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A novel class of photoinitiators with a thermally activated delayed fluorescence (TADF) property

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Photoinitiators exhibiting efficient thermally activated delayed fluorescence (TADF) are investigated. Known TADF metal complexes (copper-based structures) and purely organic molecules (carbazole/sulfone based organic structures) are used, for the first time, in the FRP of methacrylates, the CP of diepoxides and the synthesis of acrylate/diepoxide interpenetrated polymer networks, in thick films (1.4 mm), under air, under soft conditions using violet light delivered by a LED emitting at 405 nm. They are incorporated into two-component systems in combination with an iodonium salt and/or into three-component systems with iodonium salt/amine or *N*-vinylcarbazole or 9*H*-carbazole-9-ethanol (CARET) systems. A comparison with non-TADF analogues highlights the benefits of the TADF process. Using the copper complexes, the performances are better than those achieved with a conventional reference photoinitiator (bis acylphosphineoxide); the organic structures are noticeably less efficient. These systems exhibit a photoredox catalyst behavior. The involved chemical mechanism has been investigated using steady state photolysis, cyclic voltammetry, fluorescence spectroscopy, laser flash photolysis and electron spin resonance spin trapping techniques. The TADF property is found to be very important in increasing the excited state lifetime of the photoredox catalyst for better interactions with additives (i.e. a longer excited state lifetime is important to increase the yields of bimolecular reactions).

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Introduction

Within the last few decades, a large set of photoinitiators (PI) and photoinitiating systems (PISs) have been used to initiate free radical polymerization (FRP) and cationic polymerization (CP) upon light irradiation.^{1–11} The development of new PISs being able to promote FRP and CP under soft visible light especially LEDs is still a huge challenge nowadays. Among the innovative photoinitiators that have been developed recently, photoredox catalysts (PCs) have attracted increasing interest. In fact, due to the regeneration of the starting compound, small amounts of PCs could be enough to efficiently promote the polymerization process under low light intensities. The chemical mechanisms involving PCs are based on oxidation and reduction cycles (Fig. 1). To be efficient, a PC, like any usual Type II PI, must fulfill three key conditions. First, its absorption

Fig. 1 Reductive and oxidative photoredox catalytic cycles.

spectrum should have the best match with the emission spectrum of the light source together with high molar extinction coefficients. Second, it requires long lived excited states that can be easily quenched by the oxidation of reduction agents ensuring high quantum yields of reactive species.¹² Third, the values of the redox potentials are important for good reactivity. However, to become a PC, the photoinitiator must be regenerated and good reversibility to

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minimize the side reactions must be observed (the redox properties are now decisive). Many interesting and promising PIs developed in recent years operate in their first excited singlet state. The lifetimes of such states usually are on the nanosecond timescale. The design of chemical structures having long lived states deserves to be deeply investigated. To match this condition, one way might consist in using compounds exhibiting a radiative decay *via* a Thermally Activated Delayed Fluorescence (TADF) process. This concept was recently introduced in several different industrial sectors such as the fields of lighting and signage systems with the development of the organic light emitting device (OLED) technology.^{13–16} Various TADF molecules have already been synthesized. Having this TADF property requires the design of molecular structures characterized by a small S_1 - T_1 energy splitting, the small $\Delta(S_1-T_1)$ energy barrier being easily overcome by the absorption of heat and the up-conversion of electrons.¹⁷ Such compounds present a spatial separation of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) that can be achieved in rigid and highly twisted structures avoiding a conjugation between electron withdrawing and releasing units and an excessive electron density delocalization. This TADF emission occurs on a long time scale (μ s range). This property should improve the reactivity in suitable and well adapted photoredox catalysts/photoinitiators. The present paper will compare the polymerization ability of TADF *vs.* non-TADF compounds. Transition metal based complexes have been known for a long time and have notably been reported in recent studies.^{18–25} Among them, copper complexes are receiving sustained interest due to their low price, low toxicity, abundance and their high emission quantum yields.^{25–29} Interesting phosphorescence, fluorescence and delayed fluorescence properties can be realized with copper complexes as recently reported by Yersin^{26–29} and Thompson.^{30–33} As pointed out previously,³⁴ the use of copper based compounds could have an important impact thanks to the increase of the radiative decay channels through a TADF emission.^{26–29} The recent focus of numerous research studies is highlighted in a review devoted to copper complexes.¹⁵ In carefully designed copper complexes,^{26–29} the light emission, at low temperature, arises from the lowest triplet state T_1 assigned to a metal-to-ligand charge-transfer state ($^3\text{MLCT}$) involving Cu-3d and ligand- π^* orbitals; it decays in the hundred μ s time range. At room temperature, the decay occurs in the μ s range (longer than that of the prompt fluorescence) and the TADF emission is attributed to a thermally populated singlet state S_1 ($^1\text{MLCT}$) in thermal equilibrium with the lowest triplet state.

In particular, purely organic molecules also display a TADF behavior at ambient temperature as shown by C. Adachi³⁵ and reviewed by M. Y. Wong.¹⁶ Compared to luminescent Cu(I) complexes, they exhibit better chemical and thermal stability which make them more convenient in the OLED technology. In donor- π -acceptor structures, the TADF emission occurs through a reverse internal conversion (IC) from the donor $^3\pi\pi^*$ state to the triplet charge transfer state, ^3CT state, and a successive reverse intersystem crossing from the ^3CT state to the ^1CT state, the reversible $^3\pi\pi^* \rightarrow ^3\text{CT}$ energy transfer between the states being a rapid intramolecular electron exchange process.

In the context of photopolymerization reactions, only one preliminary paper has considered the first use of organic TADF PCs (carbazole based compounds such as 2,3,5,6-tetra(9*H*-carbazol-9-yl)terephthalonitrile, 2,3,5,6-tetrakis(3,6-dibromo-9*H*-carbazol-9-yl)benzonitrile, 2,3,5,6-tetrakis(*N*-carbazolyl)benzonitrile, 2,3,5,6-tetrakis(3,6-dibromo-*N*-carbazolyl)terephthalonitrile³⁶). TADF copper complexes have never been used in this area. In the past, the use of iridium complexes as PCs exhibiting excited state lifetimes in the microsecond range was shown in FRP and CP.³⁷ Therefore, we report here on the first use, in photopolymerization reactions, of known and well established³⁸ TADF and non-TADF copper-based complexes $[(\text{Cu(I)})(\text{POP})(\text{dmbpy})][\text{BF}_4^-]$ (non-TADF CuC1), $[(\text{Cu(I)})(\text{POP})(\text{dmbpy})][\text{PF}_6^-]$ (non-TADF CuC2), $[(\text{Cu(I)})(\text{POP})(\text{tmbpy})][\text{BF}_4^-]$ (TADF CuC1) and $[(\text{Cu(I)})(\text{POP})(\text{tmbpy})][\text{PF}_6^-]$ (TADF CuC2) where dmbpy is 4,4'-dimethyl-2,2'-bipyridyl, tmbpy is 4,4',6,6'-(tetramethyl-2,2'-bipyridyl) and POP is bis[2-(diphenylphosphino)phenyl]ether). These compounds shown in Fig. 2 are employed as PIs and are incorporated into two-component PISs (with an iodonium salt) and three-component PISs (with an iodonium salt and an amine or *N*-vinylcarbazole or 9*H*-carbazole-9-ethanol CARET).

The efficiency of these PISs is checked in the FRP of methacrylates, the CP of epoxides and the synthesis of acrylate/epoxide interpenetrated polymer networks, in thick films, under soft conditions, using violet light delivered by a LED at 405 nm. The polymerization profiles will be compared to those recorded with other conventional PISs. An interesting feature of this paper will concern a comparison of the relative reactivity/polymerization efficiency of TADF/non-TADF process based compounds. Due to the common interest in purely organic molecules, several compounds (Fig. 3) exhibiting a more or less TADF property,³⁹ di(4-(4-(carbazole-9-yl)phenyl)sulfone) (org 1), di(4-(4-(9-phenylcarbazol-3-yl)phenyl)sulfone) (org 2), 9,9'-(sulfonylbis(4,1-phenylene)) bis(9*H*-carbazole) (org 3) and 9,9'-(sulfonylbis(4,1-phenylene)) bis(3,6-di-*tert*-butyl-9*H*-carbazole) (org 4), will also be studied. The limits of this approach are also discussed.

The (photo) chemical mechanisms are investigated using steady state photolysis, fluorescence and laser flash photolysis.

Experimental

Materials

The investigated compounds (non-TADF CuC1,³⁸ TADF CuC1,³⁸ non-TADF CuC2, TADF CuC2, org 1,⁴⁰ org 2,⁴⁰ org 3,⁴¹ org 4³⁹)

Fig. 2 Chemical structures of the investigated copper complexes.

Fig. 3 Chemical structures of the investigated organic compounds.

are shown in Fig. 2 and 3. All compounds were prepared according to the procedures previously reported in the literature, without modifications and in similar yields. Bis-(4-*tert*-butyl-phenyl)iodonium hexafluorophosphate (Iod or Ar_2I^+) was obtained from Lambson. Ethyl 4-(dimethyl-amino)benzoate (EDB), *N*-vinyl-carbazole (NVK), 9*H*-carbazole-9-ethanol (CARET) and solvents were purchased from Sigma-Aldrich and used as received without further purification. 2,2-Bis[4-(methacryloxy-2-hydroxypropoxy)-phenyl]propane (BisGMA), triethylene glycol dimethacrylate (TEGDMA), trimethylol-propane triacrylate (TMPTA) and (3,4-epoxycyclohexane) methyl 3,4-epoxycyclohexylcarboxylate (EPOX) were obtained from Sigma Aldrich and Allnex and were used as benchmark monomers for FRP and cationic polymerization respectively (Fig. 4). The BAPO photoinitiator (bis(2,4,6-trimethyl-benzoyl)phenylphosphine oxide) was obtained from Lambson UK.

Irradiation source

A LED at 405 nm (ThorLabs; $\sim 110 \text{ mW cm}^{-2}$) was used for the irradiation of the photocurable samples.

Absorption and fluorescence experiments

The UV-vis spectra were recorded using a JASCO V-730 UV/Vis spectrophotometer. The fluorescence properties were studied using a JASCO FP-750 Spectrofluorimeter. The interaction rate constants k_q between the TADF CuC or the TADF org compounds and an additive were extracted from classical Stern-Volmer treatments ($I_0/I = 1 + k_q\tau_0 [\text{additive}]$, where I_0 and I stand for the fluorescence intensity of TADF CuC or TADF org in the absence and presence of the additive, respectively; τ_0 stands for the lifetime of the excited TADF CuC in the absence of the additive).

Laser flash photolysis

Nanosecond laser flash photolysis (LFP) experiments were carried out using a Q-switched nanosecond Nd/YAG laser ($\lambda_{\text{exc}} = 355 \text{ nm}$, 9 ns pulses; energy reduced down to 10 mJ) from Continuum (Minilite) and an analyzing system consisting of a ceramic xenon lamp, a monochromator, a fast photomultiplier, and a transient digitizer (Luzchem LFP 212).

Photopolymerization experiments

The experimental conditions for the photopolymerization reaction are given in the figure captions. The photocurable formulations were deposited on a BaF_2 pellet under air (thickness = 1.4 mm) for irradiation with different lights. The evolution of the methacrylate double-bond content of BisGMA/TEGDMA and the epoxy group content of EPOX was continuously followed using real-time FTIR spectroscopy (JASCO FTIR 6600) at about 6165 and 3700 cm^{-1} , respectively.

Results and discussion

A. Copper based TADF and non-TADF structures

A.1. Light absorption and emission properties of the studied copper complexes. Typical absorption spectra of the investigated copper complexes are presented in Fig. 5 (non-TADF CuC1 and TADF CuC1 in dichloromethane; absorption maxima at 380 nm ($\epsilon_{380 \text{ nm}} \sim 3600 \text{ M}^{-1} \text{ cm}^{-1}$) and 370 nm ($\epsilon_{370 \text{ nm}} \sim 3600 \text{ M}^{-1} \text{ cm}^{-1}$) for non-TADF CuC1 and TADF CuC1 respectively). This corresponds to a metal-to-ligand charge-transfer (MLCT) transition.³⁶ Non-TADF CuC2 and TADF CuC2 are supposed to have the same absorption properties as non-TADF CuC1 and TADF CuC1 owing to the same chromophore, respectively; only the counter anion is different. The emission spectrum of the LED at 405 nm exhibits an excellent covering with the light absorption of the investigated copper complexes. The luminescence emission of TADF CuC1 is centered at 550 nm (Fig. 6). From the crossing point of the absorption and emission spectra, the energy of the first excited triplet state S_1 is estimated to be 2.8 eV. The fluorescence lifetime of non-TADF CuC1 is equal to 0.02 μs vs. 2.5 μs for TADF CuC1.³⁸ The S_1 state is highly quenched by O_2 .³⁸

A.2. Photochemical properties of the studied copper complexes

A.2.1. Steady state photolysis. The steady state photolysis of non-TADF CuC1 and TADF CuC1 in dichloromethane, under

Fig. 4 Chemical structures of additives and monomers.

Fig. 5 UV-visible spectra of (1) non-TADF CuC1 and (2) TADF CuC1 in dichloromethane (10^{-4} M).

Fig. 6 Fluorescence spectra of TADF CuC1 in dichloromethane (1) under air and (2) under N_2 saturated medium; [TADF CuC1] = 8×10^{-5} M; λ_{exc} = 370 nm.

air, upon exposure to the LED at 405 nm is shown in Fig. 7. A slow photolysis was observed for TADF CuC1 albeit non-TADF CuC1 was rather stable. Bleaching is faster when an iodonium salt (Iod) is added. TADF CuC1 is consumed more rapidly than non-TADF CuC1 (Fig. 8) in full agreement with a stronger interaction with the TADF compound (see below for the rate constant of interaction). In the presence of Iod and EDB, bleaching also occurs (Fig. 9). It remains, however, less important in TADF CuC1/Iod/EDB than in TADF CuC1/Iod and a

photoproduct absorbing around 450 nm appears. TADF CuC1 is partly regenerated in line with the catalytic cycle.

A.2.2. Laser flash photolysis (LFP) experiments. Laser flash photolysis experiments (LFP) at 355 nm were also carried out on the different copper complexes and decay traces of the S_1 state are shown in Fig. 10 (see also Table 1). In saturated N_2 dichloromethane, a very long-lived S_1 state absorption (~ 3.5 μs) was observed at 370 nm and 400 nm for TADF CuC1 and TADF CuC2, respectively: this corresponds to the TADF lifetime. The short lifetimes observed under air (162 ns and 288 ns for TADF CuC1 and TADF CuC2, respectively) support a strong quenching by oxygen in line with Fig. 6. The transient absorption ($\Delta OD > 0$; ΔOD : change of optical density) is displayed in Fig. 11 (the $\Delta OD < 0$ range corresponds to the TADF emission). For non-TADF1 and non-TADF2, the lifetime expected is very short (within the resolution time of our LFP spectrometer) in agreement with the lack of fluorescence of these compounds (see above).

A.2.3. Interaction of TADF CuC1 with the iodonium salt. The TADF intensity decreases upon addition of Iod (Fig. 12A); the interaction rate constant k_q (Fig. 12B) is almost diffusion controlled: 3×10^9 $M^{-1} s^{-1}$ for TADF CuC1/Iod. From the determined oxidation potential of CuC1 (1.3 V by cyclic voltammetry), a negative value of the free energy change ($\Delta G_{et(TADF\ CuC/Iod)} = -0.8$ eV) has been calculated according to eqn (1) where E_{ox} , E_{red} , E^* and C are the oxidation potential of the electron donor, the reduction potential of the electron acceptor, the excited state energy level and the coulombic term for the initially formed ion pair, respectively. C is neglected as usually done in polar solvents. For the reduction potential of Iod, a value of -0.7 V vs. SCE has been used.⁴² This result is in full agreement with a very favorable interaction between the copper complex and the iodonium salt. Accordingly, a high electron transfer quantum yield ($\phi_{et(S_1)}$) of 0.67 was also calculated for (r1) for TADF-CuC1 (eqn (2)). For the non-TADF compound, no fluorescence quenching is observed in agreement with the very short excited state lifetime showing that the TADF character is crucial for (r1) to occur.

$$\Delta G_{et} = E_{ox} - E_{red} - E^* + C \quad (1)$$

Fig. 7 Steady state photolysis of (a) non-TADF CuC1 (10^{-4} M) and (b) TADF CuC1 (10^{-4} M) in dichloromethane; UV-vis spectra at different irradiation times upon LED irradiation at 405 nm.

Fig. 8 Steady state photolysis of (a) non-TADF CuC1/Iod, (b) TADF CuC1/Iod in dichloromethane and (c) non-TADF CuC1 (curve 1) vs. TADF CuC1 (curve 2) consumption in dichloromethane; ([non-TADF CuC1] = [TADF CuC1] = 2×10^{-4} M; [Iod] = 1.5×10^{-3} M). UV-vis spectra at different irradiation times upon LED irradiation at 405 nm.

$$\phi_{\text{et(S1)}} = K_{\text{sv}}[\text{Iod}]/(1 + K_{\text{sv}}[\text{Iod}]) \quad (2)$$

In spin trapping experiments on an irradiated TADF CuC2/Iod solution using phenyl-*N-tert*-butylnitron (PBN), aryl radicals were detected ($a_{\text{N}} = 14.0$ G, $a_{\text{H}} = 2.1$ G for the $\text{Ar}^\bullet/\text{PBN}$ adduct, which are in agreement with the literature data²⁵ (Fig. 13)).

The aryl radical formation (r1) observed by ESR likely explains the better reactivity of TADF CuC in the presence of Iod compared to non-TADF CuC, the $\text{Ar}^\bullet$ radical being very efficient at initiating the FRP of methacrylates. TADF CuC is also reduced by an amine (r2).²⁵ In the presence of *N*-vinyl carbazole, NVK, according to similar processes in other PI/NVK couples,⁴³ TADF CuC is expected to generate more reactive species ($\text{Ar-NVK}^\bullet$, Ar-NVK^+) that are very efficient at promoting

Fig. 9 Steady state photolysis of TADF CuC2/Iod/EDB in dichloromethane: (a) UV vis spectra at different irradiation times upon LED irradiation at 405 nm; (b) TADF CuC1/Iod (curve 1) vs. TADF CuC1/Iod/EDB (curve 2) consumption. [TADF CuC] = 2×10^{-4} M; [Iod] = 1.5×10^{-3} M; [EDB] = 3.3×10^{-3} M.

Fig. 10 Decay traces recorded at 370 nm and 400 nm after laser excitation at 355 nm of TADF CuC1 and TADF CuC2 in dichloromethane. (A and C) Under air. (B and D) Under nitrogen.

Table 1 Emission lifetime for the different studied copper complexes

	Non-TADF1	TADF CuC1	Non-TADF2	TADF CuC2
τ (μs)	<0.02 ^a	3.5 ^a	<0.02 ^a	3.5 ^a

^a From this work.

radical or cationic polymerization of methacrylates or epoxy resins. The results of the different spectroscopic techniques show, for the TADF compounds, a longer excited state lifetime

Fig. 11 Transient absorption spectrum ($\Delta OD > 0$) of the copper complexes recorded $1 \mu s$ after the laser pulse. The $\Delta OD < 0$ range corresponds to the TADF emission.

Fig. 12 (A) Fluorescence spectra of TADF CuC1 in dichloromethane as a function of $[Iod]$. (B) The corresponding Stern–Volmer plot.

Fig. 13 ESR spectra of the radicals generated in TADF CuC2/Iod and trapped by PBN in *tert*-butylbenzene upon exposure to (A) a UV lamp and (B) a LED at 477 nm; (a) experimental and (b) simulated spectra.

and a faster interaction with the iodonium salt and EDB. Therefore, a higher efficiency for the polymerization process is expected.

A.3. Photoinitiating ability of the investigated TADF and non-TADF copper complexes

A.3.1. Free radical polymerization (FRP) of methacrylates. The free radical polymerization of BisGMA-TEGDMA blends (1.4 mm thick samples) under air upon LED irradiation at 405 nm in the presence of non-TADF and TADF CuC1 based PISs was evaluated (Fig. 14A). Despite the higher molar extinction coefficients of non-TADF CuC1, a final methacrylate function conversion $FC = 60\%$ was recorded with TADF CuC1/Iod *versus* only 30% with non-TADF CuC1/Iod. The TADF (or non-TADF) CuC1/Iod/EDB is still better. The high performance character is mainly governed by its TADF behavior *i.e.* it can be seen in Fig. 14B that curve 2 (without EDB) and curve 4 (with EDB) are rather similar.

The same trend in the polymerization efficiency is observed with TADF CuC2 *vs.* non-TADF CuC2 (Fig. 14B) *i.e.* a better

Fig. 14 Polymerization profiles (methacrylate function conversion *vs.* irradiation time) of BisGMA-TEGDMA in the presence of (1) non-TADF CuC/Iod (0.5/1% w/w), (2) TADF CuC/Iod (0.5/1% w/w), (3) non-TADF CuC/Iod/EDB (0.5/1/1% w/w) and (4) TADF CuC/Iod/EDB (0.5/1/1% w/w) upon irradiation with an LED @ 405 nm; sample thickness = 1.4 mm; (A) CuC1, (B) CuC2 (the irradiation starts at $t = 10$ s).

polymerization initiating ability is found for the derivative with a TADF character. The change of EDB for NVK has almost no effect on the improvement of the TADF (or non-TADF)/Iod couples (Fig. 15). These PISs are characterized by a good ability to initiate the FRP of methacrylates; indeed using BAPO as a reference photoinitiator (BAPO is bis(2,4,6-trimethylbenzoyl) phenylphosphine oxide): $FC = 61\%$.

A.3.2. Cationic polymerization (CP) of epoxy. The photoinitiating ability of the TADF (or non-TADF) CuC2/Iod/NVK (0.5/1/1% w/w) three-component systems in the cationic polymerization of thick EPOX samples (1.4 mm) under air upon LED irradiation at 405 nm

Fig. 15 Photopolymerization profiles (methacrylate function conversion *vs.* irradiation time) of BisGMA-TEGDMA in the presence of (1) non-TADF CuC2/Iod (0.5/1% w/w), (2) TADF CuC2/Iod (0.5/1% w/w), (3) non-TADF CuC2/Iod/NVK (0.5/1/1% w/w), (4) TADF CuC2/Iod/NVK (0.5/1/1% w/w), (5) TADF CuC2/Iod/NVK (0.5/1/3% w/w) upon exposure to a LED at 405 nm (110 mW cm^{-2}); thickness = 1.4 mm; under air; the irradiation starts at $t = 10$ s.

Fig. 16 Photopolymerization profiles (epoxy function vs. irradiation time) of EPOX in the presence of (1) non-TADF CuC₂/Iod/NVK (0.5/1/1% w/w) and (2) TADF CuC₂/Iod/NVK (0.5/1/1% w/w) upon exposure to a LED at 405 nm (110 mW cm⁻²); thickness = 1.4 mm; under air; the irradiation starts at $t = 10$ s.

is shown in Fig. 16. Again, TADF CuC₂ is better than the non-TADF structure and leads to a much higher polymerization rate and final epoxy function conversion (FC = 30% vs. 12% respectively).

With the BAPO/Iod reference system, FC remains low (~10%) showing the performance of the proposed TADF compounds. The role of the counter anion (BF₄⁻ or PF₆⁻) is outlined in Fig. 17. Having a less nucleophilic anion (PF₆⁻) enhanced not only the polymerization rate but also the final epoxy function conversion (30% with TADF CuC₂ vs. 15% with TADF CuC₁).

This is in full agreement with the well-known effect of the counter anion nucleophilicity on the cationic polymerization efficiency.⁴³ Interestingly, the addition of NVK to TADF CuC₂/Iod improved the initiating ability (Fig. 18). Even more remarkable, the addition of CARET to TADF CuC₂/Iod still increased the polymerization performances.

A.3.3. Interpenetrated polymer network synthesis. The three-component system was also used to initiate simultaneously the radical and cationic polymerization of a TMPTA/EPOX blend upon LED irradiation at 405 nm to obtain a hybrid polymeric network. Using TADF CuC₂/Iod/NVK, conversions of 80% and 20% were obtained for the acrylate double bond and the epoxy group (Fig. 19). A tack-free polymer was obtained.

A.4. Chemical mechanisms. The overall reaction mechanisms involved in the three-component systems are displayed in Fig. 20 and 21 where the initiation step of the FRP of BisGMA/TEGDMA or TMPTA occurs through (1), (2), (3), (5) and the CP

Fig. 17 Polymerization profiles (epoxy function vs. irradiation time) of EPOX in the presence of (1) TADF CuC₁/Iod (0.5/1% w/w) and (2) TADF CuC₂/Iod (0.5/1% w/w) upon irradiation with a LED at 405 nm (110 mW cm⁻²); sample thickness = 1.4 mm; the irradiation starts at $t = 10$ s.

Fig. 18 Photopolymerization profiles (epoxy function vs. irradiation time) of EPOX in the presence of (1) TADF CuC₂/Iod (0.5/1% w/w), (2) TADF CuC₂/Iod/NVK (0.5/1/1% w/w), and (3) TADF CuC₂/Iod/CARET (0.5/1/1% w/w) upon exposure to a LED at 405 nm (110 mW cm⁻²); thickness = 1.4 mm; under air; the irradiation starts at $t = 10$ s.

Fig. 19 Synthesis of TMPTA/EPOX (50/50% w/w) interpenetrated polymer networks (thickness = 1.4 mm) upon exposure to a LED at 405 nm under air in the presence of TADF CuC₂/Iod/NVK (0.5/1/1% w/w). (A) Monomer conversions: (1) acrylate double bond and (2) epoxy functions. (B) IR spectra before and after polymerization; the methacrylate and epoxy peaks at ~6160 cm⁻¹ and ~3700 cm⁻¹ are indicated. The irradiation starts at $t = 10$ s.

of EPOX through (1), (2), (3), (4), (5). In CuC/Iod/EDB, Ar[•], EDB^{•(-H)}, and EDB⁺ are generated. In the presence of *N*-vinyl carbazole, NVK, or CARET, according to similar processes noted in other PI/Iod/NVK systems,⁴⁴ TADF CuC is expected to generate more reactive species (Ar-NVK[•], Ar-NVK⁺; CARET^{•(-H)}, CARET⁺) that are very efficient at promoting the radical or cationic polymerization of methacrylates or epoxy resins.

B. Organic structures as TADF compounds

The radical polymerization profiles of BisGMA-TEGDMA obtained upon LED irradiation at 405 nm, under air, in the presence of

Fig. 20 Chemical mechanisms for the CuC/Iod/Caret or CuC/Iod/EDB photoredox systems.

Fig. 21 Chemical mechanisms for the CuC photoredox catalysts.

Fig. 22 Photopolymerization profiles (methacrylate functions vs. irradiation time) of BisGMA/TEGDMA in the presence of: (1) org 1/Iod (0.5/1% w/w), (2) org 2/Iod (0.5/1% w/w), (3) org 1/Iod/EDB (0.5/1/1% w/w/w) and (4) org 2/Iod/EDB (0.5/1/1% w/w/w) upon exposure to LED at 405 nm (110 mW cm^{-2}); thickness = 1.4 mm; under air; the irradiation starts at $t = 10 \text{ s}$.

the purely organic compounds are displayed in Fig. 22 and 23. The inhibition times are rather long. The org 2/Iod couple is better than org 1/Iod. The addition of EDB improves the performance; but org 2/Iod/EDB remains better than org 1/Iod/EDB (Fig. 22). The org 3/Iod couple and org 3/Iod/EDB are even better (Fig. 23). The most remarkable result, however, concerns org 4 which leads to the best results (in terms of the rate of polymerization and conversion) when used in org 4/Iod and org 4/Iod/EDB systems.

The org 1/Iod and org 2/Iod couples exhibit photostability (Fig. 24), in contrast to the fast decomposition observed above for the copper complexes. The org 1 and org 2 have very short singlet state lifetimes in solvent (e.g. 2.55 ns and 1.55 ns, respectively⁴⁰).

Fig. 23 Photopolymerization profiles (methacrylate functions vs. irradiation time) of BisGMA/TEGDMA in the presence of (1) org 3/Iod (0.5/1% w/w), (2) org 4/Iod (0.5/1% w/w), (3) org 3/Iod/EDB (0.5/1/1% w/w/w), (4) org 4/Iod/EDB (0.5/1/1% w/w/w) upon exposure to a LED at 405 nm ($I = 110 \text{ mW cm}^{-2}$); thickness = 1.4 mm; under air; the irradiation starts at $t = 10 \text{ s}$.

Fig. 24 Steady state photolysis of (A) org 1/Iod, (B) org 2/Iod in ACN/dichloromethane (50 : 50), (C) TADF CuC1/Iod in dichloromethane; ([org 1] = [org 2] = $3 \times 10^{-4} \text{ M}$; [TADF CuC] = $2 \times 10^{-4} \text{ M}$; [Iod] = $1.5 \times 10^{-3} \text{ M}$). UV vis spectra at different irradiation times upon LED irradiation at 405 nm (110 mW cm^{-2}).

No data are available for org 3: the absence of delayed emission in powder samples was just noted³¹ and, in our experiments, the TADF emission in a solvent medium is very weak which prevented any lifetime measurements by LFP. These three structures have presumably a low TADF behaviour. In contrast, org 4 has undoubtedly a TADF behaviour: the luminescence decay of org 4 in oxygen-free toluene exhibits two components³⁹ (a short one in the ns range that corresponds to the prompt fluorescence and a long one in the 100 μ s range assigned to the TADF emission), the photoluminescence quantum yield is 0.69. This org 4 compound led to the best polymerization results in agreement with its TADF character.

Conclusions

In the present paper, metal-based and metal-free structures exhibiting a thermally activated delayed fluorescence behavior are studied in detail as potential photoinitiators/photoredox catalysts. The reactivity/efficiency of TADF vs. non TADF copper complexes in the FRP of methacrylates or the CP of epoxides, in thick samples (1.4 mm), upon LED exposure at 405 nm, under air, was compared. A clear enhancement of the final conversions was evidenced when using both TADF copper complexes and TADF organic molecules. Therefore, the role of this specific TADF property is clearly outlined. Moreover, the performances are similar to or better than those achieved with a conventional reference photoinitiator (BAPO). The design of other organic structures or copper complexes will be presented in forthcoming papers.

Conflicts of interest

There are no conflicts to declare.

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