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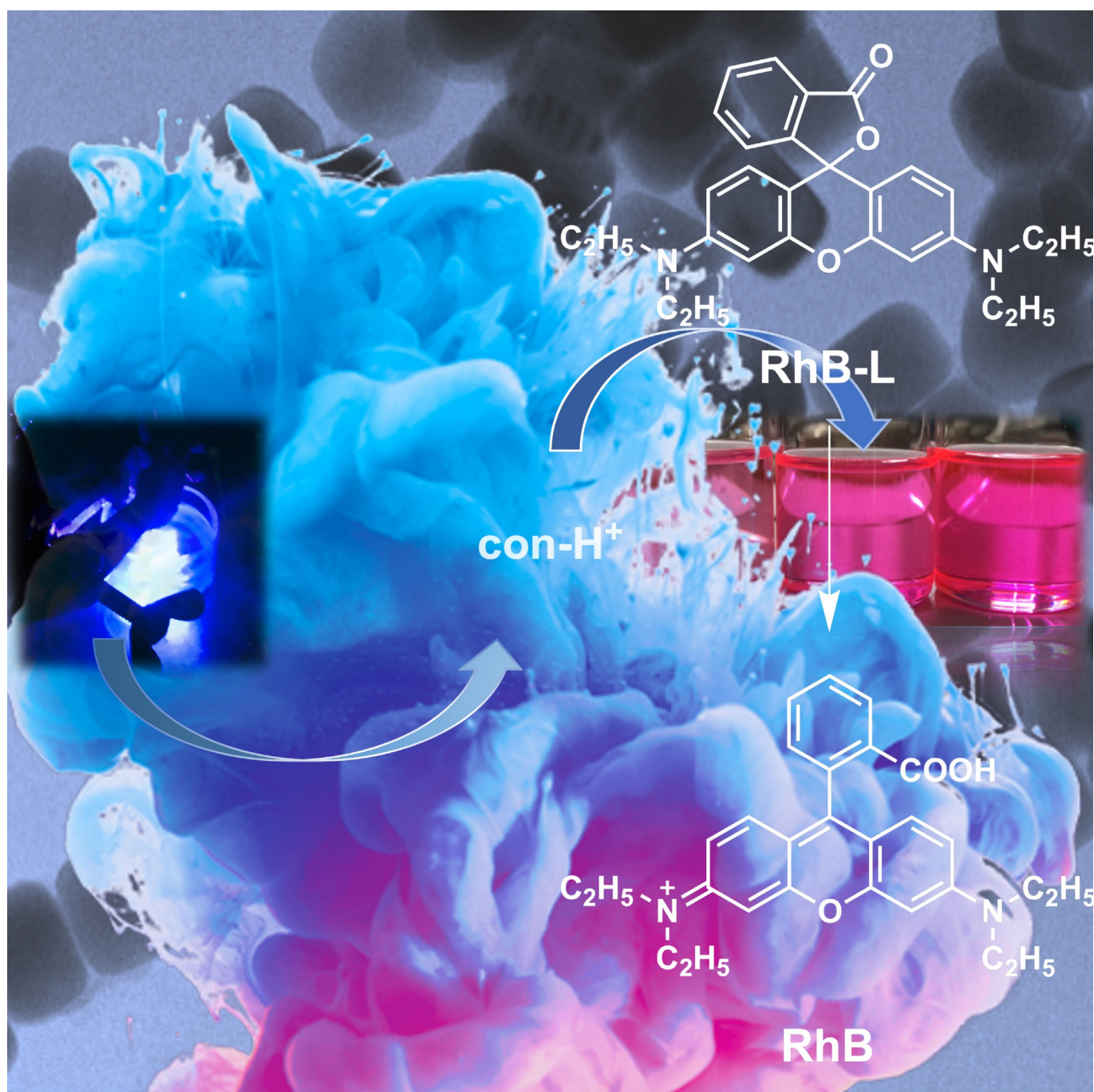European Chemical
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▌**Photochemistry**

Mediated Generation of Conjugate Acid by UV and Blue Sensitizers with Upconversion Nanoparticles at 980 nm
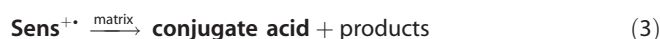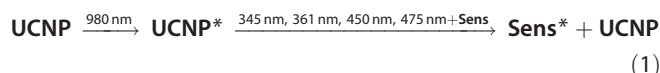
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Abstract: NIR and UV exposure of systems comprising up-conversion nanoparticles (**UCNP**) based on NaYF$_4$:Tm/Yb@NaYF$_4$, a sensitizer absorbing either in the blue or UV region, and an onium salt with weak coordinating anion resulted in formation of conjugate acid (con-H$^+$). That was namely Ivocerin (di(4-methoxybenzoyl)diethylgermane), ITX (2-iso-propyl thioxanthone), anthracene, pyrene, rubrene, camphore quinone, and a strong fluorescent coumarin (1,1,6,6,8-pentamethyl-2,3,5,6-tetrahydro-1H,4H-11-oxa-3a-aza-benzo[de]anthracene-10-one). Quantification occurred by treatment with Rhodamine B lactone whose color switched to intensive red after photolytic formation of con-H$^+$. Exposure with a NIR laser at 980 nm resulted in less con-H$^+$ compared to 395 nm where all sensitizers absorb radiation. **UCNP** did not mainly interfered formation of con-H$^+$. The different rates obtained in both experiments responsibly explain the failure and success to initiate polymerization of epoxides applying ether 980 nm or 395 nm excitation, respectively.

Assisted photoreactions via upconversion nanoparticles (**UCNP**) gained increased attention in the last years.[1–10] They convert longwave radiation into shortwave emission, namely NIR light into UV and blue light. This led to several developments in biomedicine,[11] bioimaging,[12] security inks against counterfeiting,[1,13,14] dentistry,[15] photopolymerization,[2,10,16–18] controlled polymer synthesis following an ATRP protocol,[9,10] 3D printing[3]—just to name some important fields where these fascinating materials have received remarkable attention. Their application combines the benefits of two radiation sensitive technologies; that is the use of highly reactive photosenistizers with absorption either in the UV or blue part while NIR radiation triggers this event by upconversion. It can penetrate deeper into materials since scattering of NIR radiation exhibits a third less scattering compared to UV radiation.[19] This led to developments facilitating the generation of 13 cm deep cured materials applying laser excitation at 980 nm.[17] In addition, a system based on upconversion nanoparticles resulted in cationic polymerization of cyclohexene oxide while the addition of substrates carrying an α-hydrogen such as 4-methoxybenzyl alcohol whose abstraction results in formation of a nucleophilic radical applying a system comprising the **UCNP**, titanocene and an iodonium salt.[16] It has been accepted that such nucle-
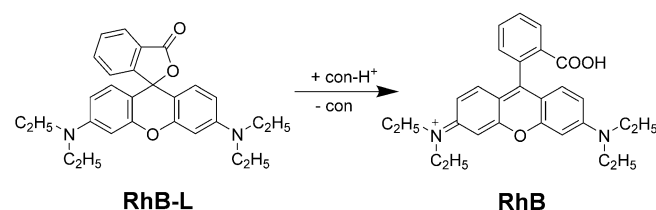
ophilic radicals derived from ether or benzyl patterns result in a chain reaction with an onium salt[20] explaining the high reactivity disclosed in the case of cyclohexene oxide.[16] Beside the **UCNP**s, there were also upconverting glasses reported to convert longer wavelength radiation into shorter wavelength emission.[21]

Early studies of this work attempted to initiate cationic polymerization of common epoxides based on a system comprising **UCNP**, blue light sensitive sensitizer and an onium salt. No cationic polymerization was observed. This directed our research to explore such systems much deeper in detail. Most reports lack to quantify the amount on conjugate acid formed by the reaction between the photoexcited sensitizer (**Sens***) and the onium salt [Eqs. (1)–(3)]. The latter derived either from iodonium or sulfonium cations. Oxidative electron transfer proceeds from **Sens*** to On$^+$ resulting in the respective cation radical **Sens$^{+\cdot}$** and **On$^\cdot$** [Eq. (2)]. Only **Sens$^{+\cdot}$** contributes to formation of conjugated acid (con-H$^+$) [Eq. (3)]. We prefer to operate with this terminology as with proton or H$^+$ because "naked" H$^+$ does not exist in the systems investigated.

$$\text{UCNP} \xrightarrow{980\,nm} \text{UCNP*} \xrightarrow{345\,nm,\ 361\,nm,\ 450\,nm,\ 475\,nm + \text{Sens}} \text{Sens*} + \text{UCNP} \tag{1}$$

$$\text{Sens*} + \text{On}^+ \rightarrow \text{Sens}^{+\cdot} + \text{On}^\cdot \tag{2}$$

$$\text{Sens}^{+\cdot} \xrightarrow{matrix} \text{conjugate acid} + \text{products} \tag{3}$$

Equation (1) requires an optimal overlap between the emission spectrum of the radiation generated to obtain an optimal amount on intermediates such as **Sens*** whose reaction with the onium salt in Equation (2) results in the cation radical of the sensitizer. The latter successfully generates conjugate acid whose amount can be quantified by Rhoadamine B (**RhB**) formed by reaction with of Rhodamine B lactone (**RhB-L**) with con-H$^+$ as shown in Scheme 1. Although this reaction has been known for a long time, only a few reports applied this chemistry to probe quantitatively the amount of con-H$^+$. This enables to compare different systems regarding their efficiency to generate con-H$^+$.

Nevertheless, it additionally addresses the necessity to have available the overlapping integral (OvInt(λ)) of the product between the emission spectrum of the radiation released by the UCNP ($I_{UCNP}(\lambda)$) and the absorption of the sensitizer ($\varepsilon_{Absorber}(\lambda)$) [Eq. (4)]. Surprisingly, such considerations giving access to the

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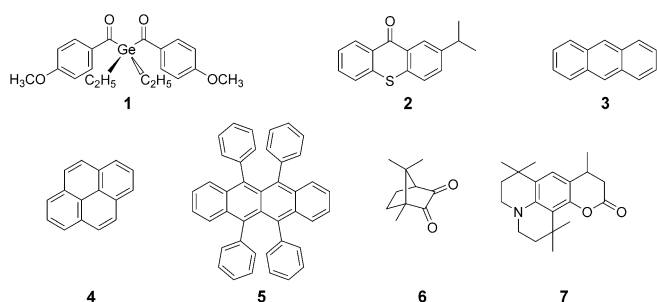47798 Krefeld (Germany)
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Scheme 1. Ring opening reaction of **RhB-L** (colorless) in the presence of acidic species to **RhB** (red colored) which is used to quantify the generation of acidic species (original in ref. [22]), application to probe con-H$^+$ in photopolymerization system see ref. [23].

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information needed disclosed above have not received the necessary attention yet though cationic initiated photopolymerization occupies a large field.

$$\text{OvInt}(\lambda) = \int \left[I_{\text{UCNP}}(\lambda) \times \varepsilon_{\text{Absorber}}(\lambda) \right] d\lambda \qquad (4)$$
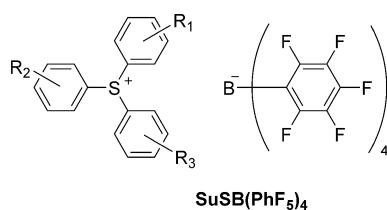
Scheme 2 depicts the structures of the sensitizers chosen. Either a nucleophilic radical[20] formed by Norrish type 1 cleavage (**1**) or an excited state (**2**–**7**)[24] determine the efficiency of con-H$^+$ formation. Most of these studies focused to employ the initiation of cationic polymerization in combination with an onium salt. In here, we investigate the generation of con-H$^+$ according to the reaction framework shown by Equations (1)–(3) via **UCNP**s. These sensitizers absorb in the UV and blue region.

Table 1. Spectral properties of photosensitizers (λ_{max} (nm): wavelength for maximum of absorption, ε_{max} (M^{-1} cm^{-1}): extinction coefficient at the absorption maximum), overlapping integral (OvInt(λ)) as defined by Equation (4), and absorption as defined by the ratio of radiation released by the **UCNP** with respect to the overall radiation released by **UCNP** called as absorption yield considering the red curve in Figure 1. Experiments were pursued in toluene. The unit of (OvInt(λ)) relates to M^{-1} keeping in mind that the emission was normalized and appears here with no unit.

Sensitizer	λ_{max} [nm]	ε_{max} [M^{-1} cm^{-1}]	(OvInt(λ)) [$10^{-4} \times$ M^{-1}]	Absorption yield [%]
1	412	780	1.95	12
2	385	6600	35.9	19
3	338	56000	49.5	27
4	356	8720	42.6	4
5	527	1400	150	50
6	472	38	0.45	55
7	370	19000	118	29

Scheme 2. Chemical structure of the photosensitizers.

Generation of con-H$^+$ typically occurs in the presence of a co-initiator. Iodonium and sulfonium salts can take this function. In this study, a sulfonium salt with weak coordinating anion[25] moved into the focus since this should not exhibit so many unexpected side reactions as reported for iodonium cations[26] (Scheme 3).

Table 1 summarizes the properties of the sensitizers, their maximum of absorption and extinction coefficient, and additionally the overlapping integral (OvInt(λ)) as disclosed by Equation (4). Figure 1 exhibits the overlapping integrals of the sensitizers **1**, **2** and **6** while supporting information shows the overlapping integrals of **3**, **4**, **5** and **7** (Supporting Information Figure SI5). They appear regarding their size in the order of **6** < **5** < **7** < **3** < **2** < **1** < **4**. It clearly images the differences where OvInt(λ) plays a major role.
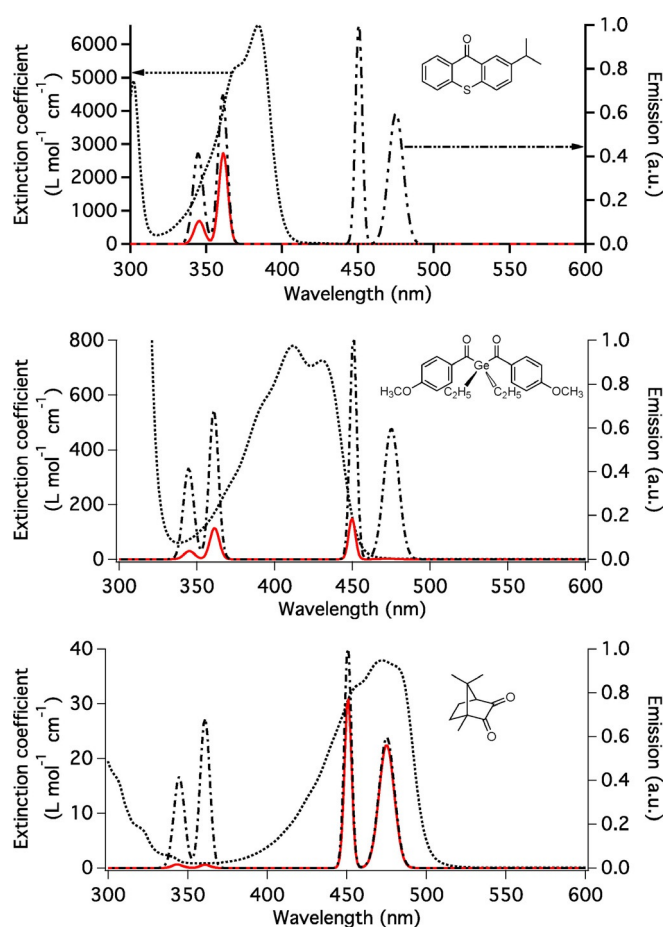

Figure 1. Overlapping integrals (red) of the absorption spectra of various absorbers and the emission of **UCNP**. Experiments were pursued in toluene.

Scheme 3. Chemical structure of the co-initiator used to generate acidic species based on the sulfonium salt **SuSB(PhF$_5$)$_4$**. The substitution R$_1$, R$_2$ and R$_3$ pattern at the phenyl ring was not disclosed by the supplier, see Supporting Information for more details.

All experiments in the NIR employed equivalent 2×10^{-3} M concentration of sensitizer and an equivalent amount of the co-initiator using toluene as solvent. Irradiation was performed with a NIR laser operating with an intensity of 125 W cm^{-2} in combination with 1 g L^{-1} **UCNP**. The solutions obtained appeared in an acceptable optical appearance for the experi-

ments and exhibited overall less activity to generate con-H$^+$ (Supporting Information Figure SI6). The high intensity of the NIR laser was necessary to enhance the amount of emitted UV radiation[7] even though some sensitizers possess a higher reactivity with lower intensity (Supporting Information Figure SI7). These measurements were compared with conventional UV light using an UV-LED ($\lambda = 395$ nm and an intensity of 230 mW cm^{-2}). Supporting Information describes the light sources.

Figure 2 shows the quantified con-H$^+$ of the systems after irradiation for 60 min in combination with **UCNP** and after 10 min irradiation with an UV-LED. The generation of acidic species appears much higher in the case of UV light excitation. Furthermore, sensitizers absorbing blue light exhibit a higher yield of con-H$^+$ in presence of **UCNP**. This might be possible due to a higher amount of emitted blue light compared to the emitted UV light, as it can be seen in Figure 1 for the emission of the **UCNP**. Nevertheless, **5** shows poor activity in both cases. The low triplet formation yield can be seen as one reason.[27] However, **7** exhibiting a fluorescence quantum yield close to unity does not fit in this scheme.[28]
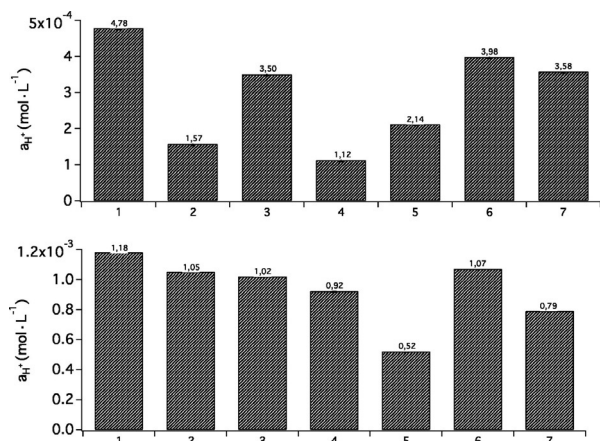

Figure 2. Conjugate acid formed by the sensitizers **1**–**7** (a) with an irradiation time of 60 min with NIR Laser and (b) with an irradiation time of 10 min with UV-LED. Experiments were pursued in toluene.

Table 2 compares the yield of generated conjugate acid Q_{con-H^+} for the initiating systems as defined by the ratio of the number of conjugate acid molecules (N_{con-H^+}) with respect to the number of sensitizer molecules (N_{Sens}). Exposure with UV leads to much higher yields compared to NIR radiation. Particularly only UV absorbing systems such as **2**, **3** and **4** exhibit a yield appearing up to six times higher. The remaining systems depict around the doubled amount of generated conjugate acid.

To get a deeper view of the systems, time-dependent measurements were performed. Figure 3 shows formation of conjugate acid as a function of time for the sensitizers **1**, **2** and **6** considering irradiation with NIR of UV. As can be seen in Figure 3, the initial slope at the beginning of the curves is much steeper than the slopes with NIR light. The significant higher laser intensity was necessary to achieve comparable

Table 2. Yield of acidic species after irradiation for 60 min with NIR-laser and 10 min with UV-LED. Excitation on the UV or Blue part occurred at 395 nm. Experiments were pursued in toluene.

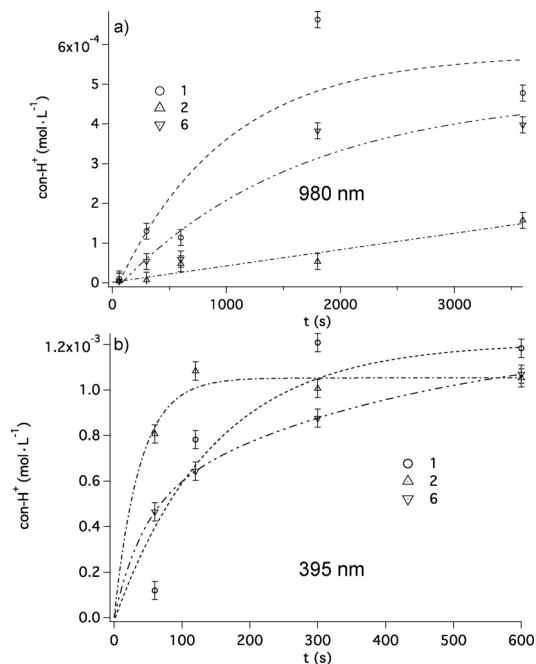| Sensitizer | $Q_{con-H^+} = \frac{N_{con-H^+}}{N_{Sens}}$. | | Rate constant | |
	NIR	UV	NIR [M^{-1} s^{-1}]	UV [M^{-1} s^{-1}]
1	0.24	0.59	5.4×10^{-7}	8.3×10^{-6}
2	0.08	0.53	4.1×10^{-8}	2.3×10^{-5}
3	0.06	0.46	9.8×10^{-8}	1.1×10^{-6}
4	0.18	0.51	3.2×10^{-8}	7.4×10^{-6}
5	0.11	0.26	1.1×10^{-7}	3.7×10^{-6}
6	0.20	0.53	2.6×10^{-7}	9.3×10^{-6}
7	0.18	0.40	2.0×10^{-7}	9.8×10^{-6}

Figure 3. Time-dependent generation of conjugate acid (con-H$^+$) of selected sensitizers with the sulfonium salt of Scheme 3 operating as co-initiator exposed with (a) NIR laser at 125 W cm^{-2} employing 980 nm, and (b) UV-LED at 230 mW cm^{-2} (solvent: toluene).

concentration on conjugate acid with the LED. The laser exhibited a size of 4.8 mm shining on a large area sample (details in Supporting Information). On the other hand, the LED exposed according to its beam characteristics a much larger area compared to the laser. Furthermore, one still needs to keep in mind that the upconversion process generates $\ll 1\%$ radiation in the UV and blue range.[29–31]

Table 2 summarizes the rate constants for the systems. In general, the exposure with UV light leads as expected again to higher rate constants compared to NIR exposure. In addition, consideration of the number of conjugate acid formed (N_{con-H^+}) with respect to the number of sensitizers N_{sens} shows a general higher ratio in the case of UV exposure although the difference appears moderate compared to NIR exposure in the case of **1** and **4**–**7**. Within the same exposure series, data show similar size in the case of UV exposure of **4** whose number depicts less amount on Q_{con-H^+}. This may be caused by the absorption

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yield introduced in Table 1 because pyrene only absorbs in the UV range. Consideration of the rate constants shown in Table 2 supports these findings by comparison of NIR and UV data. Also here, **2** exhibits a low efficiency considering the series of NIR exposure while it depicts the highest value in the case of UV exposure. It demonstrates again the necessity for quantification the amount of con-H$^+$ particular for the surrounding chosen.

In addition, rate constants do not really follow neither a trend disclosing the absorption yield as introduced in Table 1 nor the triplet yields reported in other solvents earlier (**1**: close to unity as concluded from photochemical studies;[32] **2**: 0.84;[33] **3**: 0.58;[34] **4**: 0.38 at infinite dilution, 0.18 at 10^{-3} M concentration;[35] **5**: 0.009;[27] **6**: close to unity as concluded from photochemical studies;[36] **7**: about zero because fluorescence quantum yield close to unity[28]).

The procedure disclosed in this contribution shall be recommended for those researchers pursuing research in the field of cationic polymerization where discussion of mechanism moves into the focus. It helped in our case to understand why NIR-sensitized polymerization of epoxides did not succeeded although it worked in the case of UV exposure at 395 nm using the same composition. Thus, hypothesis that the nucleophilic surface might inhibit cationic polymerization can be ruled out by our investigations employing RhB-L as optode to determine the quantitative amount of conjugate acid formed. It additionally gives a drawback why other systems succeeded.[16] Different excitation conditions presumably resulting in distinct amounts on conjugate acid that successfully initiates cationic polymerization can explain these findings.[16]

Acknowledgements

Conflict of interest

The authors declare no conflict of interest.

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