broadened PDI proton signals 4 and 5 prior to illumination (black) and after the light is turned on (red). The proton signals 4 and 5 appear as one broad signal just above the noise level and vanish immediately after the light is turned on.
3. Investigation of a common photoswitch

3.1 General information

**Materials:**

The solvent THF-d$_8$ was purchased from Deutero GmbH. 1,3,3-Trimethylindlino-6'-nitrobenzopyrolospiran 1 was purchased from TCI chemicals and was used without further purification.

**In situ UVNMR-illumination experiments:**

All measurements were conducted on a Bruker Avance III HD 600 (600.13 MHz) spectrometer with a fluorine selective TBIF probe in combination with our new UVNMR-illumination device described in section 1. The samples were illuminated by a high power UV LED (Laser Components, 365 nm, 2.06 W, LEUVA66X00RV00).

The samples described here, all contained a solution of 1 mM 1,3,3-trimethylindlino-6'-nitrobenzopyrolospiran 1 in 300 µL of THF-d$_8$.

**Preparation blank:**

To measure the required UV/Vis spectrum of a blank sample, 300 µL THF-d$_8$ were transferred into the NMR tube, the glass insert was inserted and the tube was sealed airtight with our customized screw cap.

**Blank measurement:**

The blank measurement was conducted prior to the kinetic investigations. The blank was put into the NMR spectrometer to reach a temperature of 300 K or 180 K respectively. Then a blank UV/Vis spectrum was recorded. The resulting integration time given by the UV/Vis spectrometer determined the d11 delay in the NMR pulse program (section 1.4), which was necessary for latter automation. An NMR spectrum was also taken as quality control, which ensured correct sample preparation.

**Preparation sample:**

The 1,3,3-trimethylindlino-6'-nitrobenzopyrolospiran 1 was added to the blank sample, the glass insert was inserted into the sample and the tube sealed airtight with our customized screw cap.

**Sample measurement:**

After a first proton spectrum without illumination, the photoswitching process of 1 to its open form 2 was observed by a row of $^1$H NMR spectra under continuous illumination with 365 nm. One UV/Vis spectrum was automatically recorded prior to every NMR measurement (section 1.4). When the absorption maxima of the open species 2 reached a plateau at 300 K, the illumination was turned off and a row of $^1$H NMR one scan spectra (one spectrum every 8 seconds with UV/Vis recordings) were recorded to follow the thermal back reaction to 1. At 180 K a row of $^1$H NMR spectra was taken every 20 min because of the drastically increased half-life $t_{1/2}$ of 2. Quantification of the NMR signals was derived from the integrals of the methyl group (1) of 1 and the corresponding signal of 2. Assignments were made by evaluating standard sets of 1D and 2D NMR spectra like $^1$H, $^1$H-$^1$H-COSY, $^1$H,$^1$H-TOCSY, $^1$H,$^1$H-NOESY, $^1$H,$^{13}$C-HSQC, $^1$H,$^{13}$C-HMBC. For the numeration see Figure S15. The chemical shifts were referenced to the solvent signals. The UV/Vis absorption maximum at 533 nm was taken for half life determination of 2. Evaluation of the half life $t_{1/2}$ was done by the exponential fit function of Origin 8.
3.2 Assignments of 1 and its open form 2

Assignments were made by evaluating standard sets of 1D and 2D NMR spectra (see Figure S16-S20).

The open form 2 could not be assigned at 300 K as it started to photodegrade very fast (< 30 min) under continuous illumination with 365 nm preventing a full 2D NMR set. All other species (1 at 300 K, 1 at 180 K and 2 at 180 K) could be assigned in a straightforward manner.

Figure S16. Assignment of 1 and its open form 2 in THF-d8 at 300 K (top) and 180 K (bottom). $^1$H chemical shifts are highlighted blue, $^{13}$C chemical shifts are highlighted red. The assignment of the open from 2 at 300 K was not possible due to rapid degradation under continuous illumination with 365 nm.
Figure S17. $^1$H-$^1$H-COSY of spiropyran 1 and its open form 2 in THF-d$_8$ at 180 K.

Figure S18. $^1$H-$^1$H-NOESY of spiropyran 1 and its open form 2 in THF-d$_8$ at 180 K. Mixing time 200 ms.
Figure S19. $^1$H,$^{13}$C-HSQC of spiropyran 1 and its open form 2 in THF-d$_8$ at 180 K.

Figure S20. $^1$H,$^{13}$C-HMBC of spiropyran 1 and its open form 2 in THF-d$_8$ at 180 K.
3.3 NMR and UV/Vis build up and decay curves of 2

3.3.1 Isomerization experiments at 300 K

Figure S21. *In situ* recorded UV/Vis spectra of a solution of 1 in 300 μL THF-d₈ at 300 K A) buildup of the open form 2 under continuous illumination with 365 nm (increase of absorbance from 450-650 nm) B) excerpt of the UV/Vis spectrum from 450-650 nm showing the thermal back reaction of 2 to 1 once the light is turned off.

It is to be noted that the UV/Vis spectra recorded with the UVNMR-illumination setup sometimes show negative absorbances (as shown e.g. in S21). These negative absorbances are caused by slight deviations in the distance and/or positioning of the reflector and the dip probe between blank and actual measurement.

Figure S22. Excerpt of NMR spectra showing the photoswitch 1 in a solution of 300 μL THF-d₈ at 300 K prior to illumination (bottom) and the mixture of 1 and 2 once the photostationary state is reached (top) under illumination with 365 nm.

To evaluate the half-life τ₁/₂ of 2 in THF-d₈ at 300 K the light was turned off once the photostationary state was reached and one UV/Vis spectrum was taken every eight seconds. Afterwards the absorbance of the maximum at 533 nm (belonging to the open form 2) was taken and plotted against the elapsed time (Figure S23). Those values were then fitted via exponential decay in Origin8 (ExpDec1). Using the equation shown in Figure S23 a half-life of 17.4 s was determined for 2 in THF-d₈ at 300 K.
Figure S23. Plotted decay of the absorbance of 2. After the photostationary state was reached the light was turned off to evaluate the half-life of 2 in THF-d₈ at 300 K. The absorbance values were taken from the maximum at 533 nm (see Figure S21B). Origin8 was used to fit the data via exponential decay (ExpDec1).

Figure S24. A) UV/Vis spectrum of 1 (1 mM) in THF in a 1 mm path length cuvette at ambient temperature. B) UV/Vis spectrum of 1 (1 mM) in THF with the in situ UVNMR-illumination device at 300 K. Until ~325 nm both spectra are comparable (respective absorbance maxima are 341 nm for A and 344 nm for B). Below 325 nm major differences can be observed between two methods probably because of the reduced reflectance of PTFE (from below 380 nm) and reduced transmittance of the glass insert at shorter wavelengths.
3.3.2 Isomerization experiments at 180 K

**Figure S25.** *In situ* recorded UV/Vis spectra of a solution of 1 in 300 μL THF-d₈ at 180 K. A) buildup of the open form 2 under continuous illumination with 365 nm (increase of absorbance from 450-650 nm) B) excerpt of the UV/Vis spectrum from 425-655 nm showing that the thermal back reaction of 2 to 1 is prevented by the reduced temperature.

**Figure S26.** Excerpt of NMR spectra showing the photoswitch 1 in a solution of 300 μL THF-d₈ at 180 K prior to illumination (bottom) and the mixture of 1 and 2 once the photostationary state is reached (top) under illumination with 365 nm.

3.4 Photodegradation

It was observed that the photoswitch system of 1 and 2 is very prone to photodegradation at 365 nm. Both at 300 K and 180 K photodegradation starts after around 25-45 min preventing a study of the system under continuous illumination with 365 nm. Hence only 2 at 180 K could be structurally assigned unambiguously as the thermal back reaction could be prevented by the reduced temperature and so the light could be turned off without the decrease in intensity of signals of 2. Figure S27 shows the photodegradation of 1 and 2 under continuous illumination with 365 nm in THF-d₈ at 180 K. The UV/Vis spectrum (Figure S27A) loses the characteristic absorbance of the open form 2 from 425-625 nm and even the dominant absorbance of 1 loses some absorbance at around 375 nm indicating that not only 2 but also 1 gets photodegraded under continuous irradiation. Figure S27B shows a row of NMR spectra corresponding to the UV/Vis spectra of Figure S27A. Here the strength of NMR
Supporting Information

Spectroscopy is showing as it immediately confirms that not only the open form 2 but also the initial photoswitch 1 is completely degraded after overnight illumination with 365 nm.

Figure S27. Degradation of the photoswitch 1 and its open form 2 under continuous illumination with 365 nm in THF-d₈ at 180 K. A) in situ recorded UV/Vis spectra show the combined absorbance of the photostationary state of 1 and 2 (red) is mostly gone after overnight illumination (blue) indicating photodegradation of 1 and 2. B) row of NMR spectra corresponding to the UV/Vis spectra unambiguously confirm a full photodegradation of 1 and 2 under continuous illumination.

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