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Photoswitchable, metal-free parahydrogen-induced polarization enabled by a phosphorus biradicaloid†

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Visible light-controlled nuclear spin hyperpolarization was demonstrated in parahydrogen activation using a metal-free phosphorus biradicaloid photoswitch. Experiments demonstrated an efficient photoresponse of the observed hyperpolarization. Two orders of magnitude signal enhancements were observed at 9.4 T. The mechanistic details of the underlying processes are provided.

Chemical activation of small molecules, such as dihydrogen, using metal-free substances has attracted significant attention in the search for novel, more sustainable catalysts. In this regard, for example, frustrated Lewis pairs based on various basic and acidic centers have garnered a lot of interest.[1–4] At the same time, photoactivated catalysis is another actively developed branch of chemistry that has significant potential, especially regarding the use of visible light to harness solar energy. Light can provide additional capabilities in switching chemical reactivity to gain better control over catalytic and various other reactions, including dihydrogen activation. Beyond catalytic areas, chemical activation of parahydrogen, a spin-0 isomer of dihydrogen, is employed in generating chemical substances with hyperpolarized nuclear spins.[5–7] Parahydrogen-induced polarization (PHIP) is an actively developed field in NMR spectroscopy, which allows for dramatic signal enhancements, placing NMR in terms of sensitivity on the level comparable to optical spectroscopy.[8–11] The combination of these three areas (metal-free activation of H_2, photoreactions, and PHIP) constitutes the essence of this communication.

Illuminated NMR and *in situ* illumination techniques have become valuable tools for studying light-assisted chemical processes directly within the NMR spectrometer.[12,13] These methods enable real-time observation of photochemical reactions and photocatalytic mechanisms under controlled illumination, expanding the scope of NMR in photochemistry. At the same time, light-assisted PHIP, or photo-PHIP, using metal complexes is a scarcely explored area of research, while its metal-free counterpart is completely unexplored.[10] Several types of photo-PHIP experiments were documented in which ejection of either hydride or substrate ligands facilitates subsequent activation of parahydrogen or coordination of another ligand.[14–19] In particular, it was shown that a rapid activation of parahydrogen by highly reactive photogenerated 16-electron Ru complexes allows for the detection of oscillating zero-quantum coherences, something that is entirely hidden in much slower thermal processes.[10] Moreover, NMR signal enhancements practically of theoretical maximum were observed in such photo-PHIP experiments.[19] In some cases, using laser pulsing, it was possible to estimate the kinetics of the rapid dihydrogen activation with time resolution comparable to optical spectroscopy-based flash photolysis techniques,[20] making photo-PHIP a valuable tool for mechanistic studies. It was demonstrated that hydrogenation reactions facilitated by visible light can show strong signal enhancements of hydrogenation products, which was impossible without the photoactivation.[21] It was shown that photoswitching of azobenzene molecules from *cis* to *trans* isomers can be investigated in signal amplification by chemical exchange (SABRE), a parahydrogen-based hyperpolarization technique harnessing reversible exchange of hydrides and other ligands.[22] Recently, it was also reported that photoejection of ligands can be useful in optimizing conditions for efficient generation of hyperpolarized substrates in SABRE.[23] All these examples are describing photo-PHIP experiments wherein metal complexes were involved in the chemical process.

Herein, we demonstrate that photosensitivity of a metal-free five-membered heterocyclic phosphorus biradicaloid, **1**[24,25] (Fig. 1), enables photoswitching of the nuclear spin hyperpolarization effects observed in the parahydrogen activation process.

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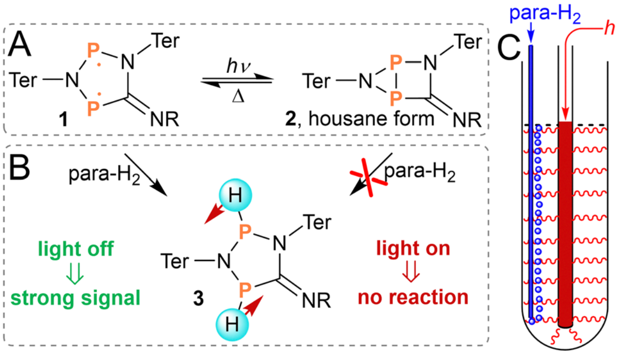

Fig. 1 Schematic illustration of photoswitching activity of **1** and its coupling to PHIP experiments (Ter = 2,6-Mes$_2$-C$_6$H$_3$, *R* = Dmp = 2,6-dimethyl phenyl). (A) Chemical equation showing the formation of the housane form upon visible light irradiation ($h\nu$, λ_{max} = 647 nm) of **1**, which can be reversed in the thermal process (Δ). (B) Two pathways of the reaction with para-H$_2$ during the light-on and light-off conditions, highlighting that upon the irradiation there are no PHIP effects expected since the formed housane (**2**) is inactive towards H$_2$ activation. In contrast, when the light is off, the active **1** molecules are present or generated in the thermal reaction from the housane form, enabling the formation of hyperpolarized **1**-H$_2$ addition product **3**. (C) A sketch of the experimental setup for the photo-PHIP experiments with **1**, including a solution-immersed optical fiber (OD 1 mm) with a roughened surface for efficient light distribution in a valved 5 mm NMR tube and a thin capillary (OD 360 μm) supplying para-H$_2$.

The reaction kinetics parameters are measured to quantify the rate of thermal reaction leading to the formation of the active biradicaloid from the inactive housane form (**2**) produced in the photoreaction (Fig. 1A). Based on these observations, we characterize the observed effects as slow photo-PHIP experiments in analogy to similar experiments with metal complexes. We discuss, however, a striking difference from the metal complexes, in which, typically, a photo-induced ejection of hydride ligands occurs, leading to the formation of active 16-electron complexes,[10,15,17] whereas the inactive housane form is produced in the case of **1** under light irradiation conditions (λ_{max} = 647 nm).[24,25]

Phosphorus biradicaloids constitute an interesting class of open-shell molecules[26] in which radical centers form a singlet electron ground state and, therefore, do not introduce any deleterious effects to NMR measurements related to the presence of free radicals. Moreover, they demonstrate a remarkable reactivity towards activation of small molecules such as ethylene, CO, and dihydrogen. The latter was utilized in PHIP experiments, wherein four- and five-membered phosphorus biradicaloids provided significant signal enhancements of ^{1}H and ^{31}P nuclei in thermally activated reactions with parahydrogen (para-H$_2$).[24]

The basic idea of metal-free photo-PHIP experiments, which we report in this communication with **1**, is illustrated in Fig. 1. Exposing the biradicaloid solutions to visible light yields the housane form **2** (Fig. 1A) of the molecule that cannot activate H$_2$ (Fig. 1B). Hence, by switching on the light, it is possible to suspend the reactivity of **1** towards para-H$_2$. Consequently, while the light is on, para-H$_2$ can be introduced into the biradicaloid samples by bubbling the gas without sensible conversion of **1** into its hydrogen addition product **3** (Fig. 1C). Switching off the light facilitates the thermal back-conversion of the housane form into the active **1** that in turn activates para-H$_2$, leading to the formation of the hyperpolarized **3** (Fig. 1B). Therefore, photoswitching can be used to control the hyperpolarization effects in this biradicaloid system as well as the chemical H$_2$ addition reaction.

The experiments were performed using 52 mM solutions of **1** in toluene-d8. Hydrogen gas enriched in para-isomer to 92%, referred to as simply para-H$_2$ in the following text, was used in this study. A detailed description of the setup and experimental conditions is presented in the ESI.†

First, we confirmed that the thermally activated interaction without light irradiation leads to the observation of pronounced nuclear spin hyperpolarization effects (see the reaction with para-H$_2$ and **1** depicted on the left side in Fig. 1A and B). To conduct the experiments, para-H$_2$ was bubbled through the solutions of **1** for 5 s inside the NMR magnet, followed by the detection of ^{1}H NMR spectra according to the PASADENA[6,8] experimental protocol. This process led to the formation of the hyperpolarized **1**-H$_2$ addition product **3** with strongly enhanced ^{1}H NMR resonances at relatively high (9.4 T) and low (1 T) magnetic fields (Fig. 2).

At the higher field, the enhanced signals appear as a set of four antiphase doublets of doublets corresponding to two para-H$_2$-originating protons ("a" and "b"; see the top of Fig. 2) of the hyperpolarized **1**-H$_2$ addition product **3**. This shape of the signal takes place because of *J*-coupling between "a" and "b" ^{1}H nuclei as well as *J*-coupling of those nuclei to two ^{31}P centers (P and P′) in the adduct molecule. At the lower field, this shape was reproduced only qualitatively, as illustrated in Fig. 2. The chemical shift difference in Hz in this case was smaller than the ^{1}H–^{31}P *J*-coupling constants ($^1J_{HP}$ and $^1J_{HP'}$). The average signal enhancements were estimated to be *ca.* 250-fold at 9.4 T (Fig. 1A) and >2000 (Fig. 1B) at 1 T (see the details of the procedure in the ESI†).

At the next step, we conducted experiments with light-controlled switching of **1** into its housane form **2**, which is inactive in the activation of H$_2$, since a *trans*-annular P–P is present and the biradical character has therefore disappeared. Briefly, the experimental protocol was as follows (see the ESI† for more details). A 52 mM solution of biradicaloid in toluene-d8 was placed under Ar in a gas-tight tube equipped with a 1 mm fused silica optical fiber in the center and a 360 μm capillary for adding para-H$_2$ gas, as schematically illustrated in Fig. 1C. The stripped and roughened end of the optical fiber was immersed into the solution to assure efficient distribution of the laser light inside the liquid sample. Thereafter, a red-light laser diode (638 nm) was connected to the other end of the optical fiber to convert **1** into the housane form. After the complete change of the solution color to pale yellow, the sample was saturated with para-H$_2$ by bubbling the gas through the capillary to 6 bar pressure in the tube. After that, the sample tube was placed into the 9.4 T magnet for NMR experiments. Both procedures (gas bubbling and tube relocation) were performed under continuous irradiation of the solution with

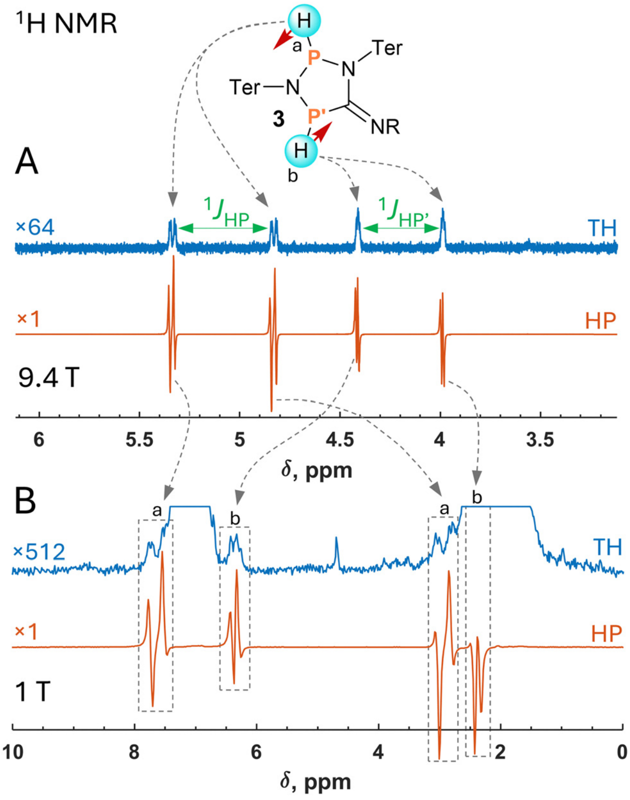

Fig. 2 ^{1}H NMR spectra acquired after para-H_2 bubbling over 5 s through a 0.052 M toluene-d8 solution of **1** under 4 bar pressure at 9.4 (A) and 1 (B) T magnetic fields. In each case, the blue (upper) spectra represent thermal (TH) signals after the relaxation, and the red (lower) spectra represent the level of hyperpolarized (HP) signals of the generated **1**-H_2 addition product **3**. For comparing signal amplitudes, the multiplication factors are shown on the left for each spectrum. Signal assignments for the para-H_2 originating hydrogens ("a" and "b") are shown by dashed arrows and the structure on the top of the figure. The horizontal green double-sided arrows illustrate splitting due to $^1H-^{31}P$ J-coupling between the added hydrogens and the corresponding phosphorus atoms (P and P′). $\pi/4$-pulses were used to measure the hyperpolarized spectra to maximize the signal amplitudes according to the PASADENA protocol.[6,8]

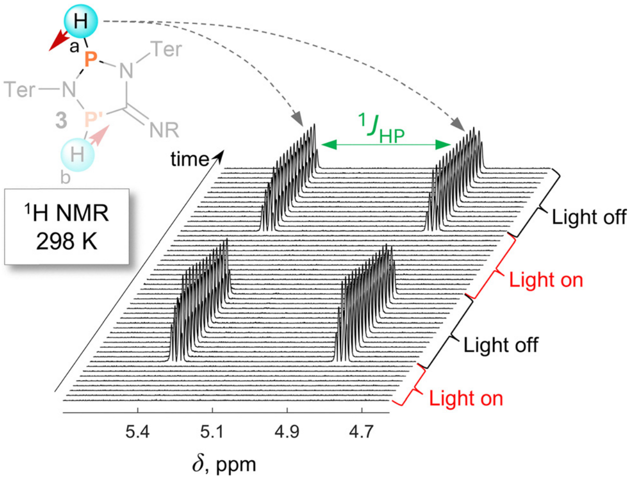

Fig. 3 A series of ^{1}H NMR spectra acquired every 7 s at 298 K in a 9.4 T magnet from a toluene-d8 solution of **1** (0.052 M) and para-H_2 (6 bar) during "light-on/light-off" periods. The "a" proton signal region is shown in the figure. The spectra are presented in the absolute value mode of the real part to avoid unnecessary complexity due to the antiphase shape. The original appearance of the hyperpolarized signals is similar to that of the corresponding spectrum shown in Fig. 2A. Moreover, the first spectrum in the series was subtracted from the whole set to remove the background. The spectra demonstrate a sensitive response to switching off the light with strong hyperpolarized signals during the "light-off" periods.

the laser light to prevent any reaction with para-H_2. A pseudo-2D NMR experiment with the repetition of the spectra accumulation every 7 s was started to monitor changes during the consequent switching of the light irradiation (Fig. 3).

In the beginning, when the light was still on, no enhanced ^{1}H NMR signals were observed in the spectra (see bottom traces in Fig. 3). Thereafter, when the laser diode was switched off, strongly enhanced signals were observed. The next light-on/off repetitions showed a clear response of the hyperpolarization to the state of the light. It was also clear that the switching time of the hyperpolarization is fast (<7 s), highlighting the high efficiency of the interaction between the light and **1**. Note that for the sake of simpler presentation and in contrast to Fig. 2A, Fig. 3 shows the real part of the antiphase ^{1}H signals in the absolute value mode. Before such processing, the observed enhanced signals in the photoswitching experiments at 9.4 T had the same antiphase shape as that shown in Fig. 2A. Moreover, only the "a" proton signal is depicted. The corresponding full-range spectra are presented in Fig. S4 in the ESI.†

It is worth noting that we have not observed any changes of signal phases or amplitude modulations as a function of time duration between switching off the light and the ^{1}H NMR detection. Such effects were observed in the so-called fast photo-PHIP experiments performed using various metal dihydride complexes like $[Ru(PPh_3)_3(CO)(H)_2]$ upon interaction with para-H_2 followed by the laser-induced ejection of the dihydride ligands.[10,14,15,17] This phenomenon is associated with a periodic evolution of the zero-quantum coherences ($\hat{I}_+\hat{S}_-$ and $\hat{I}_-\hat{S}_+$ terms) of the ^{1}H spin pair formed after the rapid activation of para-H_2 by the active 16-electron complexes.[10,15,18] In the case of para-H_2 activation by biradicaloid **1**, the reaction does not proceed as fast, so that the zero-quantum coherence averages out to zero in the course of the thermal reaction. This process leaves out only the longitudinal two-spin order term ($\hat{I}_z\hat{S}_z$), which is completely analogous to the experiments performed without photoswitching and illustrated by Fig. 2A for a 9.4 T field. Therefore, our observation confirms that **1-2** photoswitching can be attributed to the so-called slow photo-PHIP realm, wherein the periodic zero-quantum coherence evolution (quantum beats) are not observable due to the relatively slow para-H_2 activation.

There are also other remarkable differences between these metal-free and metal complex-based photo-PHIP. In the case of **1**, the para-H_2 activation is an irreversible process, meaning that when the initial material is consumed, the hyperpolarization effects cannot be observed anymore. The presence of this effect was visible in a gradually dropping amplitude of the enhanced signals after several switch-on and switch-off cycles (see Fig. S5 in the ESI†). In contrast, metal dihydride complexes can eject two hydrogens and activate para-H_2 multiple times before the potentially noticeable complex degradation. In this regard, it is interesting to know how many photoswitching cycles the hyperpolarization can last before the full consumption of **1** due to the formation of the **1**-H_2 addition product **3**.

The latter is defined by the rate of thermally activated back-conversion of the housane form **2** to the active biradicaloid **1** after the light is switched off. This is justified since the activation of para-H_2 is a significantly faster process; therefore, the back-conversion is the rate-limiting reaction in this system. To assess the rate of this reaction, a separate kinetic measurement experiment was conducted without para-H_2 (Fig. S7 in the ESI†), which provided the rate constant value of $0.0015 \pm 0.0001\ s^{-1}$ at room temperature. Taking this into account, it is possible to estimate the rough amount of biradicaloid **1** recovered between the repetitive NMR spectra acquisitions every 7 s during the light-off periods in the para-H_2 experiment shown in Fig. 3. In the beginning of the experiment, it was 0.54 mM. The measured recovery rate also implies that without photoswitching of the reaction, the initial concentration of **1** in both active and housane forms would drop irreversibly by a factor of two after only *ca.* 66 spectra accumulations (see also the ESI† for details). This conclusion highlights that the light control is specifically useful when the irreversible conversion of **1** to **3** must be interrupted for a prolonged observation of the hyperpolarization.

Similar experiments with the light-controlled switching of the spin hyperpolarization were performed using a low-field 1 T NMR spectrometer (Fig. S9 in the ESI†). Similarly, as in the 9 T experiments, the photoreaction enables switching of the hyperpolarization effects, confirming the conclusions made based on the high-field experiments. With the low-field instrument, however, the hyperpolarization effects were less pronounced due to worse field homogeneity, which led to the significant mutual cancellation of the multiplet components with opposite phases in the enhanced antiphase ^1H signals. It seems that the observed line broadening was induced by the presence of the optical fiber tip inside the sample tube and the detection region of the low-field instrument, interfering with the shimming of the magnet. Elucidation of the exact physical or technical mechanism for this issue is beyond the scope of our communication and will be addressed in future reports. At the same time, we assume that with a better shimming of the magnet or an alternative arrangement of the optical system, this can be significantly improved, and the result of the low-field experiment measurements can be even more impressive since the signal enhancement is an order of magnitude higher than that for the high field (Fig. 2B).

Conclusions

Herein we report the first example of metal-free activation of para-H_2 coupled to photoswitching of the active biradicaloid **1** into its inactive housane form **2**. This functionality makes it possible to interrupt the activation of para-H_2 and the formation of the hyperpolarized **1**-H_2 addition product **3**, allowing for precise control of the ^1H spin hyperpolarization process. This effect is in striking contrast to the reported photo-PHIP examples using metal complexes, wherein photoactivation facilitates the observation of the hyperpolarization effect. We believe that this is an initial demonstration that can be further developed, including, *e.g.*, ^{31}P detection through the polarization transfer from the hyperpolarized ^1H nuclei, adding another dimension to providing an even cleaner NMR hyperpolarization response to the applied light. In addition, we believe that rational molecular design can lead to photosensitive metal-free biradicaloids that reversibly add dihydrogen. For instance, this could potentially be achieved by substituting the Ter and R groups (Fig. 1) with alternative chemical moieties,[25,27] as such modifications have already been shown to influence the stability,[28] reactivity,[29] and photochemistry[30] of related biradicaloids. In this case, exposing the samples to light can induce conversion of the dihydrogen addition product (**3**) to housane form (**2**), effectively opening the way for the self-recovery of the active biradicaloid (**1**). With **1**, activating para-H_2 irreversibly, the hyperpolarization activity stops as long as the **1**-H_2 addition product **3** is irreversibly formed, whereas with the sensible degree of reversibility, the system will sustain a reasonable amount of the active biradicaloid component, while the light will continuously drag it into the housane form. Such investigations would result in interesting additional modalities, enriching the scope of experiments and available active systems in photo-PHIP research.

Author contributions

This work was carried out through the following contributions: V. V. Z.: conceptualization, funding acquisition, resources, supervision, investigation, validation, visualization, and writing – original draft; K. K.: investigation, validation, and writing – review and editing; J. B.: conceptualization, resources, supervision, validation, and writing – review and editing; A. S.: conceptualization, funding acquisition, resources, supervision, validation, and writing – review and editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the ESI.† In addition, data for this article, including raw NMR data folders, are available at fairdata.fi at **https://doi.org/10.23729/fd-ecd54a34-163c-3bf8-9fc7-399b31d69bc4**.

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