Wavelength-Tunable Light-Induced Polymerization of Cyanoacrylates Using Photogenerated Amines

Enrico Faggi,[a] *Jordi Aguilera,*[b] *Rubén Sáez,*[b] *Ferran Pujol,*[b] *Jordi Marquet,*[a] *Jordi Hernando,*[a,*] *and Rosa María Sebastián*[a,*]

[a] Departament de Química, Universitat Autònoma de Barcelona, 08193 Cerdanyola del Vallès, Spain

[b] CUANTUM Medical Cosmetics S.L., 08193 Cerdanyola del Vallès, Spain

KEYWORDS: cyanoacrylates, photopolymerization, photocleavable amine protection group

ABSTRACT

Cyanoacrylate photopolymerization has already been described, but it generally requires the use of organometallic photoinitiators and highly reactive monomers, which often leads to photoinitiator-monomer mixtures with limited stability. In this work we report a method to tackle these limitations, which relies on the use of amines bearing photoremovable protecting groups as light-responsive nucleophilic cyanoacrylate initiators. By exploiting the versatility of amine

photorelease strategies, we have developed a series of all-organic initiators that: (a) enable fast, on demand photocuring of commercial formulations of various cyanoacrylates, including less reactive, biologically-relevant long alkyl chain monomers; (b) show wavelength-tunability along the UV-visible spectrum and good thermal stability in the dark; (c) lead to polymeric materials with excellent adhesive behavior. Because of this combination of properties, photogenerated amines appear as ideal candidates to bring cyanoacrylate photopolymerization into real application, especially in the biomedical field.

INTRODUCTION

Cyanoacrylates (CAs) are low-viscosity, fast-acting liquid adhesives with high bonding strength to diverse materials upon polymerization (e.g. glass, paper, wood, plastic, textile).[1,2] As such, they have been widely applied as general adhesives for industrial and consumer markets since first CA-based "super glues" were commercially introduced in the 1950s. Nowadays, their use has spread to the medical, veterinary and cosmetic fields, where CAs are employed as bio-compatible adhesives or sealants for replacing sutures and staples,[3] in dentistry,[4,5] and for gluing fake nails or eyelashes extension.[6] In addition, CAs are currently finding application in other emerging areas, such as in drug-delivery systems,[7,8] 3D printing processes,[9,10] high-resolution lithography,[11] and forensic sciences.[12,13]

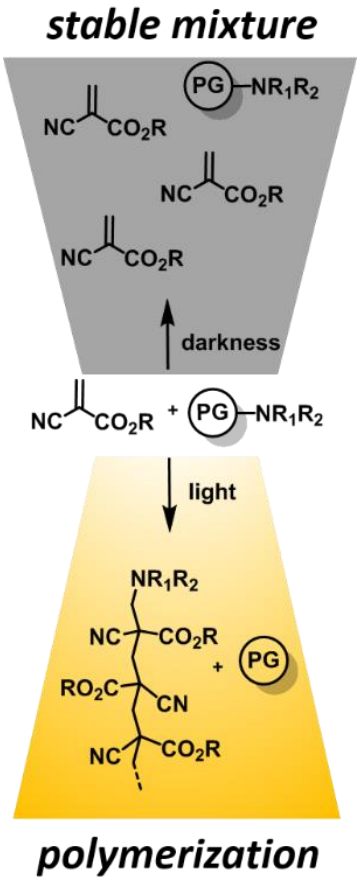
Although free radical initiation has also been described,[14] CA polymerization is normally triggered by anionic or neutral nucleophiles.[1-2] Industrially, these nucleophiles can be sprayed on the surfaces to be glued before cyanoacrylate is applied, thus greatly enhancing the curing rate.[1-2] However, this is not possible in many other cases (e.g. wound closure), where the polymerization

rate is ultimately limited by the concentration of naturally occurring activating nucleophiles. An alternative approach to minimize the adhesive setting time of CAs would be light-induced polymerization, especially for long alkyl chain monomers (e.g. octyl 2-cyanoacrylate), which are less reactive but possess superior properties for many applications (i.e. lower toxicity, and higher stability, viscosity and flexibility).[1-2] More importantly, photopolymerization would enable spatial and temporal control of CA adhesives using light as an external stimulus, which should not only ameliorate their performance in current applications but also open new avenues for the use of cyanoacrylates. Unfortunately, while this is a very popular strategy extensively applied to radical and cationic polymerization reactions, much less progress has so far been achieved in the field of light-induced anionic polymerization, mainly due to the need for further development of anionic (or nucleophilic) photoinitiators.[15-18]

Actually, only a very limited number of photoinitators have been described to promote CA light-induced polymerization, which essentially function for very reactive, short alkyl chain cyanoacrylates (i.e. methyl 2-cyanoacrylate and ethyl 2-cyanoacrylate). Most of these photoinitiators consist of organometallic compounds such as chromium,[19,20] platinum[21] and tungsten[20] complexes as well as metallocenes,[22-25] which generate anionic or neutral nucleophiles via ligand substitution reactions upon irradiation. Reports of all-organic photoinitiators for CA polymerization are even more scarce (pyridinium[26] and phosphonium[27] salts, and crystal violet leuconitrile and malachite green leucohydroxide[28]), and none of them were tested in neat cyanoacrylate, since dilution in inert solvents was needed. In view of these precedents, the preparation of metal-free photoinitiators that could be directly used in commercial formulations of more biologically-relevant, long alkyl chain cyanoacrylates is required, especially aiming to bring CA photopolymerization into real application in the biomedical field. In addition, wavelength

tunability of the latent photoinitiators would be highly desired, thus allowing the most appropriate excitation wavelength to be selected in every case.

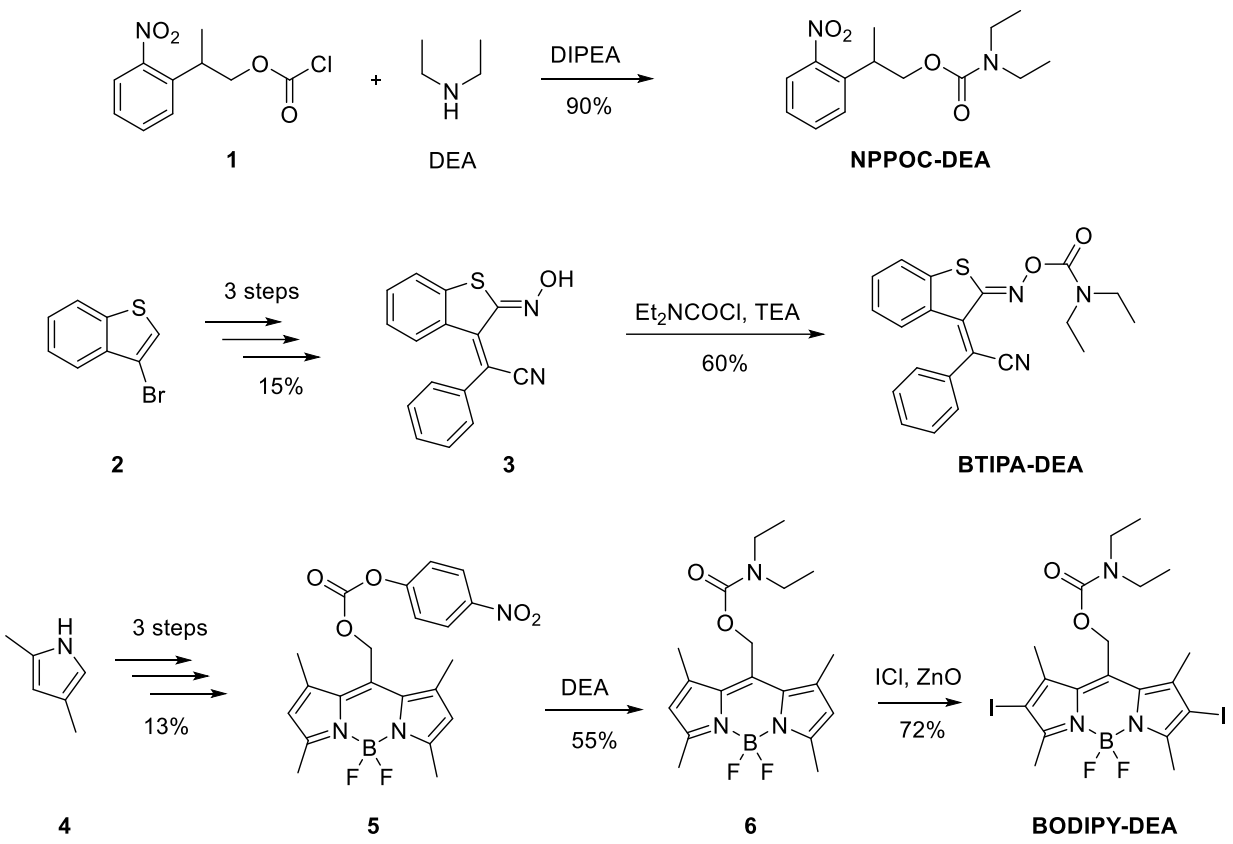
To address all these challenges at once, in this work we propose the use of photogenerated amines for CA polymerization (Scheme 1). Our strategy relies on two core principles. First, the well-known activity of free amines as nucleophilic activators of cyanoacrylate polymerization.[1-2,29] Second, the development of a plethora of photoremovable protecting groups (PG) during the last years that enable the light-induced release of amines with a wide range of irradiation wavelengths, expanding from the UV to the visible and even near-infrared regions.[30]



Scheme 1. Strategy proposed in this work for the light-induced polymerization of cyanoacrylates based on photoreleasable amines.

RESULTS AND DISCUSSION

Design and synthesis of photoinitiators. Photoreleasable amines have already been used in light-induced polymerization processes,[31] either as nucleophiles that directly trigger polymer curing[26,32,33] or as bases for activating the actual initiator of the reaction.[34-37] However, owing to the high reactivity of CAs, care has to be taken in this case when selecting the photoremovable group for amine protection, since it should not contain nucleophilic centers capable to initiate cyanoacrylate polymerization in the dark prior to light irradiation. According to this design concept and aiming to develop an extended palette of photoinitiators for CA polymerization, we explored herein three different, well-established PGs for primary and secondary amines based on a carbamate linker: (a) the UV-responding nitrophenylpropyloxycarbonyl group (NPPOC), initially introduced for nucleotide and nucleoside chemistry[38] and already exploited for the preparation of photocatalysts for thiol-Michael addition reactions with acrylates;[39] (b) the violet light-absorbing benzothiophene imino-phenylacetonitrile (BTIPA) group, which was developed for peptide synthesis;[40] (c) a green light-absorbing, diiodated boron-dipyrromethene (BODIPY) derivative, which was recently derived to enable efficient photorelease of a variety of functional groups,[41] including amines.[42] Based on these light-responsive groups, we designed carbamates **NPPOC-DEA**, **BTIPA-DEA**, and **BODIPY-DEA** (Scheme 2), which should release a secondary amine (diethylamine, DEA) upon irradiation with distinct illumination sources. DEA was chosen because it is a powerful initiator of CA polymerization that has been described to activate cyanoacrylate formulations for biomedical applications.[43] Indeed, when a droplet of DEA was added to any of the liquid CA monomers investigated in this work, very fast, local polymerization was observed.



Scheme 2. Synthesis of photoinitiators **NPPOC-DEA**, **BTIPA-DEA**, and **BODIPY-DEA**.

Scheme 2 summarizes the synthetic procedures applied to prepare the three photoinitiators used. **NPPOC-DEA** (as a racemic mixture) was synthesized in only one step and in high yield (90%) by simple reaction between 2-(2-nitrophenyl)propyl chloroformate (**1**) and free DEA in the presence of DIPEA, as already described.[39] **BTIPA-DEA** was prepared in 4 steps and 9% yield starting from commercially available 3-bromothianaphthalene (**2**). First, key intermediate **3** was obtained following a previously reported procedure,[40] and by reaction with diethylcarbamoyl chloride, the target photoinitiator was afforded. **BODIPY-DEA** was synthesized through a 5-steps procedure from 2,4-dimethyl-1*H*-pyrrole (**4**), which was converted into BODIPY derivative **5** as already described.[42] From this compound, carbamate **6** was prepared by reaction with DEA in the presence of pyridine and, upon posterior electrophilic iodination with ICl and ZnO, **BODIPY-**

DEA was finally obtained. The overall yield for the preparation of this compound was rather low (5%) due to both the cumbersome purification of the low-solubility BODIPY derivatives obtained along the synthesis and the limited efficiency of the first step in our hands. HPLC analysis of the photoinitiators prepared demonstrated that all of them were obtained with high purity (*ca.* 99% or higher).

Photochemical characterization of NPPOC-DEA, BTIPA-DEA and **BODIPY-DEA.** Figure 1a depicts the absorption spectra of the three photoinitiators prepared in acetonitrile. Clearly, they absorb in different spectral regions ($\lambda_{abs,max}$ = 254, 415 and 550 nm, Table 1), which should allow DEA photorelease using distinct irradiation wavelengths: UV (**NPPOC-DEA**), violet (**BTIPA-DEA**) and green (**BODIPY-DEA**) light. In the case of UV excitation, it cannot be overlooked that CAs present non negligible absorption at ca. $\lambda < 350$ (Figure S1). For this reason and the broad absorption tail shown by **NPPOC-DEA**, this compound was not irradiated at its absorption maximum but at significantly lower energies (λ_{exc} = 355 nm). On the contrary, illumination of visible-light absorbing photoinitiators **BTIPA-DEA** and **BODIPY-DEA** could be conducted at wavelengths closer to their spectral maxima (λ_{exc} = 405 and 532 nm, respectively).

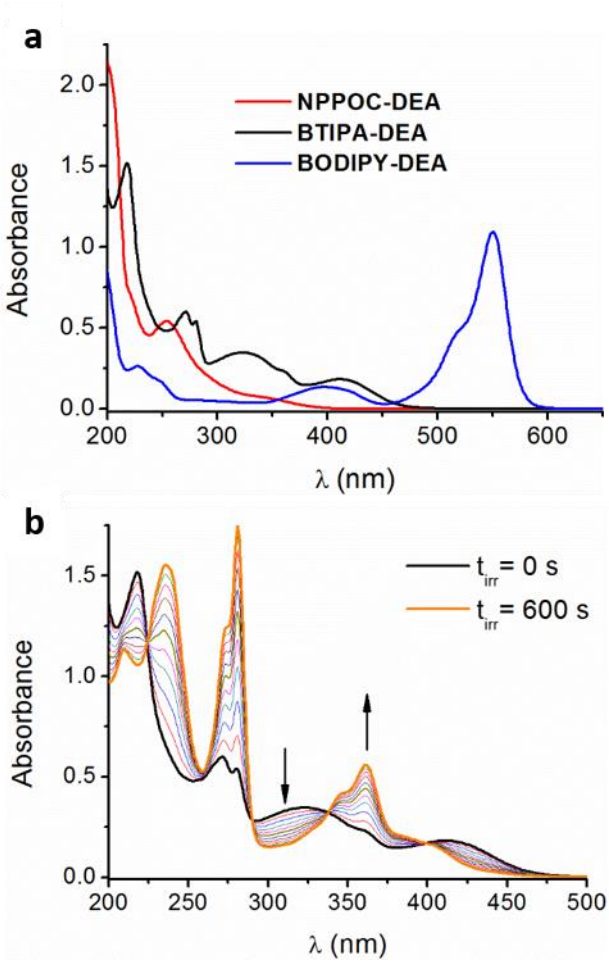


Figure 1. (a) Absorption spectra of **NPPOC-DEA** (c = 1.60·10^{-4} M), **BTIPA-DEA** (c = 4.76·10^{-5} M), and **BODIPY-DEA** (c = 1.68·10^{-5} M) in acetonitrile. (b) Variation of the absorption spectra of **BTIPA-DEA** (c = 4.76·10^{-5} M) in acetonitrile upon continuous irradiation at λ_{exc} = 405 nm (power = 2.8 mW). Spectra recorded every 60 s for a total irradiation (t_{irr}) of 600 s. The arrows show the spectral changes in time.

Table 1. Photochemical properties of **NPPOC-DEA**, **BTIPA-DEA** and **BODIPY-DEA**[a]

Compound	$\lambda_{abs,max}$ (nm)	$\varepsilon_{abs}^{\lambda_{max}}$ (M^{-1} cm^{-1})	Φ_{ph} [b,c]	$\Phi_{ph}\,\varepsilon_{abs}^{\lambda_{max}}$ (M^{-1} cm^{-1})	$\Phi_{ph}\,\varepsilon_{abs}^{\lambda_{exc}}$ (M^{-1} cm^{-1})[c]
NPPOC-DEA	254	4990	0.10	499	47
BTIPA-DEA	415	3845	0.081	311	303
BODIPY-DEA	550	65180	$5.9\ 10^{-4}$	38	22

[a] In acetonitrile at room temperature. [b] Photoreaction quantum yield. [c] λ_{exc} = 355, 405 and 532 nm for **NPPOC-DEA**, **BTIPA-DEA** and **BODIPY-DEA**, respectively.

To investigate their light-induced response, we first irradiated diluted solutions of the three photoinitiators in acetonitrile and monitored the changes observed by UV-vis absorption spectroscopy (Figures 1b and S2). For all the compounds, dramatic spectral variations were registered, which according to previous data[39,40,42] could be ascribed to the photolysis of the carbamate groups and release of the corresponding DEA molecules. To corroborate these results, additional photoexcitation experiments were performed in concentrated CD_3CN solutions of **NPPOC-DEA**, **BTIPA-DEA** and **BODIPY-DEA** that were analyzed by ^{1}H NMR (Figures 2 and S3-S4). In all the cases, gradual disappearance of the ^{1}H NMR signals of the initial compounds was observed upon continuous irradiation, which largely faded after sufficiently long irradiation times. Moreover, new sets of resonances corresponding to the photoinduced products concomitantly appeared. In particular, the two multiplets arising from free DEA at δ = 2.63 and 1.07 ppm were clearly identified for **NPPOC-DEA** and **BTIPA-DEA**, while the other ^{1}H NMR signals formed could be tentatively assigned to the *o*-nitro-α-methyl-styrene (**7**)[39] and benzo[4,5]thieno[2,3-b]quinolone-11-carbonitrile (**8**)[40] main by-products described in previous works (Scheme 3). It must be noted that compound **8** bears a nucleophilic pyridine group and,

therefore, it could participate in the initiation of CA polymerization together with free DEA. In the case of **BODIPY-DEA**, signals of free DEA were not observed, while two new multiplets at $\delta =$ 3.01 and 1.26 ppm arose during irradiation, the chemical shift and multiplicity of which were in accordance with an amine of general formula NEt_2R. Formation of amine **9** was therefore proposed, and subsequently confirmed by HPLC-MS analysis (Figure S5). Although different signals were observed in the chromatogram, the most intense peak could be unambiguously assigned to the protonated form of **9**. We speculate that, upon irradiation, **BODIPY-DEA** releases CO_2, DEA and a benzylic BODIPY cation, which cannot form the expected alcohol[42] in anhydrous media and, instead, readily reacts with DEA to afford amine **9**. Actually, the affinity of free amines for this very electrophilic carbocation was already observed,[42] and it is the reason why the iodination step is performed at the end of the synthetic pathway during the preparation of **BODIPY-DEA**. It must be noted that **9** is a tertiary amine that can also activate CA polymerization.[29] Therefore, upon irradiation of **BODIPY-DEA** in cyanoacrylate solution, we expect polymerization to be initiated either directly by the photoreleased DEA molecules or by amine **9**.

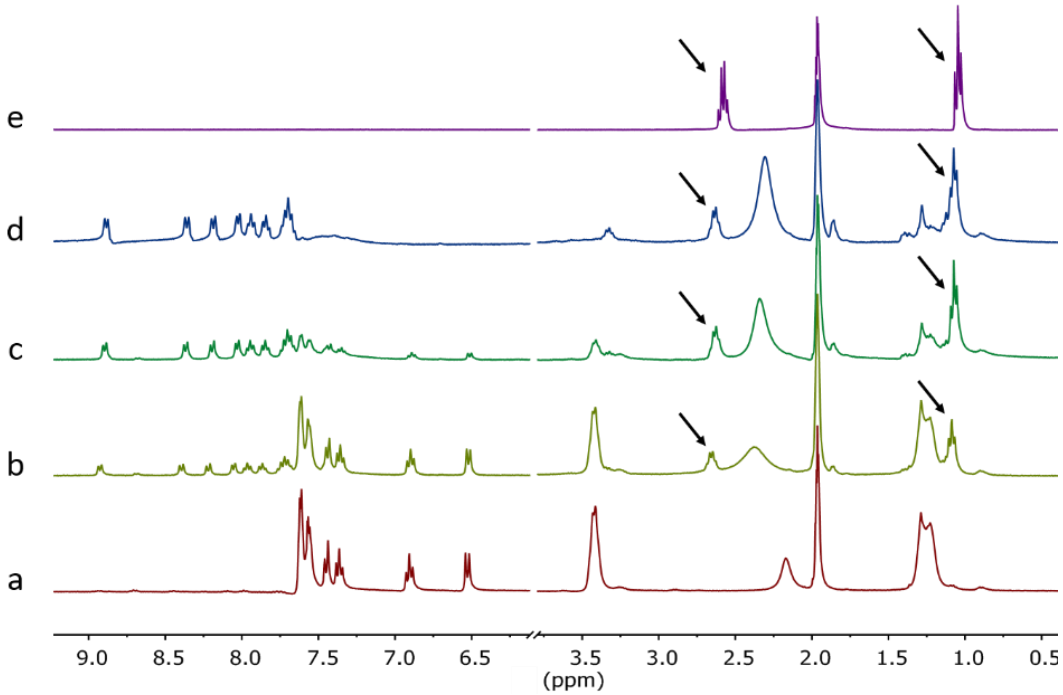
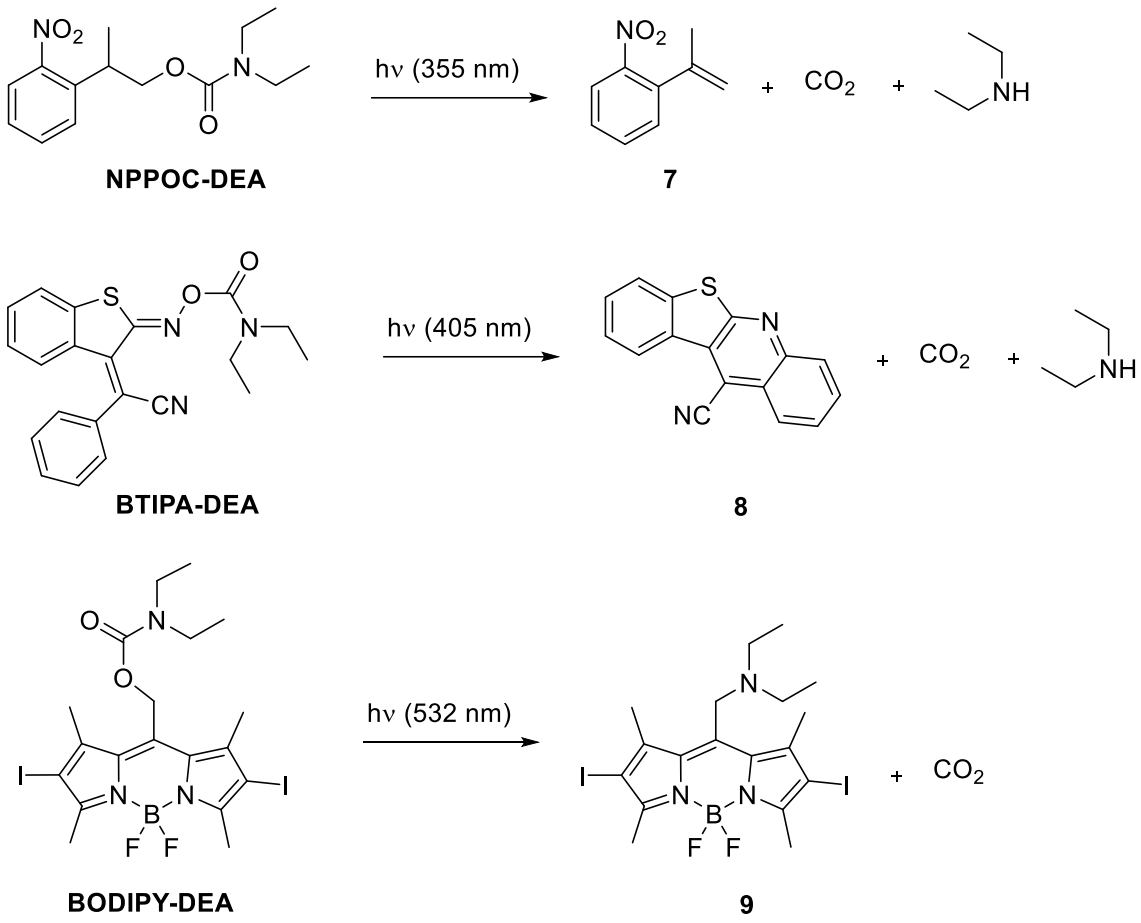


Figure 2. ^{1}H NMR spectra (360 MHz, CD_3CN) of: (a) **BTIPA-DEA**; (b-d) **BTIPA-DEA** after (b) 20 min, (c) 40 min, and (d) 60 min irradiation at 405 nm (power = 280 mW); (e) free DEA. The arrows show the signals due to free DEA.



Scheme 3. Photolysis reactions established for **NPPOC-DEA**, **BTIPA-DEA** and **BODIPY-DEA** in acetonitrile.

To assess the efficiency of amine photorelease from **NPPOC-DEA**, **BTIPA-DEA** and **BODIPY-DEA**, their photoreaction quantum yields (Φ_{ph}) were determined in acetonitrile by means of UV-vis absorption measurements (Table 1). For **NPPOC-DEA** and **BTIPA-DEA**, rather large Φ_{ph} values were measured ($\Phi_{ph} \sim 0.1$), which indicate that they undergo very effective light-induced deprotection. On the other hand, a very low photolysis quantum yield was registered for **BODIPY-DEA** ($\Phi_{ph} = 5.9\ 10^{-4}$), in agreement to the results reported for similar products.[42] However, it must be taken into account that the efficacy of photoreactions does not only depend

on the quantum yield of the process, but also on the absorptivity of the irradiated compound at the excitation wavelength (i.e. on the Φ_{ph} ε_{abs} factor, Table 1). As a consequence, the much larger molar extinction coefficient of **BODIPY-DEA** compared to **NPPOC-DEA** and **BTIPA-DEA** largely counterbalances for the difference in Φ_{ph} values. Actually, if all the compounds were illuminated with the same photon flux at their absorption maxima, amine photorelease from **BODIPY-DEA** would only take place with about 10-fold less efficiency according to our data. This, together with its red-shifted absorption with respect to **NPPOC-DEA** and **BTIPA-DEA**, makes it a very appealing photoinitiator for CA polymerization.

Photopolymerization of cyanoacrylates. To evaluate the scope of the photoinitiators developed in this work to promote light-induced CA polymerization, a wide range of cyanoacrylate monomers were considered: highly reactive ethyl 2-cyanoacrylate (ECA) and methoxyethyl 2-cyanoacrylate (BMCA), as well as long alkyl chain, less reactive butyl 2-cyanoacrylate (BCA), hexyl 2-cyanoacrylate (HCA) and 2-octyl 2-cyanoacrylate (OCA). For each of these monomers, two different batches were subjected to photopolymerization experiments. On one hand, we directly tested the commercial CA samples received (**ECA_0**, **$BMCA_0$**, **BCA_0**, **HCA_0**, **OCA_0**), which contain radical scavengers (e.g. butylated hydroxytoluene) and acids (e.g. boron trifluoride, sulfur dioxide) to prevent premature, undesired radical and anionic polymerization, respectively. Since the nature and concentration of acid stabilizers vary for each cyanoacrylate monomer, they could differently interact with the amine molecules released during light-induced polymerization and, as such, hamper the comparison of the results obtained for distinct CAs. In fact, when determining the acid content on these samples by viscosity acid value determination (AVD) measurements upon free amine addition,[44] strikingly distinct results were encountered for the CA monomers under investigation (Table S1), which however may also be affected by their different

reactivity. For this reason, a second batch of CA samples was prepared, where an acid stabilizer (methanesulfonic acid, MSA) was added to each of the commercial formulations of cyanoacrylate monomers until they presented the same AVD value (**ECA_{st}**, **$BMCA_{st}$**, **BCA_{st}**, **HCA_{st}**, **OCA_{st}**, Table S1). Therefore, we expect the photopolymerization results obtained for these additional samples to directly report on the intrinsic response of each of the CA monomers considered to the light-induced activation process triggered by the three photoinitiators prepared.

Different methods are described in the literature to assess the efficacy of the (photo)activation of cyanoacrylate polymerization, including IR absorption spectroscopy, gravimetric experiments, calorimetric measurements or even visual determination of the viscosity increase by analyzing the rotation of magnetic stirring bars.[19-29] In this work we primarily performed calorimetric experiments in order to allow simple, fast and repetitive in situ analysis of photopolymerization for the large number of conditions scanned (i.e. 3 photoinitiators and 5 CA monomers), while preventing possible artifacts arising in visual viscosity measurements due to the different mechanical properties of the cyanoacrylates tested. In our calorimetric experiments, very small volumes of liquid CA samples (75 μL) were used to minimize heat diffusion effects on their thermal behavior, to which rather low photoinitiator concentrations were added (15 mM), in agreement to previous works on cyanoacrylate photopolymerization.[19-24]

Because of the exothermic character of CA polymerization, temperature increments (typically, ΔT = 7-16 ºC) were registered upon continuous illumination for all the monomer-photoinitiator pairs investigated (Figures 3a and S6), and a solid, tack-free polymeric material was finally obtained in all the cases (Figure 3b). Since no polymerization was observed in control experiments performed in the absence of photoinitiator or light irradiation, this clearly demonstrates the capacity of **NPPOC-DEA**, **BTIPA-DEA** and **BODIPY-DEA** to light-induce the curing of all

types of cyanoacrylates. Noticeably, colored polymers were formed for all the photoactivators assayed (pale yellow for **NPPOC-DEA**, bright yellow for **BTIPA-DEA**, and intensely pink for **BODIPY-DEA**), which result from the visible-light absorbing properties of the unreacted fraction of these compounds and of the by-products formed. To quantify the efficiency of CA photopolymerization, we took as a reference the time at which each sample reached half of the overall thermal increase associated with polymer curing (t_{photo}). By conducting additional experiments by IR spectroscopy and visual inspection of the rotation of a magnetic stirring bar, we demonstrated that: (a) about 90% of the CA monomers had reacted by t_{photo} according to the decrement in the =C-H stretching band at 3127 cm^{-1} (Figure S7); (b) rotation of the stirring bar ceased slightly before t_{photo} (~ 4-10 seconds, as found for **ECA_0+BTIPA-DEA** and **OCA_0+BTIPA-DEA** mixtures), as a relatively small increase in viscosity is enough to prevent it.[45]

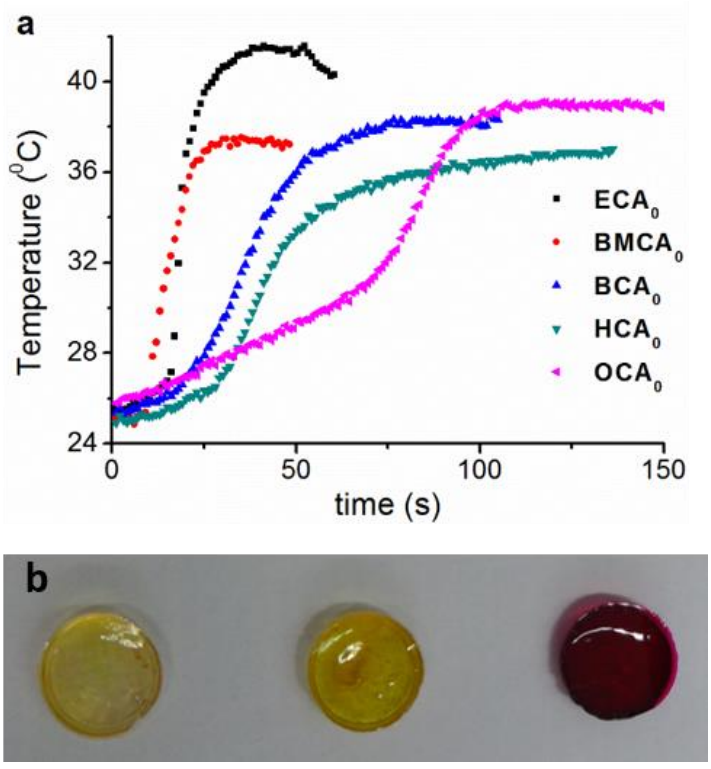


Figure 3. (a) Photopolymerization exotherms of the mixtures containing **BTIPA-DEA** and commercial CA monomers (λ_{exc} = 405 nm, power = 280 mW). (b) Polymers obtained upon illumination of **ECA$_0$**-photoinitiator mixtures (left: **NPPOC-DEA**; center: **BTIPA-DEA**; right: **BODIPY-DEA**).

Table 2 shows the t_{photo} values measured for all the samples investigated. Different conclusions can be derived from this data. First, the presence of additional acid stabilizer in **ECA$_{st}$**, **BMCA$_{st}$**, **BCA$_{st}$**, **HCA$_{st}$** and **OCA$_{st}$** monomers resulted in longer photoinitiation times, which confirms that polymerization takes place via nucleophilic activation upon amine photorelease. To further corroborate this result, a systematic analysis of t_{photo} variation with the concentration of acid stabilizer was performed for **BTIPA-DEA** upon addition of increasing amounts of methanesulfonic acid to **ECA$_0$**. As expected, this led to a continuous enlargement of the photopolymerization time (Figure S8).

Table 2. Photopolymerization times (t_{photo}) for different CA monomer-photoinitiator pairs[a,b]

Monomer	NPPOC-DEA[c,f]	BTIPA-DEA[d,f]	BODIPY-DEA[e,f]
ECA$_0$	28 s	18 s	108 s
ECA$_{st}$	75 s	34 s	143 s
BMECA$_0$	13 s	15 s	100 s
BMECA$_{st}$	49 s	38 s	126 s
BCA$_0$	84 s	37 s	126 s

BCA_{st}	91 s	51 s	169 s
HCA_0	88 s	42 s	138 s
HCA_{st}	99 s	64 s	177 s
OCA_0	94 s	76 s	168 s
OCA_{st}	110 s	91 s	185 s

[a] Determined as the time at which half of the overall thermal increase is reached for the exotherms registered for each sample at room temperature; average of 3 independent measurements. [b] $c_{photoinitiator}$ = 15 mM. [c] λ_{exc} = 355 nm, photon flux = 8.9 10^{-7} Einstein s^{-1}, light intensity: 465 mW cm^{-2}. [d] λ_{exc} = 405 nm, photon flux = 9.5 10^{-7} Einstein s^{-1}, light intensity: 1120 mW cm^{-2}. [e] λ_{exc} = 532 nm, photon flux = 1.1 10^{-6} Einstein s^{-1}, light intensity: 390 mW cm^{-2}. [f] In the absence of irradiation, polymerization of the monomer-photoinitiator mixtures was observed at a much longer time scale both in air (> 30 min) and when stored in closed, opaque polypropylene bottles: **NPPOC-DEA** (from 4 months in ECA to more than 6 months in OCA) **BTIPA-DEA** (from 40 min in ECA to 2 h in OCA), and **BODIPY-DEA** (from 2 days in ECA to 6 days in OCA).

Based on t_{photo} evaluation, we also ascertained differences in the efficacies of the three photoinitiators assayed at rather similar photon fluxes (~ 1 10^{-6} Einstein s^{-1}), which were consistent for each of the CA monomers tested and generally followed the trend of their $\Phi_{ph}\,\varepsilon_{abs}^{\lambda_{exc}}$ values in acetonitrile. **BTIPA-DEA** and, in a lesser extent, **NPPOC-DEA** led to the shortest photopolymerization times, whereas 2- to 8-fold larger t_{photo} values were determined for **BODIPY-DEA** as a result of its lower photoreaction quantum yield. In the latter case, the slower curing time may also be ascribed to the generation of tertiary amine **9**, which is sterically hindered and probably less prone to initiate CA polymerization. Notably, the photoinitiator-dependent variation in t_{photo} was found to decrease for the less active cyanoacrylates (i.e. BCA, HCA and, especially, OCA), which we attribute to the different contributions of amine photodeprotection and intrinsic monomer reactivity to the overall rate of the photopolymerization process in each case. This can

be clearly inferred from the analysis of t_{photo} for the more photoactive initiators **BTIPA-DEA** and **NPPOC-DEA**. For those compounds, much shorter photopolymerization times were measured for ECA and BMECA than for the other monomers, as expected owing to their higher reactivity.[1-2] Therefore, one can assume that the very low t_{photo} values encountered in this case (e.g. t_{photo} = 13 or 15 s for **BMECA$_0$** and **NPPOC-DEA** or **BTIPA-DEA**, respectively, Table 2) essentially report on the fast rate of amine photodeprotection accomplished for those two photoinitiators. As a consequence, the fact that larger photocuring times were registered for long alkyl chain CAs with **NPPOC-DEA** and **BTIPA-DEA** under the same irradiation conditions (e.g. t_{photo} = 94 and 76 s for **OCA$_0$**, respectively) indicates that the photopolymerization rate of these monomers is limited by their low reactivity in this case (i.e. slow nucleophile activation and/or propagation steps). As for **BODIPY-DEA**, amine light-induced deprotection takes place in a longer time scale and, consequently, ultimately determines photopolymerization kinetics even for the less reactive monomers. Hence, this explains the rather similar t_{photo} values measured for all the cyanoacrylates under study.

In spite of this, relatively fast photopolymerization times (< 190 s) were determined in all the cases, even for the less active monomer-photoinitiator pairs considered (i.e. **OCA$_{st}$** and **BODIPY-DEA**). This is unambiguously demonstrated by comparing the light-induced results with the kinetics of thermal polymerization for the same cyanoacrylates. On one hand, the monomer-photoinitiator mixtures subjected to photopolymerization experiments were found to remain in the low viscosity, liquid state for at least 30 minutes in the dark and under ambient conditions. Actually, when stored in closed, opaque polypropylene bottles, those mixtures were stable for hours (from 40 min in ECA to 2 h in OCA for **BTIPA-DEA**), days (from 2 days in ECA to 6 days in OCA for **BODIPY-DEA**) or even months (from 4 months in ECA to more than 6 months in

OCA for **NPPOC-DEA**). On the other hand, to thermally polymerize small volumes (~ 1 mL) of the cyanoacrylates under study inside non-treated glass vials, they had to be exposed to ambient conditions for several hours (ECA and BMECA) or days (BCA, HCA and OCA). Therefore, light-induced polymerization of these monomers with any of the photoinitiators developed in this work dramatically enhances their curing time, a required feature for many applications, especially for the less reactive, but more biologically relevant, long alkyl chain cyanoacrylates.

To illustrate this result, we carried out adhesion tests on polycarbonate (Makrolon® mono clear 099 FR; PC) and poly(methyl methacrylate) (PMMA) substrates. In particular, we compared the maximum tensile strength (σ_{max}) needed to detach two strips of these materials previously glued either (a) thermally with fast-curing monomer **ECA_0**, or (b) photochemically with a mixture of **BTIPA-DEA** and **ECA_0**. As clearly shown in Table 3, photoinduced adhesion efficiently took place after just 2 min irradiation for both PC and PMMA and, actually, σ_{max} values measured in this case corresponded to substrate failure instead of adhesive debonding. By contrast, only partial thermal curing was observed after 30 min with **ECA_0**, which allowed PC and PMMA sticks to be detached by applying low to modest tensile strengths. Actually, efficient thermal adhesion required a much longer period (24 h), only after which mechanical substrate failure was registered in our experiments. Therefore, this demonstrates the capacity of light-induced polymerization using photoreleasable amines to dramatically accelerate the adhesion process of cyanoacrylates, even in the case of high-reactivity monomers such as ECA.

Table 3. Mechanical performance of thermally- and photochemically-cured ECA adhesives.

Substrate	**Adhesive**	**σ_{max} at 30 min** (MPa) [a]	**σ_{max} at 24 h** (MPa) [a]
PC	**ECA_0**	5.50 ± 1.07	16.52 ± 1.93 [c]

	ECA_0+BTIPA-DEA[b]	10.89 ± 0.42 [c]	11.76 ± 3.11 [c]
PMMA	**ECA_0**	1.50 ± 0.38	8.40 ± 1.35 [c]
	ECA_0+BTIPA-DEA[b]	7.28 ± 1.28 [c]	8.98 ± 2.68 [c]

[a] Maximum tensile strength registered 30 min and 24 h after gluing two plastic sticks; average of three replicates. [b] $c_{\mathbf{BTIPA\text{-}DEA}}$ = 15 mM; irradiation conditions: 405 nm, 280 mW, 2 min. [c] σ_{max} corresponding to substrate failure instead of detachment.

Characterization of photogenerated CA polymers. To assess the efficiency of photopolymerization, we analyzed the polymers obtained by means of ^{1}H NMR. In all the cases, ^{1}H NMR spectra of photopolymerized materials showed no residual olefinic signals (Figure S9), thus demonstrating that CA monomers had reacted quantitatively under our experimental conditions. To evaluate the effect of photopolymerization on the properties of the cyanoacrylate polymers generated, we determined their molecular weight distribution by gel permeation chromatography (GPC). In particular, we focused on the commercially received formulations of three of the CA monomers investigated in this work: **ECA_0**, **BCA_0** and **OCA_0**, which are excellent models of high-, intermediate- and low-reactivity cyanoacrylates. For these monomers, molecular weights distributions were measured both upon photopolymerization with **NPPOC-DEA**, **BTIPA-DEA** and **BODIPY-DEA** as well as after slow, glass-initiated thermal polymerization at ambient conditions. Because of the well-known instability of polycyanoacrylates, which can undergo depolymerization and subsequent repolymerization to afford low molecular weight "daughter" polymer chains even in the solid state,[46] GPC experiments were performed right after polymer formation and a slight amount of MSA was added to slow down degradation upon dissolution (as demonstrated in Figure S10 for thermally cured polymers). The number average molecular weight (M_n) values obtained in this way are shown in Table 4 (see Figure S11 for molecular weight distributions). As evidenced by dispersity values, broad distributions with low molecular weight

tails were obtained in most cases, to which inevitable CA depolymerization after polymer dissolution may contribute.

Table 4. Number average molecular weight (M_n, g mol^{-1}) and dispersity ($Đ$) of photogenerated cyanoacrylate polymers[a]

Monomer	NPPOC-DEA	BTIPA-DEA	BODIPY-DEA	Thermal[b]
ECA$_0$	$5.59 \cdot 10^4$ (1.83)	$4.98 \cdot 10^4$ (1.85)	$7.24 \cdot 10^4$ (1.69)	$5.92 \cdot 10^4$ (2.34)[c]
BCA$_0$	$8.57 \cdot 10^4$ (3.23)[d]	$5.08 \cdot 10^4$ (3.22)[e]	$4.19 \cdot 10^4$ (2.18)	$1.56 \cdot 10^5$ (3.25)[f]
OCA$_0$	$2.04 \cdot 10^5$ (2.73)	$2.25 \cdot 10^5$ (3.21)	$2.49 \cdot 10^5$ (1.80)	$2.74 \cdot 10^5$ (2.80)

[a] As determined by GPC for freshly prepared polymers, which were photogenerated as described in Table 2; calibration made by using PMMA standards. $Đ$ values shown in parentheses. [b] Slow, glass-initiated thermal polymerization under ambient conditions (16 hours). [c] Bimodal distribution with M_n = 6.17 10^4 and 2.28 10^5 g mol^{-1}. [d] Bimodal distribution with M_n = 4.53 10^4 and 3.53 10^5 g mol^{-1}. [e] Bimodal distribution with M_n = 1.34 10^5 and 1.06 10^6 g mol^{-1}. [f] Bimodal distribution with M_n = 1.91 10^5 and 9.32 10^5 g mol^{-1}.

For **ECA$_0$** and **OCA$_0$** similar molecular weight distributions and M_n values were measured for thermally- and photochemically-cured samples. Therefore, this demonstrates that no detrimental effects in polymer chain length, structure and dispersity arise from the much faster polymerization times achieved upon irradiation of photoactivable amines. Actually, this is in agreement with the high adhesion forces described above for photocured samples of **ECA$_0$**+**BTIPA-DEA** even at very short times. In the case of **BCA$_0$**, more diverse results were obtained for the different polymerization conditions assayed. Thus, very broad, nearly bimodal molecular weight distributions were measured after thermal curing and photopolymerization with **NPPOC-DEA** and **BTIPA-DEA**, the highest M_n values being obtained thermally and for **NPPOC-DEA**. In spite of

this, large polymer chain lengths were observed in all the cases that resemble those registered for **ECA_0**. Consequently, excellent adhesive properties must also expected for light-sensitive **BCA_0** formulations prepared from the color-tunable photoactivable amines developed in this work.

CONCLUSIONS

In this work we described a new strategy to accomplish cyanoacrylate photopolymerization based on the use of photogenerated amines. Aiming to develop an extended palette of photoinitiators allowing excitation along the UV-visible spectrum, we prepared three different light-responsive carbamate derivatives of diethylamine, a well-known cyanoacrylate curing agent. Upon irradiation of these compounds, amine photorelease was induced, which we exploited to initiate cyanoacrylate polymerization. In this way, very fast, on demand polymer curing was achieved even for poorly reactive, biologically-relevant long alkyl chain cyanoacrylates, while no polymerization was observed in the dark. Noticeably, when applied to light-controlled material bonding, photogenerated amines led to a dramatic reduction of setting times, without detrimentally affecting neither the final adhesion strength nor the molecular weight of the final polymers obtained. This, in combination with the organic, metal-free nature of the initiators, their wavelength-tunability and their capacity to activate multiple cyanoacrylate commercial formulations, makes the photopolymerization strategy developed in this work very promising. Of especial relevance would be its use in the biomedical field, where high performance applications could be targeted that might outweigh the cost of photoinitiator synthesis.

EXPERIMENTAL SECTION

Materials and general methods. Reagents and solvents for the synthesis of **NPPOC-DEA**, **BTIPA-DEA**, and **BODIPY-DEA** were purchased and used without further purification. When required, solvents were dried using standard procedures. Reactions requiring an inert atmosphere were conducted under nitrogen or argon using standard Schlenk techniques. CA monomers ECA, BMCA, BCA, HCA and OCA were provided by Cuantum Medical Cosmetics S.L. and used as received. Methanesulfonic acid was further added to these CA monomers to increase their stability against nucleophiles. Thin-layer chromatography (TLC) was performed using Merck aluminum backed plates of TLC silica gel 60 F254, and flash column chromatography was carried out using silica gel (60 Å pore size, 230−400 μm mesh size). NMR spectra were recorded using Bruker spectrometers DPX-250, DXP360, and AVANCE-III 400 (250 MHz (^{1}H); 62.5 MHz (^{13}C), 360 MHz (^{1}H); 90 MHz (^{13}C) and 400 MHz (^{1}H); 100 MHz (^{13}C), respectively). ^{1}H and ^{13}C chemical shifts are reported in ppm relative to tetramethylsilane, using residual proton and ^{13}C resonances from solvent as internal standards. Infrared spectra were recorded using a Bruker Tensor 27 instrument equipped with an ATR Golden Gate cell and a diamond window. High resolution ESI mass spectra were registered in a Bruker MicroTOF-Q spectrometer using a direct inlet system. HPLC analyses were carried out on a Waters 2690 separations module equipped with a Waters 996 photodiode array detector and a chiral Daicel OD column (0.46 cm x 25 cm). Isocratic elution was performed with 90% hexane and 10% 2-propanol. To irradiate the photoinitiators and induce CA photopolymerization, the following illumination sources were used: the second (λ_{exc} = 532 nm) and third harmonic (λ_{exc} = 355 nm) of a ns-pulsed Nd:YAG laser (Brilliant, Quantel); a cw diode laser (λ_{exc} = 405 nm, SciTec).

Synthesis of NPPOC-DEA. This compound was prepared from commercially available products DEA and 2-(2-nitrophenyl)propyl chloroformate (**1**) in the presence of DIPEA according to a

reported procedure (90% yield).[39] ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.72 (dd, J = 8.2, 1.5 Hz, 1H), 7.61 – 7.43 (m, 2H), 7.34 (ddd, J = 8.2, 7.1, 1.5 Hz, 1H), 4.28 – 4.15 (m, 2H), 3.68 (h, J = 7.0 Hz, 1H), 3.21 (bs, 2H), 3.08 (bs, 2H), 1.35 (d, J = 7.0 Hz, 3H), 1.05 (bs, 3H), 0.90 (bs, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.5, 150.5, 137.8, 132.5, 128.2, 127.2, 123.9, 69.0, 41.8, 41.2, 33.4, 18.0, 13.8, 13.4.

Synthesis of BTIPA-DEA. *Synthesis of (Z)-2-((Z)-2-(hydroxyimino)benzo[b]thiophen-3(2H)-ylidene)-2-phenylacetonitrile* (**3**). Intermediate **3** was prepared from 3-bromothianaphthalene (**2**) according to a 3-step reported procedure (15% yield overall).[40] ^{1}H NMR (250 MHz, DMSO-d_6): δ 13.18 (bs, 1H), 7.72−7.49 (m, 6H), 7.40−7.28 (m, 1H), 6.90 (ddd, J = 8.4, 7.3, 1.4 Hz, 1H), 6.40 (d, J = 8.2 Hz, 1H).

*Synthesis of **BTIPA-DEA***. This photoinitiator was prepared adapting a procedure described for a similar compound.[47] Diethylcarbamoyl chloride (103 µL, 0.81 mmol) was dissolved in anhydrous DCM (5 mL) and added dropwise to a stirred solution of **3** (150 mg, 0.54 mmol) and triethylamine (228 µL, 1.62 mmol) in anhydrous DCM (5 mL). The solution was heated at reflux for 4 hours. After this time, the solution was cooled, diluted with DCM (30 mL) and washed with water (3 x 20 mL) and brine (3 x 20 mL). The organic phase was then dried over anhydrous Na_2SO_4 and the solvent evaporated in vacuo. The product was purified by flash column chromatography over silica gel (hexane:AcOEt 9:1 to 2:1) to afford the pure product as a yellow powder (122 mg, 0.32 mmol, 60% yield). Melting point: 164-166 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.45 (m, 5H), 7.29-7.27 (m, 2H), 6.86-6.82 (m, 1H), 6.60 (d, J = 8.2 Hz, 1H), 3.42 (bs, 4H), 1.29-1.23 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.9 (Cq), 152.2 (Cq), 141.7 (Cq), 138.5 (Cq), 134.2 (Cq), 132.1 (CH), 131.9 (Cq), 130.3 (CH), 129.9 (2 x CH), 128.7 (2 x CH), 127.3 (CH), 125.7 (CH), 123.1 (CH), 118.4 (Cq), 111.8 (Cq), 43.1 (CH_2), 42.1 (CH_2), 14.2 (CH_3), 13.4 (CH_3). ATR-IR: υ_{max} (cm^-

^{1}) 2924, 2194, 1738, 1412, 1259. HRMS (ESI) (*m/z*) calculated for $C_{21}H_{19}N_3NaO_2S$ ($[M + Na]^+$): 400.1090; experimental: 400.1102.

Synthesis of BODIPY-DEA. *Synthesis of (5,5-difluoro-1,3,7,9-tetramethyl-5H-4λ^4,5λ^4-dipyrrolo[1,2-c:2',1'-f][1,2,3]diazaborinin-10-yl)methyl (4-nitrophenyl)carbonate* (**5**). Compound **5** was prepared from 2,4-dimethyl-1*H*-pyrrole (**4**) according to a 3-step reported procedure.[42] ^{1}H NMR (360 MHz, DMSO-d_6): δ 8.34 (d, *J* = 9.2 Hz, 2H), 7.50 (d, *J* = 9.2 Hz, 2H), 5.56 (s, 2H), 2.54 (s, 6H), 2.46 (s, 6H).

Synthesis of (5,5-difluoro-1,3,7,9-tetramethyl-5H-4λ4,5λ4-dipyrrolo[1,2-c:2',1'-f][1,2,3]diazaborinin-10-yl)methyl N-N'-diethylcarbamate (**6**). To a solution of **5** (1.20 g, 2.71 mmol) in dry THF (60 mL), pyridine was added (196 µL, 2.44 mmol, 0.9 eqs.) under a nitrogen atmosphere. After the mixture was stirred for 15 min at room temperature, DEA (420 µL, 4.06 mmol, 1.5 eqs.) was added. The reaction was then stirred in the dark during 16 h. After that time, solvents were evaporated, and the crude residue was dissolved in DCM (80 mL). The organic layer was washed with 1 M HCl (2 × 50 mL), 0.1 M NaOH (2 × 50 mL) and brine (2 × 50 mL), then dried with $MgSO_4$ and, finally, the solvent was evaporated in vacuo. The crude mixture was then purified by flash chromatography on silica gel using DCM as the eluent. Compound **6** was obtained as an orange-pink powder (562 mg, 1.49 mmol, 55% yield). Melting point: 164-167 °C. ^{1}H NMR (360 MHz, $CDCl_3$): *δ* 6.07 (s, 2H), 5.27 (s, 2H), 3.32 (q, *J* = 7.1 Hz, 2H), 3.21 (q, *J* = 7.1 Hz, 2H), 2.53 (s, 6H), 2.38 (s, 6H), 1.14 (t, *J* = 7.1 Hz, 3H), 1.04 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 156.4 (Cq), 155.3 (Cq), 141.8 (Cq), 134.5 (Cq), 132.9 (Cq), 122.2 (CH), 58.3 (CH_2), 42.2 (CH_2), 41.4 (CH_2), 15.6 (CH_3), 14.8 (CH_3), 14.3 (CH_3), 13.5 (CH_3). ATR-IR: υ_{max} (cm^{-1}) 2963, 1699, 1555, 1427, 1158. HRMS (ESI) (*m/z*) calculated for $C_{19}H_{26}BF_2N_3NaO_2$ ($[M + Na]^+$): 400.1982; experimental: 400.1987.

*Synthesis of **BODIPY-DEA***. To a suspension of **6** (360 mg, 0.95 mmol) and ZnO (280 mg, 3.42 mmol) in dry THF (25 mL), a solution of ICl (465 mg, 2.86 mmol, 3 equiv) in dry THF (5 mL) was added at 0 °C and under nitrogen atmosphere. The ice bath was removed and the reaction mixture was stirred for 30 minutes, after which the solvent was evaporated. The crude product was purified by flash chromatography on silica gel (hexane:DCM 1:1 to DCM only). **BODIPY-DEA** was obtained as a dark purple powder (430 mg, 0.68 mmol, 72% yield). Melting point: 178-180 °C. ^{1}H NMR (360 MHz, $CDCl_3$): δ 5.29 (s, 2H), 3.34 (q, J = 7.2 Hz, 2H), 3.21 (q, J = 7.2 Hz, 2H), 2.63 (s, 6H), 2.43 (s, 6H), 1.16 (t, J = 7.1 Hz, 3H), 1.05 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.8 (Cq), 154.9 (Cq), 143.8 (Cq), 133.9 (Cq), 132.8 (Cq), 87.1 (Cq), 58.7 (CH_2), 42.3 (CH_2), 41.5 (CH_2), 18.1 (CH_3), 16.4 (CH_3), 14.3 (CH_3), 13.5 (CH_3). ATR-IR: υ_{max} (cm^{-1}) 2978, 1699, 1538, 1162, 985. HRMS (ESI) (*m/z*) calculated for $C_{19}H_{24}BF_2I_2N_3NaO_2$ ($[M + Na]^+$): 651.9915; experimental: 651.9913.

Photochemical characterization. Steady-state UV-vis absorption measurements were recorded on a HP 8453 spectrophotometer using 1 cm-thick quartz cuvettes in acetonitrile (HPLC quality). DEA photorelease from **NPPOC-DEA** (λ = 355 nm), **BTIPA-DEA** (λ = 405 nm) and **BODIPY-DEA** (λ = 532 nm) was monitored by: (a) registering UV-vis absorption spectra under continuous irradiation of diluted acetonitrile solutions ($c \sim 1.68 \cdot 10^{-5}$ M – $1.60 \cdot 10^{-4}$ M); (b) measuring ^{1}H NMR spectra upon continuous illumination of concentrated CD_3CN solutions (c ~ 10 mg mL^{-1}). Photorelease quantum yields (Φ_{ph}) in acetonitrile solution were determined from the UV-vis absorption measurements using the methodology reported in ref. 48 and the following reference data: (a) **NPPOC-DEA**: the photorelease quantum yield reported for this compound in methanol (Φ_{ph} = 0.20 [39]); (b) **BTIPA-DEA** and **BODIPY-DEA**: the photoisomerization quantum yield

reported for the closed isomer of 1,2-bis(5-chloro-2-methyl-3-thienyl)perfluorocyclopentene in hexane ($\Phi_{ph} = 0.13$ [49]).

Stabilization of CA monomers. The batches of CA monomers commercially acquired were already loaded with certain amounts of acid (typically, SO_2) and radical (typically, butylated hydroxytoluene (BHT)) stabilizers. To estimate the quantity of acid stabilizers in these samples that could interfere with the amine nucleophiles released during the photopolymerization experiments, a viscosity acid value determination technique previously described was employed.[44] In this technique, an organic solution of a tertiary amine is mixed quickly with 0.5 mL of a chosen CA monomer. The resulting mixture is manually stirred with a wooden stick until it cannot be separated from the mixture anymore, as it gets stuck in it. The time elapsed between the mixing and the sticking is defined as t_{AVD}. t_{AVD} is used to quantify the amount of acid stabilizers, which were found to be different for each type of CA monomer (Table S1). For this reason, a new batch of cyanoacrylate monomers was prepared, in which increasing quantities of an acid stabilizer (methanesulfonic acid) were added to each sample until all of them presented the same t_{AVD} (t_{AVD} ~ 210 s).

Photopolymerization experiments. To characterize the light-induced polymerization of CAs, calorimetric experiments were performed. In each of these experiments, a closed polypropylene well (diameter: 8 mm) was filled with 75 µL of a liquid CA monomer where the photoinitiator of choice had been previously dissolved (15 mM). Full dissolution was achieved in all cases after shaking the preparation during 10 minutes. The absence of undissolved photoinitiator was visually checked every time. The sample was then irradiated with a selected laser beam (spot size ~ 0.5 cm^2) at room temperature (**NPPOC-DEA**: λ = 355 nm, power = 300 mW, photon flux = 8.9 10^{-7} Einstein s^{-1}; **BTIPA-DEA**: λ = 405 nm, power = 280 mW, photon flux = 9.5 10^{-7} Einstein s^{-1};

BODIPY-DEA: λ = 532 nm, power = 250 mW, photon flux = 1.1 10^{-6} Einstein s^{-1}) and its temperature was monitored with an infrared probe and recorded every second until minimal thermal changes were observed. In all the cases, an increase of temperature (typically, ΔT = 7-16 ºC) was observed as a consequence of CA polymerization, which is a strongly exothermic process. To estimate the time period needed for photopolymerization to occur, we determined the time at which the sample temperature rise was half of the overall increase observed during the calorimetric experiment (i.e. when $T = T_0 + 0.5\ \Delta T$). Because of the sigmoidal shape of temperature variation for most cases, this means that t_{photo} corresponds to the time at which the temperature variation is higher and, assuming fast heat diffusion for the small sample volume, at which polymerization reaction rate reaches its maximum. Several replicates (n = 3) were conducted for each CA monomer-photoinitiator pair and reproducible t_{photo} values were retrieved. Additional calorimetric experiments were undertaken where a small Teflon stirring bar was added to the polypropylene well (~ 50 rpm), which was found to stop spinning when the sample became viscous enough as a result of photopolymerization. In all the cases, this phenomenon was observed to occur slightly before t_{photo}. Finally, we also monitored the photopolymerization of **BCA_0** with **BTIPA-DEA** by means of IR spectroscopy. To this end, the ATR-IR spectra of **BCA_0** monomer, a fully cured **BCA_0**+**BTIPA-DEA** mixture and a **BCA_0**+**BTIPA-DEA** mixture at t_{photo} = 37 s were acquired in the same conditions. The integrals (I) of the peaks at 3150 cm^{-1} (=C-H stretching band) and 2900 cm^{-1} (-C-H stretching band) were compared. For **BCA_0**, I_{3150}/I_{2900} = 0.0506; for the fully cured **BCA_0**+**BTIPA-DEA** mixture, I_{3150}/I_{2900} = 0 as the peak at 3150 cm^{-1} is not present; for a **BCA_0**+**BTIPA-DEA** mixture at t_{photo}= 37 s, I_{3150}/I_{2900} = 0.0055. From this data we estimated that in the latter case the mixture is composed by 89% polymer and 11% monomer.

Thermal polymerization experiments. For sake of comparison with the results of the photopolymerization experiments, thermal polymerization of CAs was also conducted by simply adding 0.5 mL of each monomer in a non-passivated glass vial and storing the sample at room temperature and in the dark for the appropriate time (typically, overnight).

Characterization of CA polymers. The molecular weight distribution of thermally- and light-cured CA polymers was determined by gel permeation chromatography using an Agilent Technologies 1260 Infinity chromatograph and THF as solvent. The instrument is equipped with three gel columns: PLgel 5μm Guard/50×7.5 mm, PLgel 5μm 10000 Å MW 4K−400K, and PL Mixed gel C 5μm MW 200−3M. Calibration was made by using PMMA standards. In each experiment, the freshly-prepared polymer sample of interest was dissolved (5 mg/mL) in THF containing 0.05% MSA and immediately analyzed by GPC (1 mL/min flow; 40 °C column temperature).

Adhesion test. The adhesion test was carried out following the specifications of the "ISO 4587 Adhesives Tensile Lap Shear Strength Rigid to Rigid" standard method, using an Instron 3366 instrument. The test has been performed on PC (Makrolon® mono clear 099 FR) and PMMA rectangular cuboid (100 x 20 x 2 mm) specimens bound with 25 μL of two different adhesives: **ECA_0** alone and a 15 mM solution of **BTIPA-DEA** in **ECA_0**. The lap joint area was approximately 100 mm^2. In the case of the **ECA_0**+**BTIPA-DEA** mixture, the specimens were clamped together and the lap joint area was irradiated at 405 nm (power = 280 mW) during 2 minutes, and then they were left standing during 30 min or 24 h. In the case of **ECA_0** alone, the specimens were clamped together after the application of the adhesive, and left standing during 30 min or 24 h.

ASSOCIATED CONTENT

Supporting Information. Additional data on the synthesis of the photoinitiators (NMR, IR and HRMS spectra, HPLC chromatograms), and on the polymerization and characterization of cyanoacrylates. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

* (J.H.) E-mail: jordi.hernando@uab.cat

* (R.M.S.) E-mail: rosamaria.sebastian@uab.cat

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

ACKNOWLEDGEMENTS

Financial support by MINECO/FEDER (RTC-2016-5683-1 project within "Retos Colaboración" program and CTQ2015-65439-R project) and by Generalitat de Catalunya (2017 SGR00465 project) is gratefully acknowledged. We also thank Sara Ortego and Feliu Pizà for their help.

ABBREVIATIONS

CA, cyanoacrylate; NPPOC, nitrophenylpropyloxycarbonyl group; BTIPA, benzothiophene imino-phenylacetonitrile group; BODIPY, boron-dipyrromethene dye; DEA, diethylamine; DIPEA, *N*,*N*-diisopropylethylamine; ECA, ethyl 2-cyanoacrylate; BMCA, methoxyethyl 2-cyanoacrylate; BCA, butyl 2-cyanoacrylate; HCA, hexyl 2-cyanoacrylate; OCA, 2-octyl 2-

cyanoacrylate; TAD, total acid determination; t_{photo}, photopolymerization time; GPC, gel permeation chromatography; M_n, number average molecular weight; TLC, thin-layer chromatography; DCM, dichloromethane; THF, tetrahydrofuran; MSA, methanesulfonic acid; PC, polycarbonate (Makrolon® mono clear 099 FR) ; PMMA, poly(methyl methacrylate).

REFERENCES

(1) Fink, J. K. In *Reactive Polymers Fundamentals and Applications*, 2nd ed.; William Andrew Publishing: Norwich, 2013; pp. 317-330.

(2) Burns, B. Polycyanoacrylates. In *Encyclopedia of Polymer Science and Technology*, 4th ed.; JohnWiley & Sons: Hoboken, 2016; Volume 4, pp. 1–27.

(3) Petrie, E. M. Cyanoacrylate Adhesives in Surgical Applications. In *Progress in Adhesion and Adhesives*, 1st ed.; Mittal, K. L., Ed.; Scrivener Publishing LLC: Beverly, 2015; pp. 245-298.

(4) Herod, E. Cyanoacrylates in Dentistry: a Review of the Literature. *J. Can. Dental Assoc.* **1990**, *56*, 331-334.

(5) Fadaie, P.; Atai, M.; Imani, M.; Karkhaneh, S. G. Cyanoacrylate–POSS Nanocomposites: Novel Adhesives with Improved Properties for Dental Applications. *Dental Mater.* **2013**, *29*, e61-e69.

(6) Papay, K. L. Vitamin/Mineral-Enriched Cyanoacrylate Cosmetic, U.S. Patent 5,866,106A, February 2, 1999.

(7) Torchilin, V. P. Multifunctional, Stimuli-Sensitive Nanoparticulate Systems for Drug Delivery. *Nat. Rev. Drug Discov.* **2014**, *13*, 813-827.

(8) Zhang, T.; Tang, Y.; Zhang, W.; Liu, S.; Zhao, Y.; Wang, W.; Wang, J.; Xu, L.; Liu, K. Sustained Drug Release and Cancer Treatment by an Injectable and Biodegradable Cyanoacrylate-Based Local Drug Delivery System. *J. Mater. Chem. B* **2018**, *6*, 1216-1225.

(9) Lozo, B.; Stanic, M.; Jamnicki, S.; Poljacek, S. M.; Muck, T. Three-Dimensional Ink Jet Prints–Impact of Infiltrants. *J. Imag. Sci. Technol.* **2008**, *52*, 051004.

(10) Ligon, S. C.; Liska, R.; Stampfl, J.; Gurr, M.; Mülhaupt, R. Polymers for 3D Printing and Customized Additive Manufacturing. *Chem. Rev.* **2017**, *117*, 10212-10290.

(11) Dammel, R. R.; Sakamuri, R.; Lee, S. -H.; Rahman, M. D.; Kudo, T.; Romano, A.; Rhodes, L.; Lipian, J.; Hacker, C.; Barnes, D. A. Cycloolefin/Cyanoacrylate (COCA) Copolymers for 193 nm and 157 nm Lithography. *Adv. Resist. Technol. Process* **2002**, *4690*, 101-110.

(12) Wargacki, S. P.; Lewis, L. A.; Dadmun, M. D. Understanding the Chemistry of the Development of Latent Fingerprints by Superglue Fuming. *J. Forensic Sci.* **2007**, *52*, 1057-1062.

(13) Bentolila, A.; Totre, J.; Zozulia, I.; Levin-Elad, M.; Domb, A. J. Fluorescent Cyanoacrylate Monomers and Polymers for Fingermark Development. *Macromolecules* **2013**, *46*, 4822-4828.

(14) Duffy, C.; Zetterlund, P. B.; Aldabbagh, F. Radical Polymerization of Alkyl 2-Cyanoacrylates. *Molecules* **2018**, *23*, 465.

(15) Photopolymerization: Fundamentals and Applications. Scranton, A. B., Bowman, C. N., Peiffer, R. W., Eds.; ACS Symposium Series No. 673; American Chemical Society: Washington, 1997.

(16) Yagci, Y.; Jockush, S.; Turro, N. J. Photoinitiated Polymerization: Advances, Challenges, and Opportunities. *Macromolecules* **2010**, *43*, 6245-6260.

(17) Crivello, J. V.; Reichmanis, E. Photopolymer Materials and Processes for Advanced Technologies. *Chem. Mater.* **2014**, *26*, 533-548.

(18) Dadashi-Silab, S.; Doran, S.; Yagci, Y. Photoinduced Electron Transfer Reactions for Macromolecular Syntheses. *Chem. Rev.* **2016**, *116*, 10212-10275.

(19) Kutal, C.; Grutsch, P. A.; Yang, D. B. A Novel Strategy for Photoinitiated Anionic Polymerization. *Macromolecules* **1991**, *24*, 6872-6873.

(20) Paul, R. B.; Kelly, J. M.; Pepper, D. C.; Long, C. Photoinduced Anionic Polymerization of Cyanoacrylates using Substituted Pyridine Pentacarbonyl Complexes of Tungsten or Chromium. *Polymer* **1997**, *38*, 2011-2014.

(21) Palmer, B. J.; Kutal, C.; Billing, R.; Hennig, H. A New Photoinitiator for Anionic Polymerization. *Macromolecules* **1995**, *28*, 1328-1329.

(22) Yamaguchi, Y.; Palmer, B. J.; Kutal, C.; Wakamatsu, T.; Yang, D. B. Ferrocenes as Anionic Photoinitiators. *Macromolecules* **1998**, *31*, 5155-5157.

(23) Yamaguchi, Y.; Kutal, C. Benzoyl-Substituted Ferrocenes: An Attractive New Class of Anionic Photoinitiators. *Macromolecules* **2000**, *33*, 1152-1156.

(24) Sanderson, C. T.; Palmer, B. J.; Morgan, A.; Murphy, M.; Dluhy, R. A.; Mize, T.; Amster, J.; Kutal, C. Classical Metallocenes as Photoinitiators for the Anionic Polymerization of an Alkyl 2-Cyanoacrylate. *Macromolecules* **2002**, *35*, 9648-9652.

(25) Wojciak, S.; Attarwala, S. Radiation-Curable, Cyanoacrylate-Containing Compositions, European Patent 0963420B1, February 26, 1998.

(26) Arsu, N.; Önen, A.; Yagci, Y. Photoinitiated Zwitterionic Polymerization of Alkyl Cyanoacrylates by Pyridinium Salts. *Macromolecules* **1996**, *29*, 8973-8974.

(27) Önen, A.; Arsu, N.; Yagci, Y. Photoinitiated Polymerization of Ethyl Cyanoacrylate by Phosphonium Salts. *Angew. Makromol. Chem.* **1999**, *264*, 56-59.

(28) Jarikov, V. V.; Neckers, D. C. Anionic Photopolymerization of Methyl 2-Cyanoacrylate and Simultaneous Color Formation. *Macromolecules* **2000**, *33*, 7761-7764.

(29) Johnston, D. S.; Pepper, D. C. Polymerisation via Macrozwitterions, 2. Ethyl and Buthyl Cyanoacrylates Polymerised by Pyridine and Polivinylpyridine. *Makromol. Chem.* **1981**, *182*, 407-420.

(30) Klán, P.; Solomek, T.; Bochet, C. G.; Blanc, A.; Givens, R.; Rubina, M.; Popik, V.; Kostikov, A.; Wirz, J. Photoremovable Protecting Groups in Chemistry and Biology: Reaction Mechanisms and Efficacy. *Chem. Rev.* **2013**, *113*, 119-191.

(31) Suyama, K.; Shirai, M. Photobase Generators: Recent Progress and Application Trend in Polymer Systems. *Prog. Polym. Sci.* **2009**, *34*, 194-209.

(32) Chae, K. H. Thermal Curing Reaction of Poly(Glycidyl Methacrylate) Using Photogenerated Amines from Oxime-Urethane Derivatives. *Macromol. Rapid Commun.* **1998**, *19*, 1-4.

(33) Chae, K. H.; Lee, C. S.; Kim, J. H. One Component Photo-Curing Agent for Epoxy Resins Based on Multifunctional Photobase Generators Containing Oxime-Urethane Groups. *Pol. Adv. Technol.* **2011**, *22*, 1427-1433.

(34) Sun, X.; Gao, J. P.; Wang, Z. Y. Bicyclic Guanidinium Tetraphenylborate: A Photobase Generator and a Photocatalyst for Living Anionic Ring-Opening Polymerization and Cross-Linking of Polymeric Materials Containing Ester and Hydroxy Groups. *J. Am. Chem. Soc.* **2008**, *130*, 8130-8131.

(35) Salmi, H.; Allonas, X.; Ley, C.; Defoin, A.; Ak, A. Quaternary Ammonium Salts of Phenylglyoxylic Acid as Photobase Generators for Thiol-promoted Epoxide Photopolymerization. *Polym. Chem.* **2014**, *5*, 6577-6583.

(36) Kuroshi, P. K.; Dove, A. P. Photoinduced Ring-Opening Polymerisation of L-Lactide via a Photocaged Superbase. *Chem. Commun.* **2018**, *54*, 6264-6267.

(37) Zhang, X.; Xi, W.; Gao, G.; Wang, X.; Stansbury, J. W.; Bowman, C. N. *o*‑Nitrobenzyl-Based Photobase Generators: Efficient Photoinitiators for Visible-Light Induced Thiol-Michael Addition Photopolymerization. *ACS Macro Lett.* **2018**, *7*, 852-857.

(38) Giegrich, H.; Eisele-Bühler, S.; Herman, C.; Kvasyuk, E.; Charubala, R.; Pleiderer, W. New Photolabile Protecting Groups in Nucleoside and Nucleotide Chemistry - Synthesis, Cleavage Mechanisms and Applications. *Nucleosides Nucleotides* **1998**, *17*, 1987-1996.

(39) Xi, W.; Peng, H.; Aguirre-Soto, A.; Kloxin, C. J.; Stansbury, J. W.; Bowman, C. N. Spatial and Temporal Control of Thiol-Michael Addition via Photocaged Superbase in Photopatterning and Two-Stage Polymer Networks Formation. *Macromolecules* **2014**, *47*, 6159-6165.

(40) Hayes, C. O.; Bell, W. K.; Cassidy, B. R.; Willson, C. G. Synthesis and Characterization of a Two Stage, Nonlinear Photobase Generator. *J. Org. Chem.* **2015**, *80*, 7530-7535.

(41) Slanina, T.; Shrestha, P.; Palao, E.; Kand, D.; Peterson, J. A.; Dutton, A. S.; Rubinstein, N.; Weinstain, R.; Winter, A. H.; Klán, P. In Search of the Perfect Photocage: Structure−Reactivity Relationships in *meso*-Methyl BODIPY Photoremovable Protecting Groups. *J. Am. Chem. Soc.* **2017**, *139*, 15168-15175.

(42) Sitkowska, K.; Feringa, B. L.; Szymanski, W. Green-Light-Sensitive BODIPY Photoprotecting Groups for Amines. *J. Org. Chem.* **2018**, *83*, 1819-1827.

(43) Zhang, S.; Ruiz, R. Wound Healing Compositions Based on Cyanoacrylates and 5,5-Disubstitutedhydantoins, Including Phenytoin. European Patent 2603552B1, August 9, 2011.

(44) Cooke, B. D.; Allen, K. W. Cyanoacrylates and their Acid Values, *Int. J. Adhesion Adhesives 13*, **1993**, 73-76.

(45) Szanka, I.; Szanka, A.; Kennedy, J. P. Rubbery Wound Closure Adhesives. II. Initiators for and Initiation of 2-Octyl Cyanoacrylate Polymerization. *J. Polym. Sci., Part A: Polym. Chem.* **2015**, *53*, 1652-1659.

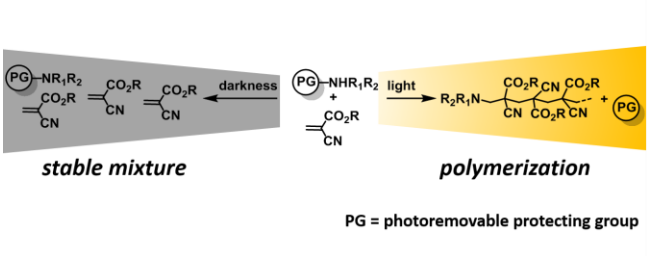
(46) Robello, D. R.; Eldridge, T. D.; Swanson, M. T. Degradation and Stabilization of Polycyanoacrylates, *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 4570-4581.

(47) McNamara, Y. M.; Bright, S. A.; Byrne, A. J.; Cloonan, S. M.; McCabe, T.; Williams, D. C.; Meegan, M. J. Synthesis and Antiproliferative Action of a Novel Series of Maprotiline Analogues. *Eur. J. Med. Chem.* **2014**, *71*, 333-353.

(48) Lees, A. J. A Photochemical Procedure for Determining Reaction Quantum Efficiencies in Systems with Multicomponent Inner Filter Absorbances. *Anal. Chem.* **1996**, *68*, 226-229.

(49) Higashiguchi, K.; Matsuda, K.; Asano, Y.; Murakami, A.; Nakamura, S.; Irie, M. Photochromism of Dithienylethenes Containing Fluorinated Thiophene Rings. *Eur. J. Org. Chem.* **2005**, 91-97.

Table of contents graphic



Supporting Information for:

Wavelength-Tunable Light-Induced Polymerization of Cyanoacrylates Using Photogenerated Amines

Enrico Faggi,[a] *Jordi Aguilera,*[b] *Rubén Sáez,*[b] *Ferran Pujol,*[b] *Jordi Marquet,*[a] *Jordi Hernando,*[a,*] *and Rosa María Sebastián*[a,*]

[a] Departament de Química, Universitat Autònoma de Barcelona, 08193 Cerdanyola del Vallès, Spain

[b] CUANTUM Medical Cosmetics S.L., 08193 Cerdanyola del Vallès, Spain

TABLE OF CONTENTS:

1. ^{1}H NMR, ^{13}C NMR, IR, HRMS SPECTRA AND HPLC CHROMATOGRAMS OF PHOTOINITIATORS AND INTERMEDIATES…….....S3

2. ABSORPTION SPECTRA OF CA MONOMERS……S17

3. AMINE PHOTORELEASE FROM NPPOC-DEA AND BODIPY-DEA……...….S18

4. TOTAL ACID DETERMINATION OF CYANOACRYLATE MONOMERS……..S22

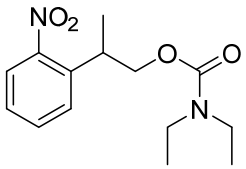
5. PHOTOPOLYMERIZATION OF CYANOACRYLATE MONOMERS……...S23

6. CHARACTERIZATION OF POLYCYANOACRYLATES……S26

7. REFERENCES…….…….S29

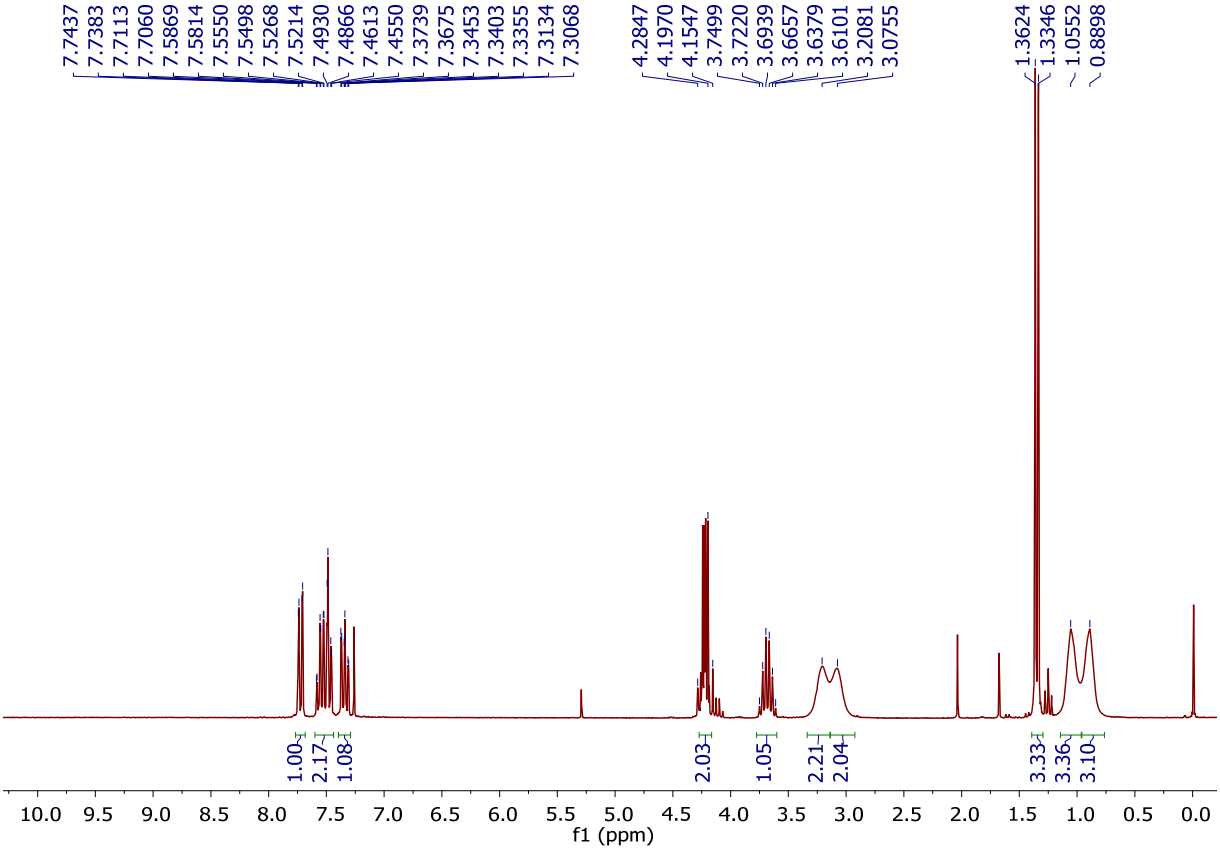
1. ^{1}H NMR, ^{13}C NMR, IR AND HR-MS SPECTRA OF PHOTOINITIATORS AND INTERMEDIATES

NPPOC-DEA. ^{1}H NMR and ^{13}C NMR spectra are shown for **NPPOC-DEA**, which perfectly agree with previously reported data.[1] Chiral HPLC chromatogram is also shown for this compound.

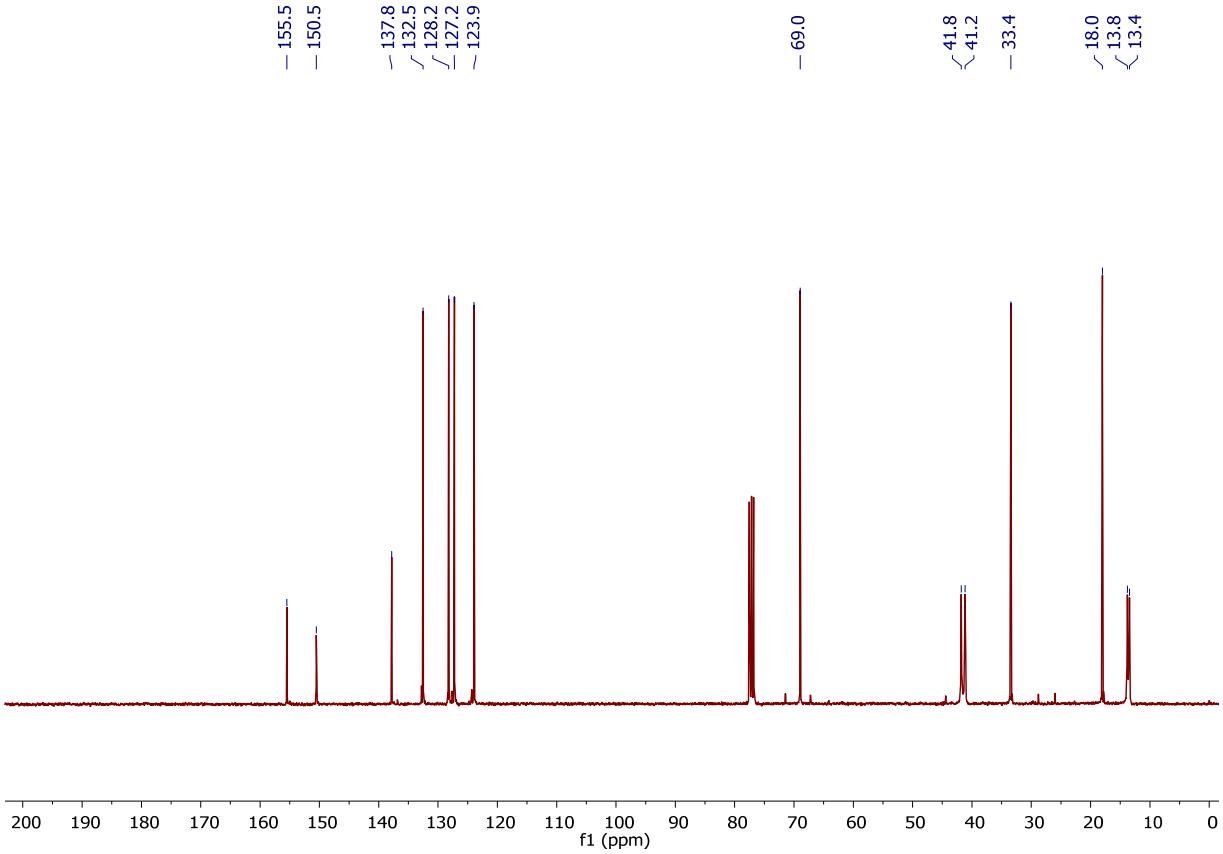


NPPOC-DEA

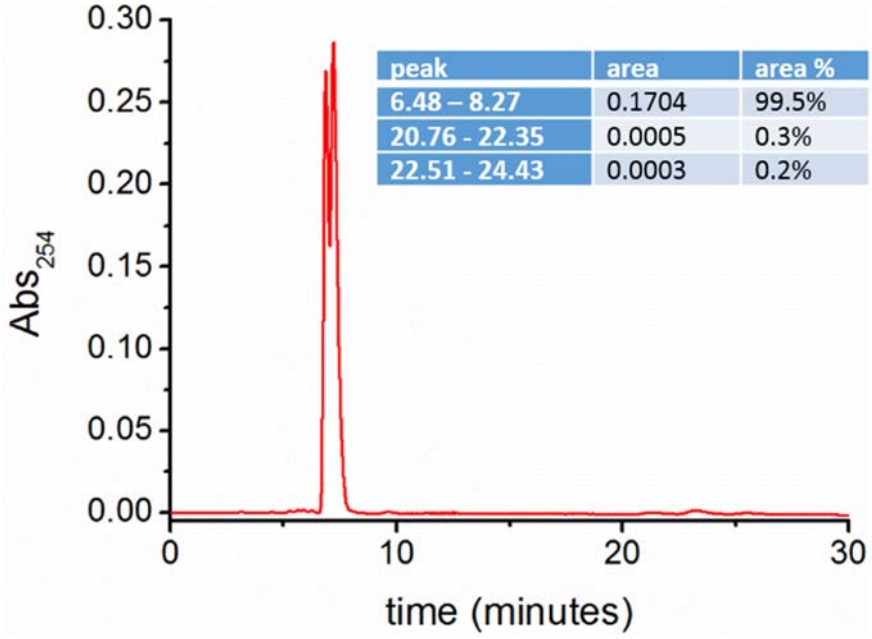
^{1}H NMR (250 MHz, $CDCl_3$)



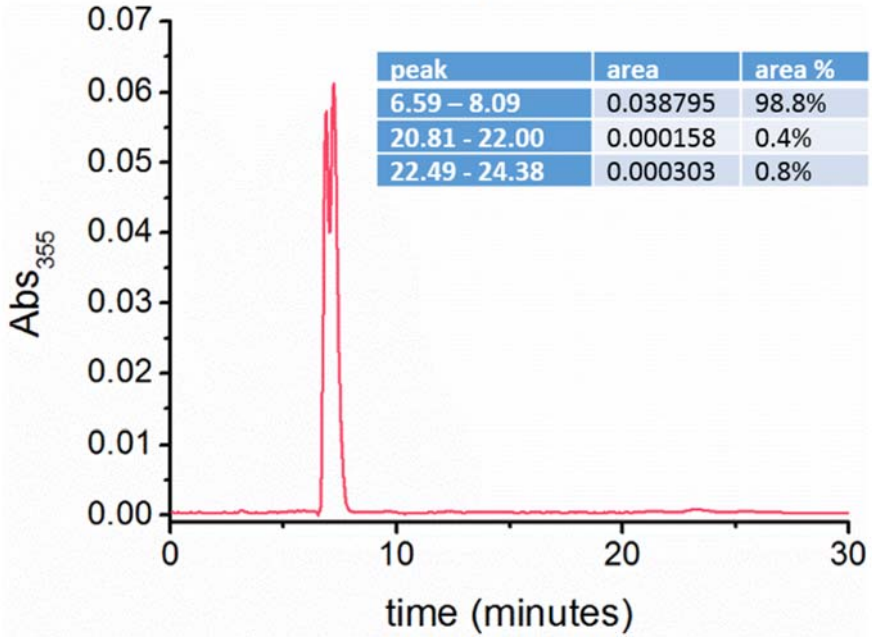
^{13}C NMR (90 MHz, $CDCl_3$)



Chiral HPLC

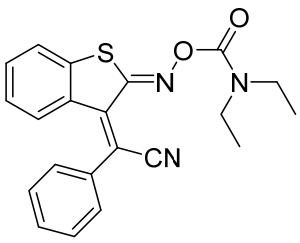


peak	area	area %
6.48 – 8.27	0.1704	99.5%
20.76 - 22.35	0.0005	0.3%
22.51 - 24.43	0.0003	0.2%



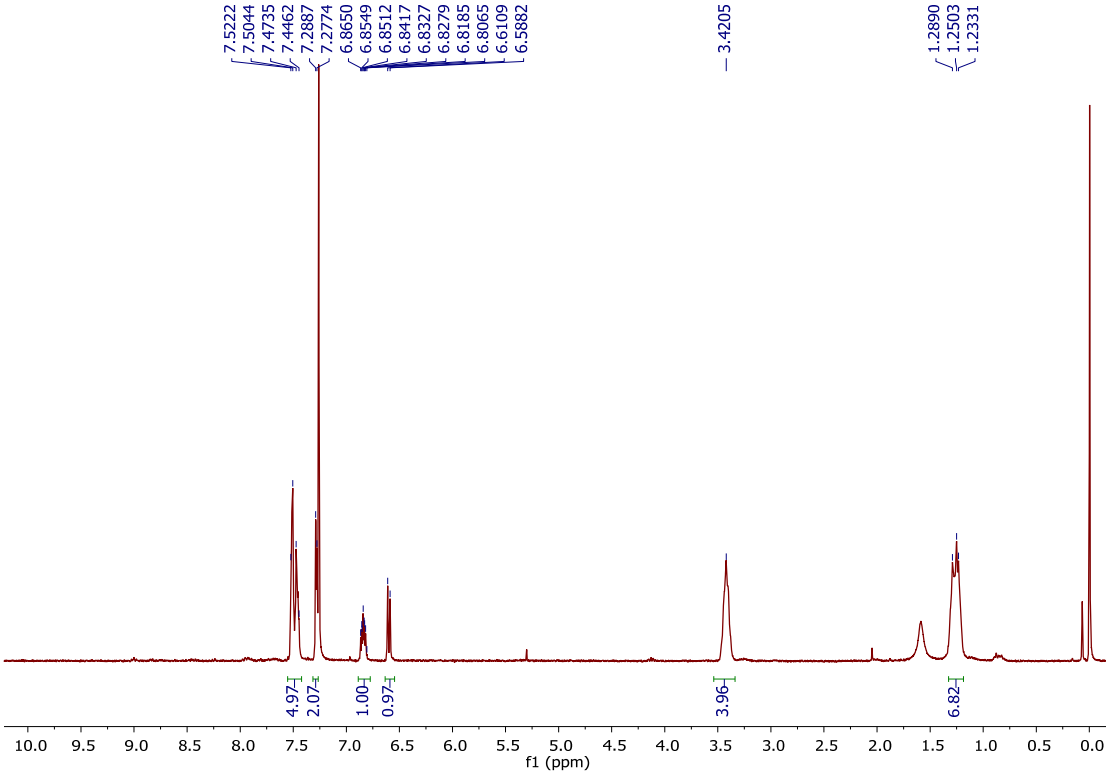
peak	area	area %
6.59 – 8.09	0.038795	98.8%
20.81 - 22.00	0.000158	0.4%
22.49 - 24.38	0.000303	0.8%

BTIPA-DEA. Spectral data and HPLC chromatogram are given for the target photoinitiator.

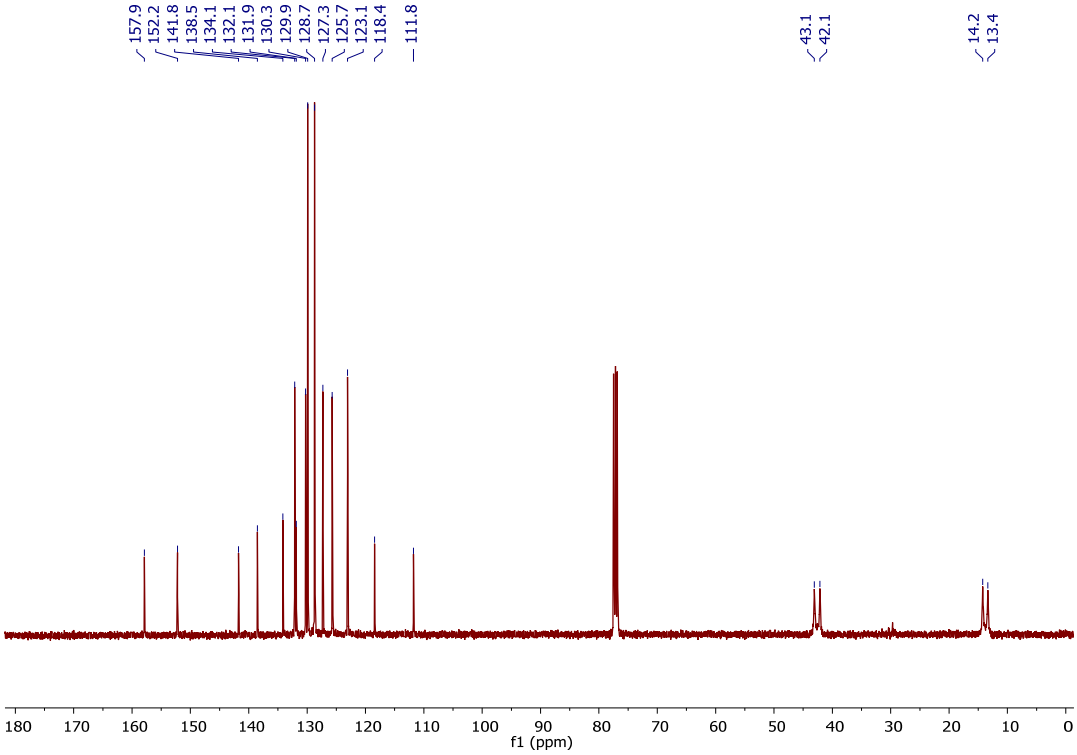


BTIPA-DEA

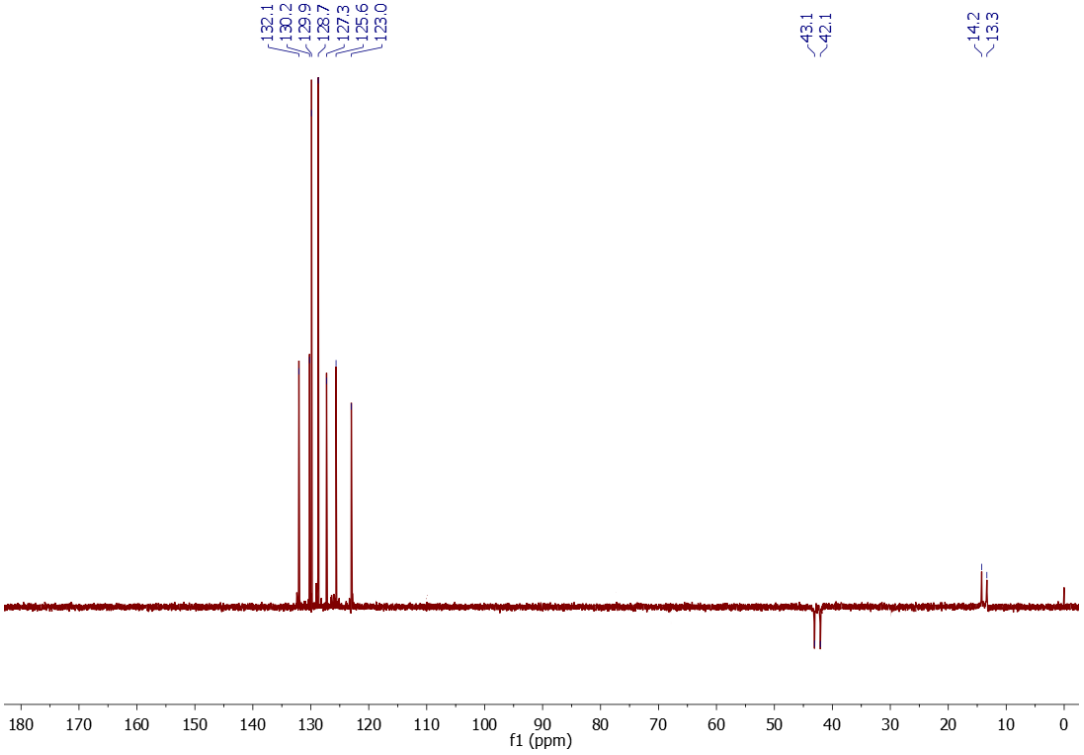
^{1}H NMR (360 MHz, $CDCl_3$)



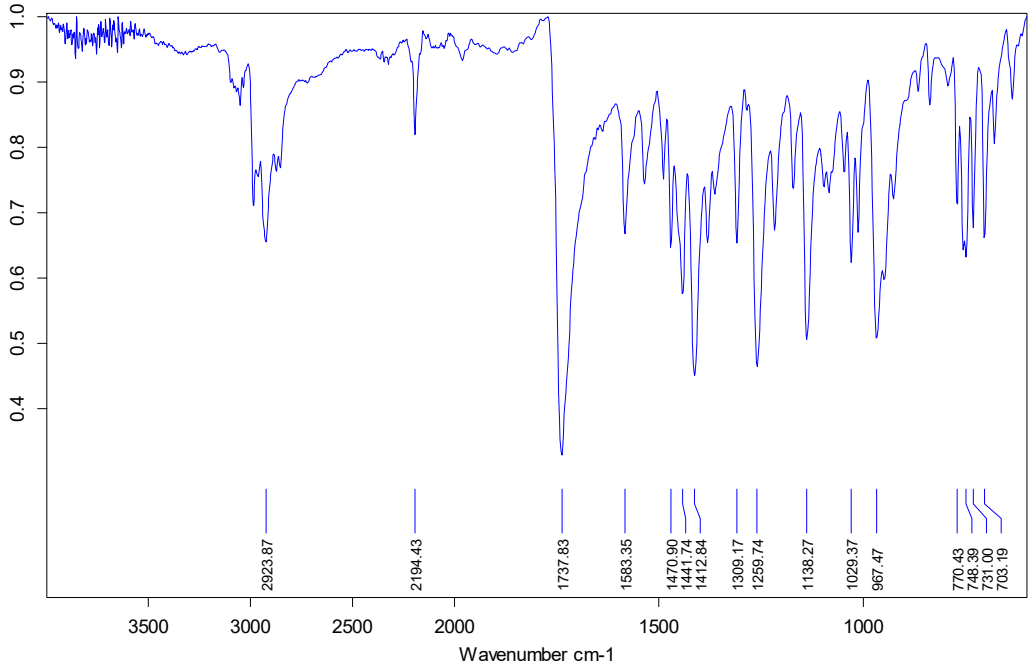
^{13}C NMR (90 MHz, $CDCl_3$)



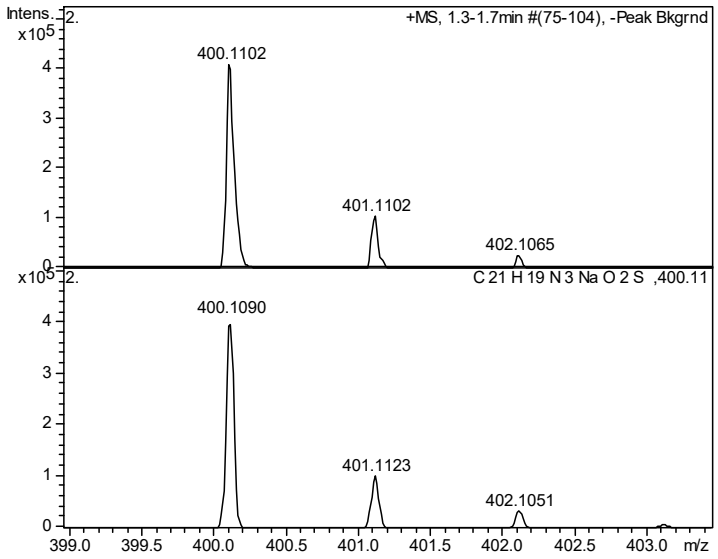
DEPT 135 (90 MHz, $CDCl_3$)



ATR-IR

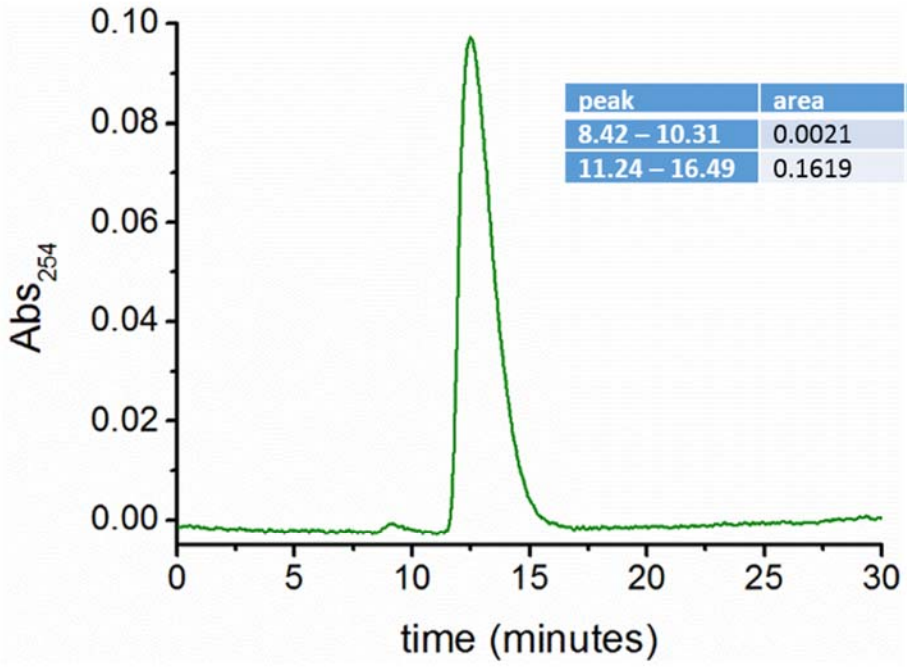


HR-MS (ESI$^+$)

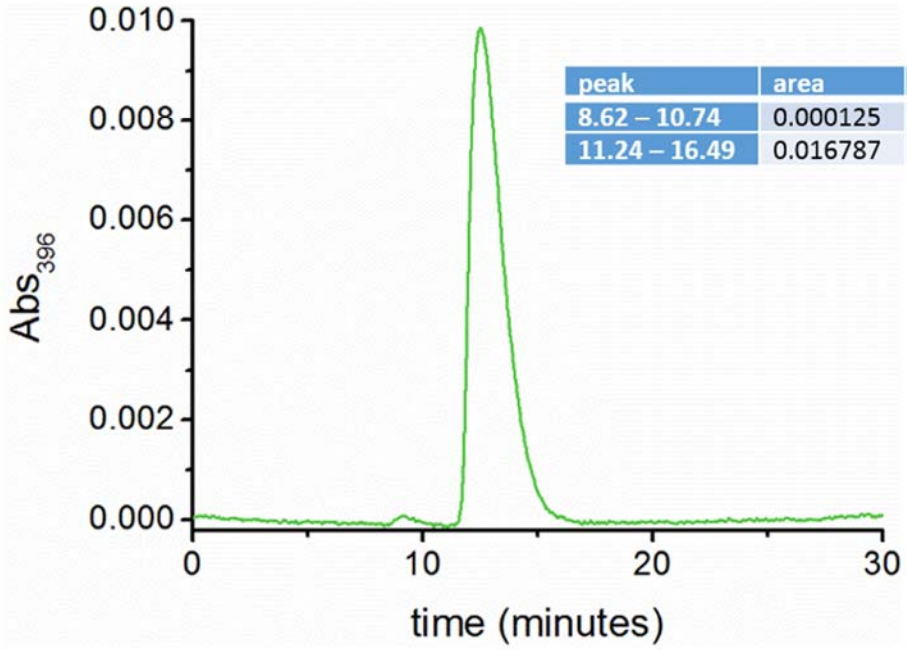


Meas. m/z	Formula	m/z	err [mDa]	err [ppm]	mSigma
400.1102	C21H19N3NaO2S	400.1090	-1.2	-2.9	10.0

HPLC

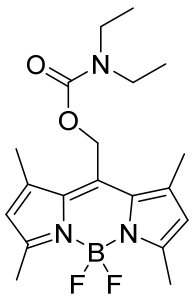


peak	area	area %
8.42 – 10.31	0.0021	1.3%
11.24 – 16.49	0.1619	98.7%



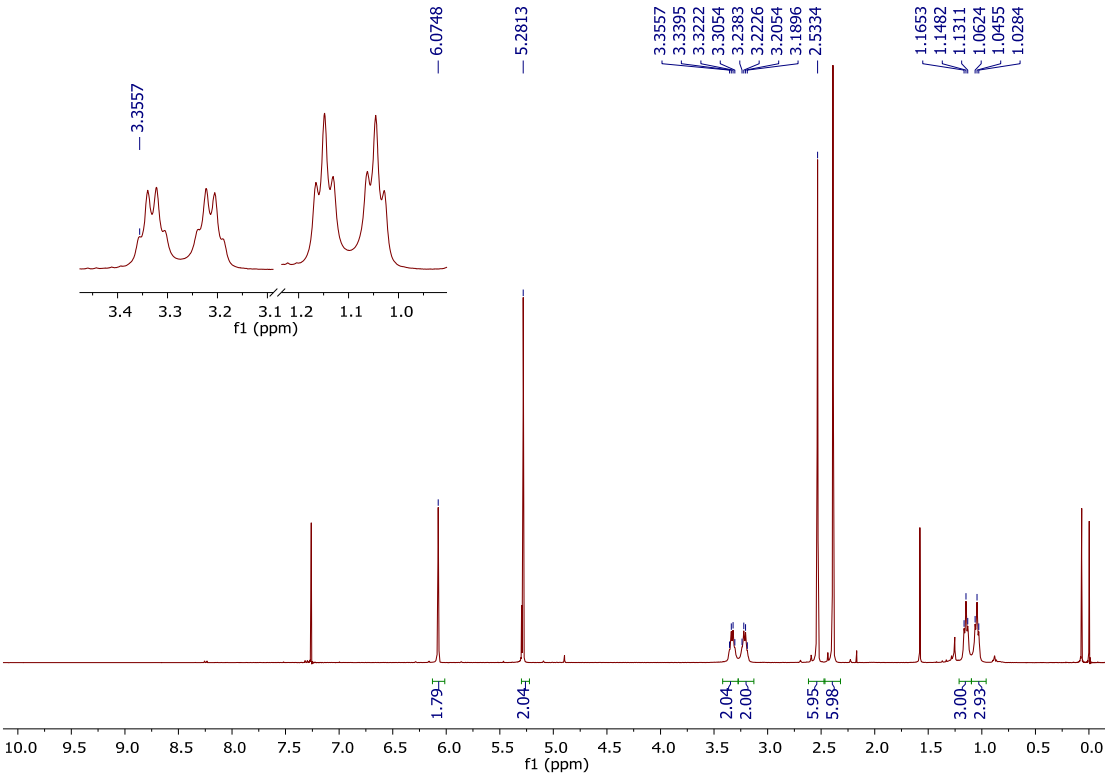
peak	area	area %
8.62 – 10.74	0.000125	0.7%
11.24 – 16.49	0.016787	99.3%

BODIPY-DEA. Spectral data are given for both intermediate **6** and the target photoinitiator. HPLC chromatogram of the photoinitiator is also shown.

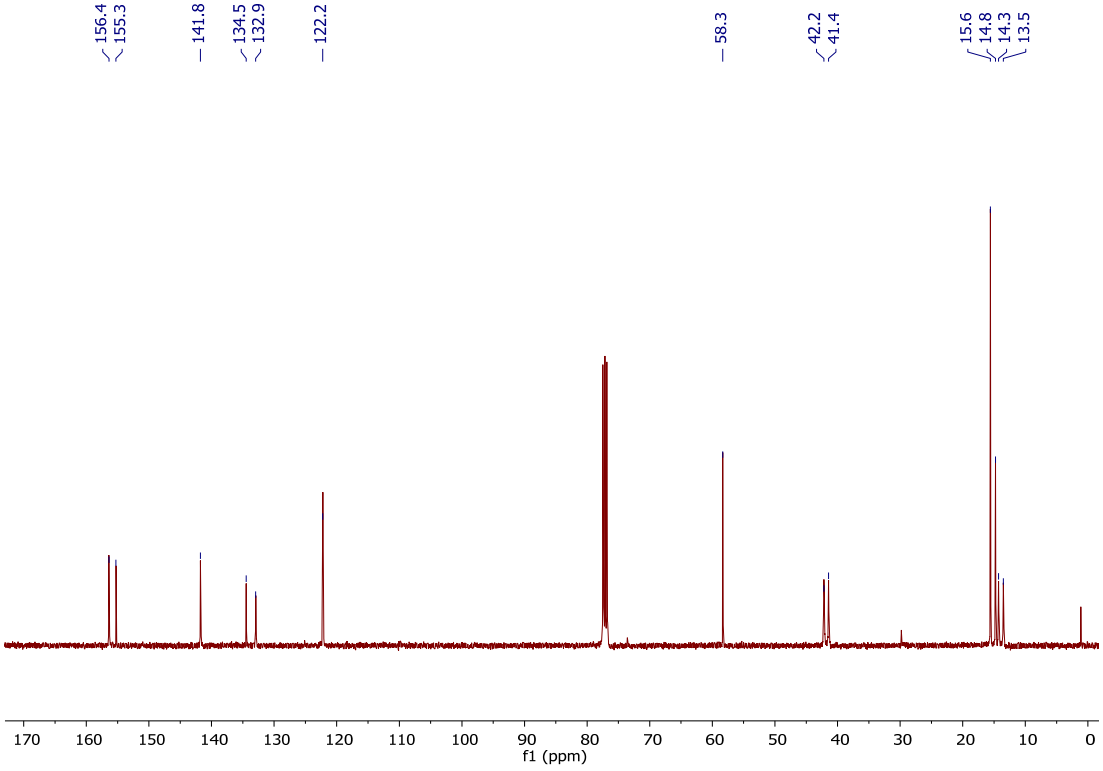


6

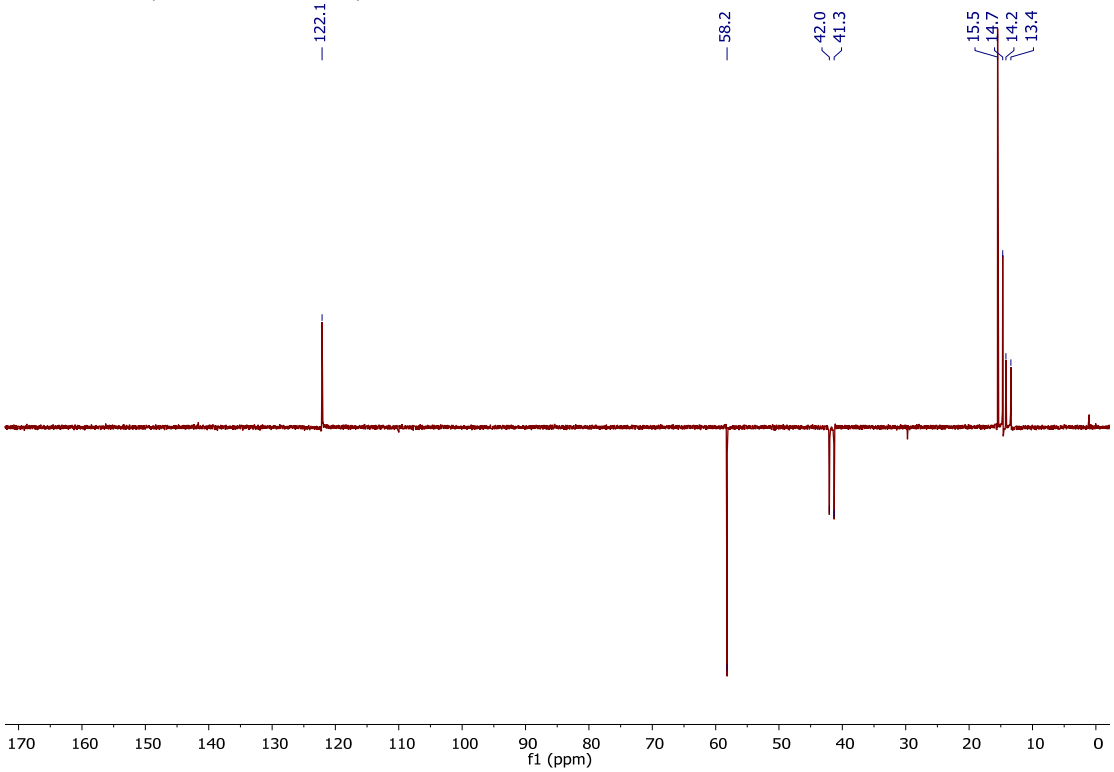
^{1}H NMR (360 MHz, $CDCl_3$)



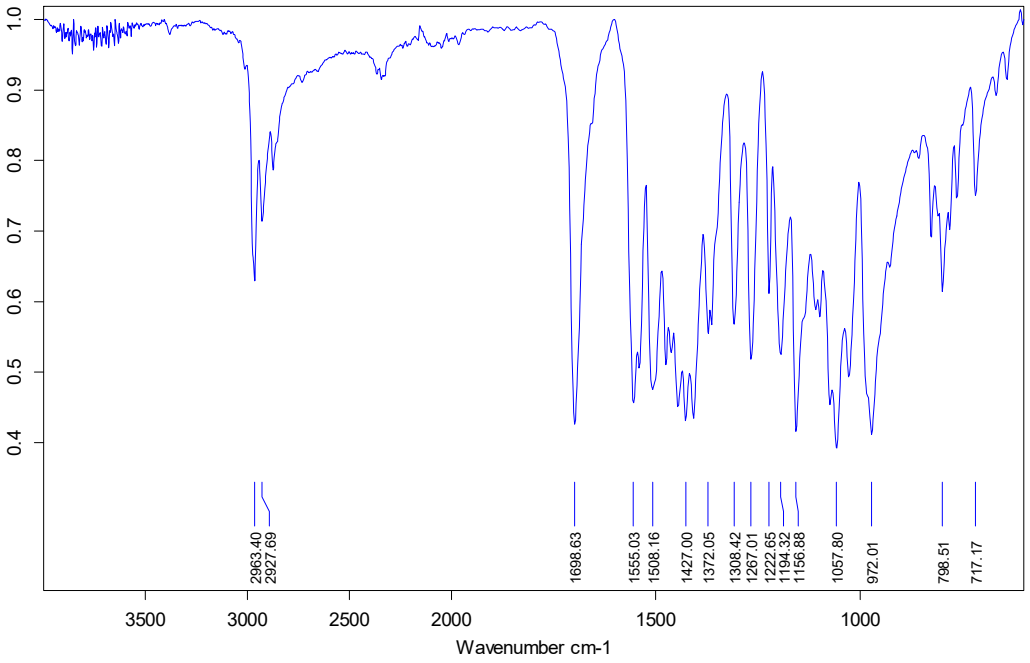
^{13}C NMR (90 MHz, $CDCl_3$)



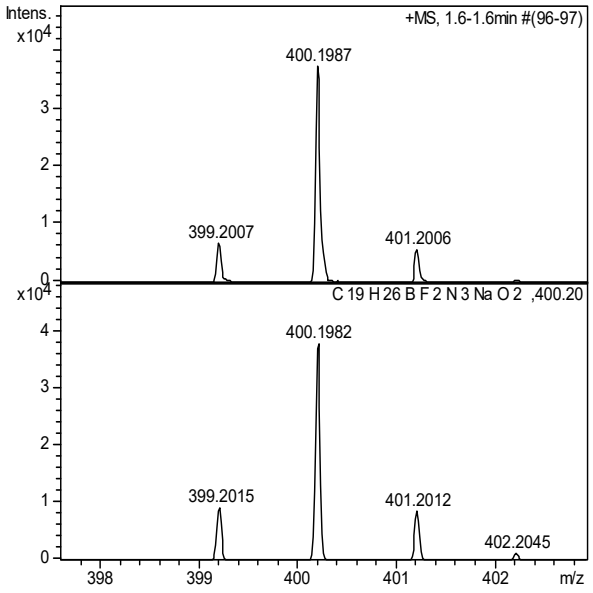
DEPT 135 (90 MHz, $CDCl_3$)



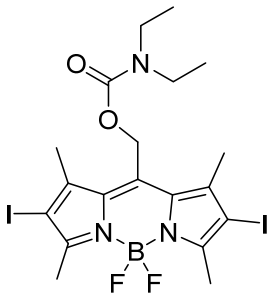
ATR-IR



HR-MS (ESI$^+$)

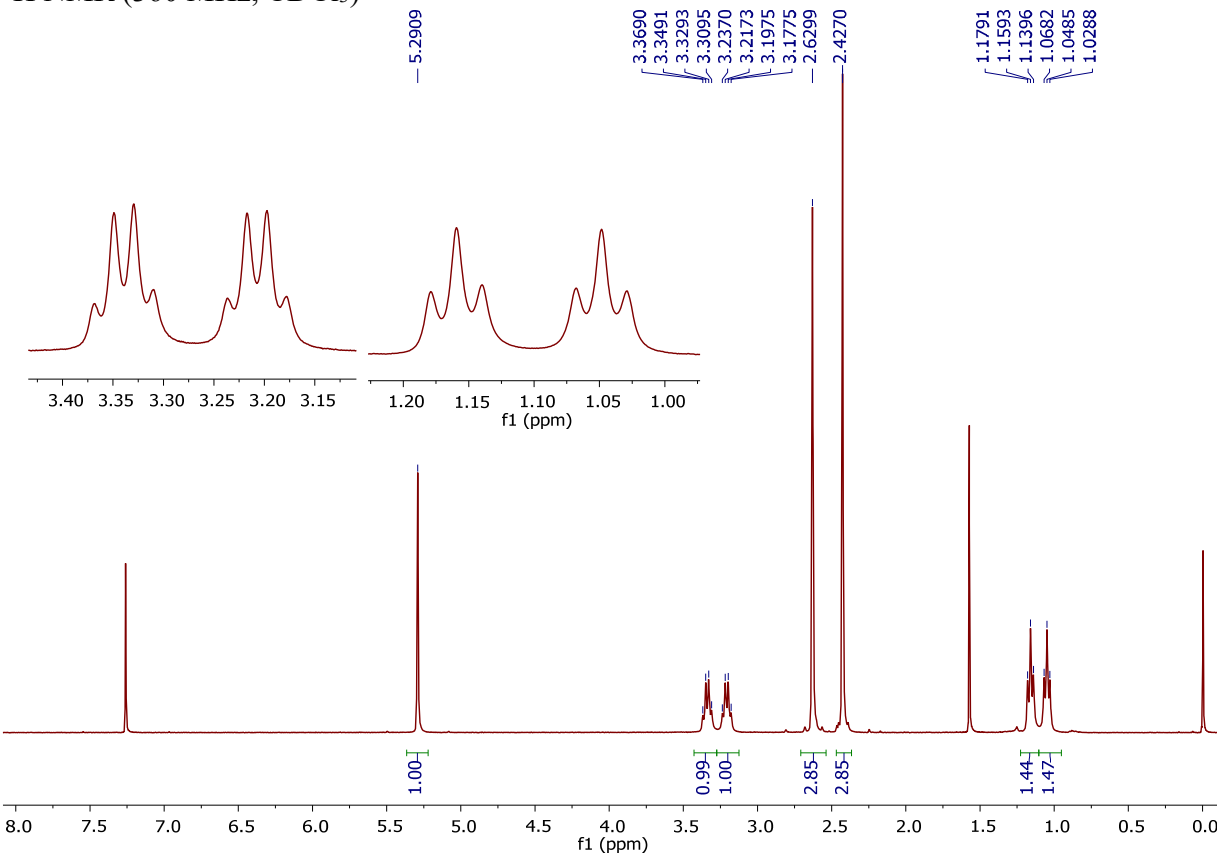


Meas. m/z	Formula	m/z	err [mDa]	err [ppm]	mSigma
400.1987	C19H26BF2N3NaO2	400.1982	-0.5	-1.2	44.7

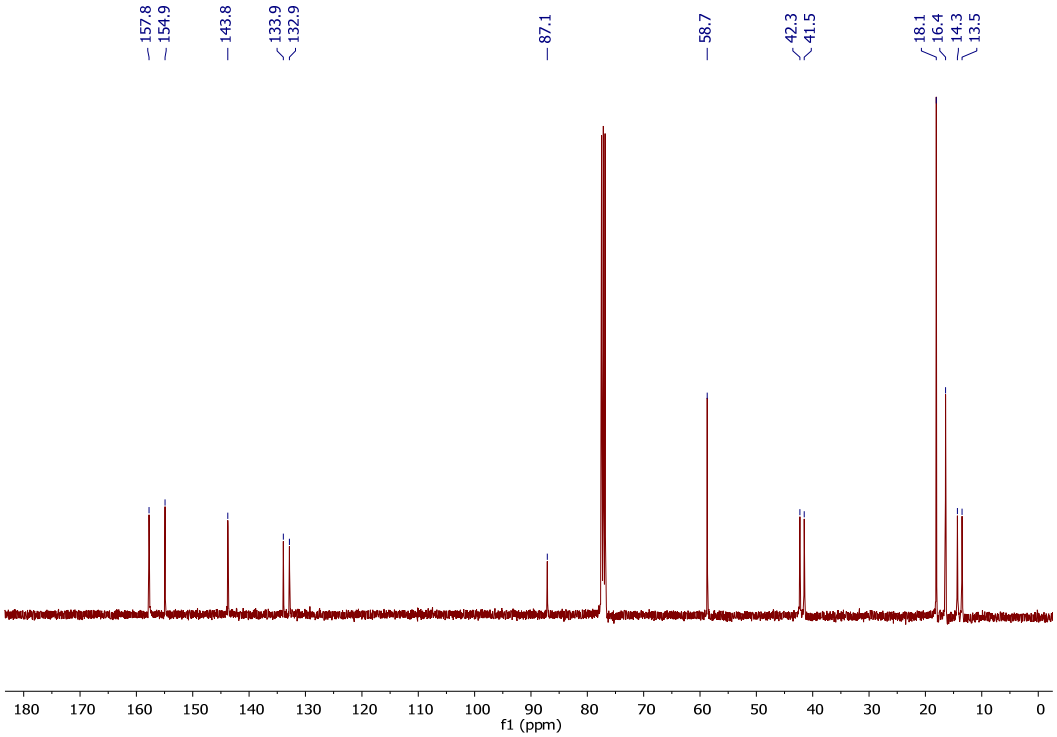


BODIPY-DEA

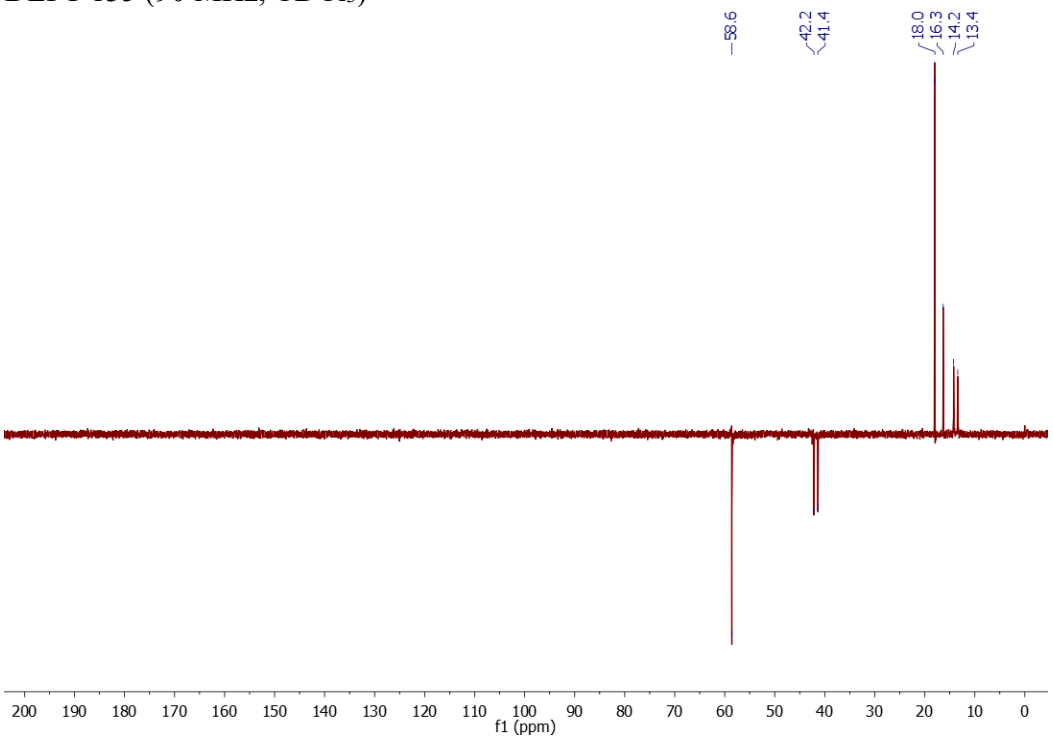
^{1}H NMR (360 MHz, $CDCl_3$)



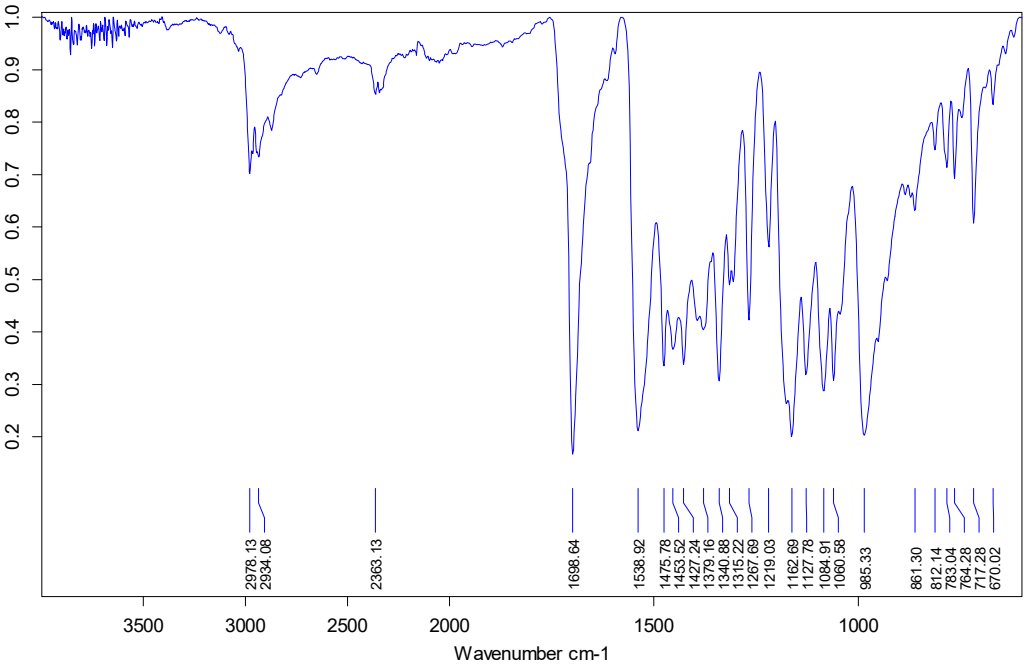
^{13}C NMR (90 MHz, $CDCl_3$)



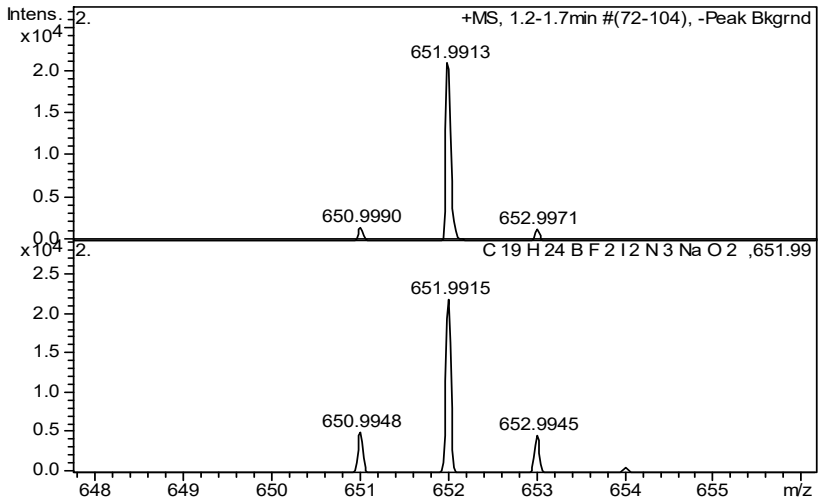
DEPT 135 (90 MHz, $CDCl_3$)



ATR-IR

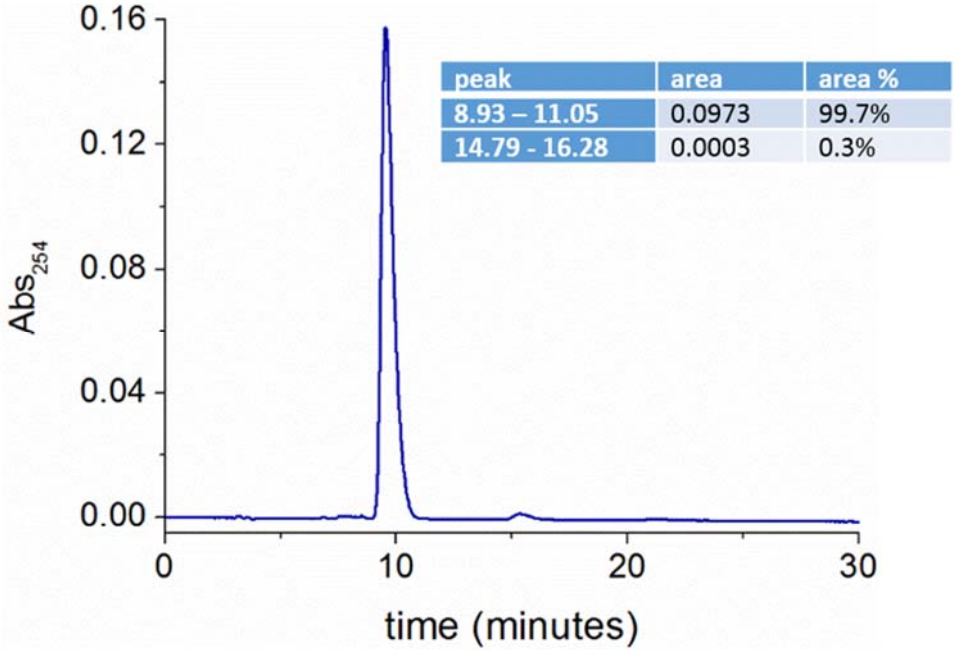


HR-MS (ESI$^+$)

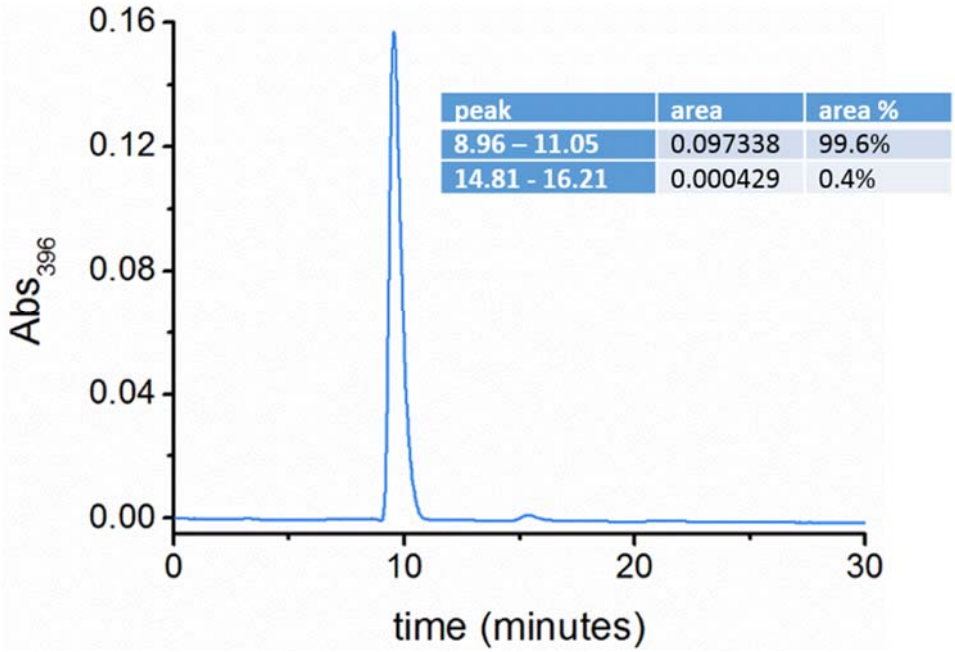


Meas. m/z	Formula	Calc.m/z	err [mDa]	err [ppm]	mSigma
651.9913	C19H24BF2I2N3NaO2	651.9915	0.1	0.2	113.9

HPLC



peak	area	area %
8.93 – 11.05	0.0973	99.7%
14.79 - 16.28	0.0003	0.3%



peak	area	area %
8.96 – 11.05	0.097338	99.6%
14.81 - 16.21	0.000429	0.4%

2. ABSORPTION SPECTRA OF CA MONOMERS

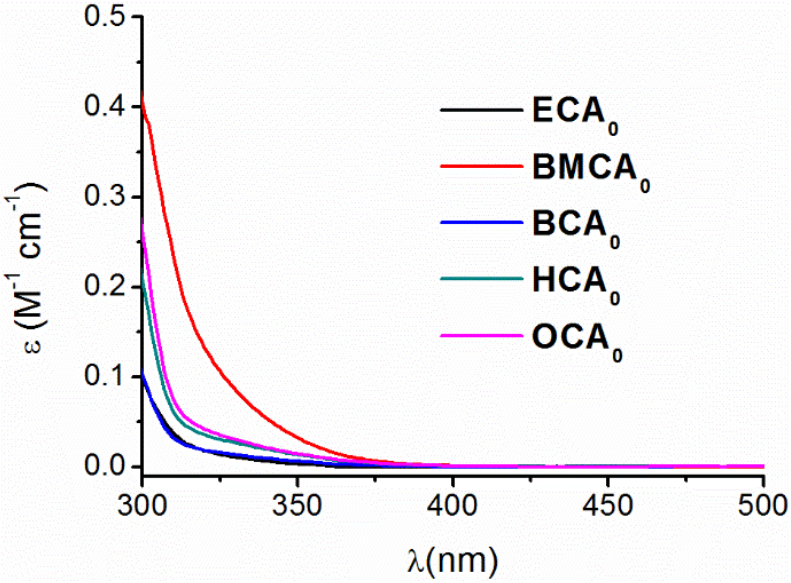


Figure S1. Absorption spectra of neat **ECA_0**, **$BMCA_0$**, **BCA_0**, **HCA_0** and **OCA_0**.

3. AMINE PHOTORELEASE FROM NPPOC-DEA AND BODIPY-DEA

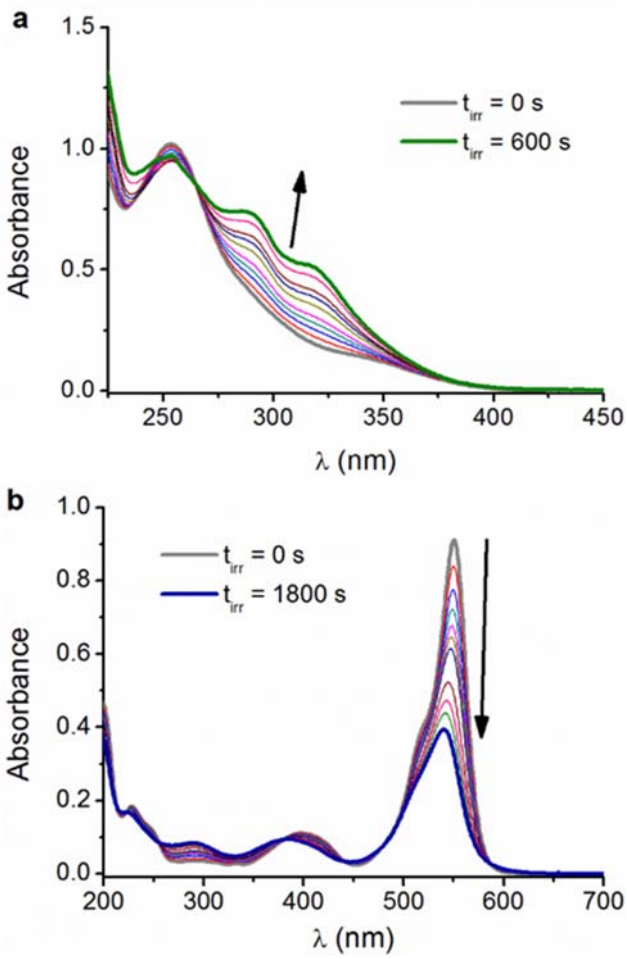


Figure S2. (a) Variation of the absorption spectra of **NPPOC-DEA** (c = $3.17 \cdot 10^{-4}$ M) in acetonitrile upon continuous irradiation at λ_{exc} = 355 nm (power = 3.5 mW). Spectra recorded at different times (0-600 seconds). The arrow shows the spectral change in time. (b) Variation of the absorption spectra of **BODIPY-DEA** (c = $1.48 \cdot 10^{-5}$ M) in acetonitrile upon continuous irradiation at λ_{exc} = 532 nm (power = 28.2 mW). Spectra recorded at different times (0-1800 seconds). The arrow shows the spectral change in time.

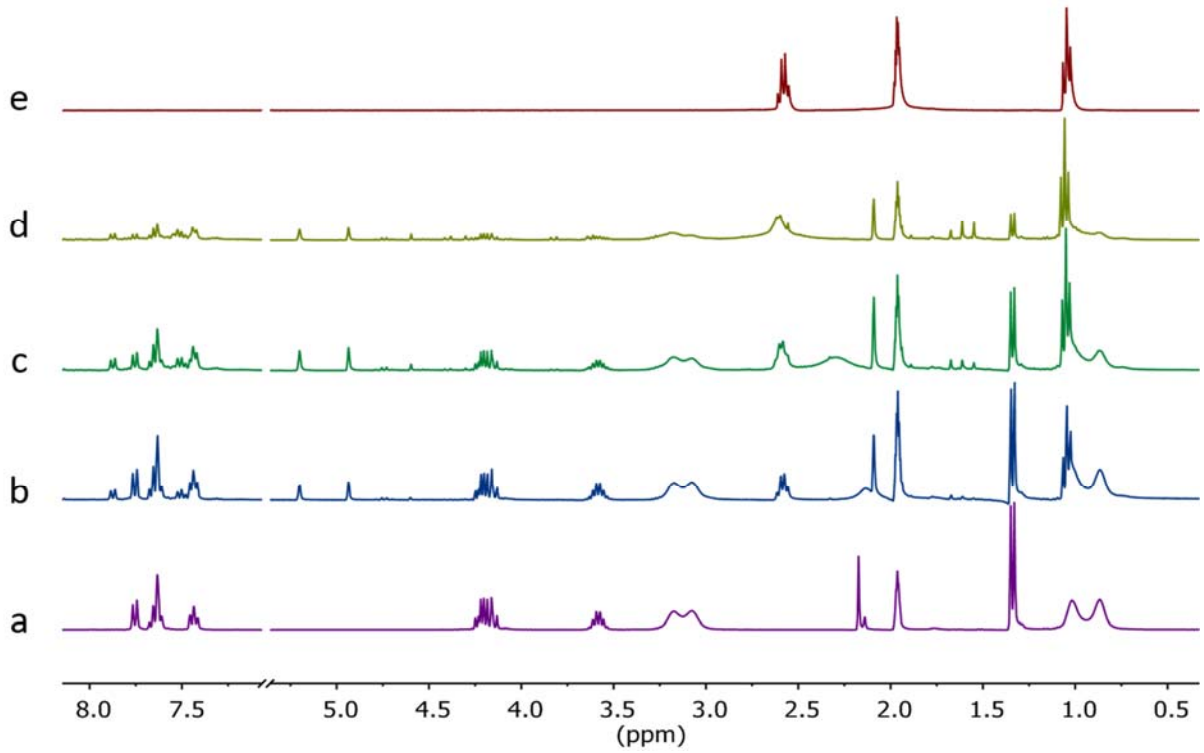


Figure S3. Variation of the ^{1}H NMR spectrum (360 MHz, CD_3CN) of **NPPOC-DEA** (*c* = 35 mM) upon continuous irradiation at λ_{exc} = 355 nm (power = 300 mW). Spectra recorded at different times (0, 25, 60 and 130 minutes; spectra (a)-(d)). For sake of comparison, the ^{1}H NMR spectrum (360 MHz, CD_3CN) of DEA is also shown (spectrum (e)).

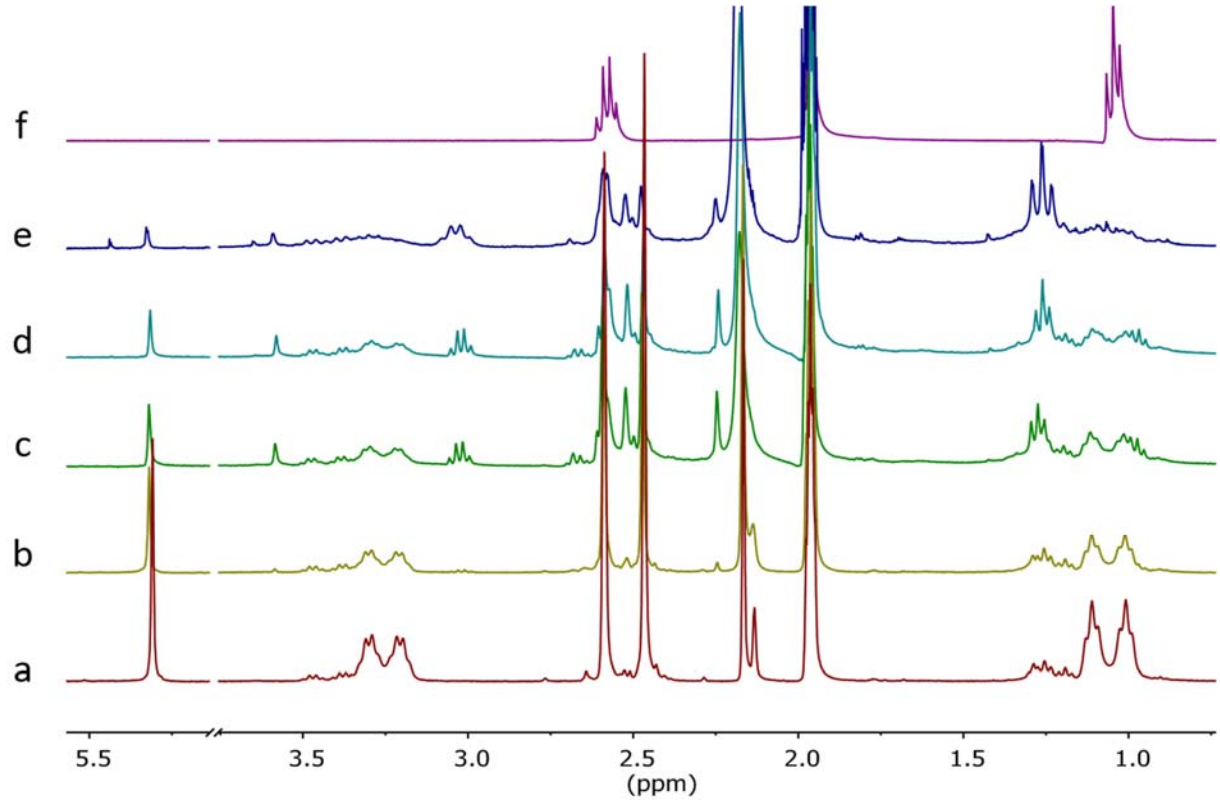


Figure S4. Variation of the ^{1}H NMR spectrum (360 MHz, CD_3CN) of **BODIPY-DEA** (*c* = 17 mM) upon continuous irradiation at λ_{exc} = 532 nm (power = 250 mW). Spectra recorded at different times (0, 25, 90, 180 and 300 minutes; spectra (a)-(e)). For sake of comparison, the ^{1}H NMR spectrum (360 MHz, CD_3CN) of DEA is also shown (spectrum (f)).

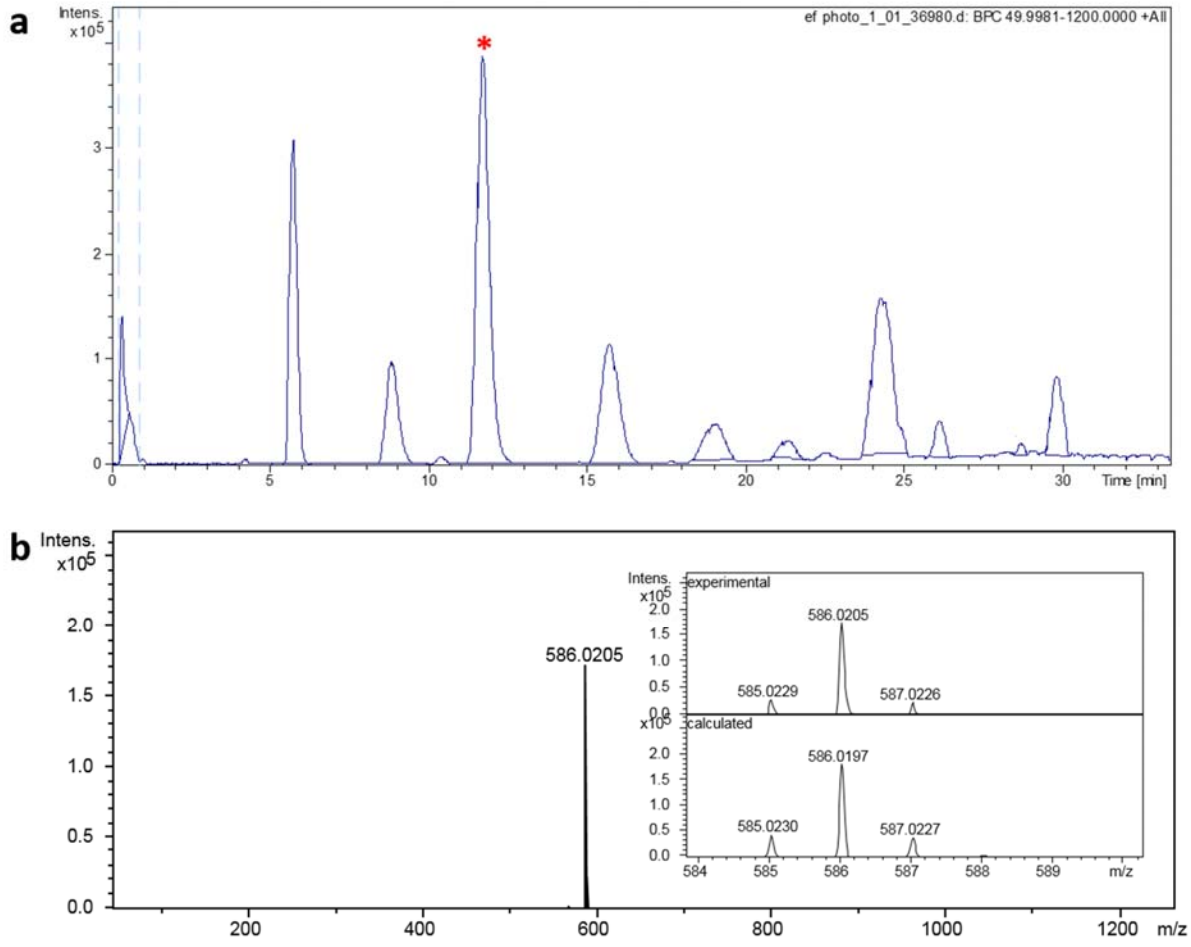


Figure S5. (a) HPLC-MS chromatogram of **BODIPY-DEA** in acetonitrile after irradiation (λ_{exc} = 532 nm; power = 250 mW; 300 minutes). (b) HRMS spectrum of the most intense peak of the chromatogram, eluted at 11.7 minutes. Inset: detail of the experimental (above) and calculated (below) HRMS spectrum of $[\mathbf{9}\cdot H]^+$ ion. In addition, the peak eluted at 15.8 minutes is attributed to the $[\mathbf{BODIPY\text{-}DEA}\cdot Na]^+$ ion (experimental m/z = 651.9894; calculated m/z = 651.9917).

4. ACID VALUE DETERMINATION OF CYANOACRYLATE MONOMERS

Table S1. Viscosity acid value determination of CA monomers

Monomer	t_{AVD} **(s)**
ECA_0	40
ECA_{st}	210
$BMCA_0$	22
$BMCA_{st}$	210
BCA_0	65
BCA_{st}	210
HCA_0	120
HCA_{st}	210
OCA_0	140
OCA_{st}	210

5. PHOTOPOLYMERIZATION OF CYANOACRYLATE MONOMERS

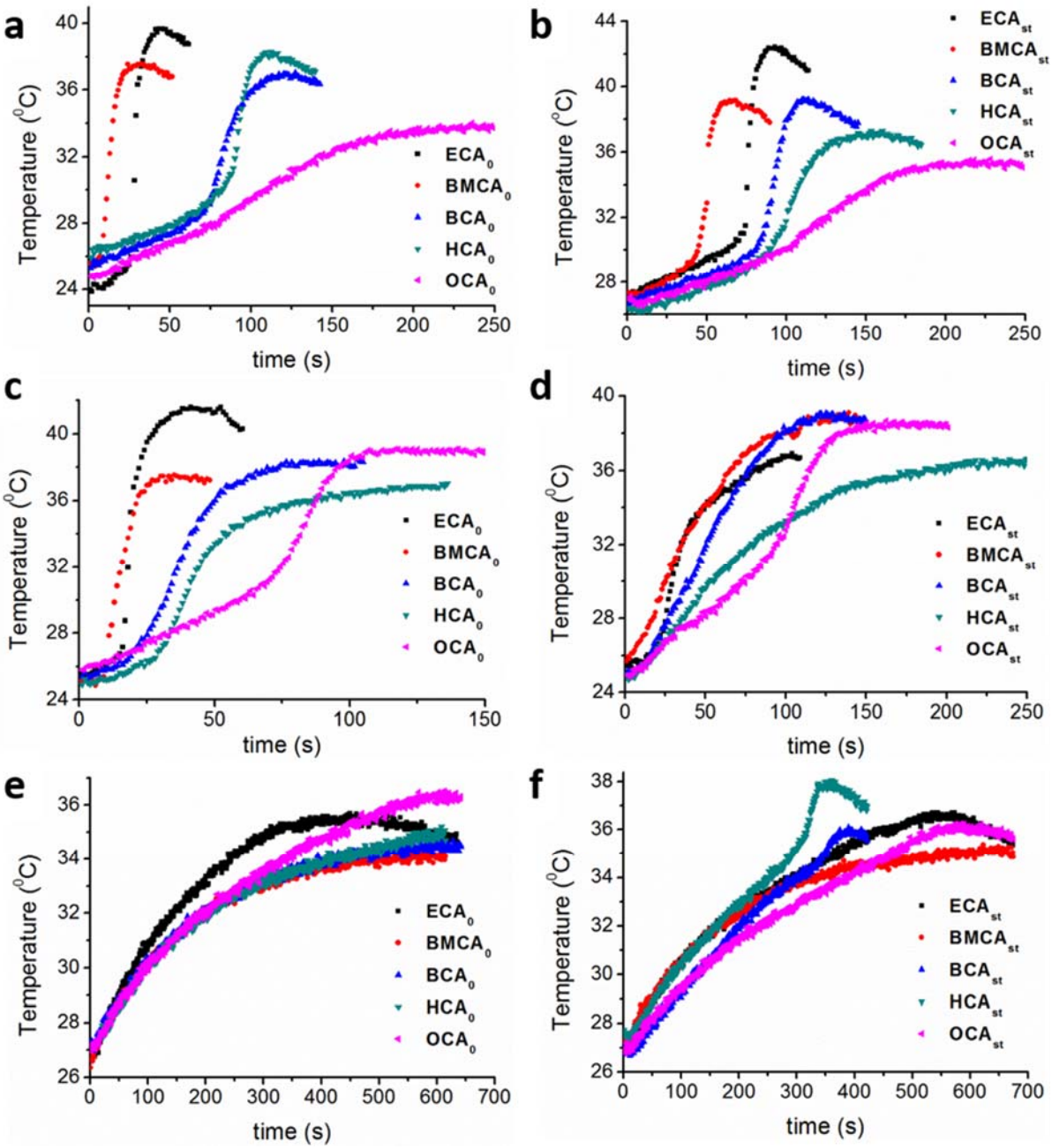


Figure S6. Photopolymerization exotherms measured for: (a) **NPPOC-DEA** and commercial monomers; (b) **NPPOC-DEA** and stabilized monomers ([**NPPOC-DEA**] = 15 mM; λ_{exc} = 355 nm; power = 300 mW); (c) **BTIPA-DEA** and commercial monomers; (d) **BTIPA-DEA** and

stabilized monomers ([**BTIPA-DEA**] = 15 mM; λ_{exc} = 405 nm; power = 280 mW); (e) **BODIPY-DEA** and commercial monomers; (f) **BODIPY-DEA** and stabilized monomers ([**BODIPY-DEA**] = 15 mM; λ_{exc} = 532 nm; power = 250 mW).

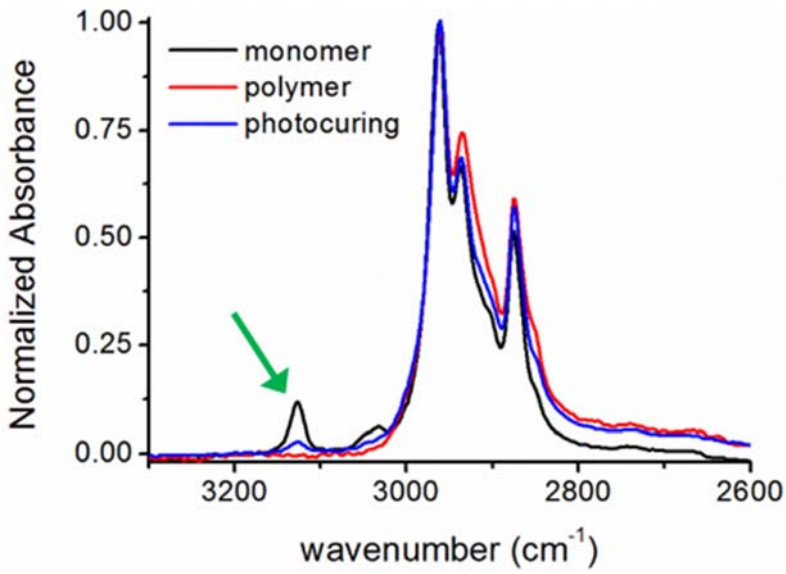


Figure S7. IR spectra of **BCA$_0$** monomer, a fully cured **BCA$_0$**+**BTIPA-DEA** mixture and a **BCA$_0$**+**BTIPA-DEA** mixture at t_{photo}= 37 s. The arrow shows the peak at 3127 cm^{-1}, which decreases as polymerization takes place.

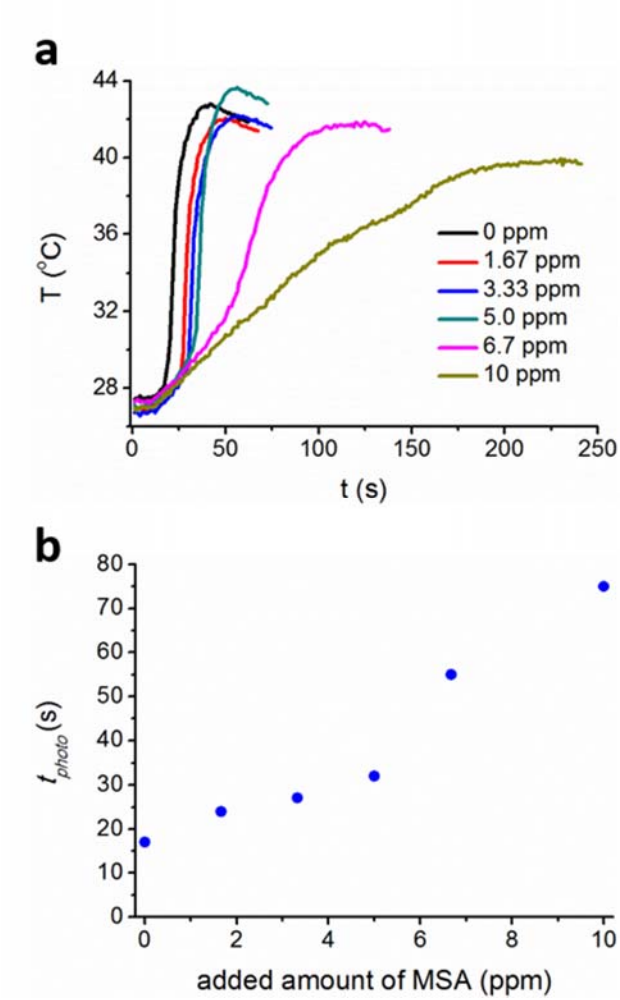


Figure S8. (a) Photopolymerization exotherms measured for mixtures of **BCA_0** and **BTIPA-DEA** (15 mM) upon increasing addition of methanesulfonic acid. (b) Variation of the polymerization time (t_{photo}) with the added quantity of methanesulfonic acid.

6. CHARACTERIZATION OF POLYCYANOACRYLATES

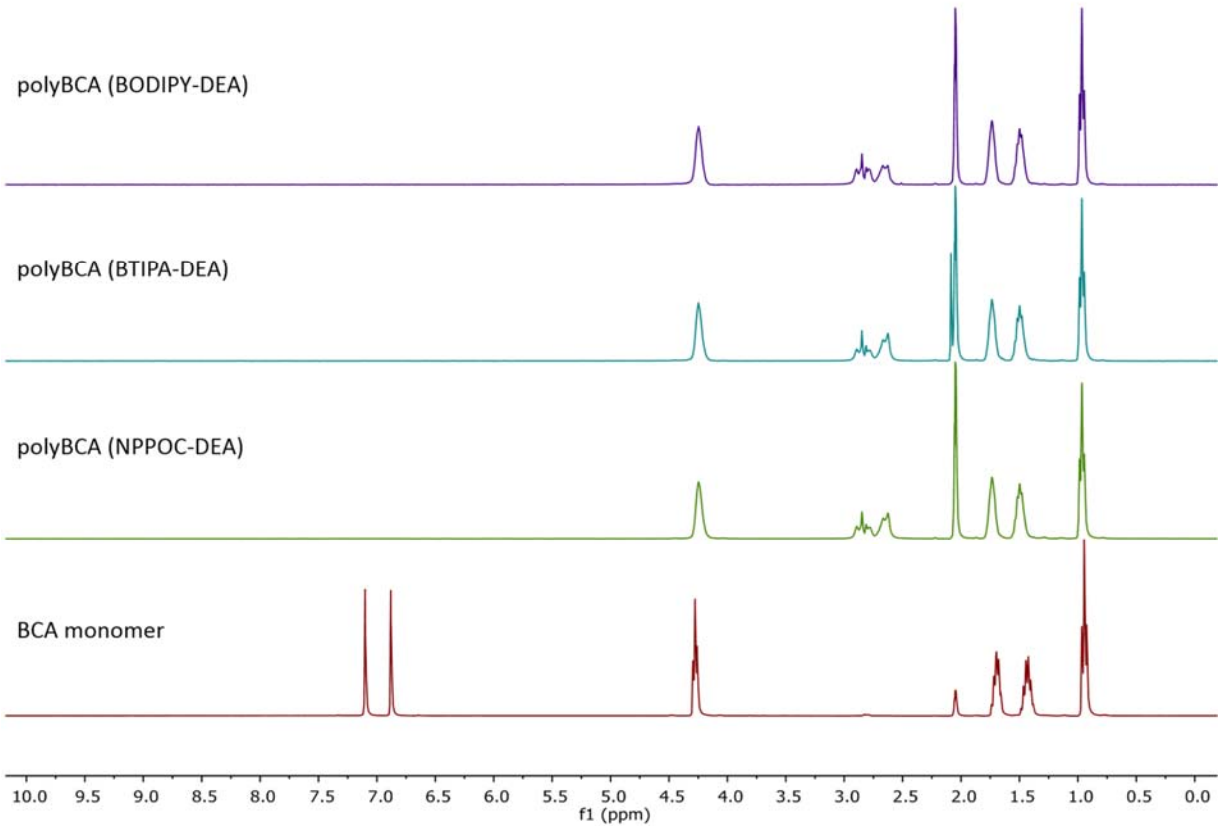


Figure S9. ^{1}H-NMR spectra (360 MHz, acetone-d_6) of **BCA_0** in its monomeric form and after photopolymerization with **BODIPY-DEA**, **BTIPA-DEA** and **NPPOC-DEA**.

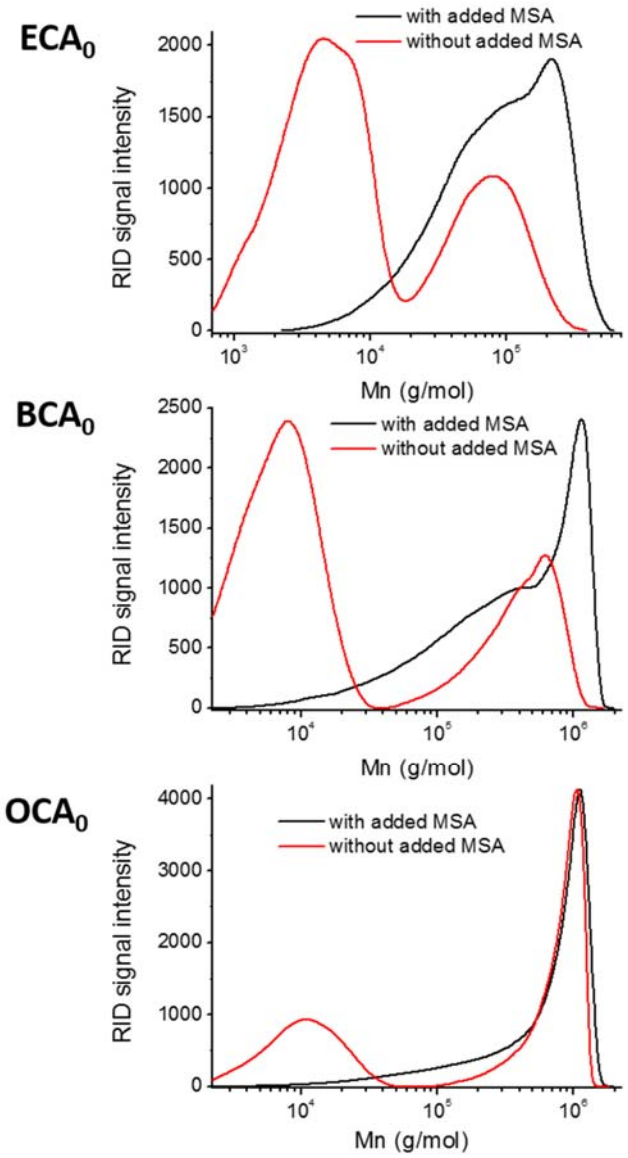


Figure S10. GPC traces for polycyanoacrylates obtained upon either thermal polymerization. Red lines: polymers dissolved in THF; black lines: polymers dissolved in THF containing 0.05% of MSA (methanesulfonic acid).

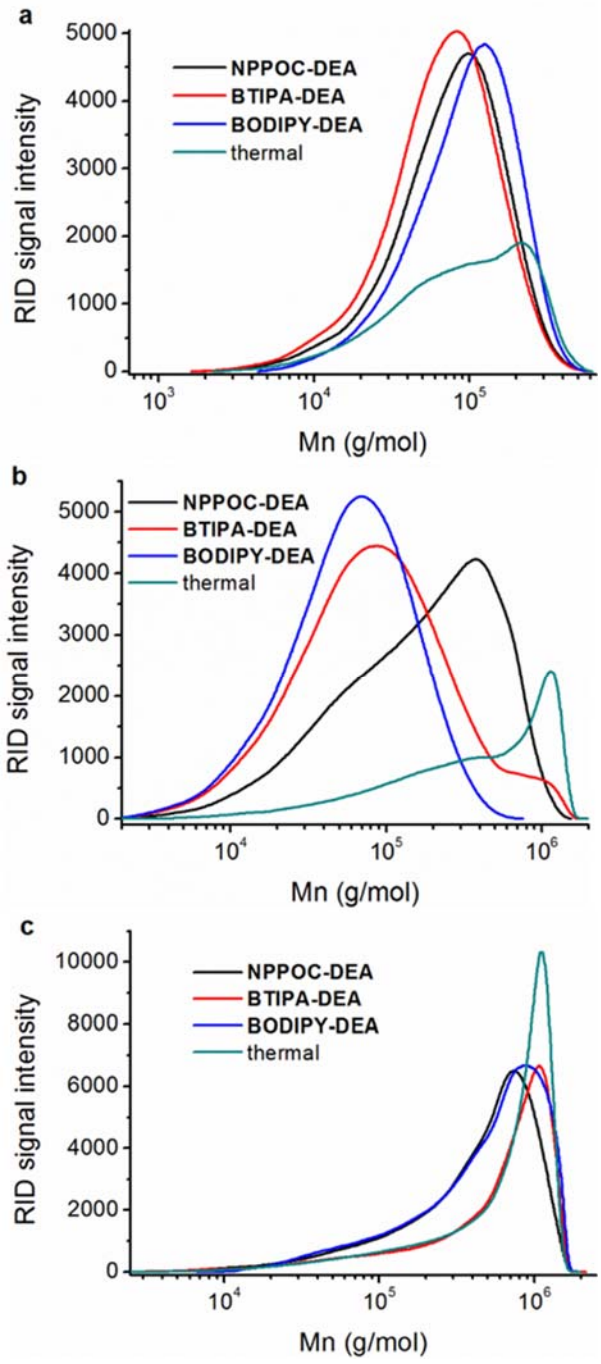


Figure S11. GPC traces for polycyanoacrylates obtained upon either photopolymerization or thermal polymerization of (a) **ECA$_0$**, (b) **BCA$_0$** and (c) **OCA$_0$**.

7. REFERENCE

(1) Xi, W.; Peng, H.; Aguirre-Soto, A.; Kloxin, C. J.; Stansbury, J. W.; Bowman, C. N. Spatial and Temporal Control of Thiol-Michael Addition via Photocaged Superbase in Photopatterning and Two-Stage Polymer Networks Formation. *Macromolecules* **2014**, *47*, 6159-6165.