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## Journal Pre-proofs

UV irradiation of Cu-based complexes with aliphatic amine ligands as used in living radical polymerization

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## UV irradiation of Cu-based complexes with aliphatic amine ligands as used in living radical polymerization

Evelina Liarou,<sup>\*a</sup> Michael Staniforth, James S. Town,<sup>a</sup> Arkadios Marathianos,<sup>a</sup> Maria Grypioti,<sup>a</sup> Yongguang Li,<sup>a</sup> Yujing Chang,<sup>a</sup> Spyridon Efstathiou,<sup>a</sup> Ellis Hancox,<sup>a</sup> Alan M. Wemyss,<sup>a</sup> Paul Wilson,<sup>a</sup> Bryn A. Jones,<sup>a</sup> Mohammed Aljuaid,<sup>a</sup> Vasilios G. Stavros<sup>a</sup> and David M. Haddleton<sup>\*a</sup>

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In honor of the 70<sup>th</sup> birthday of Professor Robin N. Perutz.

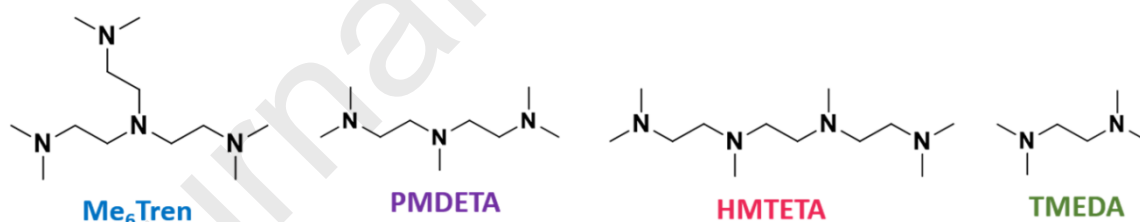
The effect UV irradiation on Cu(II)-based complexes with aliphatic amine ligands is investigated. Four aliphatic amines are used as ligands and Cu(II)Br<sub>2</sub> as the metal source for the formation of catalyst complexes that can be used for the photoinduced Cu-RDRP of methyl acrylate. Different characterization techniques such as transient electronic absorption spectroscopy (TEAS), ultraviolet-visible (UV-Vis) spectroscopy, electrospray ionization time of flight mass spectrometry (ESI-ToF-MS) and cyclic voltammetry (CV) are applied in order to provide insights into the catalyst behaviour upon photoirradiation. The excited-state dynamics, the electrochemical behaviour of the Cu(II)/Cu(I) redox couples and the detection of different species upon complexation of the ligand to the metal center (before and after UV irradiation) are further depicted in the quality of the obtained polymers.

### Introduction

Controlled/living radical polymerization of vinyl monomers (methacrylates, acrylates, acrylamides, styrene) has revolutionized the field of polymer science. Transition metal mediated/catalyzed methodologies were introduced in 1995 using low valent Ru(II)<sup>1</sup> and Cu(I)<sup>2</sup> complexes in conjunction with alkyl halides. Up until this point, ionic and ionic-related polymerisation were most successful requiring the use of very anhydrous conditions and pure reagents and solvents. The transition metal-based radical techniques such as Atom Transfer Radical Polymerization (ATRP)<sup>1, 2</sup> and Single Electron Transfer Living Radical Polymerization (SET-LRP),<sup>3-6</sup> emerged as powerful tools for the synthesis of numerous materials, with different architectures and functionalities, in a variety of media and under different conditions without the requirement of rigorously removing water and other protic impurities or the need for protecting groups for monomers containing such functionality.<sup>7-14</sup> These methods depend on an activation-deactivation equilibrium between active and dormant species, related to the transition metal complex ( $M^n X/L$ ) which activates an alkyl halide ( $P_n-X$ ) leading to  $M^{n+1} X_2/L$  and a  $P_n$  radical leading to chain growth.<sup>15-17</sup> As in other living polymerisations, the chain length is determined by the  $[monomer]/[R-X]$  with the  $\alpha$ -terminus derived from the initiator ( $R-X$ ) and the  $\omega$ -group of the halide. Initiation and propagation occur *via* reversible homolytic bond cleavage of the  $R-X$  bond and the low concentration of resulting radicals means chain termination *via* second order radical/radical reaction is minimised. This allows for the design and control of the transition metal complex through external stimuli such as electrochemical<sup>18</sup> and photochemical methods.<sup>17, 19, 20</sup>

The application of photochemistry in these systems offers numerous advantages such as mild reaction conditions, spatial and temporal control, is environmentally friendly and non-invasive and as a result it has been proved to be an excellent candidate for triggering organic reactions and polymerizations.<sup>21-32</sup> Hawker and colleagues, utilizing visible light and a photoactive iridium complex ( $fac-[Ir(ppy)_3]$  ( $ppy = 2$ -pyridylphenyl)), reported the synthesis of well-defined poly(methyl methacrylate) (PMMA) with spatiotemporal control.<sup>33, 34</sup> Yagci and co-workers reported the synthesis of PMMA applying different conditions, such as in the presence and absence of photoinitiators and photosensitizers, as well as different applied wavelengths.<sup>35-38</sup> Matyjaszewski and colleagues have reported the synthesis of acrylates and methacrylates by employing low loadings (parts per million) of copper catalyst under visible light, as well as in different media.<sup>22, 39</sup> Haddleton and colleagues have investigated the photoinduced Cu-mediated Reversible Deactivation Radical Polymerization (Cu-RDRP) of various acrylates utilizing excess of an aliphatic tertiary amine under UV irradiation reaching near-quantitative conversions at different molar masses.<sup>17</sup>

The versatility of these photo-regulated systems has led researchers to understand the mechanism of photoRDRP in an attempt to provide insights into the transition metal complex behaviour. The catalyst mainly consists of the transition metal (copper (Cu) in this current study) and the ligand(s) (herein aliphatic amines). Consequently, as the catalyst has a determining role on transferring the halogen and regulating the equilibrium between active and dormant species, the impact of photo-irradiation is important. Haddleton and co-workers reported that an excess of the aliphatic amine ligand (relative to  $\text{Cu(II)Br}_2$ ) is required so as to maintain excellent control over the polymerization by varying the composition of the catalyst ( $\text{Cu(II)Br}_2$  and tris[2-(dimethylamino)ethyl]amine ( $\text{Me}_6\text{Tren}$ ) as ligand) for the polymerization of acrylates.<sup>17</sup> UV-vis spectroscopy was applied to follow the polymerization and monitor the effect of UV irradiation on the components of the polymerization over time. They proposed that the photoexcitation of free  $\text{Me}_6\text{Tren}$  is responsible for the C-Br bond homolysis, which occurs through an outer-sphere single-electron transfer (OSET) when the alkyl halide initiator is present, with the occurring radical initiating the polymerization. Moreover, this OSET process results in  $\text{Me}_6\text{Tren}$  radical cations and Br anions that participate in the oxidation of the generated active species, into  $\text{Cu(II)Br}_2/\text{Me}_6\text{Tren}$ . Matyjaszewski's group investigated the mechanism of activation and radical regeneration in photoATRP by performing a series of experiments with several reaction conditions, and experimental and kinetic simulation techniques.<sup>40</sup> Based on their findings, the (re)generation of the activator occurs from the photochemical reduction of Cu(II) complexes when excess of the amine ligand is employed, with the latter getting oxidized to form a ligand-based radical cation, capable of initiating a new chain. Barner-Kowollik and colleagues investigated the initiation mechanism of photoRDRP utilizing pulsed-laser polymerization (PLP) and high resolution mass spectrometry, highlighting the important role of the ligand which acts as a reducing agent.<sup>41</sup> They demonstrated that upon UV irradiation, scission of the initiator's C-Br bond occurs which subsequently provides radicals that can propagate and also react with Cu(II) species. Upon UV irradiation, an electron transfer reaction takes place between the photoexcited ligand and Cu(II) moieties leading to the generation of Cu(I) species, and apart from that, it was proposed that the Cu(II) complex gets excited and subsequently quenched by the free ligand, generating the analogous Cu(I) complex and the ligand radical cation. All the aforementioned approaches highlight the importance of the excess ligand on photoinduced-RDRP and by utilizing different analytical (*i.e.* spectroscopic) techniques, interesting insights on the mechanism have been reported. However, a limited number of different ligands have been employed for these investigations, with  $\text{Me}_6\text{Tren}$  having been the most extensively studied ligand for photo-induced Cu-RDRP.



**Scheme 1.** Chemical structures of the aliphatic amines used as ligands in this investigation

Herein, the application of different characterization methods and analytical techniques including UV-Vis spectroscopy, ESI-ToF-MS and CV give insights into the effect of UV irradiation (broad band  $\lambda_{\text{max}} \sim 360$  nm) on the transition metal complex, when different aliphatic amines are employed as ligands (**Scheme 1**) and  $\text{Cu(II)Br}_2$  as the metal source. In order to investigate in depth the excited-state behaviour of these complexes, the  $[\text{Cu(II)(Me}_6\text{Tren)Br}_2]$  and the  $[\text{Cu(II)(PMDETA)Br}_2]$  complexes are studied through TEAS. Furthermore, the different catalytic complexes are employed for the photoinduced Cu-RDRP of methyl acrylate in organic media, leading to differences in the molecular characteristics of the obtained PMAs.

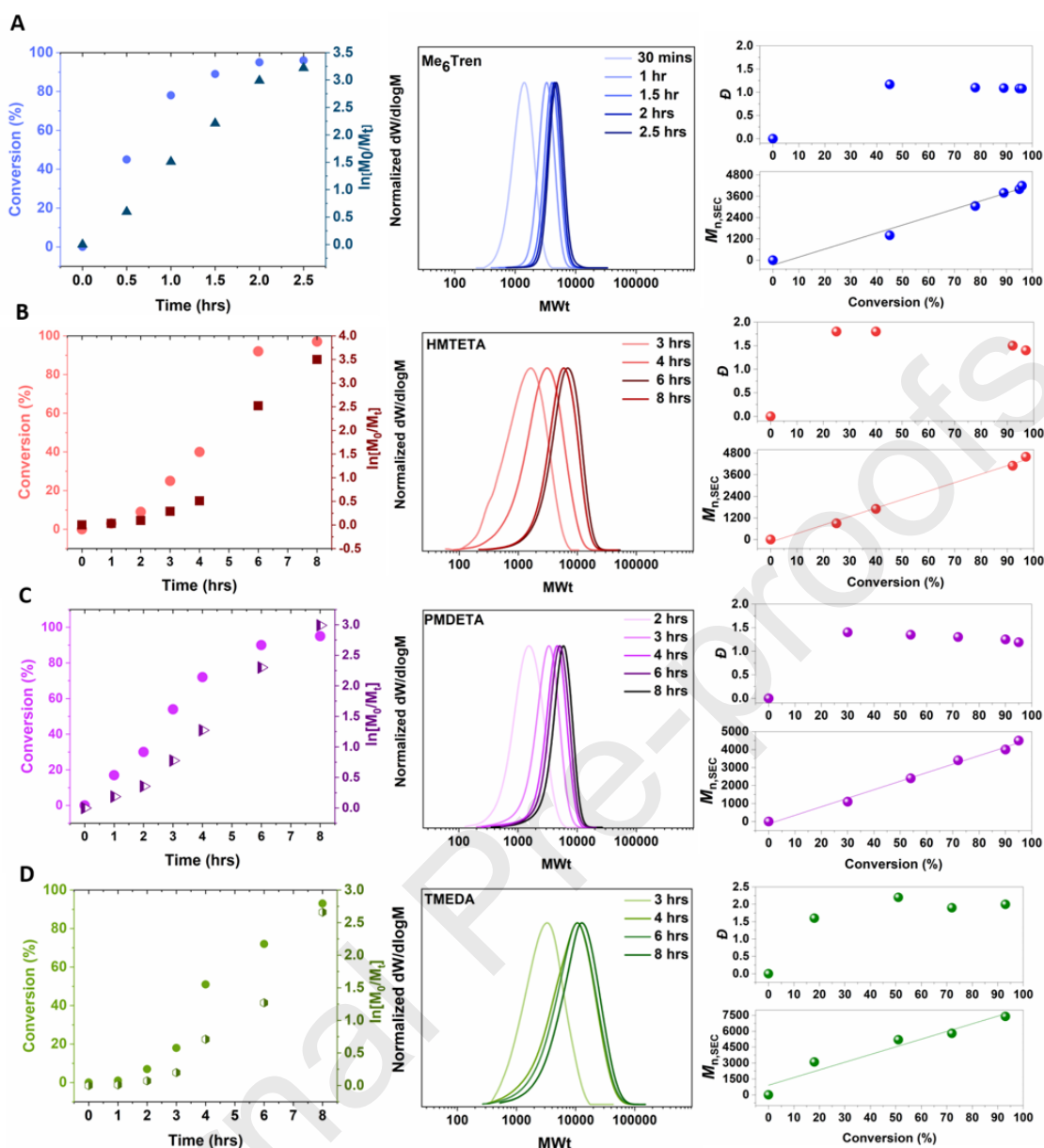
## Results and Discussion

Initially, different Cu-based complexes with aliphatic amine ligands (L) were prepared *in situ* in dimethyl sulfoxide (DMSO), including tris[2-(dimethylamino)ethyl]amine (Me<sub>6</sub>Tren) (tripodal, 4N), 1,1,4,7,10,10-Hexamethyltriethylenetetramine (HMTETA) (linear tetradentate, 4N), N,N,N',N'',N'''-Pentamethyldiethylenetriamine (PMDETA) (tridentate, 3N) and tetramethylethylenediamine (bidentate, 2N) (TMEDA) as ligands and Cu(II)Br<sub>2</sub> as metal source. Subsequently, the different complexes were employed for the photoinduced Cu-RDRP of methyl acrylate (MA) with ethyl  $\alpha$ -bromoisobutyrate (EBiB) as the initiator, following the ratio [MA]:[EBiB]:[L]:[Cu(II)Br<sub>2</sub>]=[50]:[1]:[0.02]:[0.12], in 50 % v/v DMSO, under a UV "nail lamp" with broad band emission and  $\lambda_{\text{max}} \sim 360$  nm. As previously reported, the use of Me<sub>6</sub>Tren (in excess with respect to Cu(II)Br<sub>2</sub>) leads to control over the polymerization with well-defined polyacrylates and low dispersities. Kinetic experiments showed that, as expected, the rate of the polymerization was very fast (**Table 1**) and the semi-logarithmic plot of  $\ln[M_0/M_t]$  versus time follows linear trend, indicating that the reaction is first order with respect to [monomer] and the generation of the radicals is constant (**Figure 1A**). Moreover, the experimental  $M_n$  values ( $M_{n,\text{SEC}}$ ) exhibited very good agreement with the theoretical values ( $M_{n,\text{th}}$ ) which was also depicted by the linear evolution of  $M_{n,\text{SEC}}$  with respect to monomer conversion. When HMTETA, a linear tetradentate aliphatic amine similar to Me<sub>6</sub>Tren was employed as ligand, although the  $M_{n,\text{SEC}}$  showed linear behaviour with conversion and there was agreement between  $M_{n,\text{SEC}}$  and  $M_{n,\text{th}}$ , the  $\ln[M_0/M_t]$  versus time plot exhibited deviations from first order behaviour with respect to monomer. This indicates that the [propagating chains] was not constant throughout the polymerization and possibly there was an increase at high conversions (**Figure 1B**). Moreover, slower polymerization rates were observed compared to Me<sub>6</sub>Tren (quantitative conversion after 2.5 hours) with the monomer conversion reaching 97% after 8 hours (**Table 1**). The dispersity of the polymers was higher than in the case of Me<sub>6</sub>Tren with  $D = 1.4$  at 97% conversion. When PMDETA (tridentate aliphatic amine) was used as ligand, good control over the molecular weights was observed as previously (**Table 1, Figure 1C**), although the dispersity values for PMA were slightly higher in comparison to the results obtained when Me<sub>6</sub>Tren was used, reaching  $D \sim 1.18$  at 95% monomer conversion (after 8 hours). Although the  $\ln[M_0/M_t]$  versus time slightly deviated from the first order trend, there was not clear curvature of the plot that would indicate inconsistency on the radical generation. When the bidentate TMEDA was utilized, the  $M_{n,\text{SEC}}$  values deviated from the theoretical and the dispersity was higher than in the previous cases, reaching  $D \sim 1.90$  (**Table 1**). Moreover, the rate of polymerization was slightly slower than when tetradentate and tridentate ligands were used, reaching 90% monomer conversion after 8 hours (**Figure 1D**) and the  $\ln[M_0/M_t]$  did not increase linearly in time.

**Table 1.** <sup>1</sup>H NMR and THF-SEC analysis for the photoinduced Cu-RDRP of MA (targeted DP=50) with different aliphatic amines as ligands<sup>a</sup>

Aliphatic amine	Time (hrs)	Conv. (%) <sup>b</sup>	$M_{n,SEC}$ <sup>c</sup> (g/mol)	$M_{n,th.}$ (g/mol)	$\bar{D}$
<b>Me<sub>6</sub>Tren</b> (tripodal, 4N)	0.5	45	1,400	2,100	1.17
	1	78	3,100	3,500	1.10
	1.5	89	3,900	4,000	1.09
	2	95	4,200	4,300	1.08
	2.5	98	4,400	4,400	1.08
<b>HMTETA</b> (linear, 4N)	1	3	-	-	-
	2	9	-	-	-
	3	25	900	1,200	1.80
	4	40	1,700	1,900	1.80
	6	92	4,100	4,200	1.50
<b>PMDETA</b> (3N)	1	17	-	-	-
	2	30	1,100	1,500	1.40
	3	54	2,410	2,500	1.35
	4	72	3,400	3,300	1.30
	6	90	4,000	4,100	1.22
<b>TMEDA</b> (2N)	1	1	-	-	-
	2	7	-	-	-
	3	18	3,100	970	1.60
	4	51	5,200	2,400	2.20
	6	72	5,800	3,300	2.00
	8	93	7,400	4,200	1.90

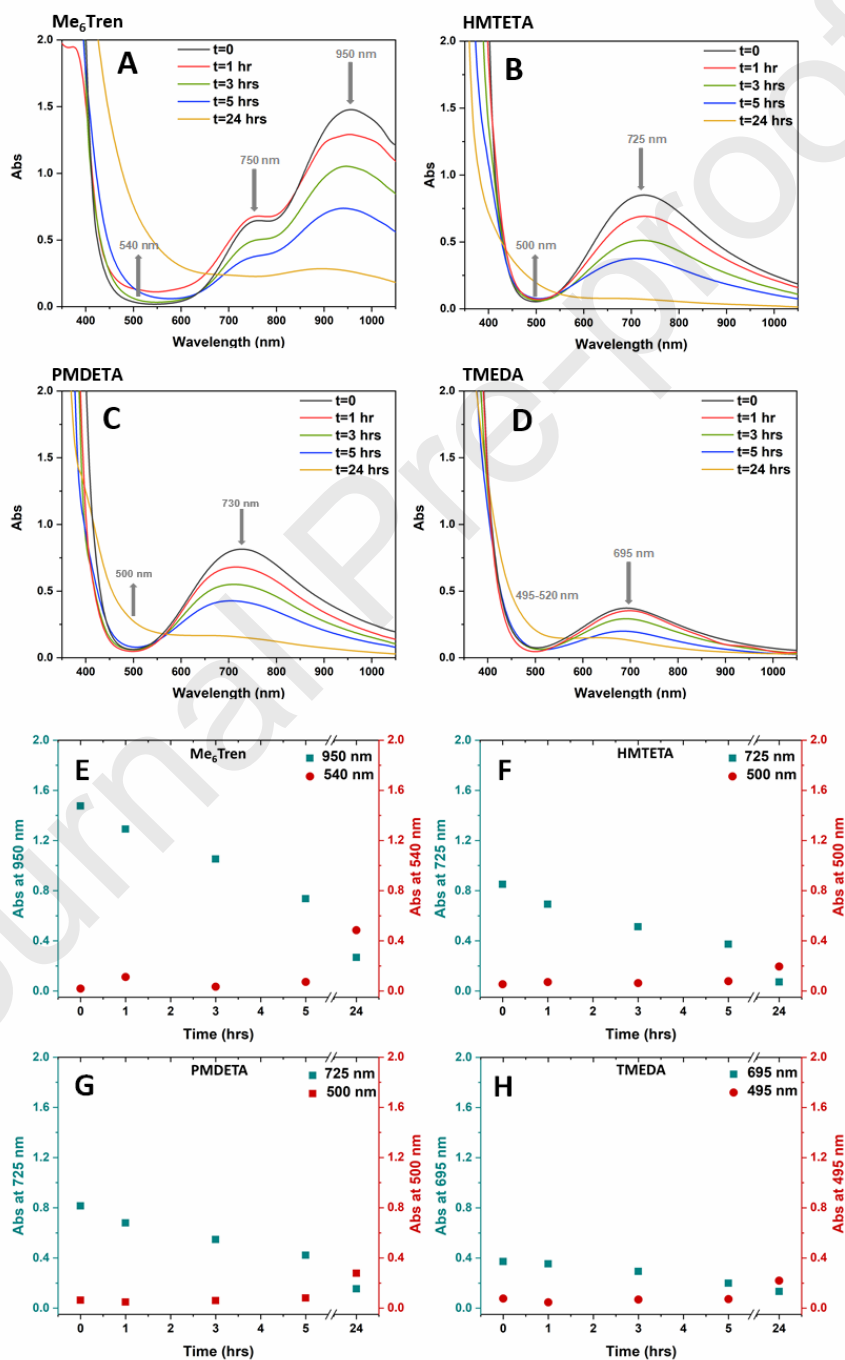
<sup>a</sup> For all the polymerizations the conditions were [MA]:[EBiB]:[L]:[Cu(II)Br<sub>2</sub>]=[50]:[1]:[0.02]:[0.12], in 50 % v/v DMSO, under a UV lamp with broad band emission and  $\lambda_{max} \sim 360$  nm. <sup>b</sup> Monomer conversion obtained through <sup>1</sup>H NMR in CDCl<sub>3</sub>. <sup>c</sup> Determined by THF SEC analysis and expressed as molecular weight equivalents to PMMA narrow molecular weight standards.



**Figure 1.** Kinetic plots of conversion and  $\ln[M_0/M_t]$  over time, THF-SEC derived molecular weight distributions, and  $M_{n,SEC}$  and dispersity ( $\bar{D}$ ) versus monomer conversion for PMA with targeted DP=50 with **A)** Me<sub>6</sub>Tren, **B)** HMTETA, **C)** PMDETA and **D)** TMEDA as ligands under UV lamp with broad band  $\lambda_{max} \sim 360$  nm and  $[MA]:[EBiB]:[L]:[Cu(II)Br_2]=[50]:[1]:[0.02]:[0.12]$ .

Since the evolution of the photoinduced Cu-RDRP of MA exhibited differences when different ligands were used (**Figure S1**), we were interested in investigating the behaviour of the different catalysts upon UV irradiation. Initially, deoxygenated solutions of the complexes in DMSO and  $[Cu(II)Br_2]:[L]=1:6$  (conditions also applied for polymerization) were prepared and studied through UV-Vis spectroscopy, upon exposure to UV irradiation. As has been extensively reported, the maximum absorbance at  $\sim 700$  nm is attributed to the d-d transitions of the d<sup>9</sup> Cu(II) complex. It should be noted that deviations from the literature can be attributed to the different solvents used, since the solvent can play an important role on the coordination of Cu-complexes.<sup>42</sup> For the  $[Cu(II)(Me_6Tren)Br_2]$  complex, the characteristic maximum absorbance is found at 950 nm, with a second absorbance feature at 750 nm (**Figure 2A**). The reduction of these maxima, indicative of the reduction of Cu(II) to Cu(I) and possibly attributed to a ligand-to-metal charge transfer (LMCT), was highly evident even after a short period of exposure at UV irradiation (**Figures 2A&E**). Noteworthy is that apart from a consistent reduction in  $[Cu(II)(Me_6Tren)Br_2]$  during the first 5 hours of UV irradiation, after 24 hours a scattering slope is evident,

indicating that changes in the physical properties of the complex take place without excluding the hypothesis of Cu(0) particle generation and accumulation. When the  $[\text{Cu(II)(HMTETA)Br}_2]$  complex was monitored, a reduction of the characteristic band at 725 nm was also evident, indicating the generation of Cu(I) from Cu(II) (**Figures 2B&F**). In comparison to  $[\text{Cu(II)(Me}_6\text{Tren)Br}_2]$ , the reduction of the  $[\text{Cu(II)(HMTETA)Br}_2]$  complex was slower and at lower degree, an observation that can potentially corroborate the slower rate of polymerization when HMTETA is used as ligand (**Table 1, Figure 1B**). In the case of PMDETA used as ligand, the absorbance reduction at 730 nm was similar to the  $[\text{Cu(II)(HMTETA)Br}_2]$ , indicating a slower rate of Cu(II) reduction to Cu(I), and again conformed with the slower rates of polymerization (**Figures 2C&G**). The  $[\text{Cu(II)(TMEDA)Br}_2]$  characteristic band at 695 nm exhibited the lowest degree of reduction (**Figures 2D&H**) compared to the other complexes. This observation might be correlated with the polymerization results when TMEDA was used as ligand and give insight into the generation of Cu(I) when the bidentate TMEDA is employed for the formation of  $[\text{Cu(II)(TMEDA)Br}_2]$ .

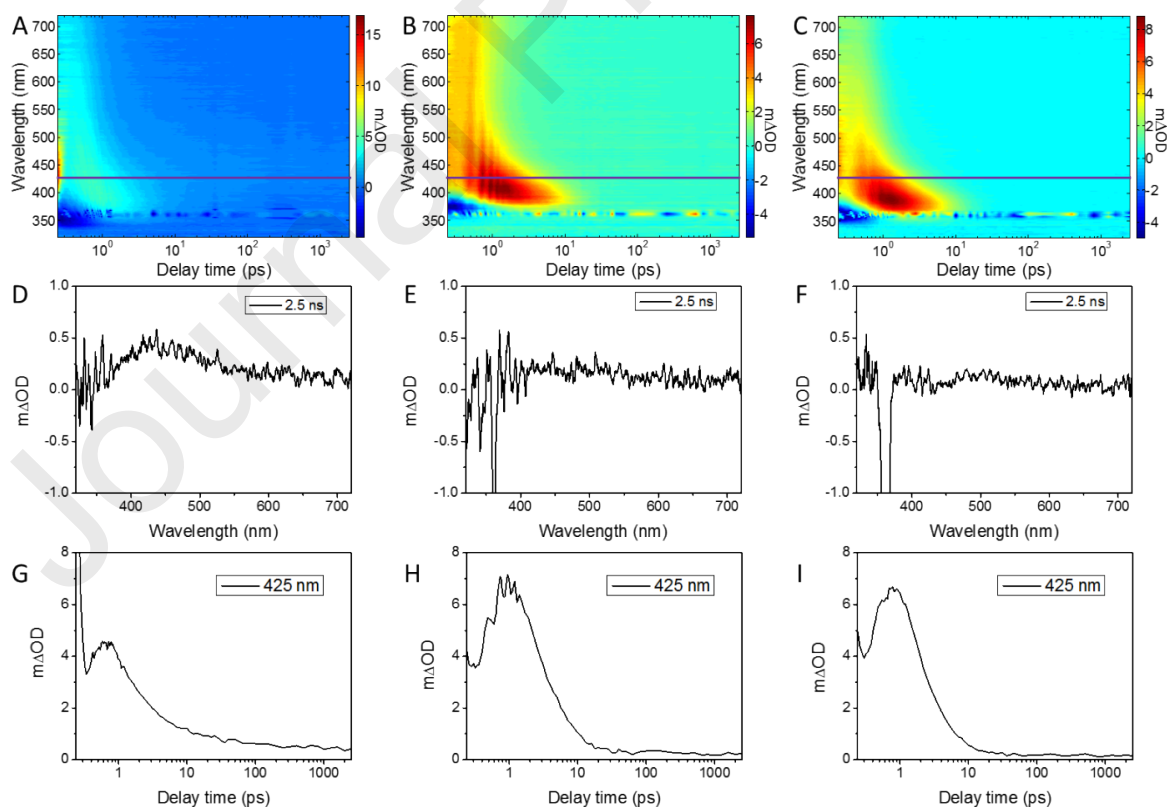


**Figure 2.** Time-dependent UV-Vis spectra and kinetic profile of the Cu-based complexes with A), E) Me<sub>6</sub>Tren, B), F) HMTETA, C), G) PMDETA and D), H) TMEDA following broadband irradiation with  $\lambda_{\text{max}} \sim 360$  nm.



A possible hypothesis is that the two N atoms that comprise TMEDA restrict the mobility of the tetrahedral complex or, as has been reported, the methyl groups on the N atoms create steric effects, rendering the complex inefficient in abstracting the halogen atom and form radicals.<sup>43</sup> In general, the differences in the evolution of the absorption bands when different ligands were used, were attributed to the different coordination geometry of the Cu complex when aliphatic amines with different numbers of N atoms are used, thus leading to different catalytic activity. Upon UV irradiation, these differences become even more apparent due to the photo-reduction of Cu(II) by the excited free ligand.

Consequently, we were interested in exploring the dynamics of the catalyst upon UV irradiation and on account of this, TEAS was employed for the comparison of the complexes that exhibited the greatest control over the polymerization. As such, the [Cu(II)(Me<sub>6</sub>Tren)Br<sub>2</sub>] complex was compared with the [Cu(II)(PMDETA)Br<sub>2</sub>] complex, as well as with Cu(II)Br<sub>2</sub> in the absence of ligand. These results are illustrated in the false-colour heat maps following excitation with 0.5 mW 365 nm radiation (**Figures 3A-C**). Each of the false-colour heat maps starts with a large (10s of mΔOD) absorption feature centred at ~400 nm, which persists on the timescale of the instrument response (~80 fs, see Supporting Information). This feature likely includes mostly contributions from the solvent/glass of the flow cell and has not been included in **Figures 3A-C**, for ease of visualisation on the relevant signal from the sample. As shown, a broad, but much weaker absorption feature which spans from 400 to 700 nm is also present, with a corresponding ground state bleach (negative feature) around the excitation wavelength. This feature blue shifts, narrows, and grows in intensity, within the first 1 ps after photoexcitation, eventually becoming centred again on ~400 nm. Subsequently, this decays within ~5-10 ps, and a very small positive absorption offset persists throughout the temporal window of the experiment, suggesting that a small amount of photoproduct is created. This long lived state is evident in the non-zero transient absorption spectrum taken at 2.5 ns delay time, shown in **Figures 3D-F**, as well in the non-zero offset at long delay times in lineouts of the TEAS, taken at 425 nm probe wavelength (purple lines **Figures 3A-C**), and shown in **Figures 3G-I**. It is hypothesised that the differences in the UV-Vis absorption upon irradiation are caused by transitioning from Cu(II) to Cu(I) (with some contribution growing possibly from Cu(0) over time). As such, we suggest that the long-lived state observed is due to the creation of small amounts of Cu(I) complexes. The large amount of noise in all three TEAS (and the large negative feature observed in **Figure 3F**) around 365 nm is caused by scatter from the pump pulse which could not be thoroughly removed.

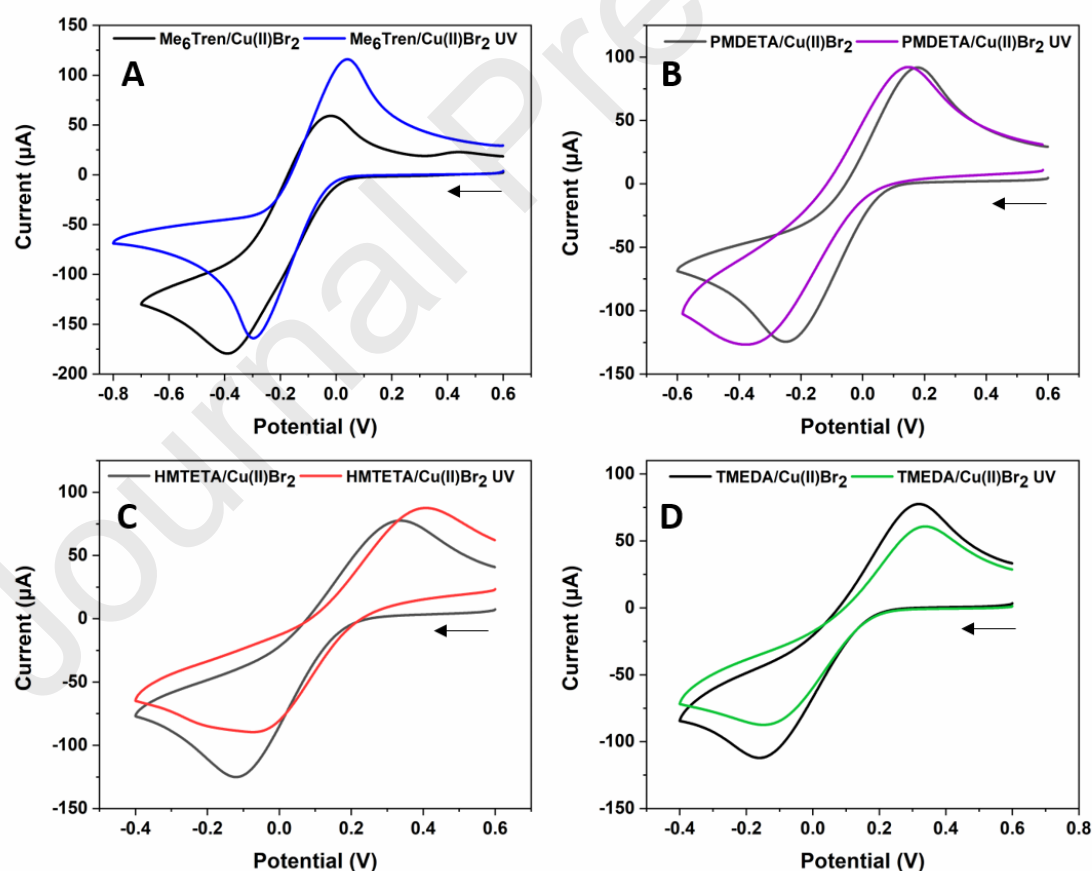


**Figure 3.** TEAS generated false-colour heat maps of **A)** Cu(II)Br<sub>2</sub>, **B)** [Cu(II)(Me<sub>6</sub>Tren)Br<sub>2</sub>] and **C)** [Cu(II)(PMDETA)Br<sub>2</sub>], transient absorption spectra taken 2.5 ns after photoexcitation for **D)** Cu(II)Br<sub>2</sub>, **E)**

[Cu(II)(Me<sub>6</sub>Tren)Br<sub>2</sub>] and F [Cu(II)(PMDETA)Br<sub>2</sub>] and lineouts taken at 425 nm probe wavelength (purple line in A-C) for G Cu(II)Br<sub>2</sub>, H [Cu(II)(Me<sub>6</sub>Tren)Br<sub>2</sub>] and I [Cu(II)(PMDETA)Br<sub>2</sub>].

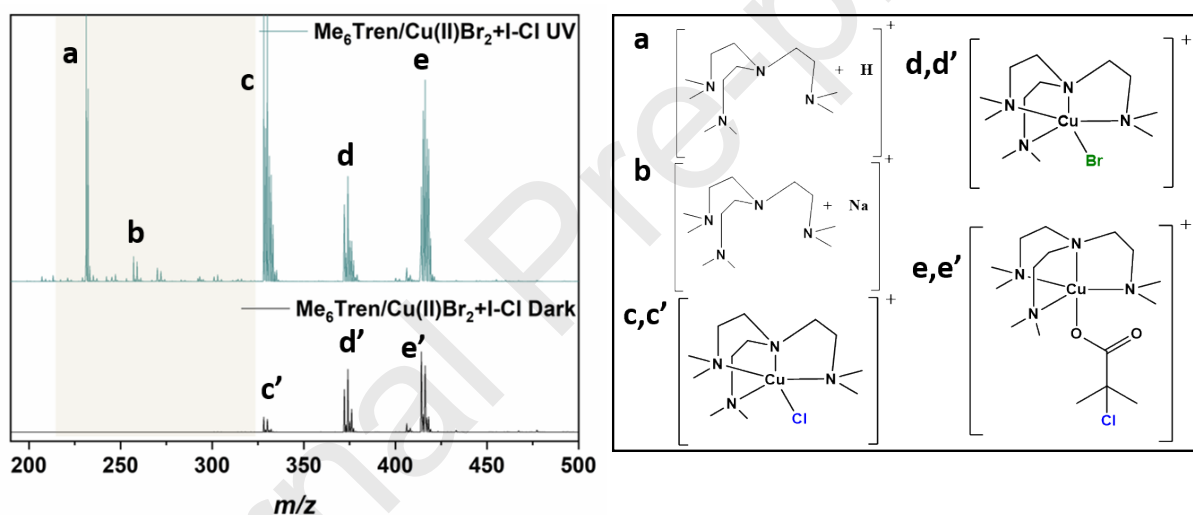
All three false-colour heat maps are qualitatively similar, with the exception of an oscillating signal, with a peak to peak separation of  $\sim 220$  fs, which is clearly present in the [Cu(II)(Me<sub>6</sub>Tren)Br<sub>2</sub>] complex (Figures 3B&H) and persists for at least 1 ps. This is also present but much weaker in the [Cu(II)(PMDETA)Br<sub>2</sub>] (Figures 3C& I) complex, and while an accurate peak to peak separation cannot be extracted, the frequency appears identical to that observed in [Cu(II)(Me<sub>6</sub>Tren)Br<sub>2</sub>]. Such an oscillatory signal is not observed in the Cu(II)Br<sub>2</sub> alone (Figures 3A&G). Similar TEAS were recorded when changing the halogen to chlorine, but no beat was observed (Figure S2). This suggests that both the ligand and the halogen are playing a role in the oscillatory signal observed in [Cu(II)(Me<sub>6</sub>Tren)Br<sub>2</sub>] and [Cu(II)(PMDETA)Br<sub>2</sub>]. As such, we postulate here that the beat we observe in the transient absorption spectra is caused by the system oscillating between two different oxidation states of Cu, possibly caused by motion of the bromine between the copper and the ligand.

Subsequently, CV studies were carried out so as to provide information about changes in the redox properties of the complexes upon UV irradiation. For the CV measurements, solutions of different complexes were prepared in DMSO and CV measurements were performed under a N<sub>2</sub> atmosphere (See Supporting Information). The voltammogram of [Cu(II)(Me<sub>6</sub>Tren)Br<sub>2</sub>] shows reduction (Cu(II) to Cu(I)) during the cathodic trace and corresponding oxidation peak during the anodic trace, as has been previously reported.<sup>44</sup> Although before UV irradiation the redox couple did not exhibit a “perfect” quasi-reversible behaviour, upon UV irradiation the quasi-reversible behaviour was clear, possibly due to stabilization of the complex (Figure 4A). The half-wave potential ( $E_{1/2}$ ) in both cases was negative, but after UV irradiation an increase from -0.200 V (before UV) to -0.130 V (after UV) was observed.



**Figure 4.** Cyclic voltammograms of A) [Cu(II)(Me<sub>6</sub>Tren)Br<sub>2</sub>], B) [Cu(II)(PMDETA)Br<sub>2</sub>], C) [Cu(II)(HMTETA)Br<sub>2</sub>] and D) [Cu(II)(TMEDA)Br<sub>2</sub>] complexes with 0.01 M concentration, in a 0.1 M tetrabutylammonium hexafluorophosphate (NBu<sub>4</sub>PF<sub>6</sub>) solution in DMSO with scan rate 0.5 V/s vs. Ag/AgCl.

When the tridentate  $[\text{Cu(II)(PMDETA)Br}_2]$  complex was measured before irradiation, reduction and oxidation were clearly observed during the cathodic and anodic trace (**Figure 4B**), exhibiting a quasi-reversible behaviour ( $\Delta E_p=470$  mV $\gg$ 60 mV, Table S). After UV irradiation, although the anodic peak does not show significant changes, the cathodic wave exhibits alterations shifting to more negative values, possibly indicative of deviation from a reversible redox reaction. The peak-to-peak separation exhibits differences before and after UV irradiation, 470 mV and 320 mV respectively, showing that more energy is needed for the reduction of the complex after UV irradiation, an observation that can be probably attributed to the different amount of species available for reduction. The  $[\text{Cu(II)(HMTETA)Br}_2]$  complex exhibited changes on the cathodic wave after UV irradiation, showing important decrease (**Figure 4C**). Apart from the shift in the potential, a second peak in the cathodic wave was observed, probably attributed to a second population available for reduction. This might be attributed to changes in the coordination sphere of the metal complex upon exposure to UV light. It should be noted that due to the significant decrease of the cathodic peak, the peak-to-peak separation values could not be identified precisely after UV irradiation. In the case of  $[\text{Cu(II)(TMEDA)Br}_2]$  both the anodic and cathodic traces were decreased upon UV irradiation (**Figure 4D**), an observation that led us to hypothesize that electrochemically the effect of UV irradiation on the catalyst complex is not as significant as in the other complexes examined. This information might provide an explanation on the behaviour of the TMEDA ligand (and the analogous TMEDA/Cu(II)Br<sub>2</sub> complex) on the polymerization results which exhibited significant differences from the other cases. In all cases, the  $\Delta E_p$  values exhibited values much higher than 60 mV. These trends, although qualitatively examined, provide some information on the effect of UV light on the behaviour of redox couples that govern photoinduced Cu-RDRP and are reflected in the quality of the obtained polymers when the different ligands are used.



**Figure 5.** ESI-MS spectra of  $[\text{Cu(II)(Me}_6\text{Tren)Br}_2]$  in the presence of a Cl-initiator before and after UV irradiation in MeOH (left) and chemical structures corresponding to the ESI-MS peaks (right).

Finally, ESI-ToF-MS was employed to investigate potential photoproducts that occur after photo-irradiation of the complexes and can be detected through ESI as positively charged species in the gas phase. Apart from the individual complexes, a solution of  $[\text{Cu(II)(Me}_6\text{Tren)Br}_2]$  combined with a chlorine-based initiator (**Figure 5**) was examined before and after exposure to UV light, to investigate the possibility of halogen exchange between the metal complex and the initiator. In all complexes, peaks corresponding to  $[\text{L} + \text{H}]^+$ ,  $[\text{L-CuBr} + \text{H}]^+$  and  $[\text{L-CuBr}_2 + \text{H}]^+$  were detected in the positive ion mode. Apart from  $\text{H}^+$  charged species, all of the samples included  $\text{Na}^+$  charged species. For the  $[\text{Cu(II)(Me}_6\text{Tren)Br}_2]$  complex the main species detected were the  $[\text{Cu(Me}_6\text{Tren)} + \text{H}]^+$ ,  $[\text{Cu(Me}_6\text{Tren)Br}]^+$  and the  $[\text{Cu(Me}_6\text{Tren)(OCH}_3)]^+$  (**Figure S4-A**) both before and after UV irradiation. Apart from these intact complex species, free ligand  $[\text{Me}_6\text{Tren} + \text{H}]^+$  and  $[\text{Me}_6\text{Tren} + \text{Na}]^+$  were detected and only after UV irradiation a small peak corresponding to  $[(\text{Me}_6\text{Tren)(OCH}_3) + \text{Na}]^+$  was found. Based on the TEAS results, it should be noted that when  $\text{Me}_6\text{Tren}$  is used, any changes in the complexation of the metal are significantly fast and it would be difficult to be monitored. For the  $[\text{Cu(II)(HMTETA)Br}_2]$  complex, the main species detected, apart from  $[\text{L} + \text{H}]^+$ , were the  $[\text{Cu(HMTETA)Br}]^+$ ,  $[\text{Cu(HMTETA)Br}_2]^+$  and  $[\text{Cu(HMTETA)}_2(\text{OH})_2 + \text{Na}]^+$ . Furthermore, although before UV irradiation a peak attributed to  $[\text{Cu}_2(\text{HMTETA})_2\text{Br}(\text{OCH}_3)_2]^+$  was detected, it was absent after UV irradiation (**Figure S4-B**).

For the TMEDA-based complex the assignment of the peaks was a challenging task since many species were detected including  $[\text{Cu}(\text{TMEDA})]^+$  and  $[\text{Cu}(\text{TMEDA})_2]^+$ ,  $[\text{Cu}(\text{TMEDA})_2\text{Br}(\text{OH})]^+$ ,  $[\text{Cu}(\text{TMEDA})_2\text{Br}_2]^+$  and  $[\text{Cu}_2(\text{TMEDA})_2\text{Br}_2]^+$  as well as  $[\text{Cu}_2(\text{TMEDA})_2\text{Br}_4 + \text{Na}]^+$ . The species detected only after UV irradiation were the  $[\text{Cu}(\text{TMEDA})_2\text{Br}]^+$ ,  $[\text{Cu}_2(\text{TMEDA})_2(\text{OCH}_3)_2]^+$  and  $[\text{Cu}_2(\text{TMEDA})_2\text{O}_4]^+$  (**Figure S4-C**). The existence of many species in the solution of the TMEDA-based complex might also be a factor that affects the polymerization and, thus the obtained polymers exhibit high dispersity and molecular weights.

For the  $[\text{Cu}(\text{II})(\text{PMDETA})\text{Br}_2]$  complex the main species assigned were the  $[\text{Cu}(\text{PMDETA})]^+$ ,  $[\text{Cu}(\text{PMDETA})(\text{OCH}_3)]^+$ ,  $[\text{Cu}(\text{PMDETA})_2(\text{OH})_2 + \text{H}]^+$  and  $[\text{Cu}(\text{PMDETA})\text{Br}_2]^+$  both before and after UV exposure (**Figure S4-D**). However, peaks that correspond to intact  $[\text{Cu}(\text{PMDETA})(\text{OH})]^+$  (as well as  $[\text{CuO}(\text{PMDETA})]^+$ ) and  $[\text{CuO}(\text{PMDETA})\text{Br} + \text{Na}^+]$  were observed only after UV irradiation. For the solution in which, apart from the  $[\text{Cu}(\text{II})(\text{Me}_6\text{Tren})\text{Br}_2]$  complex a chlorine initiator was added, a main peak at 328.16  $m/z$  was detected corresponding to  $[\text{Cu}(\text{Me}_6\text{Tren})\text{Cl}]^+$  as well as at 372.11  $m/z$  the  $[\text{Cu}(\text{Me}_6\text{Tren})\text{Br}]^+$  showing that exchange of the halogen between the complex and the initiator takes place (**Figure 5**). Noteworthy is the peak at 414.20  $m/z$  attributed to reactions taking place between the complex and the initiator, with the latter complexing with the ligand and corresponding to  $[\text{Cu}(\text{Me}_6\text{Tren})(\text{C}_3\text{H}_6\text{Cl})]^+$  (**Figure 5, e&e'**). As a result, many different charged species were detected through ESI-MS for each complex, with all of them including not only the complexation of the Cu-metal centre with the ligand and the halogen, but also the occupation of vacant coordination sites with solvent. The determination of the oxidation state of copper was avoided since the several species could have a positive charge due to the imbalance of copper and the counterion or due to a radical formed by the ligand.

## Conclusions

In summary, the effect of UV irradiation on Cu-based complexes including different aliphatic amine ligands has been investigated. Different characterization techniques such as UV-Vis spectroscopy, TEAS, CV and ESI-MS provided information about the behaviour of  $[\text{Cu}(\text{II})(\text{Me}_6\text{Tren})\text{Br}_2]$ ,  $[\text{Cu}(\text{II})(\text{PMDETA})\text{Br}_2]$ ,  $[\text{Cu}(\text{II})(\text{HMTETA})\text{Br}_2]$  and  $[\text{Cu}(\text{II})(\text{TMEDA})\text{Br}_2]$  upon exposure to UV light. The investigation of the excited-state dynamics, the redox behaviour and the different species generated upon complexation of the ligand to the metal center, before and after UV irradiation are further depicted in the quality of the polymers obtained after utilization of these transition metal complexes for the photoinduced Cu-RDRP of MA.

## Conflicts of interest

There are no conflicts to declare.

Data described in this paper is available from The University of Warwick repository at [www.warwick.ac.uk/WRAP.xxxxxxxx](http://www.warwick.ac.uk/WRAP.xxxxxxxx)

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Author statement

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## UV irradiation of Cu-based complexes with aliphatic amine ligands as used in living radical polymerization

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### Highlights

The effect UV irradiation on Cu(II)-complexes with aliphatic amine ligands of importance in polymer synthesis is investigated

Transient electronic absorption spectroscopy (TEAS) shows that when Me<sub>6</sub>Tren is used, any changes in the complexation of the metal are significantly fast and it would be difficult to be monitored.

An investigation of the excited-state dynamics, the redox behaviour and the different species generated before and after UV irradiation in copper mediated living radical polymerization

### Graphical abstract

