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Corresponding Author:	Julien Pinaud, Ph.D Institut Charles Gerhardt de Montpellier Montpellier, Occitanie FRANCE
Corresponding Author's Institution:	Institut Charles Gerhardt de Montpellier
Corresponding Author E-Mail:	julien.pinaud@umontpellier.fr
Order of Authors:	Julien Pinaud, Ph.D
	Emeline Placet
	Patrick Lacroix-Desmazes
	Thi Kim Hoang Trinh
	Jean Pierre Malval
	Abraham Chemtob
	Loïc Pichavant
	Valérie Héroguez
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TITLE:

Photogeneration of N-Heterocyclic Carbenes: Application in Photoinduced Ring-Opening Metathesis Polymerization

AUTHORS AND AFFILIATIONS:

Julien Pinaud[1], Emeline Placet[1], Patrick Lacroix-Desmazes[1], Thi Kim Hoang Trinh[2,3], Jean Pierre Malval[2,3], Abraham Chemtob[2,3], Loïc Pichavant[4], Valérie Héroguez[4]

[1]Université de Montpellier, Montpellier, France
[2]Université de Haute-Alsace, Mulhouse, France
[3]Université de Strasbourg, Strasbourg, France
[4]Université de Bordeaux, Pessac, France

Corresponding Author:

Julien Pinaud
julien.pinaud@umontpellier.fr
Tel: 33 (0)4 67 14 39 99

Email Addresses of Co-authors:

Emeline Placet (emeline.placet@enscm.fr)
Patrick Lacroix-Desmazes (patrick.lacroix-desmazes@enscm.fr)
Thi Kim Hoang Trinh (thi-kim-hoang.trinh@uha.fr)
Jean Pierre Malval (jean-pierre.malval@uha.fr)
Abraham Chemtob (abraham.chemtob@uha.fr)
Loïc Pichavant (loic.pichavant@enscbp.fr)
Valérie Héroguez (valerie.heroguez@enscbp.fr)

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SUMMARY:

We describe a protocol to photogenerate N-heterocyclic carbenes (NHCs) by UV irradiation of a 2-isopropylthioxanthone/imidazolium tetraphenylborate salt system. Methods to characterize the photoreleased NHC and elucidate the photochemical mechanism are proposed. The protocols for ring-opening metathesis photopolymerization in solution and miniemulsion illustrate the potential of this 2-component NHC photogenerating system.

ABSTRACT:

We report a method to generate the N-heterocyclic carbene (NHC) 1,3-dimesitylimidazol-2-ylidene (IMes) under UV-irradiation at 365 nm to characterize IMes and determine the corresponding photochemical mechanism. Then, we describe a protocol to perform ring-opening metathesis polymerization (ROMP) in solution and in miniemulsion using this NHC-photogenerating system. To photogenerate IMes, a system comprising 2-isopropylthioxanthone (ITX) as the photosensitizer and 1,3-dimesitylimidazolium tetraphenylborate ($IMesH^+BPh_4^-$) as the protected form of NHC is employed. $IMesH^+BPh_4^-$ can be obtained in a single step by anion exchange between 1,3-dimesitylimidazolium chloride and sodium tetraphenylborate. A real-time steady-state photolysis setup is described, which hints that the photochemical reaction proceeds in two consecutive steps: 1) ITX triplet is photo-reduced by the borate anion and 2) subsequent proton transfer takes place from the imidazolium cation to produce the expected NHC IMes. Two separate characterization protocols are implemented. Firstly, CS_2 is added to the reaction media to evidence the photogeneration of NHC through formation of the IMes-CS_2 adduct. Secondly, the amount of NHC released *in situ* is quantified using acid-base titration. The use of this NHC photo-generating system for the ROMP of norbornene is also discussed. In solution, a photopolymerization experiment is conducted by mixing ITX, $IMesH^+BPh_4^-$, $[RuCl_2(p\text{-}cymene)]_2$ and norbornene in CH_2Cl_2, then irradiating the solution in a UV reactor. In a dispersed medium, a monomer miniemulsion is first formed then irradiated inside an annular reactor to produce a stable poly(norbornene) latex.

INTRODUCTION:

In chemistry, N-heterocyclic carbenes (NHCs) species fulfill the twofold role of ligand and organocatalyst[1]. In the former case, the introduction of NHCs has resulted in the design of metal transition catalysts with improved activity and stability[2]. In the latter case, NHCs have proved to be superior catalysts for manifold organic reactions[3,4]. Despite this versatility, handling bare NHCs is still a significant challenge[5], and producing these highly reactive compounds so they are released *in situ* and “on demand” is a very attractive goal. Consequently, several strategies have been developed to release NHC in the reaction media which mostly rely on the use of thermolabile progenitors[6-8]. Surprisingly, while this could unleash a novel generation of photoinitiated reactions useful for macromolecular synthesis or preparative organic chemistry[6], generation using light as stimulus has been scarcely explored. Recently, a first photo-generating system able to produce NHC has been unveiled[9]. It consists of 2 components: 2-isopropylthioxanthone (ITX) as photosensitive species and 1,3-dimesitylimidazolium tetraphenylborate ($IMesH^+BPh_4^-$) as the NHC protected form. Consequently, in the following paragraphs, we report a method to generate the N-heterocyclic carbene (NHC) 1,3-dimesitylimidazol-2-ylidene (IMes) under UV-irradiation at 365 nm, characterize it, and determine the photochemical mechanism. Then, we describe a protocol to perform ring-opening metathesis polymerization (ROMP) in solution and in miniemulsion using this NHC photogenerating system.

In the first portion, we report a synthesis protocol to produce $IMesH^+BPh_4^-$. This protocol is based on anion metathesis between the corresponding imidazolium chloride ($IMesH^+Cl^-$) and sodium tetraphenylborate ($NaBPh_4$). Then, to demonstrate the *in situ* formation of NHC, two protocols involving the irradiation at 365 nm of a $IMesH^+BPh_4^-$/ITX solution in a photoreactor are described. The first consists of monitoring the deprotonation of the imidazolium cation $IMesH^+$ through ^1H NMR spectroscopy. Direct evidence for formation of the desired NHC (IMes) is provided in a second method, where the adduct IMes-CS_2 is successfully isolated, purified, and characterized.

The second section describes two protocols that shed light on the photochemical mechanism involving the NHC two-component photogenerating system $IMesH^+BPh_4^-$/ITX. Firstly, an original real-time steady state photolysis experiment reveals that electron transfer is induced by photo-excitation of ITX in the presence of tetraphenylborate. Electron donor properties of this borate anion[10] drives a photoreduction of $^3ITX^*$ triplet excited-state into $ITX^{\bullet -}$ radical anion through a so-called photo-sensitized reaction. The formation of NHC confirms that $ITX^{\bullet-}$ species may further abstract a proton from $IMesH^+$ to produce the desired NHC. Based on acid/base titration using phenol red pH indicator as titrant, a second original protocol is implemented that allows the determination of the yield of released NHC.

In the third section, we describe a protocol in which the above-mentioned photogenerated IMes can be exploited in photopolymerization. Of primary interest is ring-opening metathesis polymerization (ROMP), because this reaction is still at a preliminary stage of development with regard to photoinitiation[11,12]. Initially limited to ill-defined and highly sensitive tungsten complexes, photoinduced ROMP (photoROMP) has been extended to more stable complexes based on W, Ru, and Os transition metals. Despite the variety of precatalysts, almost all photoROMP processes rely on the direct excitation of a single photoactive precatalyst[13]. By contrast, we use radiation to create the NHC imidazolidene ligand (IMes), which can react subsequently with a non-photoactive Ru precatalyst $[RuCl_2(p\text{-cymene})]_2$ dimer[9]. In this method, the photogeneration of NHC ligand drives the *in situ* formation of a highly active ruthenium-arene NHC complex known as $RuCl_2(p\text{-cymene})(IMes)$ (Noels' catalyst)[14,15]. Using this indirect methodology, two distinct photoROMP experiments of norbornene (Nb) are performed: 1) in solution (dichloromethane) and 2) in aqueous dispersed system from a monomer miniemulsion[16].

PROTOCOL:

1. NHC Photogenerating System: Synthesis and Reactivity

1.1. Synthesis of 1,3-dimesitylimidazolium tetraphenylborate ($IMesH^+BPh_4^-$)

1.1.1. Preparation of the solution of 1,3-dimesitylimidazolium chloride ($IMesH^+Cl^-$) in ethanol.

1.1.1.1. Add 1.00 g (2.93 mmol) of 1,3-dimesitylimidazolium chloride to a 50 mL round bottom flask equipped with a stir bar.

1.1.1.2. Dissolve the 1,3-dimesitylimidazolium chloride in 30 mL of ethanol.

1.1.2. Preparation of the solution of sodium tetraphenylborate ($NaBPh_4$) in ethanol.

1.1.2.1. Add 1.35 g (3.92 mmol) of sodium tetraphenylborate to a 50 mL round bottom flask equipped with a stir bar.

1.1.2.2. Dissolve the sodium tetraphenylborate in 30 mL of ethanol.

1.1.3. Generation of 1,3-dimesitylimidazolium tetraphenylborate ($IMesH^+BPh_4^-$)

1.1.3.1. Add (dropwise) the solution of sodium tetraphenylborate into the solution of 1,3-dimesitylimidazolium chloride under stirring.

1.1.3.2. Stir the reaction mixture for 10 min at room temperature.

1.1.3.3. Remove the stir bar and filter the white precipitate using a vacuum and fritted glass filter of pore size 3.

1.1.3.4. Wash the precipitate with 30 mL of ethanol and filter it (fritted glass filter with pore size 3). Wash the precipitate with 30 mL of deionized water and filter it (fritted glass filter with pore size 3).

1.1.3.5. Dry the white precipitate at 60 °C for 15 h. Analyze the product by ^{1}H and ^{13}C NMR in DMSO-d_6 according to previously reported procedures[9].

1.2. Photogeneration of NHC 1,3-dimesitylimidazol-2-ylidene, also known as IMes, by UV irradiation of the dimesitylimidazolium tetraphenylborate in the presence of isopropylthioxanthone (ITX)

1.2.1. Add 39 mg (0.062 mmol, 2 equiv.) of 1,3-dimesitylimidazolium tetraphenylborate, 7.8 mg (0.031 mmol, 1 equiv.) of ITX, and 0.5 mL of deuterated THF (previously stored over 3 Å molecular sieves) in an NMR tube.

1.2.2. Place the NMR tube inside the photochemical reactor equipped with a circular array of 16 fluorescent tubes emitting a monochromatic radiation at 365 nm and irradiate for 10 min.

1.3. Monitoring of deprotonation of $IMesH^{+}BPh_4^{-}$ by ^{1}H NMR spectroscopy

1.3.1. Analyze the deprotonation of $IMesH^{+}$ into IMes by ^{1}H NMR.

NOTE: ^{1}H NMR spectra were recorded at 25 °C on a NMR spectrometer operating at 400 MHz. TMS was used as internal standards for calibrating the chemical shifts in ^{1}H NMR.

1.3.1.1. Calibrate the integration parameters so that in the ^{1}H NMR spectra the CH_3 singlet of 1,3-dimesitylimidazolium tetraphenylborate ($\delta = 2.0$ ppm) corresponds to six.

1.3.1.2. Determine the integration value of the N-C*H*-N signal area ($\delta = 8.4$-9.4 ppm) in order to evaluate the degree of $IMesH^{+}$ deprotonation. The integration value should vary from 1 (when no deprotonation occurred, before irradiation) to 0 (when complete deprotonation of $IMesH^{+}$ has been performed).

1.4. Formation, isolation, and characterization of the 1,3-dimesitylimidazoliumdithio-carboxylate adduct (IMes-CS_2)

1.4.1. Add 0.02 mL of carbon disulfide in the as-irradiated NMR tube. The reaction media changes in color from orange/brown to dark red, indicating the formation of the IMes-CS_2 adduct.

1.4.2. Let it react for 12 h. A red precipitate forms assigned to the IMes-CS_2 adduct.

1.4.3. Filter the red precipitate (fritted glass filter with pore size 3) and dry it under air at room temperature for 12 h.

1.4.4. Solubilize the red solid in 0.5 mL of deuterated DMSO. Confirm the chemical structure by ^{1}H and ^{13}C NMR spectroscopy.

CAUTION: Carbon disulfide is highly toxic and should be handled with care under a fume hood.

2. Photochemical Mechanism

2.1. Real-time photobleaching of $IMesH^+BPh_4^-$/ITX

2.1.1. Prepare a stock solution of ITX by adding 0.76 mg (3×10^{-3} mmol) of ITX to 15 mL of dry acetonitrile (previously stored over 3Å molecular sieves).

2.1.2. Transfer 3 mL of ITX solution into a UV quartz cell covered with a rubber stopper containing 1.10 mg of $IMesH^+BPh_4^-$ (1.8×10^{-3} mmol) and a stirring micromagnet. The molar ratio ITX:$IMesH^+BPh_4^-$ is 1:3.

2.1.3. Degas the solution by bubbling nitrogen for 10 min, then irradiate the solution at 365 nm with a medium-pressure Hg-Xe lamp under continuous stirring (63 mW cm^{-2}, power of 75 mW).

2.1.4. Monitor the change of UV-absorbance at 365 nm during irradiation by using a spectrometer after passing a transmitted actinide beam.

2.1.5. Apply the same procedure (steps 2.1.1-2.1.4) for other experiments but replace $IMesH^+BPh_4^-$ with other quenchers: $IMesH^+Cl^-$ (0.61 mg, 1.8×10^{-3} mmol) or $NaBPh_4$ (0.62 mg, 1.8×10^{-3} mmol).

2.2. Quantification of photogenerated NHC by spectrophotometric titration

2.2.1. Add 1.85 mg of dimesitylimidazolium tetraphenylborate (3×10^{-4} mmol, 3 equiv.) and 0.25 mg of ITX (10^{-4} mmol, 1 equiv.) to 10 mL of dry acetonitrile.

2.2.2. Transfer 2 mL of this freshly prepared solution into a conventional spectroscopic quartz cell capped with a rubber septum.

2.2.3. Purge the colorless mixture with nitrogen before exposing the cuvette to a 365 nm LED spotlight (power of 65 mW) for 1 min.

2.2.4. After each irradiation time, add gradually 0.1 mL portions of phenol red (PR) solution (2×10^{-4} M in dry acetonitrile) into the cuvette. This latter titrating solution was prepared in advance.

2.2.5. Record a UV-vis spectrum after each 0.1 mL addition of PR solution until reaching 1 mL.

Note: The indicator solution is initially transparent and contains the bis-protonated form H_2PR. After its addition, acid/base reaction with NHC causes the formation of the pink bivalent anion PR^{2-} with a maximum absorption at 580 nm. Plotting the absorbance at 580 nm as a function of the titrant volume gives two intersecting straight lines, indicative of the titration endpoint.

2.2.6 Repeat the same procedure (steps 2.2.1-2.2.5) with the same ITX/$IMesH^+BPh_4^-$ solution irradiated for longer times: 2 min, 5 min, and 10 min. For each time, a new must be prepared.

Note: At the equivalence point in the acid-base titration:

$$[\mathrm{IMes}] \times \mathrm{V} = 2[\mathrm{PR}] \times \mathrm{V_{eq}} \qquad (1)$$

Where $[\mathrm{IMes}]$ is the concentration of photogenerated IMes released in the UV cuvette, V is the initial volume of $IMesH^+BPh_4^-$/ITX solution, [PR] is the concentration of PR, and $\mathrm{V_{eq}}$ is the total volume of PR added into the UV cuvette at the titration end-point. Therefore, the yield of IMes released upon irradiation of $IMesH^+BPh_4^-$/ITX solution is obtained from equation (2):

$$\mathrm{Yield}\ (\%) = \frac{2 * [\mathrm{PR}] \times \mathrm{V_{eq}}}{[\mathrm{IMesH^+BPh_4^-}] \times \mathrm{V}} \times 100 \qquad (2)$$

Where $[\mathrm{IMesH^+BPh_4^-}]$ is the initial concentration of $IMesH^+BPh_4^-$.

The validity of the method is checked by titrating a free IMes solution (1×10^{-4} M in acetonitrile) using a similar acetonitrile PR solution as a titrant (2×10^{-4} M).

3. Photoinduced Ring-Opening Metathesis Polymerization

3.1. PhotoROMP of Nb in solution

3.1.1. Add 1 g (11 mmol, 540 equiv.) of Nb, 120 mg (0.196 mmol, 10 equiv.) of 1,3-dimesitylimidazolium tetraphenylborate, 12 mg (19.6 mmol, 1 equiv.) of dichloro(para-cymene)ruthenium dimer, and 25 mg (0.098 mmol, 5 equiv.) of ITX in a 20 mL test tube equipped with a stir bar.

3.1.2. Dissolve the solids in 10 mL of dichloromethane and cap the tube with a rubber septum.

3.1.3. Purge the mixture by bubbling nitrogen gas through a syringe needle for 15 min.

3.1.4. Place the tube inside the photochemical reactor equipped with a circular array of 16 fluorescent lamps (emitting at 365 nm) and irradiate for 10 min. The solution becomes viscous, indicating that high-molecular weight polyNb is formed.

3.1.5. Precipitate the polymer by pouring the solution into 300 mL of methanol.

3.1.6. Filter the polymer (fritted glass filter with pore size 3) and dry it at 60 °C for 8 h.

3.1.7. Analyze the polymer by ^{1}H NMR according to reported procedures[9] by dissolving about 10 mg of polymer in 0.5 mL of CD_2Cl_2.

3.1.8. Analyze the polymer by size exclusion chromatography according to reported procedures[9], using THF as eluent and dissolving 10 mg of polymer in 1 mL of THF.

3.2. PhotoROMP of Nb in miniemulsion

3.2.1. Preparation of Nb miniemulsion.

3.2.1.1. Dissolve 15.0 g of neutral surfactant polyoxyethylene (100) stearyl ether in 150 mL of milliQ water

3.2.1.2. Introduce the aqueous phase in the annular LED photoreactor closed with rubber septum and place the reactor under the airtight sonication probe.

3.2.1.3. Degas the solution by bubbling nitrogen during 1 h.

3.2.1.4. Mix 4.94 g of Nb (5.2×10^{-2} mol; 510 equiv.; 25 w%), 2.85 mL of hexadecane (10 w%), and 6 mL of dichloroethane (32.5 w%) in a 50 mL round bottom flask closed with a rotaflo. Degas the solution with a freeze-pump-thaw cycle.

3.2.1.5. Add 6 mL of dichloroethane (32.5 w%) in a second 50 mL round-bottom flask closed with a rotaflo. Degas the solution by freeze-pump-thaw. Add 162 mg of 1,3-dimesitylimidazolium tetraphenylborate (2.6×10^{-4} mol, 5 equiv.), 33 mg of ITX ($1.3\ 10^{-4}$ mol, 2.5 equiv.), and 30 mg of dichloro(p-cymene)ruthenium(II) dimer (4.9×10^{-5} mol, 1 equiv.) under inert atmosphere (glovebox) to the flask.

3.2.1.6. Mix the two organic solutions containing the monomer and the catalytic mixture under a nitrogen flux, and introduce 15 g of the final organic solution inside the photoreactor, containing the aqueous phase under stirring.

3.2.1.7. Stir the two phases during 1 h to form a rough macroemulsion. Sonicate during 10 min (power 50%; pulse on-time: 5 s, off-time: 5 s) to form the miniemulsion.

3.2.2. Photopolymerization of NB miniemulsion.

3.2.2.1. Replace the airtight sonication probe by the LED lamp equipped with a water cooling system and protected by a cladding tube under a nitrogen flux.

3.2.2.2. Place the closed reactor inside the photocabinet to prevent exposure to UV radiation.

3.2.2.3. Irradiate the monomer miniemulsion for 100 min to obtain polymer latex. During irradiation, particle size and monomer conversion can be determined as explained below.

3.2.3. Determination of particle size, conversion and molecular weight.

3.2.3.1. Collect 4 mL of miniemulsion sample during irradiation process.

3.2.3.2. Add 20 µL of miniemulsion in a glass cuvette containing 5 mL water to prepare a 250x diluted sample for particle size analysis by dynamic light scattering (DLS).

3.2.3.3. Dissolve 100 µL of miniemulsion in 500 µL of THF to measure the Nb conversion by gas chromatography (GC), with hexadecane as internal standard (GC retention times: t^{GC}_{Nb} = 1.77 min; $t^{GC}_{dodecane}$ = 13.25 min).

3.2.3.4. Precipitate the rest of the sample in 20 mL of acetone. Filter the polymer. Dry the polymer under a vacuum and measure the molecular weight by size exclusion chromatography (SEC) [SEC in tetrahydrofuran (THF) (1 mL min^{-1}) with trichlorobenzene as the flow marker, using both refractometric and UV detectors].

CAUTION (Part 1-3): Possibly hazardous sources of light emitting in the UV and visible range are used in the described experiments. These lamps can present a reasonably foreseeable risk of harming the eyes and skin of lab members. Consequently, all measures possible should be put in place by the experimenter to reduce the risks to as low as is reasonably practicable. A list of common measures includes the isolation of the light source inside a protective casing (photocabinet, for example), training of all workers, placing the hazardous sources of light in well-designated laboratories or fume hoods with restricted access, providing suitable safety gears (safety goggles blocking UVA irradiation are sufficient for all described protocols), and displaying appropriate warning and safety signs.

REPRESENTATIVE RESULTS:

Step 1.1 describes the efficient anion metathesis between 1,3-dimesitylimidazolium chloride ($IMesH^+Cl^-$) and sodium tetraphenylborate ($NaBPh_4$) to yield 1,3-dimesitylimidazolium tetraphenylborate ($IMesH^+BPh_4^-$). The desired photolatent NHC is obtained in excellent yield (98%). **Figure 1** shows ^{1}H and ^{13}C NMR spectra, both testifying that a pure product exhibiting the correct structure is obtained.

Step 1.2 describes how to generate the N-HC IMes by irradiating the mixture $IMesH^+BPh_4^-$/ITX (2/1 equiv.) in THF-d_8 solution.

Step 1.3 shows that it is possible to assess the conversion of $IMesH^+$ in IMes by monitoring the deprotonation of $IMesH^+BPh_4^-$ through ^{1}H NMR spectroscopy. **Figure 2** shows that proton H_a (8.63 ppm, **Figure 2a**) on carbon 2 adjacent to the two nitrogen atoms disappears partially after 10 min irradiation (53%, **Figure 2b**). The reaction was performed by irradiating the mixture $IMesH^+BPh_4^-$/ITX (2/1 equiv.) in THF-d_8 solution.

Step 1.4 shows that it is possible to isolate the formed NHC by reacting the as-irradiated medium (see protocol 1.2) with CS_2. The red precipitate formed in THF-d_8 is collected, dried, and dissolved in DMSO-d_6. As can be seen in the ^{13}C NMR spectrum (**Figure 2c**), all the characteristic resonances are consistent with IMes-CS_2 adduct. This result indirectly confirms the *in situ* generation of the targeted IMes NHC.

Step 2.1: Thioxanthone derivatives make up a well-established class of photoinitiators generally employed in combination with a second component referred to as "co-initiators". Their absorption spectra appear with a maximum in the range of 340-420 nm. The nature of the co-initiator determines the mechanism of initiation. Three general initiation mechanisms have been described: 1) triplet-triplet energy transfer (in this case, from ^{3}ITX* to $^3BPh_4^-$*); 2) electron transfer from the electron donor BPh_4^- to ^{3}ITX*; and 3) direct H abstraction of $IMesH^+$ by ^{3}ITX*. Mechanism 1 can be discarded since the triplet energy order $E_T(BPh_4^-) > E_T(ITX)$ is established by conventional computational procedure.

Step 2.1 provides evidence as to whether mechanism 2 or 3 is operating. **Figure 3** shows the evolution of absorbance values of characteristic ITX absorption band at 365 nm during irradiation for three different bicomponent mixtures: $IMesH^+BPh_4^-$/ITX, $IMesH^+Cl^-$/ITX, and $NaBPh_4$/ITX. The absence of decay for $IMesH^+Cl^-$ supports the incapacity for electronically excited ITX to abstract a hydrogen from the imidazolium cation (mechanism 3). In contrast, photobleaching of ITX is visible in the two systems containing the BPh_4^- anions; although, the decay rates are different in these two cases. This result emphasizes the critical role played by the tetraphenylborate anion. Consequently, the photoreduction of ITX by tetraphenylborate (mechanism 2) is proven to be the primary step in the formation of the NHC. **Figure 4** displays a hypothetical and complete mechanism in which the $ITX^{\bullet-}$ radical anion may abstract a proton from $IMesH^+$ to release the free NHC IMes.

Step 2.2 shows evidence in favor of this mechanism. This method reveals the progressive release of NHC during irradiation. It is a method to determine the amount of released NHC based on acid/base titration using phenol red (PR) pH indicator as titrant. A maximum yield of 50% is achieved after 5 min of irradiation (**Figure 5**), and a control experiment with free IMes enables validation of the method.

Step 3.1 describes photoROMP of NB (540 equiv.) in dichloromethane using a photolatent mixture composed of $IMesH^+BPh_4^-$/ITX (10/5 equiv.) (to produce NHC IMes) and the well-known inactive $[RuCl_2(p\text{-cymene})]_2$ dimer (1 equiv.). It is recognized that the simple reaction of Ru precatalyst with the imidazolidene ligand IMes is a means to generate *in situ* the highly active ruthenium-arene complex $RuCl_2(p\text{-cymene})$(NHC), also known as Noels' catalyst. Irradiation is performed in a conventional photochemical reactor (λ_{max} = 365 nm) at room temperature. Complete conversion is achieved after only 10 min of irradiation as measured by ^{1}H NMR spectroscopy (**Figure 6**), suggesting successful formation of the highly active ruthenium-arene complex bearing an NHC ligand. In addition, polyNb [with a number-average molecular weight of 288 kDa and relatively narrow dispersity values ($Đ$ = 1.5)] is obtained as determined by size exclusion chromatography.

Step 3.2 describes a miniemulsion photoROMP procedure. High conversions (70-80%) are achieved (**Figure 7**). As can be seen in **Figure 8**, the initial droplet size measured by DLS is 92 nm. The final particles exhibit a size of 102 nm (0.140) close to the initial droplet size. TEM observations show perfectly spherical particles with sizes in agreement with DLS data.

FIGURE LEGENDS:

Figure 1: NMR characterization of $IMesH^+BPh_4^-$. (a) ^{1}H NMR spectrum in DMSO-d_6 (400 MHz)

of 1,3-dimesitylimidazolium tetraphenylborate ($IMesH^+BPh_4^-$), δ_{ppm} : 2.13 (s, 12H), 2.36 (s. 6H), 6.69 (t, 4H), 7.17 (m, 20H), 8.27 (s, 2H), 9.64 (s, 1H,); (b) ^{13}C NMR spectrum of the same compound in DMSO-d_6 (100 MHz), δ_{ppm} : 16.58, 20.23, 121.35, 124.49, 125.02, 129.24, 130.29, 134.00, 135.35, 138.19, 140.06, 162.58. T_m = 212 °C (DSC). This figure has been modified from a previous publication[9].

Figure 2: NMR monitoring of $IMesH^+BPh_4^-$ deprotonation and subsequent synthesis of IMes-CS_2. ^1H NMR spectra of $IMesH^+BPh_4^-$/ITX (2/1 equiv.) mixture in THF-d_8 (a) before UV exposure and (b) after 10 min irradiation at 365 nm (0.12 mW cm^{-2}) in a photochemical reactor; shown are (c) ^{13}C NMR spectra in DMSO-d_6 of the precipitate recovered after addition of CS_2. This figure has been modified from a previous publication[9].

Figure 3: Evidence for photolysis mechanism. Real-time photobleaching experiments in acetonitrile (irradiation: 365 nm, 63 mW cm^{-2}): ITX, and ITX with three different quenchers: $IMesH^+Cl^-$, $NaBPh_4$, and $IMesH^+BPh_4^-$. ITX: quencher molar ratio is 1:3. ([ITX] = 2.0×10^{-4} M).

Figure 4: Photomechanism pathway to IMes. Photolysis mechanism of the $IMesH^+BPh_4^-$/ITX tandem system.

Figure 5: Quantification of IMes amount released. (a) Change of UV-Vis spectra of an acetonitrile solution of $IMesH^+BPh_4^-$ (3.0×10^{-4} M) and ITX (1×10^{-4} M) irradiated for 2 min (LED, 365 nm, 65 mW cm^{-2}) upon gradual addition of PR (2×10^{-4} M); (b) titration plot showing the absorbance at 580 nm for the same solution irradiated at 1, 2, or 5 min as a function of PR (titrant) volume. The insert gives the yield of photogenerated NHCs deduced from the spectrophotometric titration curve. This figure has been modified from a previous publication[9].

Figure 6: PhotoROMP in solution. ^1H NMR spectrum in CD_2Cl_2 (400 MHz) of the photopolymerization reaction medium (a) before irradiation and (b) after 10 min irradiation at 365 nm.

Figure 7: Evolution of photoROMP in miniemulsion with time. Nb conversion as a function of irradiation time in miniemulsion photoROMP.

Figure 8: Characterization of polyNb particles. Shown are DLS data (top) of Nb miniemulsion and polyNb latex obtained after photopolymerization. TEM micrograph of final latex.

DISCUSSION:

Reported here is an easy and versatile protocol for the in-situ generation of NHC upon UV-irradiation at 365 nm. The anion exchange reaction between 1,3-dimesitylimidazolium chloride and sodium tetraphenylborate provides straightforward access to the NHC protected from $IMesH^+BPh_4^-$ in quantitative yield. Nevertheless, if using another starting imidazolium salt, the solvent employed to perform the metathesis reaction should be chosen with care so that it allows the solubilization of both starting salts (imidazolium salts and sodium tetraphenylborate) and the precipitation of the imidazolium tetraphenylborate product. As such, ethanol is often the most appropriate solvent to perform this reaction.

The photogeneration of the NHC IMes by irradiation at 365 nm of the 2 components system $IMesH^+BPh_4^-$/ITX can produce NHC yields up to 50%, but lower yields can be obtained depending on the experimental conditions employed. In particular, the use of solvents containing water or protic species favors secondary reactions such as the deprotonation of these protic species by BPh_4^- and/or the reprotonation of IMes, decreasing the overall yield of released IMes. Indeed, NHC are known to be sensitive to water and other impurity traces, so it is recommended to use dried solvents when attempting to photogenerate the NHC IMes. Despite their water/protic sensitivity, NHCs are much more reactive towards metallic substrates such as $[RuCl_2(p\text{-cymene})]_2$, which allows for the ROMP of Nb to be performed in miniemulsion. It has been noticed that the presence of dioxygen can also alter the course of the reaction. Indeed, dioxygen is known to react with ITX triplet, preventing the release of IMes. Because an electron transfer is involved during the generation of NHC, the reaction is also assumed to be highly dependent on solvent polarity. Finally, when attempting to photogenerate IMes from ITX/$IMesH^+BPH_4^-$ in a reaction media, the latter should be chosen to provide good solubilization of the $IMesH^+BPh_4^-$ salt and no absorption of UV light up to 350 nm.

As opposed to other methods that rely on temperature, dilution, or pH changes to generate *in situ* NHC, this approach involves radiation as the external stimulus, with a distinctive advantage being spatial/temporal control of the reaction. Thanks to manifold polymerization reactions catalyzed/initiated by NHC, we envision that a photolatent NHC can foster new photopolymerization reactions such as photoROMP as detailed in this study. In addition, because NHCs are well-established stabilizing ligands, we believe that the photochemical preparation of organometallic complexes may benefit from this photogenerating NHC system. Finally, because NHCs are employed as reactants or catalysts in many organic chemistry reactions, their photogeneration should be of interest to chemists who wish to involve NHCs in cascade reactions at specific times.

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DISCLOSURES:

The authors have nothing to disclose.

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Figure 1. NMR characterization of IMesH+BPh4-. (a) 1H NMR spectrum in DMSO-d6 (400 MHz) of 1,3-dimesitylimidazolium

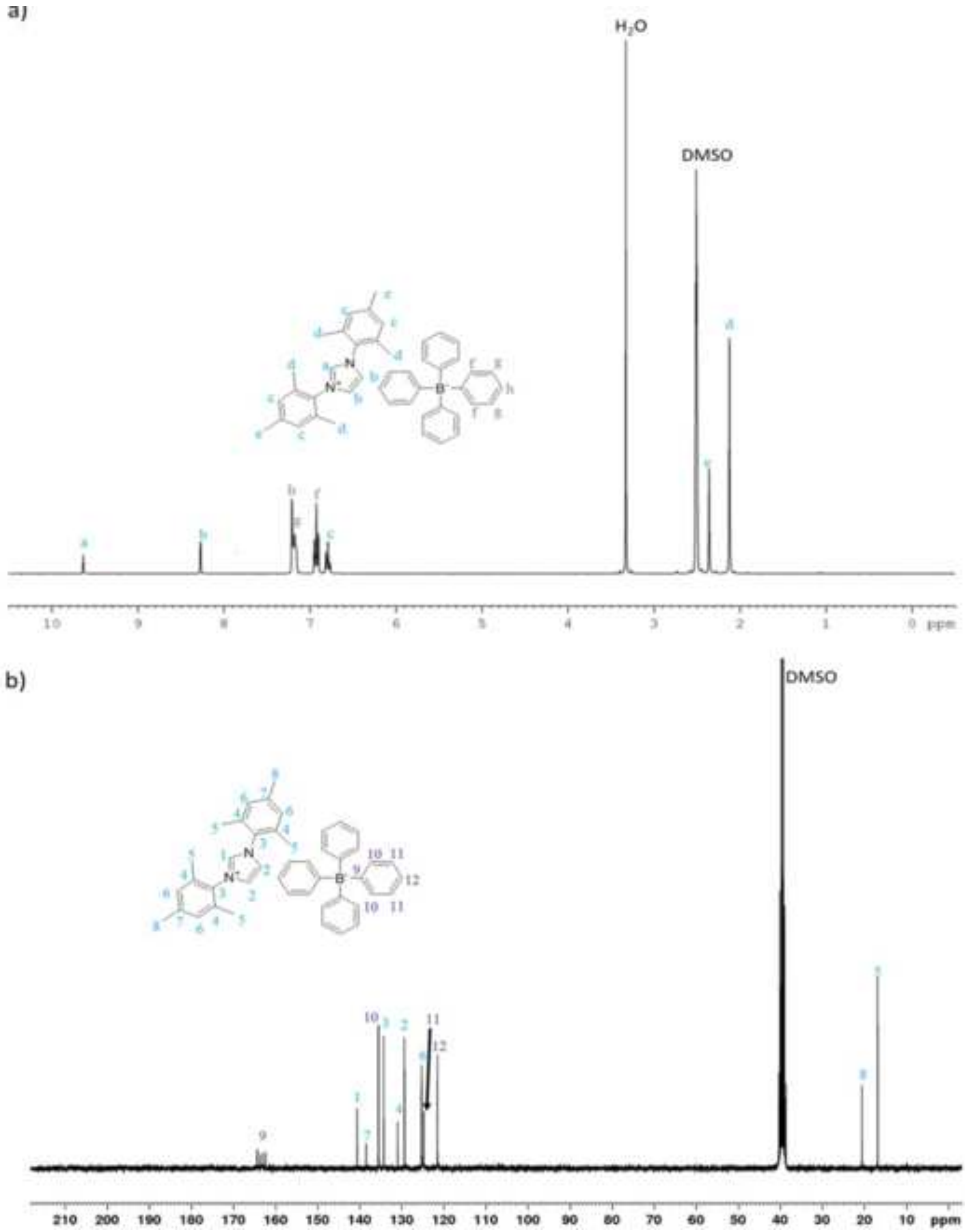

Figure 2. NMR monitoring of IMesH+BPh4- deprotonation and subsequent synthesis of IMes-CS2. 1H NMR spectra of

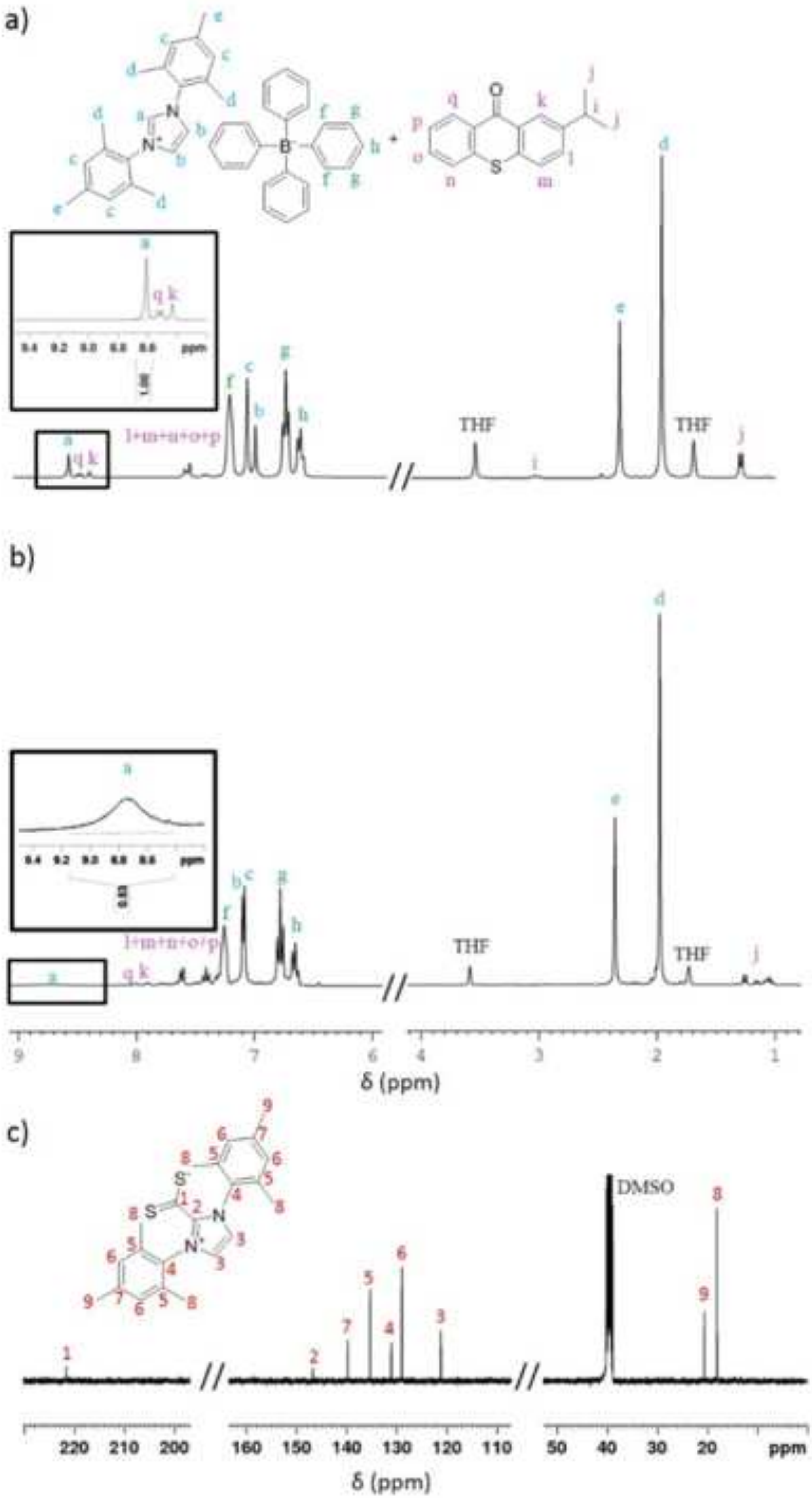

Figure 3. Evidence for photolysis mechanism. Real-time photobleaching experiments in acetonitrile (irradiation: 365 nm, 63 mW cm-2): ITX, and ITX with three different

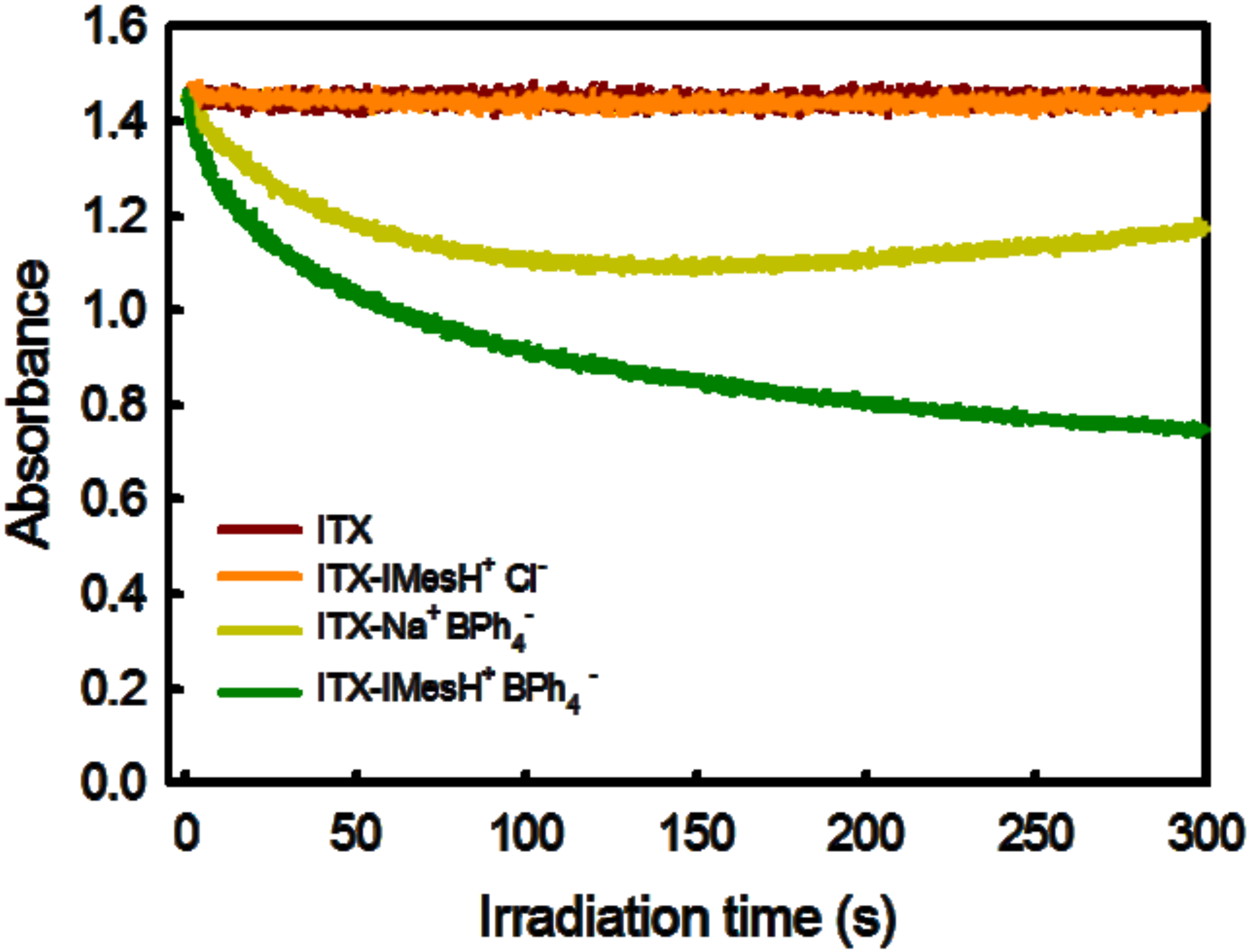

Figure 4. Photomechanism pathway to IMes. Photolysis mechanism of the IMesH+BPh4-/ITX tandem system.

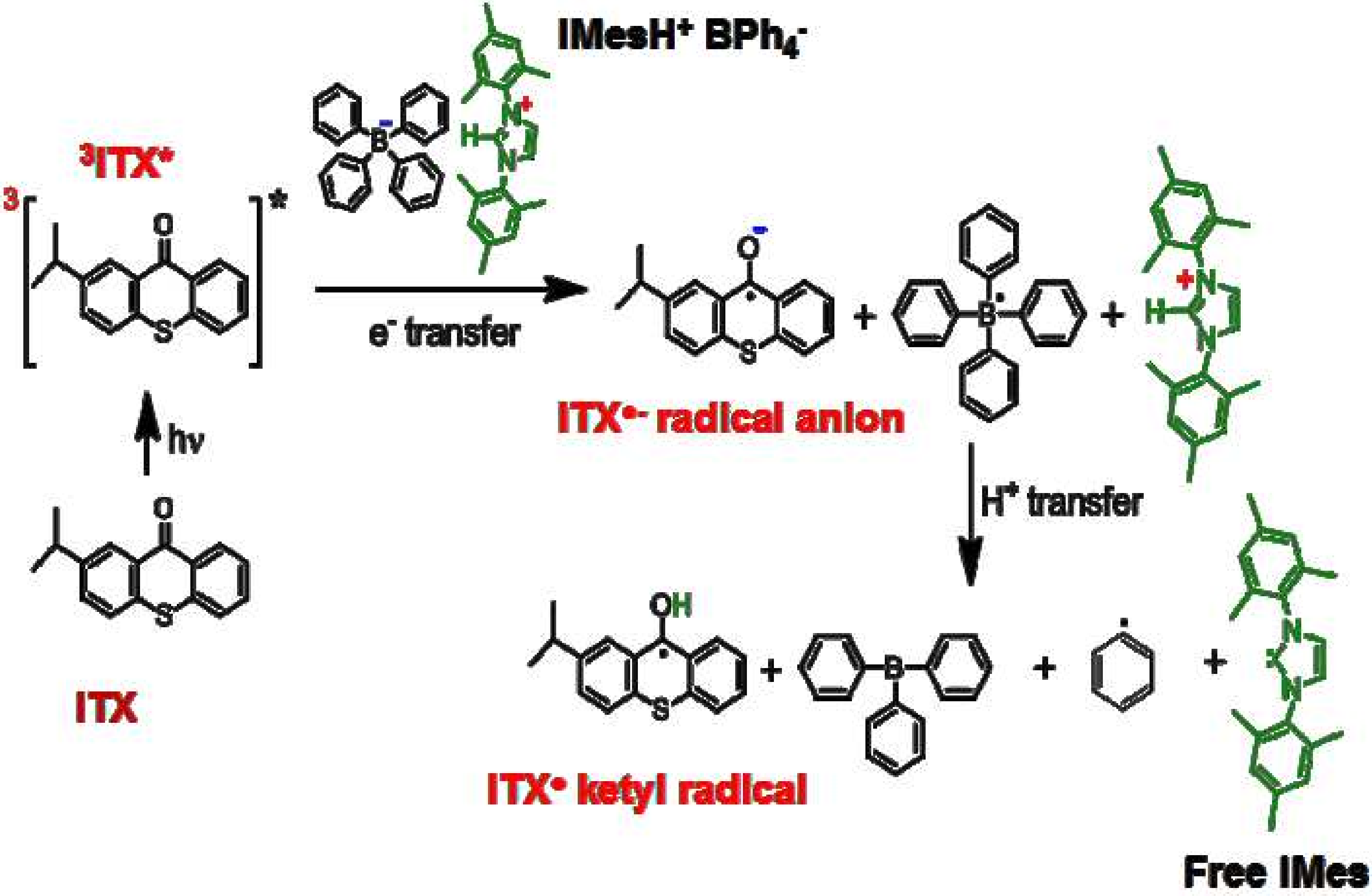

Figure 5. Quantification of IMes amount released. (a) Change of UV-Vis spectra of an acetonitrile solution of IMesH+BPh4- (3.0

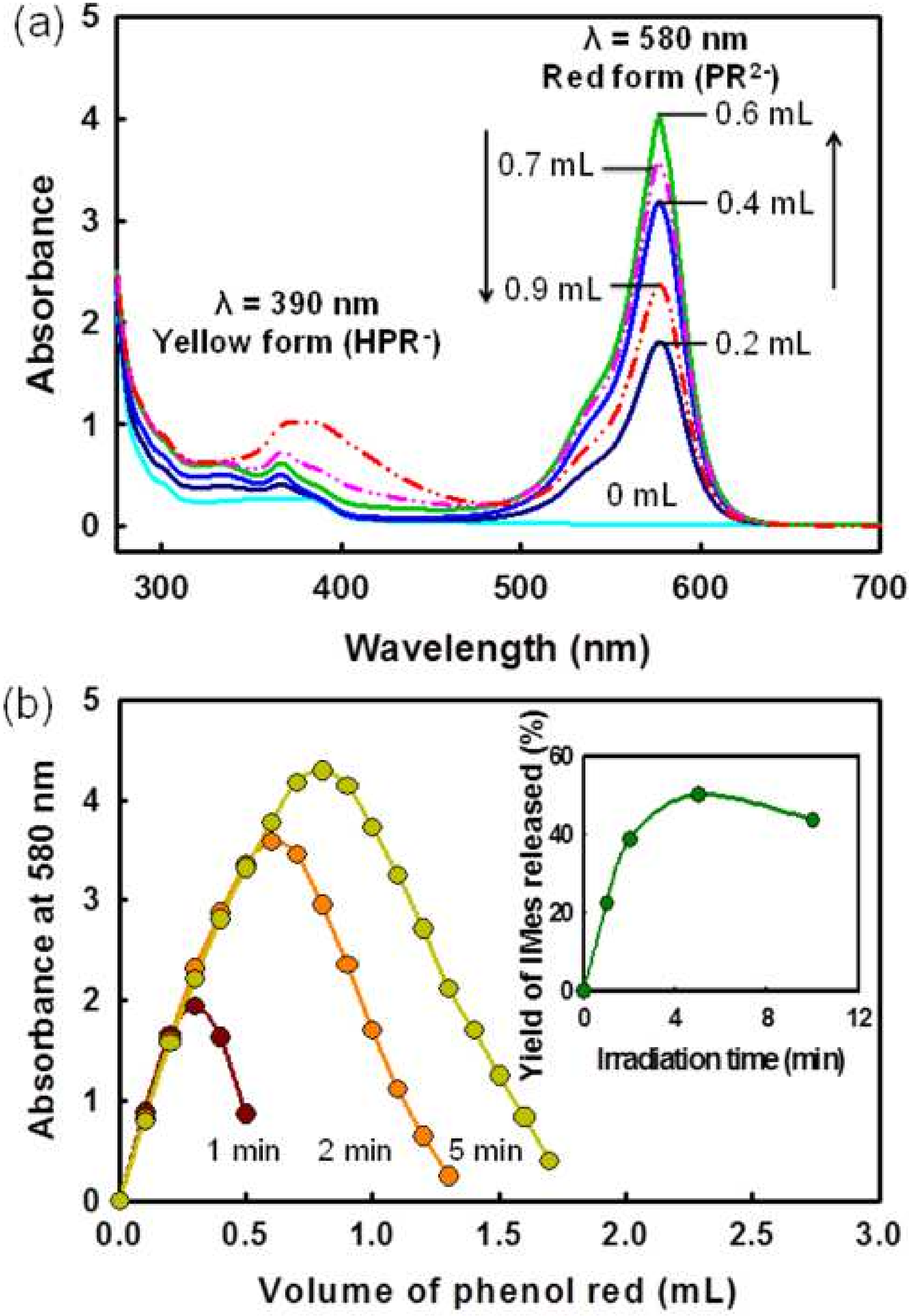

Figure 6. PhotoROMP in solution. 1H NMR spectrum in CD2Cl2 (400 MHz) of the photopolymerization reaction medium before

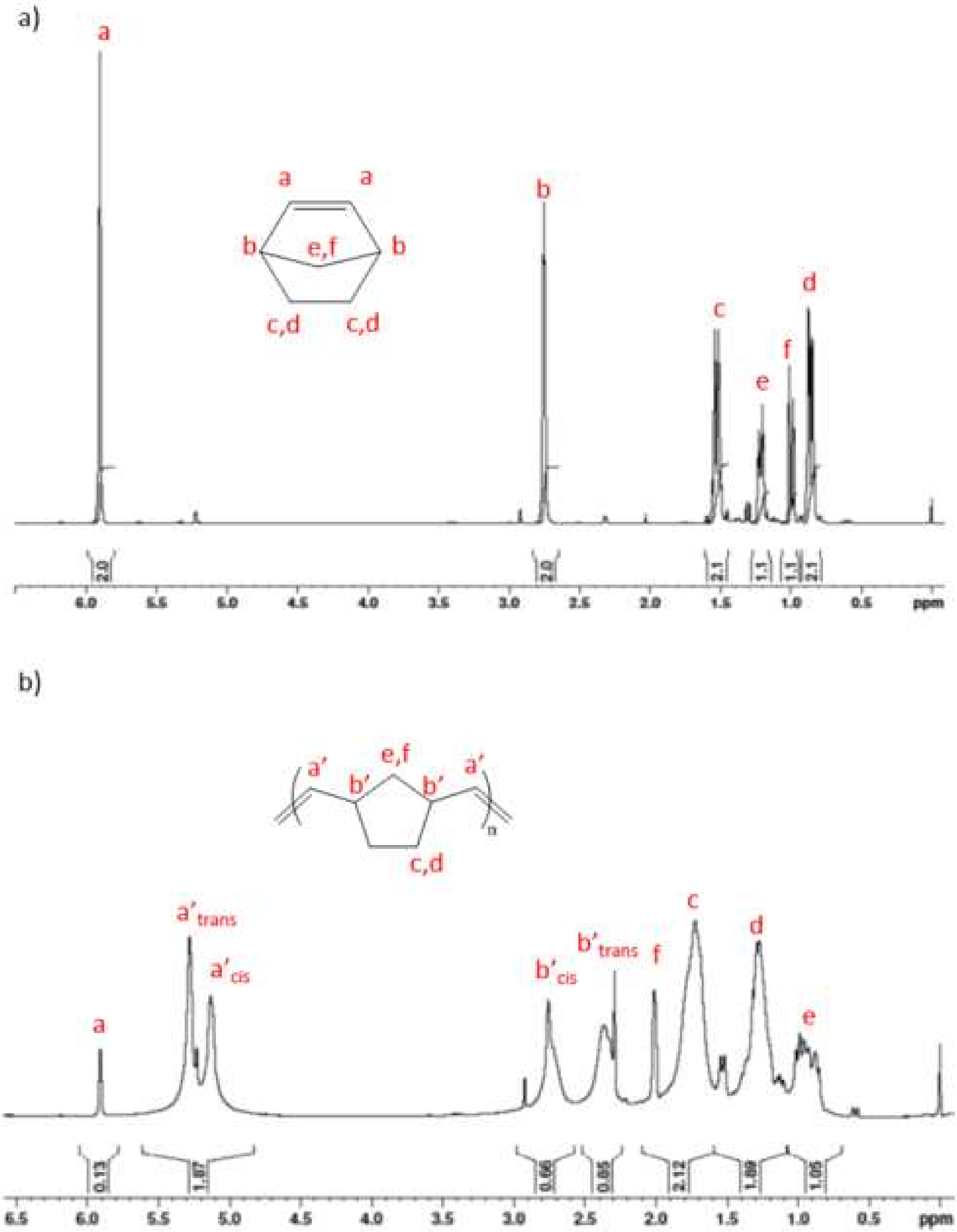

Figure 7. Evolution of photoROMP in miniemulsion with time. Nb conversion as a function of irradiation time in miniemulsion photoROMP.

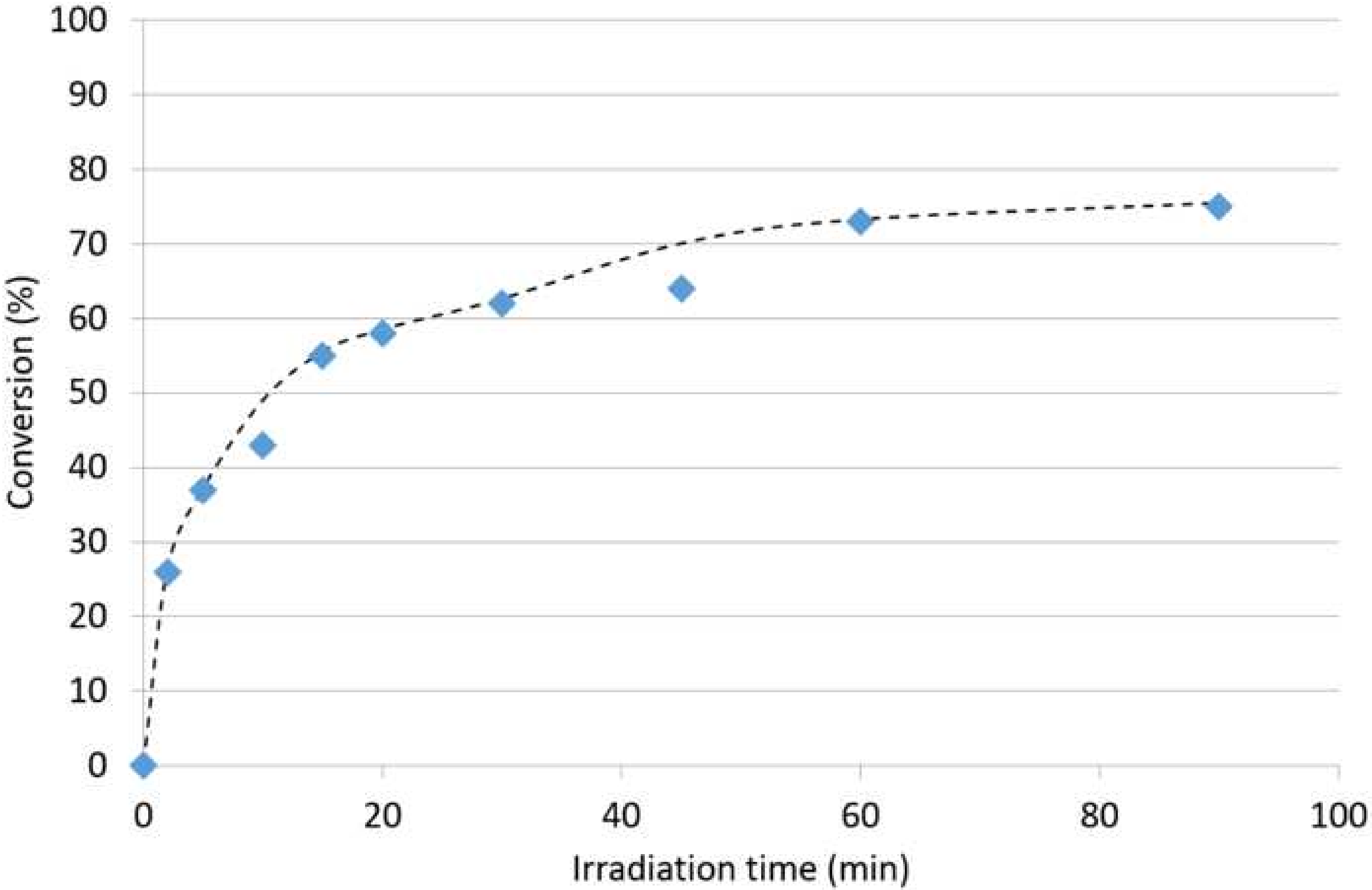

Figure 8. Characterization of polyNb particles. DLS data (top) of Nb miniemulsion and polyNb latex obtained after

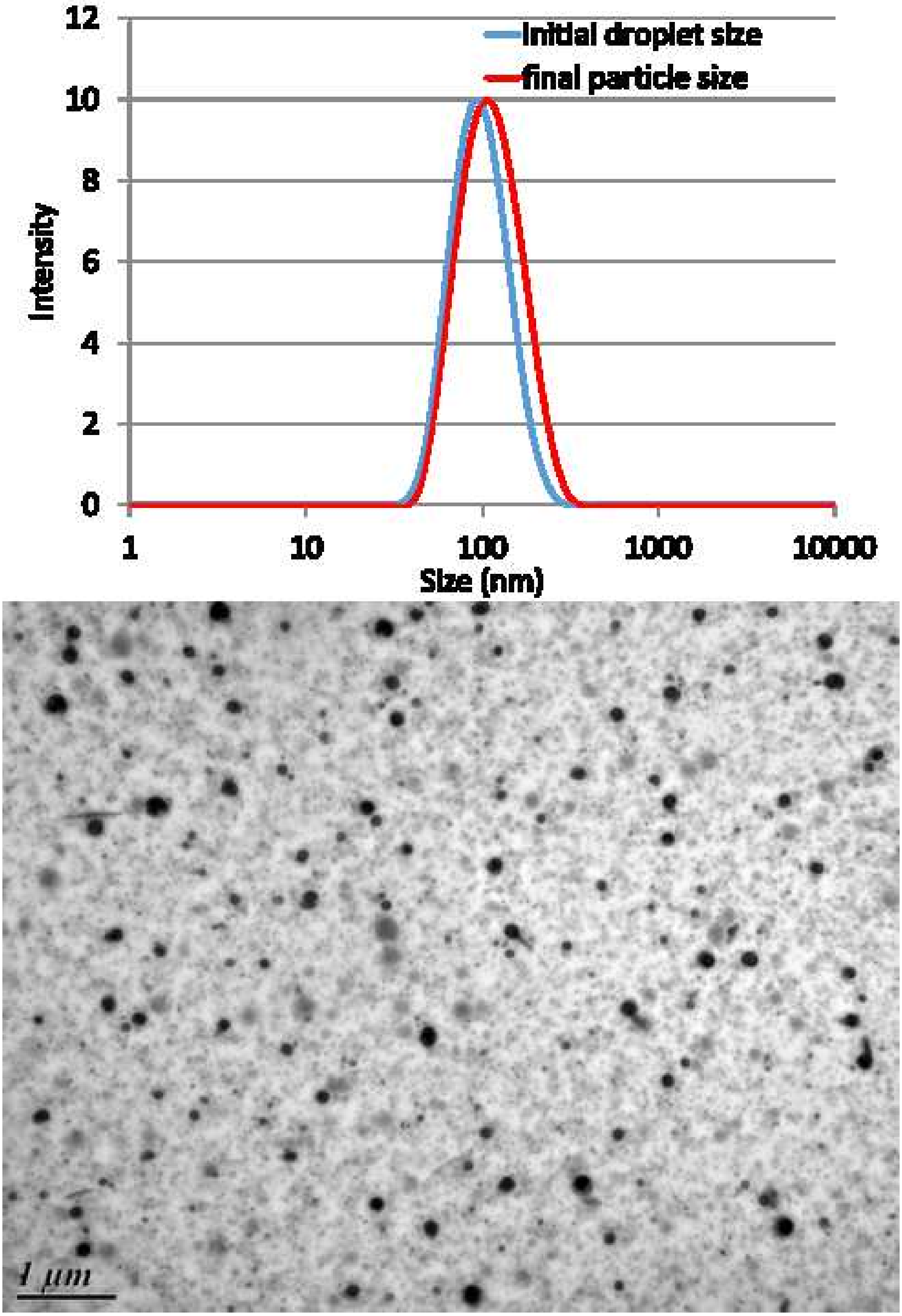

Table of Materials

Name of Material/ Equipment	Company	Catalog Number	Comments/Description
Material			
Dimesitylimidazolium chloride, 97%	ABCR	AB130859	
Sodium tetraphenylborate, 99%	ABCR	AB118843	
Dichloro(p-cymene) ruthenium dimer, 98%	ABCR	AB113524	
Norbornene, 99%	ABCR	AB171849	
Isopropythioxanthone, 97%	Sigma Aldrich	406317	
Carbon disulfide, 99.9%	Sigma Aldrich	335266	
Dichloromethane	Sigma Aldrich	270997	
Ethanol	VWR	20821.31	
Deuterated DMSO	Eurisotop	D010FE	
Deuterated THF	Eurisotop	D149CB	
1,2-Dichloroethane	Sigma Aldrich	284505	
Brij S 100	Sigma Aldrich	466387	
Hexadecane	Sigma Aldrich	H6703	
Phenol red, 98%	Sigma Aldrich	P4633	
Acetonitrile	VWR	83639.290	
1,3-Bis(mesityl)imidazol-2-ylidene, 97%	Sigma Aldrich	696188	
Equipment			
Rayonet photochemical reactor	Southern New England Ultraviolet Company	RPR-200	
UV lamps for photochemical reactor	Southern New England Ultraviolet Company	RPR-3500A	
^{1}H and ^{13}C NMR spectrometer	Bruker	Avance III HD spectrometer	
Sonication probe	BioBlock	Vibra-cell	
Gas chromatography	Varian	GC3900	
LED Lamp and Photo-cabinet	Peschl ultraviolet	novaLIGHT TLED100-365	
Dynamic Light Scattering	Malvern	zetasizer Nano ZS	

365 nm UV-LED light source coupled with a flexible light-guide	Hamamastu	LC-L1V3
UV/vis spectrometer	Perkin Elmer	Lambda 35
Hg- Xe lamp with filter centred at 365 nm	Hamamastu	LC-9588/01A
Radiometer	Ocean Optics	USB4000

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TITLE:

Photogeneration of N-Heterocyclic Carbenes: Application in Photoinduced Ring-Opening Metathesis Polymerization

AUTHORS AND AFFILIATIONS: Julien Pinaud,*[1] Emeline Placet,[1] Patrick Lacroix-Desmazes,[1] Thi Kim Hoang Trinh,[2,3] Jean Pierre Malval,[2,3] Abraham Chemtob,[2,3] Loïc Pichavant,[4] Valérie Héroguez[4]
[1] Université de Montpellier, CNRS, ICGM UMR5253 ENSCM, F-34095 Montpellier, France
[2] Université de Haute-Alsace, CNRS, IS2M UMR7361, F-68100 Mulhouse, France
[3] Université de Strasbourg, France
[4] Université de Bordeaux, CNRS, LCPO UMR5629 ENSCBP, F-33607 Pessac, France

Corresponding Author:
Julien Pinaud
julien.pinaud@umontpellier.fr
Tel: 33 (0)4 67 14 39 99

Email Addresses of Co-authors:

Emeline Placet	emeline.placet@enscm.fr
Patrick Lacroix-Desmazes	patrick.lacroix-desmazes@enscm.fr
Thi Kim Hoang Trinh	thi-kim-hoang.trinh@uha.fr
Jean Pierre Malval	jean-pierre.malval@uha.fr
Abraham Chemtob	abraham.chemtob@uha.fr
Loïc Pichavant	loic.pichavant@enscbp.fr
Valérie Héroguez	valerie.heroguez@enscbp.fr

KEYWORDS:
polymer, ring-opening, metathesis, ROMP, carbene, NHC, photochemistry, miniemulsion, photolysis, photoreactor, photoreactivity

SUMMARY:

We describe a protocol to photogenerate N-heterocyclic carbenes (NHCs) by UV irradiation of a 2-isopropylthioxanthone/imidazolium tetraphenylborate salt system. Methods to characterize the photoreleased NHC and elucidate the photochemical mechanism are proposed. Protocols for ring-opening metathesis photopolymerization in solution and miniemulsion illustrate the potential of this 2-component NHC photogenerating system.

ABSTRACT:

We report a method to generate the N-heterocyclic carbene (NHC) 1,3-dimesitylimidazol-2-ylidene (IMes) under UV-irradiation at 365 nm, to characterize it and to determine the corresponding photochemical mechanism. Then we describe protocols to perform ring-opening metathesis polymerization (ROMP) in solution and in miniemulsion using this NHC-photogenerating system. To photogenerate the NHC IMes, a system comprising 2-isopropylthioxanthone (ITX) as photosensitizer and 1,3-dimesitylimidazolium tetraphenylborate ($IMesH^+BPh_4^-$) as NHC protected form is employed. $IMesH^+BPh_4^-$ can be obtained in a single step by anion exchange between 1,3-dimesitylimidazolium chloride and sodium tetraphenylborate. A real-time steady-state photolysis set up is described, which hints that the photochemical reaction proceeds in two consecutive steps: ITX triplet is photoreduced by the borate anion, subsequent proton transfer takes place from the imidazolium cation to produce the expected NHC IMes. Two separate characterization protocols are implemented: firstly, CS_2 is added to the reaction media to evidence the photogeneration of NHC through the formation of the IMes-CS_2 adduct, and secondly, amount of NHC released *in situ* is quantified using acid-base titration. The use of this NHC photogenerating system for the ROMP of norbornene is also commented on. In solution, a photopolymerization experiment is conducted by mixing ITX, $IMesH^+BPh_4^-$, $[RuCl_2(p\text{-}cymene)]_2$ and norbornene in CH_2Cl_2 and by irradiating the solution in a UV reactor. In dispersed medium, a monomer miniemulsion is first formed, then irradiated inside an annular reactor to produce a stable poly(norbornene) latex.

INTRODUCTION:

In chemistry, N-Heterocyclic Carbenes (NHCs) species fulfill the twofold role of *ligand* and *organocatalyst*[1]. In the former case, the introduction of NHCs has resulted in the design of metal transition catalysts with improved activity and stability[2]. In the latter case, NHCs have proved to be superior catalysts for manifold organic reactions[3, 4]. Despite this versatility, handling of bare NHCs is still a significant challenge[5] and producing these highly reactive compounds in a way that they could be released *in situ* and “on demand” is a very attractive goal. Consequently, several strategies have been developed to release NHC in the reaction media, which mostly rely on the use of thermolabile progenitors[6–8]. Surprisingly, while it would unleash a novel generation of photoinitiated reactions useful for macromolecular synthesis or preparative organic chemistry[6], their generation using light as stimulus has been scarcely explored. Only very recently, a first photogenerating system able to produce NHC has been unveiled[9]. It consists of 2 components: 2-isopropylthioxanthone (ITX) as photosensitive species and 1,3-dimesitylimidazolium tetraphenylborate ($IMesH^+BPh_4^-$) acting as NHC protected form. Consequently, in the following paragraphs, we report a method to generate the N-heterocyclic carbene (NHC) 1,3-dimesitylimidazol-2-ylidene (IMes) under UV-irradiation at 365 nm, to characterize it and to determine the photochemical mechanism associated with. Then we describe protocols to perform ring-opening metathesis polymerization (ROMP) in solution and in miniemulsion using this NHC photogenerating system.

In a first part, we report herein a synthesis protocol to produce $IMesH^+BPh_4^-$. This protocol is based on anion metathesis between the corresponding imidazolium chloride ($IMesH^+Cl^-$) and sodium tetraphenylborate ($NaBPh_4$). Then, to demonstrate the *in situ* formation of NHC, two protocols have been developed involving the irradiation at 365 nm of a $IMesH^+BPh_4^-$/ITX solution in a photoreactor. The first one consists in monitoring the deprotonation of the imidazolium cation $IMesH^+$ through ^1H NMR spectroscopy. Direct evidence for the formation of the desired NHC (IMes) is provided in a second experiment where the adduct IMes-CS_2 is successfully isolated, purified and characterized.

The second section describes two protocols to shed light onto the photochemical mechanism involving the NHC two-component photogenerating system: $IMesH^+BPh_4^-$/ITX. Firstly, an original real-time steady state photolysis experiment reveals that electron transfer is induced by photo-excitation of ITX in the presence of tetraphenylborate. Electron donor properties of this borate anion[10] drives a photoreduction of $^3ITX^*$ triplet excited state into $ITX^{\bullet-}$ radical anion in a so-called photo-sensitized reaction. The formation of NHC confirms that ITX$^{\bullet-}$ species may further abstract a proton from IMesH$^+$ to produce the desired NHC. Based on acid/base titration using phenol red pH indicator as titrant, a second original protocol is implemented which allows the determination of the yield of released NHC.

In the third section, we describe protocols where the above-mentioned photogenerated IMes can be exploited in photopolymerization. Of primary interest is ring-opening metathesis polymerization (ROMP) because this reaction is still at a very preliminary stage of development with regard to photoinitiation[11, 12]. Initially limited to ill-defined and highly sensitive tungsten complexes, photoinduced ROMP (photoROMP) has been extended to more stable complexes based on W, Ru and Os transition metals. Despite the variety of precatalysts, almost all photoROMP processes rely on the direct excitation of a single photoactive precatalyst[13]. By contrast, we use radiation to create the NHC imidazolidene ligand (IMes), which can react subsequently with a non-photoactive Ru precatalyst [$RuCl_2$(*p*-cymene)]$_2$ dimer[9]. In our process, the photogeneration of NHC ligand drives the *in situ* formation of a highly active ruthenium-arene NHC complex: $RuCl_2$(*p*-cymene)(IMes) (Noels' catalyst)[14, 15]. Using this indirect methodology, two distinct photoROMP experiments of norbornene (Nb) are performed: in solution (dichloromethane) and in aqueous dispersed system from a monomer miniemulsion[16].

PROTOCOL:

1. NHC PHOTOGENERATING SYSTEM: SYNTHESIS AND REACTIVITY

1.1 Synthesis of 1,3-dimesitylimidazolium tetraphenylborate (IMesH$^+$BPh$_4^-$)

1.1.1 Preparation of the solution of 1,3-dimesitylimidazolium chloride (IMesH$^+$Cl$^-$) in ethanol.

1.1.1.1 Add 1.00 g (2.93 mmol) of 1,3-dimesitylimidazolium chloride to a 50 mL round bottom flask equipped with a stir bar.

1.1.1.2 Dissolve the 1,3-dimesitylimidazolium chloride in 30 mL of ethanol.

1.1.2 Preparation of the solution of sodium tetraphenylborate ($NaBPh_4$) in ethanol.

1.1.2.1 Add 1.35 g (3.92 mmol) of sodium tetraphenylborate to a 50 mL round bottom flask equipped with a stir bar.

1.1.2.2 Dissolve the sodium tetraphenylborate in 30 ml of ethanol.

1.1.3 Generation of 1,3-dimesitylimidazolium tetraphenylborate (IMesH$^+$BPh$_4^-$)

1.1.3.1 Add dropwise the solution of sodium tetraphenylborate into the solution of 1,3-dimesitylimidazolium chloride under stirring.

1.1.3.2 Stir the reaction mixture for 10 min at room temperature.

1.1.3.3 Remove the stir bar and filter the white precipitate using vacuum and a fritted glass filter of pore size 3.

1.1.3.4 Wash the precipitate with 30 mL of ethanol and filter it (fritted glass filter pore size 3).

1.1.3.5 Wash the precipitate with 30 mL of deionized water and filter it (fritted glass filter pore size 3).

1.1.3.6 Dry the white precipitate at 60 °C for 15 h.

1.1.3.7 Analyze the product by ^{1}H and ^{13}C NMR in DMSO-d_6 according to reported procedure[9].

1.2 Photogeneration of NHC 1,3-dimesitylimidazol-2-ylidene, also known as IMes, by UV irradiation of the dimesitylimidazolium tetraphenylborate in the presence of isopropylthioxanthone (ITX)

1.2.1 Add 39 mg (0.062 mmol, 2 equiv.) of 1,3-dimesitylimidazolium tetraphenylborate, 7.8 mg (0.031 mmol, 1 equiv.) of ITX and 0.5 mL of deuterated THF (previously stored over 3Å molecular sieves) in an NMR tube.

1.2.2 Place the NMR tube inside the photochemical reactor equipped with a circular array of 16 fluorescent tubes emitting a monochromatic radiation at 365 nm and irradiate for 10 min.

1.3 Monitoring of deprotonation of $IMesH^+BPh_4^-$ by ^{1}H NMR spectroscopy.

1.3.1 Analyze the deprotonation of $IMesH^+$ into IMes by ^{1}H NMR.

NOTE: ^{1}H NMR spectra were recorded at 25 °C on a NMR spectrometer operating at 400 MHz. TMS was used as internal standards for calibrating the chemical shifts in ^{1}H NMR.

1.3.1.1 Calibrate the integration parameters so that in the ^{1}H NMR spectra the CH_3 singlet of 1,3-dimesitylimidazolium tetraphenylborate ($\delta = 2.0$ ppm) corresponds to six.

1.2.3.2 Determine the integration value of the N-C*H*-N signal area ($\delta = 8.4 – 9.4$ ppm) in order to evaluate the degree of $IMesH^+$ deprotonation. The integration value should vary from 1 when no deprotonation occurred (before irradiation) to 0 when complete deprotonation of $IMesH^+$ has been performed.

1.4 Formation, isolation and characterization of the 1,3-dimesitylimidazoliumdithiocarboxylate adduct (IMes-CS_2)

1.4.1 Add 0.02 mL of carbon disulfide in the as-irradiated NMR tube. The reaction media changes color from orange/brown to dark red indicating the formation of the IMes-CS_2 adduct.

1.4.2 Let react for 12 h. A red precipitate forms assigned to the IMes-CS_2 adduct.

1.4.3 Filter the red precipitate (fritted glass filter of pore size 3) and dry it under air at room temperature for 12 h.

1.4.4 Solubilize the red solid in 0.5 mL of deuterated DMSO. Confirm the chemical structure by ^1H and ^{13}C NMR spectroscopy.

CAUTION: Carbon disulfide is highly toxic and should be handled with care under a fume hood.

2. PHOTOCHEMICAL MECHANISM

2.1 Real-time photobleaching of $IMesH^+BPh_4^-$ / ITX

2.1.1 Prepare a stock solution of ITX by adding 0.76 mg (3 x 10^{-3} mmol) of ITX to 15 mL of dry acetonitrile (previously stored over 3Å molecular sieves).

2.1.2 Transfer 3 mL of ITX solution into a UV quartz cell covered with a rubber stopper containing 1.10 mg of $IMesH^+BPh_4^-$ (1.8 x 10^{-3} mmol) and a stirring micromagnet. The molar ratio ITX:$IMesH^+BPh_4^-$ is 1:3.

2.1.3 Degas the solution by bubbling nitrogen for 10 min, then irradiate the solution at 365 nm with a medium-pressure Hg-Xe lamp under continuous stirring (63 mW cm^{-2}, power 75 mW).

2.1.4 Monitor the change of UV-absorbance at 365 nm during irradiation by using a spectrometer after passing a transmitted actinide beam.

2.1.5 Apply the same procedure (steps 2.1.1 to 2.1.4) for other experiments replacing $IMesH^+BPh_4^-$ by other quenchers: $IMesH^+Cl^-$ (0.61 mg, 1.8 x 10^{-3} mmol) or $NaBPh_4$ (0.62 mg, 1.8 x 10^{-3} mmol).

2.2 Quantification of photogenerated NHC by spectrophotometric titration

2.2.1 Add 1.85 mg of dimesitylimidazolium tetraphenylborate (3 x 10^{-4} mmol, 3 equiv.) and 0.25 mg of ITX (10^{-4} mmol, 1 equiv.) to 10 mL of dry acetonitrile.

2.2.2 Transfer 2 mL of this freshly prepared solution into a conventional spectroscopic quartz cell capped with a rubber septum.

2.2.3 Purge the colorless mixture with nitrogen before exposing the cuvette to a 365 nm LED spotlight (power 65 mW) for 1 min.

2.2.4 After each irradiation time, add gradually 0.1 mL portions of phenol red (PR) solution (2×10^{-4} M in dry acetonitrile) into the cuvette. This latter titrating solution was prepared in advance.

2.2.5 Record a UV-vis spectrum after each 0.1 mL addition of PR solution until 1 mL.

The indicator solution is initially transparent and contains the bis-protonated form H_2PR. After its addition, acid/base reaction with NHC causes the formation of the pink bivalent anion PR^{2-} with a maximum absorption at 580 nm. Plotting the absorbance at 580 nm as a function of the titrant volume gives two intersecting straight lines, indicative of the titration end-point.

2.2.6 Repeat the same operations (steps 2.2.1 to 2.2.5) with the same ITX/$IMesH^+BPh_4^-$ solution irradiated for longer times: 2 min, 5 min and 10 min. For each time, a new must be prepared.

At the equivalence point in the acid-base titration:

$$[\mathrm{IMes}] \times \mathrm{V} = 2[\mathrm{PR}] \times \mathrm{V_{eq}} \qquad (1)$$

where $[\mathrm{IMes}]$ is the concentration of photogenerated IMes released in the UV cuvette, V is the initial volume of $IMesH^+BPh_4^-$ / ITX solution, [PR] is the concentration of PR and $\mathrm{V_{eq}}$ is the total volume of PR added into the UV cuvette at the titration end-point. Therefore, the yield of IMes released upon irradiation of $IMesH^+BPh_4^-$ /ITX solution was obtained from equation (2):

$$\mathrm{Yield}\ (\%) = \frac{2*[\mathrm{PR}]\times \mathrm{V_{eq}}}{[\mathrm{IMesH^+BPh_4^-}]\times \mathrm{V}} \times 100 \qquad (2)$$

where $[\mathrm{IMesH^+BPh_4^-}]$ is the initial concentration of $IMesH^+BPh_4^-$.

The validity of the method is checked by titrating a free IMes solution (1×10^{-4} M in acetonitrile) using a similar acetonitrile PR solution as titrant (2×10^{-4} M).

3. PHOTOINDUCED RING-OPENING METATHESIS POLYMERIZATION

3.1 PhotoROMP of Nb in solution

3.1.1 Add 1 g (11 mmol, 540 equiv.) of Nb, 120 mg (0.196 mmol, 10 equiv.) of 1,3-dimesitylimidazolium tetraphenylborate, 12 mg (19.6 mmol, 1 equiv.) of dichloro(para-cymene)ruthenium dimer and 25 mg (0.098 mmol, 5 equiv.) of ITX in a 20 mL test tube equipped with a stir bar.

3.1.2 Dissolve the solids in 10 mL dichloromethane and cap the tube with a rubber septum.

3.1.3 Purge the mixture by bubbling nitrogen gas through a syringe needle for 15 min.

3.1.4 Place the tube inside the photochemical reactor equipped with a circular array of 16 fluorescent lamps (emitting at 365 nm) and irradiate for 10 min. The solution becomes viscous indicating that high-molecular weight polyNb is formed.

3.1.5 Precipitate the polymer by pouring the solution into 300 ml of methanol.

3.1.6 Filter the polymer (fritted glass filter pore size 3) and dry it at 60°C for 8h.

3.1.7 Analyze the polymer by ^{1}H NMR according to reported procedure[9] by dissolving about 10 mg of polymer in 0.5 ml of CD_2Cl_2.

3.1.8 Analyze the polymer by size exclusion chromatography according to reported procedure[9], using THF as eluent and by dissolving 10 mg of polymer in 1 mL of THF.

3.2. PhotoROMP of Nb in miniemulsion

3.2.1 Preparation of Nb miniemulsion:

3.2.1.1 Dissolve 15.0 g of neutral surfactant Polyoxyethylene (100) stearyl ether in 150 mL of milliQ water

3.2.1.2 Introduce the aqueous phase in the annular LED photoreactor closed with rubber septum and place the reactor under the airtight sonication probe.

3.2.1.3 Degas the solution by bubbling nitrogen during 1 h.

3.2.1.4 Mix 4.94 g of Nb (5.2 10^{-2} mol; 510 equiv.; 25 w-%), 2.85 mL of hexadecane (10 w-%) and 6 mL of dichloroethane (32.5 w-%) in a 50 mL round bottom flask closed with a rotaflo and degas the solution with freeze-pump-thaw cycle.

3.2.1.5 Add 6 mL of dichloroethane (32.5 w-%) in a second 50 mL round-bottom flask closed with a rotaflo. Degas the solution by Freeze-pump-thaw. Add 162 mg of 1,3-dimesitylimidazolium tetraphenylborate (2.6 10^{-4} mol, 5 equiv.), 33 mg of ITX (1.3 10^{-4} mol, 2.5 equiv.) and 30 mg of dichloro(p-cymene)ruthenium(II) dimer (4.9 10^{-5} mol, 1 equiv.) under inert atmosphere (glovebox) to the flask.

3.2.1.6 Mix the two organic solutions containing the monomer and the catalytic mixture under a nitrogen flux and introduce 15 g of the final organic solution inside the photoreactor containing the aqueous phase under stirring.

3.2.1.7. Stir the two phases during 1 h to form a rough macroemulsion.

3.2.1.8. Sonicate during 10 min (Power 50%; pulse-on time: 5 s, off-time: 5 s) to form the miniemulsion.

3.2.2. Photopolymerization of NB miniemulsion

3.2.2.1 Replace the airtight sonication probe by the LED lamp equipped with a water cooling system and protected by a cladding tube under a nitrogen flux.

3.2.2.2 Place the closed reactor inside the photocabinet to prevent exposure to UV radiation.

3.2.2.3 Irradiate the monomer miniemulsion for 100 min in order to obtain polymer latex. During irradiation, particle size and monomer conversion can be determined as explained below.

3.2.3 Determination of particle size, conversion and molecular weight

3.2.3.1 Collect 4 mL of miniemulsion sample during irradiation process.

3.2.3.2 Add 20 µL of miniemulsion in a glass cuvette containing 5 mL water to prepare a 250 times diluted sample for particle size analysis by dynamic light scattering (DLS).

3.2.3.3 Dissolve 100 µL of miniemulsion in 500 µL of THF to measure the Nb conversion by gas chromatography (GC) with hexadecane as internal standard (GC retention times: t^{GC}_{Nb} = 1.77 min; $t^{GC}_{dodecane}$ = 13.25 min).

3.2.3.4 Precipitate the rest of the sample in 20 mL of acetone. Filter the polymer. Dry the polymer under vacuum and measure the molecular weight by size exclusion chromatography (SEC) (SEC in tetrahydrofuran (THF) (1 mL min^{-1}) with trichlorobenzene as the flow marker, using both refractometric and UV detectors).

CAUTION (Part 1-3): Possibly hazardous sources of light emitting in the UV and visible range are used in the described experiments. These lamps can present a reasonably foreseeable risk of harming the eyes and skin of workers. Consequently, all measures possible should be put in place by the experimenter to reduce the risks to as low as is reasonably practicable. A list of common measures includes isolation of the light source inside a protective casing (photocabinet for example), training of all workers, placing the hazardous sources of light in well designated laboratories or fume hood with restricted access, providing suitable safety gears: safety goggles blocking UVA irradiation are sufficient for all described protocols and displaying appropriate warning and safety signs.

REPRESENTATIVE RESULTS:

Protocol 1.1 describes the efficient anion metathesis between 1,3-dimesitylimidazolium chloride ($IMesH^+Cl^-$) and sodium tetraphenylborate ($NaBPh_4$) to yield 1,3-dimesitylimidazolium tetraphenylborate ($IMesH^+BPh_4^-$). The desired photolatent NHC is obtained in excellent yield (98 %). Figure 1 shows a ^1H and ^{13}C NMR spectra, both testifying that a pure product exhibiting the correct structure is obtained.

Protocol 1.2 describes how to generate the N-HC IMes by irradiating the mixture $IMesH^+BPh_4^-$ / ITX (2/1 equiv.) in THF-d_8 solution.

Protocol 1.3 shows that it is possible to assess the conversion of $IMesH^+$ in IMes by monitoring the deprotonation of $IMesH^+BPh_4^-$ through ^1H NMR spectroscopy. Figure 2 shows that proton H_a (8.63 ppm, Figure 2a) on carbon 2 adjacent to the two nitrogen atoms disappears partially after 10 min irradiation (53 %, Figure 2b). The reaction was performed by irradiating the mixture $IMesH^+BPh_4^-$ / ITX (2/1 equiv.) in THF-d_8 solution.

Protocol 1.4 shows that it is possible to isolate the formed NHC by reacting the as-irradiated medium (see protocol 1.2) with CS_2. The red precipitate formed in THF-d_8 is collected, dried and dissolved in DMSO-d_6. As it can be seen in the ^{13}C NMR spectrum (Figure 2c), all the characteristic resonances are consistent with IMes-CS_2 adduct. This result confirms indirectly the *in situ* generation of the targeted IMes NHC.

Protocol 2.1 Thioxanthone derivatives are a well-established class of photoinitiators generally employed in combination with a second component referred to as "co-initiator". Their absorption spectra appear with a maximum in the range 340-420 nm. The nature of the co-initiator determines the mechanism of initiation. Three general initiation mechanisms have been described: ❶ Triplet-triplet energy transfer (in the present case from $^3ITX^*$ to $^3BPh_4^{-}{}^*$); ❷ electron transfer from the electron donor BPh_4^- to $^3ITX^*$; and, ❸ direct H abstraction of $IMesH^+$ by $^3ITX^*$. Mechanism ❶ can be discarded since the following triplet energy order, $E_T(BPh_4^-) > E_T(ITX)$ is established by conventional computational procedure. **Protocol 2.1** enables to evidence which of the two mechanisms ❷ or ❸ is operating. Figure 3 shows the evolution of absorbance values of characteristic ITX absorption band at 365 nm during irradiation for three different bicomponent mixtures: $IMesH^+BPh_4^-$ /ITX, $IMesH^+Cl^-$ /ITX and $NaBPh_4$/ITX. The absence of decay for $IMesH^+Cl^-$ supports the incapacity for electronically excited ITX to abstract a hydrogen from the imidazolium cation (mechanism ❸). In contrast, photobleaching of ITX is visible in the two systems containing the BPh_4^- anions although the decay rates are different in these two cases. This result emphasizes the critical role played by the tetraphenylborate anion. Consequently, the photoreduction of ITX by tetraphenylborate (mechanism ❷) is proved as the primary step in the formation of the NHC. **Figure 4** displays a hypothetical and complete mechanism where the $ITX^{\bullet-}$ radical anion may abstract a proton from $IMesH^+$ to release the free NHC IMes.

Protocol 2.2 shows evidence in favor of this mechanism. This method reveals the progressive release of NHC during irradiation. It is a method to determine the amount of released NHC based on acid/base titration using phenol red (PR) pH indicator as titrant. A maximum yield of 50 % is achieved after 5 min of irradiation (**Figure 5)** and control experiment with free IMes enables to validate the method.

Protocol 3.1 describes photoROMP of NB (540 equiv.) in dichloromethane using a photolatent mixture composed of $IMesH^+BPh_4^-$ /ITX (10/5 equiv.) (to produce NHC IMes) and the well-known inactive $[RuCl_2(p\text{-cymene})]_2$ dimer (1 equiv.). It is recognized that the simple reaction of Ru precatalyst with the imidazolidene ligand IMes is a means to generate *in situ* the highly active ruthenium-arene complex $RuCl_2(p\text{-cymene})(NHC)$, also known as Noels' catalyst. Irradiation is performed in a conventional photochemical reactor (λ_{max} = 365 nm) at room temperature. Complete conversion is achieved after only 10 min of irradiation as measured by ^1H NMR spectroscopy **(Figure 6)**, suggesting the successful formation of the highly active ruthenium-arene complex bearing an NHC ligand. In addition, polyNb with a number-average molecular weight of 288 kDa and a relatively narrow dispersity values ($Đ$ = 1.5) is obtained as determined by size exclusion chromatography.

Protocol 3.2 describes a miniemulsion photoROMP procedure. High conversions (70-80 %) are achieved (**Figure 7**). As can be seen in **Figure 8**, the initial droplet size measured by DLS is 92 nm. The final particles exhibit a size of 102 nm (0.140) closed to the initial droplet size. TEM observations show perfectly spherical particles with sizes in agreement with DLS data.

FIGURE LEGENDS:

Figure 1. NMR characterization of IMesH$^+$BPh$_4$$^-$. (a) ^{1}H NMR spectrum in DMSO-d_6 (400 MHz) of 1,3-dimesitylimidazolium tetraphenylborate (IMesH$^+$BPh$_4$$^-$), δ_{ppm} : 2.13 (s, 12H), 2.36 (s. 6H), 6.69 (t, 4H), 7.17 (m, 20H), 8.27 (s, 2H), 9.64 (s, 1H,); (b) ^{13}C NMR spectrum of the same compound in DMSO-d_6 (100 MHz), δ_{ppm} :16.58, 20.23, 121.35, 124.49, 125.02, 129.24, 130.29, 134.00, 135.35, 138.19, 140.06, 162.58. T_m = 212 °C (DSC). This figure has been modified from reference[9].

Figure 2. NMR monitoring of IMesH$^+$BPh$_4$$^-$ deprotonation and subsequent synthesis of IMes-CS$_2$. ^{1}H NMR spectra of IMesH$^+$BPh$_4$$^-$ /ITX (2/1 equiv.) mixture in THF-d_8: (a) before UV exposure, (b) after 10 min irradiation at 365 nm (0.12 mW cm^{-2}) in a photochemical reactor; (c) ^{13}C NMR spectra in DMSO-d_6 of the precipitate recovered after addition of CS$_2$. This figure has been modified from reference[9].

Figure 3. Evidence for photolysis mechanism. Real-time photobleaching experiments in acetonitrile (irradiation: 365 nm, 63 mW cm^{-2}): ITX, and ITX with three different quenchers: IMesH$^+$Cl$^-$, NaBPh$_4$ and IMesH$^+$BPh$_4$$^-$. ITX: quencher molar ratio is 1:3. ([ITX] = 2.0 10^{-4} M).

Figure 4. Photomechanism pathway to IMes. Photolysis mechanism of the IMesH$^+$BPh$_4$$^-$ /ITX tandem system.

Figure 5. Quantification of IMes amount released. (a) Change of UV-Vis spectra of an acetonitrile solution of IMesH$^+$BPh$_4$$^-$ (3.0×10^{-4} M) and ITX (1×10^{-4} M) irradiated during 2 min (LED, 365 nm, 65 mW cm^{-2}) upon gradual addition of PR (2×10^{-4} M), (b) Titration plot showing the absorbance at 580 nm for the same solution irradiated at 1, 2 or 5 min as a function of PR (titrant) volume. The insert gives the yield of photogenerated NHCs deduced from the spectrophotometric titration curve. This figure has been modified from reference[9].

Figure 6. PhotoROMP in solution. ^{1}H NMR spectrum in CD$_2$Cl$_2$ (400 MHz) of the photopolymerization reaction medium before irradiation (a) and after 10 min irradiation at 365 nm (b).

Figure 7. Evolution of photoROMP in miniemulsion with time. Nb conversion as a function of irradiation time in miniemulsion photoROMP.

Figure 8. Characterization of polyNb particles. DLS data (top) of Nb miniemulsion and polyNb latex obtained after photopolymerization. TEM micrograph of final latex.

DISCUSSION:

We have reported an easy and versatile protocol for the in-situ generation of NHC upon UV-irradiation at 365 nm. The anion exchange reaction between 1,3-dimesitylimidazolium chloride and sodium tetraphenylborate provides a straightforward access to the NHC protected form IMesH$^+$BPh$_4$$^-$ in quantitative yield. Nevertheless, if employing another starting imidazolium salt, the solvent employed to perform the metathesis reaction should be chosen with care so that it allows the solubilization of both starting salts (imidazolium salts and sodium tetraphenylborate) and the precipitation of the imidazolium tetraphenylborate product. As such, ethanol is most often the appropriate solvent to perform this reaction.

The photogeneration of the NHC IMes by irradiation at 365 nm of the 2 components system $IMesH^+BPh_4^-$/ITX can produce NHC yields up to 50 % but lower yields can be obtained depending on the experimental conditions employed. In particular, the use of solvents containing water or protic species favors secondary reactions such as the deprotonation of these protic species by BPh_4^- and/or the reprotonation of IMes, thus decreasing the overall yield of released IMes. Indeed, NHC are known to be sensitive to water and other impurity traces, we thus recommend using dried solvents when attempting to photogenerate the NHC IMes. Despite their water/protic sensitivity, NHCs are much more reactive towards metallic substrates such as $[RuCl_2(p\text{-cymene})]_2$, which allows for the ROMP of Nb to be performed in miniemulsion. It has been noticed that the presence of dioxygen can also alter the course of the reaction. Indeed, dioxygen is known to react with ITX triplet, preventing the release of IMes. Because an electron transfer is involved for the generation of NHC, the reaction is also assumed to be highly dependent on solvent polarity. Finally, when attempting at photogenerating IMes from ITX/$IMesH^+BPH_4^-$ in a reaction media, the latter should be chosen so that it provides a good solubilization of the $IMesH^+BPh_4^-$ salt and does not absorb UV light up to 350 nm.

As opposed to other methods that rely on temperature, dilution or change of pH to generate *in situ* NHC, our approach involves radiation as external stimulus with the distinctive advantage of spatial/temporal control of the reaction. Thanks to manifold polymerization reactions catalyzed/initiated by NHC, we envision that a photolatent NHC can foster new photopolymerization reactions such as photoROMP as detailed in this study. In addition, because NHCs are well established stabilizing ligands, we believe that the photochemical preparation of organometallic complexes may benefit from this photogenerating NHC system. Finally, NHCs are employed as reactants or catalysts in many reactions of organic chemistry, their photogeneration should be of interest to chemists who would like to involve NHCs in cascade reactions at the desired time.

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DISCLOSURES:

The authors have nothing to disclose.

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