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Metalated Porphyrins as versatile visible light and NIR photoinitiators of polymerization

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Abstract:

A series of metalated porphyrins has been prepared and used as visible light photoinitiators of polymerization activable under low light intensity. Among the six metalated porphyrins examined in this work, five of them have never been reported in the literature and specifically designed to exhibit a good solubility in monomers. Three of the proposed structures were efficient @405nm but remarkably, despite their weak absorptions at 785 nm, efficient Near Infrared (NIR) polymerization profiles could also be obtained during the free radical polymerization of a methacrylate resin. To support the experimental observation of a polymerization process, a mechanism has been proposed based on combined photochemical and photothermal pathways.

1. Introduction

Polymer products are now everywhere in our daily life and these materials can advantageously replace the traditional materials such as steel, glass, wood, stone or concrete in numerous applications.^[1-2] Polymers benefit from numerous advantages such as being lightweight, rigid or flexible on demand and these materials can also display remarkable thermal, electrical or magnetic properties. As final advantages, polymers can also be recycled or reused after application of the appropriate treatment.^[3-4] Due to their widespread use, a great deal of

efforts has been devoted to develop new routes to access to these polymeric materials. In this field, visible light photopolymerization has the capacity to replace the traditional UV photopolymerization still extensively used in industry.^[5] Indeed, UV polymerization is facing numerous drawbacks such as the requirements of using adequate precautions as an accidental exposure to UV light can cause severe eyes and skin damages. Parallel to this, expensive irradiation setups and high-energy consumption are associated with UV photopolymerization. In this context, visible light photopolymerization appears as a promising alternative as cheap and lightweight light sources such as light-emitting diodes (LEDs) can be advantageously used.^[6-10] Higher light penetration inside the photocurable resins can be also obtained, enabling to polymerize thick samples.^[11] Conversely, due to the limited light penetration with UV light, UV photopolymerization is restricted to the polymerization of thin samples. Considering that the light penetration is the key-parameter to polymerize thick samples, recently, NIR light photopolymerization has been the focus of numerous research efforts and structures such as squaraines, phthalocyanines, cyanines, Bodipys or negative photochroms such as the Donor-Acceptor Stenhouse Adducts (DASA) have been examined for this purpose.^[12-21] However, there is a constant strive to find new structures activable in the near infrared region. At present, porphyrins have only been scarcely for NIR light polymerization despite their appropriate absorptions.^[22-23] Besides, a few examples of porphyrins used as visible photoinitiators can be cited. Notably, in 2015, an interesting report mentioning the use of Zn-porphyrins as photoredox catalysts for living radical polymerization in the 435-655 nm range was published by Boyer and coworkers.^[24] But living radical polymerization could also be initiated with Co-based porphyrins or even chlorophyll, still in the visible range.^[25-29] However, in these different works, photoinitiation in the near-infrared region has never been examined. Porphyrins can be easily found in Nature, mostly complexed with iron or magnesium cations. Among the most popular porphyrins, those that can be found in hemoglobins, myoglobins, cytochromes, and chlorophylls can be cited as the most relevant examples.^[30] In our previous works, we have

shown that zinc tetraphenylporphyrin can be used in multicomponent initiating systems for both radical and cationic polymerization upon near UV or visible light (e.g. 405 nm).^[31] Therefore, in this work, a new series of metalloporphyrins has been examined as photoinitiators of polymerization and extended to longer wavelength polymerization (i.e. NIR light). Noticeably, among the six metalloporphyrins examined in this work, five of them have been designed with long aliphatic chains to improve the solubility in monomers. Considering that a sufficient solubility of photoinitiators in the monomer is primordial to efficiently initiate a polymerization process,^[32,33] several metal-free porphyrins have been rapidly discarded for metalation due to the solubility issues. As a result of this, three porphyrins were metalated with various metal cations such as Pd^{2+} , Cu^{2+} , Zn^{2+} , Fe^{2+} . Among the selected set of metalloporphyrins, the free radical polymerization (FRP) of a methacrylate resin (Mix-MA) could only be efficiently promoted at 405 nm and 785 nm under air (i.e. in oxygen inhibition conditions) with three of the synthesized porphyrins (See Figure 1). At 405 nm, a pure photochemical approach can be used to generate the initiating radicals in presence of metalloporphyrins, iodonium salt and phosphine (4-dppba). Whereas for polymerization upon NIR light (785 nm), the addition of a thermal initiator was required for a combined photochemical/photothermal approach. Indeed, the polymerization of acrylates and methacrylates is also a highly exothermic reaction as it consists in converting double bonds to single bond. As a consequence of this, if a thermal initiator is introduced into the photocurable resin, the heat released during the polymerization process can promote the decomposition of the thermal photoinitiator if a sufficient temperature is reached by the reaction media. A heater behavior for porphyrins upon NIR light is also highlighted. As a result of this, a second source of radicals can be generated in situ, improving the monomer conversion. In this study, incorporation of a well-known thermal initiator, namely BlocBuilder MA which a thermosensitive alkoxyamine,^[34-36] has been introduced in the resins so that a significant enhancement of both the polymerization speed as well as the final monomer conversion could be detected.

2. Materials and methods

2.1. Materials

The three metalloporphyrins investigated in this work were synthesized according to procedures depicted below and their corresponding chemical structures are presented in Figure 1. 1. Di-*tert*-butyl-diphenyl iodonium hexafluoro-phosphate (noted as Iod) was obtained from Lambson Ltd (UK) and 4-(diphenylphosphino) benzoic acid (4-dppba) was purchased from Tokyo Chemical Industry (TCI) Chemicals. Mix-Ma is a resin composed of three different monomers in a 33/33/33 (wt%/wt%/wt%) ratio, composed of HPMA (2-hydroxypropyl) methacrylate, 1,4-BDDMA (1,4-butanediol dimethacrylate) and UDMA (a urethane dimethacrylate). Mix-Ma has a low viscosity of 0.053 Pa. BlocBuilder MA was obtained from Arkema (See Figure 2). All the chemical compounds were selected with the highest purity available and used as received. For all the formulations mentioned in this work, weight percentages are related to the resin.

Figure 1. Chemical structures of metalloporphyrins used in this study.

Figure 2. Chemical structures of the different additives (4-dppba, Iod and BlocBuilder MA) and the monomer (Mix-MA).

2.2. Sample preparation

For the free radical polymerization, metallophorphyrins (photoinitiators), Iod (electron acceptor) and 4-dppba (electron donor) were successfully added into Mix-MA (0.1%/3%/2%, w/w), and the weight percent of the three-component photoinitiating system was calculated from the monomer content. For the four component systems, the following composition was used, namely Porph/Iod/4-dppba/BlocBuilder (0.1%/3%/2%/2%, w/w). Upon mechanical mixing at a rotation speed of 1500 rpm with a SpeedMixer (DAC 150.1 FVZ-K) (FlackTek Inc., Landrum USA), homogeneous resins could be obtained, which were stored in dark environment at room temperature before irradiation.

2.3. Irradiation source

A Laser diode emitting at 785 nm (supplied by Changchun New Industries Optoelectronics Technology Co., Ltd) has been used and the incident light intensity at the surface of the sample was 2.5 W.cm^{-2} .

2.4. Real-time Fourier transform infrared spectroscopy

For the free radical polymerization, the prepared photosensitive formulations were deposited into a 1.4 mm thick round mold or 25 μm thin films. Evolution of the C=C double bond content of Mix-MA was continuously followed using real time Fourier transform infrared spectroscopy (RT-FTIR, JASCO FTIR 4100 (JASCO, Tokyo Japan)) at about 6160 cm^{-1} and 1630 cm^{-1} , respectively. The final conversion (FC) of the reactive groups at time t during the photopolymerization was calculated using $\text{FC} = (A_0 - A_t)/A_0 \times 100\%$ (where A_0 is the initial peak area of the functional groups before irradiation and A_t is the peak area at irradiation time t).^[37,38] The set-up and procedure to follow polymerization upon NIR lights have been presented in [15-17].

2.5. Synthesis of the dyes

All compounds were characterized using the procedures and equipments (^1H and ^{13}C NMR, high resolution mass spectrometry (HRMS),...) reported elsewhere.^[39] 4-Dodecylbenzaldehyde ^[40], 2-dodecylbenzaldehyde ^[41], 2,4-dibutoxybenzaldehyde ^[42], 2-butoxy-4-diethylaminobenzaldehyde ^[43] and 9-hexyl-9*H*-carbazole-3-carbaldehyde ^[44], **Porph_1** ^[45-49], **Porph_2** ^[50], **Porph_3** ^[51], **Porph_6** ^[52-54], **Porph_7** ^[55], **Porph_8** ^[56], **Fe-Porph_1** ^[57] were synthesized, as previously reported in the literature, without modification and in similar yields.

Synthesis of 5,10,15,20-tetrakis(2,4-dibutoxyphenyl)porphyrin **Porph_4**

To a 500 mL two-necked round-bottomed flask equipped with a water condenser, a mixture of 2,4-dibutoxybenzaldehyde (25.0 g, 100 mmol, $M = 250.34 \text{ g/mol}$) in propionic acid (400 mL) was added under N_2 . The reaction solution was heated up to 130°C and then pyrrole (6.7 g, 100 mmol) was added. The mixture was stirred at 140°C for 2 h. After cooling to room temperature, the dark violet precipitate was filtered off, washed with methanol several times and dried under vacuum (7.74 g, 26% yield). $^1\text{H-NMR}$ (CDCl_3) δ : 8.80 (8H, s), 7.87 (4H, m), 6.89 (4H, s), 6.87 (4H, m), 4.28 (8H, m), 3.86 (8H, m), 2.01 (8H, m), 1.66 (8H, m), 1.55-0.51 (42H, m), -2.60 (2H, s); Anal. Calc. for $\text{C}_{76}\text{H}_{94}\text{N}_4\text{O}_8$: C, 76.6; H, 7.9; O, 10.7; Found: C, 76.4; H, 7.7; O, 10.5 %; HRMS (ESI MS) m/z : theor: 1191.7144 found: 1191.7145 $[\text{M}+\text{H}]^+$ detected).

Synthesis of 5,10,15,20-tetrakis(2-butoxy-4-diethylaminophenyl)porphyrin **Porph_5**

To a 500 mL two-necked round-bottomed flask equipped with a water condenser, a mixture of 2-butoxy-4-diethylaminobenzaldehyde (24.9 g, 100 mmol, $M = 249.35 \text{ g/mol}$) in propionic acid (400 mL) was added under N_2 . The reaction solution was heated up to 130°C and then pyrrole (6.7 g, 100 mmol) was added. The mixture was stirred at 140°C for 2 h. After cooling to room temperature, the dark violet precipitate was filtered off, washed with methanol several times and dried under vacuum (6.24 g, 21% yield). $^1\text{H-NMR}$ (CDCl_3) δ : 8.82 (8H, s), 7.82 (4H, m),

6.83 (4H, s), 6.81 (4H, m), 4.02 (8H, m), 3.42 (16H, m), 1.79 (8H, m), 1.53 (8H, m), 1.19 (24H, m), 0.98 (12H, m), -2.63 (2H, s); Anal. Calc. for $C_{76}H_{98}N_8O_4$: C, 76.9; H, 8.3; O, 5.4; Found: C, 76.8; H, 8.5; O, 5.5 %; HRMS (ESI MS) m/z: theor: 1187.7784 found: 1187.7789 $[M+H]^+$ detected).

Synthesis of [5,10,15,20-Tetrakis(4-dodecyloxyphenyl)porphyrinate]Fe (II) **Fe-Porph_2**

To a solution of **Porph_2** (1.35 g, 1 mmol, M = 1352.04 g/mol) in chloroform (100 mL) was added a solution of iron acetate (173 mg, 1 mmol, M = 173.93 g/mol) in DMF (20 mL). The mixture was refluxed for 1 h. After cooled to room temperature, the solvent was removed under reduced pressure. After washing by methanol, the crude was purified by column chromatography (SiO_2) using chloroform) as the eluent to yield [5,10,15,20-tetrakis(4-dodecyloxyphenyl) porphyrinate]Fe(II) (913 mg, 65% yield) as a purple powder. Anal. Calc. for $C_{92}H_{124}FeN_4O_4$: C, 78.6; H, 8.9; O, 4.5; Found: C, 78.8; H, 8.8; O, 4.5 %; HRMS (ESI MS) m/z: theor: 1404.8972 found: 1404.8974 (M^{+} detected).

Synthesis of [5,10,15,20-Tetrakis(4-dodecyloxyphenyl)porphyrinate]Zn (II) **Zn-Porph_2**

To a solution of **Porph_2** (1.35 g, 1 mmol, M = 1352.04 g/mol) in chloroform (100 mL) was added a solution of zinc acetate dihydrate (0.25 g, 1 mmol, M = 251.19 g/mol) in methanol (20 mL). The mixture was refluxed for 1 h. After cooled to room temperature, the solvent was removed under reduced pressure. After washing by methanol, the crude was purified by column chromatography (SiO_2) using chloroform) as the eluent to yield [5,10,15,20-tetrakis(4-dodecyloxyphenyl) porphyrinate]Zn(II) (764 mg, 54% yield) as a solid. 1H -NMR ($CDCl_3$) δ : 8.97 (8H, s), 8.11 (8H, d, J = 9 Hz), 7.27 (8H, d, J = 9 Hz), 4.26 (8H, t, J = 7 Hz), 1.99 (8H, quint, J = 7 Hz), 1.63 (8H, quint, J = 7 Hz), 1.25–1.52 (m, 64H), 0.87 (12H, t, J = 7.0 Hz); HRMS (ESI MS) m/z: theor: 1412.8914 found: 1412.8916 (M^{+} detected).

Synthesis of [5,10,15,20-Tetrakis(4-dodecyloxyphenyl)porphyrinate]Cu (II) **Cu-Porph_2**

To a solution of **Porph_2** (1.35 g, 1 mmol, $M = 1352.04$ g/mol) in chloroform (100 mL) was added a solution of copper acetate hydrate (0.18 g, 1 mmol, $M = 181.63$ g/mol) in methanol (20 mL). The mixture was refluxed for 1 h. After cooled to room temperature, the solvent was removed under reduced pressure. After washing by methanol, the crude was purified by column chromatography (SiO_2) using chloroform) as the eluent to yield [5,10,15,20-tetrakis(4-dodecyloxyphenyl) porphyrinate]Cu(II) (1.34 g, 95% yield) as a solid. Anal. Calc. for $\text{C}_{92}\text{H}_{124}\text{FeN}_4\text{O}_4$: C, 78.2; H, 8.8; O, 4.5; Found: C, 78.1; H, 8.9; O, 4.6 %; HRMS (ESI MS) m/z : theor: 1411.8919 found: 1411.8924 (M^+ detected).

Synthesis of [5,10,15,20-Tetrakis(4-dodecyloxyphenyl)porphyrinate]Pd (II) **Pd-Porph_2**

To a solution of **Porph_2** (1.35 g, 1 mmol, $M = 1352.04$ g/mol) in chloroform (100 mL) was added a solution of palladium acetate (0.22 g, 1 mmol, $M = 224.51$ g/mol) in methanol (20 mL). The mixture was refluxed for 1 h. After cooled to room temperature, the solvent was removed under reduced pressure. After washing by methanol, the crude was purified by column chromatography (SiO_2) using chloroform) as the eluent to yield [5,10,15,20-tetrakis(4-dodecyloxyphenyl) porphyrinate]Pd(II) (1.23 g, 85% yield) as a solid. $^1\text{H-NMR}$ (CDCl_3) δ : 9.05 (8H, s), 8.22 (8H, d, $J = 9$ Hz), 7.32 (8H, d, $J = 9$ Hz), 4.22 (8H, t, $J = 7$ Hz), 1.96 (8H, quint, $J = 7$ Hz), 1.61 (8H, quint, $J = 7$ Hz), 1.25–1.55 (m, 64H), 0.91 (12H, t, $J = 7.0$ Hz); HRMS (ESI MS) m/z : theor: 1454.8657 found: 1454.8659 (M^+ detected).

Synthesis of [5,10,15,20-Tetrakis(2,4-dibutoxyphenyl)porphyrinate]Zn (II) **Zn-Porph_4**

To a solution of **Porph_4** (1.19 g, 1 mmol, $M = 1191.61$ g/mol) in chloroform (100 mL) was added a solution of zinc acetate dihydrate (0.25 g, 1 mmol, $M = 251.19$ g/mol) in methanol (20 mL). The mixture was refluxed for 1 h. After cooled to room temperature, the solvent was removed under reduced pressure. After washing by methanol, the crude was purified by column

chromatography (SiO₂) using chloroform) as the eluent to yield [5,10,15,20-tetrakis(4-dodecyloxyphenyl) porphyrinate]zinc(II) (0.60 g, 48% yield) as a solid. ¹H-NMR (CDCl₃) δ: 9.38 (4H, d, J = 9.0 Hz), 8.98 (8H, s), 6.61 (4H, dd, J = 9.0 Hz, J = 2.2 Hz), 6.61 (4H, d, J = 2.2 Hz), 4.08 (8H, t, J = 6.4 Hz), 4.07 (8H, t, J = 6.4 Hz), 1.76-1.94 (16H, m), 1.46-1.64 (16H, m), 1.02 (12H, t, J = 7.3 Hz), 1.00 (12H, t, J = 7.3 Hz); HRMS (ESI MS) m/z: theor: 1252.6207 found: 1252.6205 (M⁺ detected).

3. Results and Discussion

3.1. Synthesis of porphyrins and metalloporphyrins

Eight porphyrins **Porph_1-Porph_8** were investigated in this work and the different dyes were synthesized following the Rothmund synthesis reported for the time in 1935^[58,59]. More precisely, the simplified version of the Rothmund synthesis i.e. the Adler-Longo procedure was used.^[60] This procedure consists in a condensation/oxidation reaction of pyrrole and the appropriate aldehyde in propanoic acid used as the solvent (See Scheme 1). In our case, eight aromatic aldehydes **Ald_1-Ald_7** were used and **Porph_1-Porph_8** could be obtained with reaction yields ranging from 9 to 90%.

Scheme 1. The Adler-Longo synthesis of porphyrins.

Noticeably, the reaction yields obtained for **Porph_1**^[59-63], **Porph_2**^[64], **Porph_3**^[65], **Porph_6**^[66-68], **Porph_7**^[69] and **Porph_8**^[70] are consistent with those previously reported in the literature (See Scheme 2). Only **Porph_4** and **Porph_5** were not previously reported in the literature and these two porphyrins were prepared in 26 and 21% yields respectively. However, immediately after synthesis, **Porph_3** and **Porph_5-Porph_8** were discarded from the

metalation step due to their insufficient solubilities. By using the appropriate solvent, **Porph_1**, **Porph_2** and **Porph_4** could undergo a rapid metal incorporation (Cu^{II} , Zn^{II} , Fe^{II} and Pd^{II}) so that six metalated porphyrins could be obtained with reaction yields ranging from 48% for **Zn-Porph_4** to 95% yield for **Cu-Porph_2** (See Scheme 3).

Scheme 2. Synthetic routes to porphyrins **Porph_1-Porph_8**.

Scheme 3. Synthetic routes to metalloporphyrins **Fe-Porph_1**, **Cu-Porph_2**, **Zn-Porph_2**, **Pd-Porph_2**, **Fe-Porph_2** and **Zn-Porph_4**.

3.2. Light absorption properties of metallated porphyrins

UV-visible absorption spectra of **Fe-Porph_1**, **Cu-Porph_2**, **Zn-Porph_2**, **Pd-Porph_2**, **Fe-Porph_2** and **Zn-Porph_4** were recorded in chloroform. As shown in the Figure 3, all porphyrins showed an intense absorption band around 420 nm corresponding to the Soret

band. While modifying the metal cation, the Soret band of the metalated porphyrins **Fe-Porph_1** and **Fe-Porph_2** was not shifted but broadened compared to that observed for the other metal cations. Jointly, a severe reduction of the molar extinction coefficient was detected for the Fe-based porphyrins, peaking at $150\,000\text{ L.mol}^{-1}.\text{cm}^{-1}$. The highest molar extinction coefficients were determined for **Cu-Porph_2** and **Zn-Porph_2** peaking at $436\,000$ and $465\,000\text{ L.mol}^{-1}.\text{cm}^{-1}$. Interestingly, introduction of additional electron-donating groups in **Zn-Porph_4** contributed to drastically reduce the molar extinction coefficient of **Zn-Porph_4** compared to that of **Zn-Porph_2**. Even if the absorption spectra of all porphyrins is centered in the 400-500 nm region, a non-negligible absorption can be detected in the 700-800 nm region with a molar extinction coefficient higher than $1000\text{ L.mol}^{-1}.\text{cm}^{-1}$. Absorption in this region typically corresponds to the Q-bands of the metalated porphyrins, originating from high-frequency molecular vibrations. Positions and intensities of these Q bands are notably highly dependent from the substitution pattern of the porphyrin core.[71-73] Therefore, contrarily to what is observed in the 350-450 nm region, **Zn-Porph_2** showed the weakest absorption in the near-infrared region, with a maximum absorption lower than that of **Zn-Porph_4**. It has to be noticed that the Q bands correspond to vibronic couplings between the metal cation and the peripheral organic part so that the transitions detected in the near-infrared region would not be observed for none-metalated porphyrins. Despite their low absorption in the near-infrared region, the absorption of the different metalated dyes was sufficient to be used for photoinitiation processes.

3.3. Photoinitiation ability of the porphyrin-based systems.

3.3.1. Photoinitiating ability @405nm

Photoinitiating ability of the different metalated porphyrins was examined first for the Free Radical Polymerization (FRP) of a methacrylate resin (MIX-MA) upon excitation at 405 nm in presence of iodonium salt and phosphine as additives. Absorptions of porphyrins are mainly centered in the 400-600 nm region (See Figure 3) with high molar extinction coefficients,

therefore three of them were found as efficient initiators for the polymerization of methacrylates under air (See Table 1).

Figure 3. UV-visible absorption spectra of **Fe-Porph_1**, **Cu-Porph_2**, **Zn-Porph_2**, **Pd-Porph_2**, **Fe-Porph_2** and **Zn-Porph_4** in chloroform (top) expansion of the UV-visible absorption spectra of the same porphyrins in the 500-800 nm region.

For the other porphyrin-based systems, the final methacrylate function conversion remained quite low (<30%); these latter systems were not able to overcome the oxygen inhibition. As shown in our previous work for ZnTPP, the porphyrin can sensitize the iodonium salt decomposition through r1 to generate highly efficient initiating aryl radicals (See mechanism depicted in the mechanistic part). Presence of the phosphine helps to overcome the oxygen inhibition in r4-r5 but can also regenerate the porphyrins in r6 (see below).^[31]

Table 1. Final methacrylate function conversions (FC) under air for the MIX-MA after 400s of irradiation using a LED@405nm

Initiating systems (0.1%/1%/1%)	methacrylate function conversion (FC) % (at t = 400s)
Fe-Porph_1 /Iod/4-dppba	50%
Zn-Porph_2 /Iod/4-dppba	75%
Zn-Porph_4 /Iod/4-dppba	74%

3.3.2. Photoinitiating ability Upon NIR light

Photoinitiating ability of the different metalated porphyrins was extended for the FRP of MIX-MA upon excitation at 785 nm. As mentioned in the introduction section, the polymerization of acrylate or methacrylate is exothermic so that the FRP of MIX-MA was examined for a four-component system comprising the two additives, namely the iodonium salt (Iod) and the phosphine (4-dppba) which is commonly used to reduce oxygen inhibition,^[61-62] and the thermal initiator BlocBuilder MA.

To carry out the photopolymerization experiments, the optical density at 785 nm was selected to be lower than 0.1 to ensure a good light penetration inside the photocurable resin. The absorption in monomer is slightly different than in chloroform, but the NIR absorption of the investigated compounds remain low. Indeed, for high optical density, an inner filter effect

occurs, adversely affecting the polymerization in depth by limiting the light penetration. Especially, all porphyrins examined in this work exhibit low molar extinction coefficients at 785 nm which corresponds to the irradiation wavelength, avoiding the inner filter effect. Conversely, for dyes absorbing in the near-infrared region, light-triggered heat release is well-reported and notably used for phototherapy or drug delivery. ^[63-65] In the context of photopolymerization, NIR dyes can absorb light and convert it into heat i.e. these dyes have a heater behavior. As a result of this, heat can be dissipated through the whole resin via convective heat transfer and if the temperature reached by the resin is sufficient, a thermal initiator of polymerization can be decomposed, producing initiating species. This is the reason why, in this work, polymerization processes were carried out upon NIR excitation, to decompose the iodonium salt by a pure photochemical process (r1) and concomitantly to decompose a thermal initiator by light-triggered heat release (r2-r3) corresponding to a photothermal process. The exothermicity of the polymerization reaction also participates to the heat release to promote the decomposition of the thermal photoinitiator. As the thermal initiator, Blockbuilder® MA which is a thermosensitive alkoxyamine was selected for its low decomposition temperature ranging between 50 and 70°C. ^[66-68] Choice of Blockbuilder® MA (See chemical structure in Figure 2) as the thermal initiator was motivated by the following reasons 1) BlocBuilder® MA is extensively used for the polymerization of methacrylates. 2) homolysis of the C-ON bond is well-documented in the literature 3) BlocBuilder® MA opens the way towards living radical polymerization. Indeed, thermosensitive alkoxyamines are at the basis of a polymerization technique named the nitroxide mediated polymerization (NMP) ^[67] 4) this thermal initiator exhibits a low dissociation temperature and 5) this thermal initiator is commercially available and used as a benchmark initiator in industry.

Noticeably, a NIR polymerization process could only be detected for three metalated porphyrins, namely, **Fe-Porph_1**, **Zn-Porph_2** and **Zn-Porph_4**. For the four other metalated porphyrins, no polymerization could be detected, even after 1000 s of irradiation at 785 nm. A

relatively long inhibition time could be determined with all photoinitiating systems, around 200 s, resulting from a strong oxygen inhibition despite the presence of 4-dppba in the resin (See Figure 4). The thicknesses of the samples have been controlled to check that conversion can't be ascribed to such a change of thickness. After 1000 s of irradiation, the four-component system based on **Fe-Porph_1** as the photosensitizer could reached a final methacrylate function conversion of 55%, close to that obtained with **Zn-Porph_4** (50% methacrylate function conversion). The final methacrylate function conversion without BlocBuilder MA (e.g. for Zn-Porph_2/Iod/4-dppba system) is only 30% (vs. 50% in presence of BlocBuilder), clearly showing the interest of the photothermal effect combined with the presence of thermal initiator to improve the polymerization initiating ability (see the chemical mechanisms below). Considering that the three metalated porphyrins strongly differs by the metal cation and the substitution pattern of the porphyrin core, no structure performance can be established. Besides, it can be noticed that two of the three porphyrins that were capable to initiate a polymerization process comprise a Zn^{2+} cation, giving a first trend for future works. These results are consistent with our previous works on ZnTPP @405nm^[31] and the extensive use of Zn-porphyrins as photocatalysts for the degradation of various pollutants,^[69,70,74,75] hydrogen production^[76] or CO₂ reduction.^[77-78] To support the polymerization process observed upon irradiation with a LED at 785 nm, the following equations r1-r5 can be proposed. Indeed, initiating radicals formed upon photoexcitation can be generated according to two parallel mechanisms: 1) a pure photochemical pathway which is classically observed during photopolymerization consisting in the interaction of the excited dye with the iodonium salt. As a result of this, a photoreduction process occur, reducing the iodonium salt and leading to the formation of aryl radicals which are very efficient initiating species (see equation r1). 2) Parallel the photochemical process, a photothermal effect can also take place, the dye being capable to convert the NIR light into heat. When the temperature of the photocurable resin is sufficient, the thermal initiator can decompose, providing a second source of initiating radicals (See equations r2-r3). Considering

that FRP is adversely affected by oxygen and that all polymerization experiments have been carried out under air, phosphines are classically used to overcome the oxygen inhibition by mean of the equations r4-r5.^[79] The temperature was controlled as presented by us in [15,16,17] by thermal imaging experiments. It is shown that temperature higher than 60°C can be reached after 100s of NIR irradiation allowing the decomposition of BlocBuilder.

Figure 4. Photopolymerization profiles for Mix-MA in air (methacrylate function conversion vs. irradiation time) in the presence of $\text{Ar}_2\text{I}^+/\text{PF}_6^-$ (3 wt%), 4-dppba (2 wt%), BlocBuilder MA (2 wt%), and (1) **Fe-Porph_1** (0.1 wt%), (2) **Zn-Porph_2** (0.1 wt%) and (3) **Zn-Porph_4** (0.1 wt%), using a laser diode @785 nm ($I = 2.5 \text{ W.cm}^{-2}$); thickness = 1.4 mm; the irradiation starts at $t = 17 \text{ s}$.

As interesting feature, phosphines are capable to convert the non-initiating peroxy radicals ($\text{ROO}^\bullet$) into the reactive alkoxy radicals ($\text{RO}^\bullet$) (See Scheme 4). Indeed, as reported by Buckler as soon as 1962, autoxydation of arylphosphine by peroxy radicals can occur via a radical attack of peroxy radicals on the heteroatom of phosphines, inducing a valence expansion

for the phosphor atom and furnishing a short-lived phosphoranyl radical. Finally, by mean of a β -scission, initiating species $\text{RO}^\bullet$ can be obtained.^[80-81] Parallel to this, the phosphine can also contribute to reduce the oxidized photosensitizer, regenerating it and maintaining the concentration of photosensitizer constant within the resin (See equation r6). Overall, by combining a photochemical and a thermal polymerization pathway and by using a phosphine in charge to convert the non-initiating peroxy radicals into reactive radicals, radicals of various types can be simultaneously formed, optimizing the production of radicals and resulting in remarkable polymerization profiles.

Scheme 4. Overview of the chemical mechanism.

4. Conclusion

To conclude, a series of eight porphyrins have been designed and synthesized for their subsequent metalation with various metal cations. Due to the insolubility of **Porph_3** and **Porph_5-Porph_8**, these porphyrins have been discarded for the design of photoinitiators. Six porphyrins could be successfully metalated with iron, zinc and palladium cations. When tested as photoinitiator/photosensitizer for four-component systems in the NIR, only three of them proved to be efficient and final methacrylate function conversion between 40 and 55% could be obtained with the different systems. Especially, their ability to initiate a polymerization at 785 nm has been clearly evidenced. Interestingly, Zn-porphyrins seems to be better candidates for photoinitiation, what is consistent with their well-established photocatalytic activity reported for the photodegradation of pollutant, hydrogen production or CO₂ reduction. Considering the paucity of structures examined in this work, future work will consist in developing a wide of structure to establish a structure-performance relationship in NIR systems.

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