Photochemical Insights on Intramolecular Dye-Sensitized Free-Radical Processes with a Quinoline Antenna

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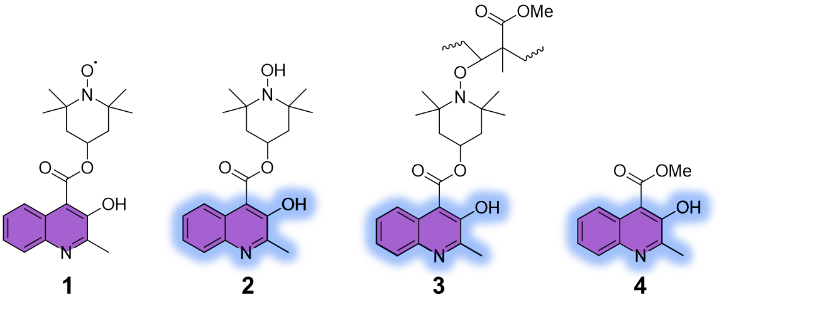
**Abstract**

Organic fluorophores containing paramagnetic nitroxides covalently tethered to the chromophoric core show a dramatic reduction in fluorescence due to intramolecular quenching of their excited states. Nonetheless, trapping of hydrogen atoms or carbon-centered radicals by the nitroxide suppresses the quenching pathway and restores the fluorescence, an effect that can be used to monitor radical scavenging processes. Herein, we synthesized a prefluorescent radical probe in which a 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) moiety was chemically coupled to a quinoline chromophore, which can directly sensitize TEMPO via energy transfer following low-intensity ultraviolet illumination. In this design, the quinoline dye effectively acts as molecular ‘antenna’ to promote the reactivity of TEMPO toward H abstraction to form the corresponding *N*-hydroxylamine. The excited TEMPO can also abstract a hydrogen from a polymeric matrix, enabling the photochemical modification of the polymer with concomitant fluorescence activation and patterning. In addition, the patterning process can be thermally reverted (‘erased’) by heating the film above the glass transition temperature of the polymer.

**Introduction**

The search for optically active donor-acceptor systems capable of converting light energy to chemical energy continues to be an area of intense research interest.[1–3] Undeniably, the design and synthesis of viable *D* *-* *A* (*D* = Donor; *A* = Acceptor) systems capable of absorbing light and funneling the absorbed energy toward a chemical process are of fundamental importance for applications in artificial photosynthesis,[4–8] photovoltaics,[9–12] and photocatalysis.[13–16] In this context, molecular systems comprised of organic chromophores can effectively capture light and transduce the resulting excitation energy into a chemical reaction. Organic chromophores can absorb radiation across the ultraviolet and visible regions of the electromagnetic spectrum with concomitant transitions from ground to excited electronic states.[1,3] Excited chromophores can then release the absorbed energy in the form of fluorescence, or by decaying back to the ground state through non-radiative relaxation processes.[17] In the presence of a suitable acceptor, however, such chromophores can transfer the absorbed energy from their excited state (*D\**) to a nearby *A*, mimicking the workings of a transmitting antenna.[18] The acceptor species can therefore be sensitized with light via energy transfer from a tethered donor and undergo, or promote, a chemical reaction.

Dual chromophore-nitroxide dyads (CNO•) have often been investigated for conversion of light energy to chemical energy based upon the ability of paramagnetic nitroxides, such as 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO), to selectively abstract a hydrogen atom or trap carbon-centered radicals, yielding the corresponding hydroxylamines or alkoxyamines, respectively.[19–22] Commonly studied hydrogen donor substrates include phenols,[23–25] thiols,[26,27] and solvents (notably, acetonitrile and toluene).[28,29] Within the dyadic system, covalent coupling between a light-absorbing organic dye and TEMPO allows sensitization of the latter by direct energy transfer from the excited chromophore.[21,22,29–32] It follows that such a design permits hydrogen abstraction or radical trapping initiated purely by a photochemical process. Herein, we synthesized compound **1** (Scheme 1), in which TEMPO was coupled with the UVA absorbing chromophore 3-hydroxy-2-methyl-4-quinolinecarboxylic acid (abbreviated as **Q**), and studied its light-induced chemical processes at low irradiation power with spectrometric techniques. Specifically, we investigated its ability to undergo H abstraction from a polymer matrix upon energy transfer from **Q** to TEMPO.

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**Scheme 1.** Chemical structures of compounds **1**-**4**. Glowing structures indicate fluorescence.

**Results and Discussion**

**Photochemistry of 1 in CH3CN and C6H6**

The absorption spectrum of **1** in CH3CN (Figure S1, Supporting Information) shows a band attributable to the quinoline (**Q**) chromophore at Abs = 340 nm, while its emission spectrum (Figure S1) reveals that the fluorescence at Em = 400 nm is largely quenched, as expected for fluorophore-TEMPO dyads and as illustrated by the comparison between the emission spectra of **Q** and **1** (Figure S2). Paramagnetic nitroxides covalently linked to fluorophores are well known to quench the excited states of the latter.[19,29,41–46,33–40] In these systems, intramolecular quenching occurs through electron exchange between the two units, which causes non-radiative relaxation of the local singlet state to the ground state of the fluorophore.[19,20,42,47] Nevertheless, hydrogen or radical trapping by TEMPO leads to the formation of a diamagnetic product, thereby disabling the quenching pathway and restoring fluorescence. Based upon these considerations, activation of the fluorescence of **Q** in compound **1** can be used to report on and quantify hydrogen abstraction or radical reaction by the nitroxide counterpart in real time. In our set up, compound **1** is irradiated at 365 nm, which delivers 330 kJ/mol of energy and is thus theoretically sufficient to sensitize TEMPO upon energy transfer from the quinoline antenna.[31] The mechanism for energy transfer is plausible given the observation that **1** is non-fluorescent due to intramolecular quenching, suggesting that chromophore and nitroxide are separated by a distance that is appropriate for energy transfer.[33] Relative to energy transfer, the shorter-range electron exchange mechanism for quenching the fluorescence of **1** requires a much closer donor-acceptor distance, on the order of a few Angstroms, and decreases significantly as the fluorophore to nitroxide distance is increased.[17,33] We therefore adopted a design for the chemical structure of **1** that minimizes separation between the **Q** and TEMPO units.

Illumination of an aerated CH3CN solution of **1** at 365 nm does not produce any detectable change in the absorption or emission spectra (Figure S1). Irradiation of **1** in C6H6 in otherwise identical conditions leads to analogous results (Figure S3). This result is in agreement with the previously observed behaviours of other quinoline-TEMPO antenna systems, for which it has been noted that quinoline-TEMPO photochemistry in pure solvents (i.e., in the absence of a good H-donor) is inefficient in aerated or oxygenated solutions. For example, Goto *et al*. successfully promoted the photochemical dissociation of a TEMPO-based alkoxyamine by intramolecular energy transfer from an excited quinoline dye,[31] while Su *et al*. exploited quinoline-sensitized TEMPO-alkoxyamine photolysis to promote the polymerization of methyl methacrylate.[32] In these reports, a quinoline antenna absorbs UVA light and transfers the energy to a TEMPO acceptor to cleave the NO-C bond of the alkoxyamine. However, the system performs only under controlled atmosphere. Based on these considerations, we irradiated a solution of **1** in CH3CN under N2 atmosphere at 365 nm. Although no changes in absorption occurred (Figure S4), a 2.75-fold increase (average of two trials) in fluorescence intensity was observed when species **1** was irradiated under N2 (Figure 1), indicating the photochemical formation of a diamagnetic product. The maximum increase in emission, observed after 60 minutes of irradiation, is comparable to the luminescence of the model compound **4** at identical concentration (Figure S5), confirming that the process is aimed at restoring the quenched fluorescence of the quinoline chromophore, rather than increasing its quantum yield. The spectra in Figure S5 also suggest that the conversion of **1** is approximately quantitative.



**Fig. 1** Emission spectra of a CH3CN solution of **1** (30 M, 20°C, Ex = 330 nm) before and after UVA irradiation (365 nm, 0-60 min, 0.4 mW cm–2) under N2 atmosphere.

We identified the product as hydroxylamine **2** (Scheme 1), which is expected to form upon partial H abstraction from acetonitrile with concomitant formation of a solvent-generated radical, •CH2CN. Literature examples reported that the •CH2CN radical can subsequently couple with a second TEMPO unit to generate an adduct, traces of which could be detected by mass spectrometry.[28,29] In our case however, GC-MS analysis of the same reaction repeated on a milligram scale did not reveal the presence of such adduct, due to the inherently low stability of *N*-alkoxyamines bearing electron-withdrawing groups and their spontaneous reoxidation to •TEMPO under air.[48–54] Nonetheless, we were able to chromatographically isolate a small quantity of a semi-stable product from a large-scale irradiation experiment under N2 (1.4 mg/mL, 22 h irradiation, CH3CN) and analyze it by GC-MS in a time sensitive fashion. A comparison between the GC chromatogram of **1** and the irradiated mixture (Figure S6) reveals that the main product appears at a retention time of 16 minutes. MS analysis of this peak (Figure S7) reports a MW of 358 m/z, in agreement with the expected value for **2**. Furthermore, FTIR-ATR of the irradiated solution also suggests this product to be hydroxylamine **2**, due to the appearance of the O-H stretching vibration at 3250 cm-1 (Figure S8). Importantly, no O-H stretching mode could be observed in the FTIR spectrum of compound **1**, nor in that of the commercial compound 3-hydroxy-2-methyl-4-quinolinecarboxylic acid (**Q**). In C6H6, under N2 atmosphere, we recorded a 1.95-fold (average of two trials) increase in the fluorescence after 60 minutes of irradiation (Figure S9). Thus, the reaction in acetonitrile appears to work better than in benzene, even though the latter is normally considered the better hydrogen donor due to its lower bond dissociation energy for the homolytic cleavage of the C-H bond.[55] This is not without precedent: Johnston *et al.* also noted that the quantum yield for the production of TEMPO-H (obtained by irradiating TEMPO with a Xe lamp) in acetonitrile was higher than in toluene.[28] In that instance, charge transfer was hypothesized to play a role. In our case, where a quinoline chromophore has been tethered to TEMPO, we speculate that this behaviour is due to a marginally shorter excited state lifetime of **Q** in C6H6. A reduction in the excited state lifetime would, in fact, decrease the likelihood of energy transfer from the chromophore to TEMPO (consequently reducing product formation) even though the rate of hydrogen abstraction from benzene is similar or greater than that in acetonitrile. Indeed, the integrated emission intensity of the model compound **4** at equimolar quantum yield concentrations is lower in C6H6 than in CH3CN (Figure S10).

Critically, it has been observed that the O-H bond in the hydrogenated derivative **2** is weak, and nitroxides can commonly reform by simple exposure of their corresponding hydroxylamines to mild oxidants, including air and molecular oxygen, even in the absence of a catalyst.[48,56] To investigate the relative stability of the species photogenerated herein, the degassed solution of **1** irradiated with ultraviolet light (Figure 1) was capped to avoid evaporation of the solvent and maintain controlled atmosphere. Emission spectra were then recorded over the course of 12 hours in otherwise identical conditions. Results (Figure S11) show that the fluorescence intensity post-activation remains constant under controlled atmosphere, suggesting that **2** is stable in the absence of air. On the contrary, a solution that was activated under N2 but later exposed to oxygen shows a slow but steady decrease in the emission intensity, consistent with the progressive decomposition of **2**.

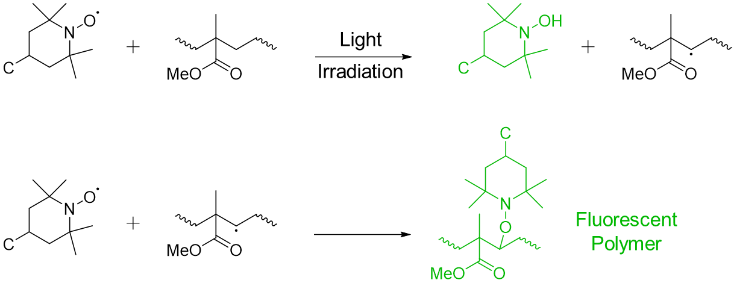
**Photochemistry of 1 in PMMA/CH3CN**

The spectroscopic behaviour of **1** is considerably altered in a 5% poly(methyl methacrylate) (PMMA) solution in CH3CN (Figure 2). Prior to irradiation, addition of the polymer causes a partial increase of the original emission intensity due to the increased viscosity of the medium and reduced rotational motion of the free dye (compare the trace at 0 min in Figures 1 and 2).[17] With sustained ultraviolet illumination, the emission spectrum of an aerated solution of **1** in the presence of PMMA (Figure 2) shows a >5-fold vertical increase of the fluorescence intensity up to 15 minutes, followed by a decrease (up to a 2.5-fold net rise) and a concomitant bathochromic shift of the emission maximum. In parallel, irradiation of **1** in 1% PMMA/CH3CN solution (Figure S13) shows the same increase-decrease and redshift trend, although it is less pronounced than at higher polymer concentration, suggesting that PMMA is an active participant in the equilibrium.



**Fig. 2** Emission spectra of a 5% PMMA in CH3CN solution of **1** (30 M, 20°C, Ex = 330 nm) before and after UVA irradiation (365 nm, 0-60 min, 0.4 mW cm–2) under air.

Previously, it has been reported that a chromophore-TEMPO dyad can form a stable photochemical product by binding to PMMA upon photochemical sensitization of the nitroxide appendix.[29,57] The mechanism for the addition, depicted for a generic chromophore-nitroxide dyad CNO•, is illustrated in Scheme 2. We thus investigated the possibility that, following ultraviolet irradiation in the presence of PMMA, a polymer adduct (**3** in Scheme 1) could result from the addition of **1** to the polymer skeleton following a H abstraction step. Binding or attachment of a fluorophore to a polymeric substrate is usually accompanied by spectral shift due to the different environment of the bound species.[17] In our case, the aggregation of **1** into the polymer matrix promotes the formation of intramolecular H-bonding at the N-position within the PMMA network, red-shifting the emission similar to what was observed for the commercial, heavily H-bonded chromophore **Q** (Figure S2). To confirm this hypothesis, PMMA was precipitated out of the solution by addition of CH3OH, after 2 hours of UVA irradiation. The precipitated polymer was then subjected to three cycles of centrifugation, sonication, and washing to eliminate any unbound dye. The residue was redissolved in CH3CN and analyzed by absorption and fluorescence spectroscopy (Figure 3), which display the bathochromically shifted signature of **1** (lEm = 435 nm), in agreement with the results shown in Figure 2. In comparison, the emission spectra of pure PMMA in CH3CN does not show any intrinsic fluorescence or irradiation effect (Figure S14). From the absorption values in Figure 3 and the extinction coefficient of **1**, we can estimate that the total amount of **1** that reacted with poly(methyl methacrylate) corresponds to ~14% of the original dye-nitroxide content.



**Scheme 2.** Light-induced reaction of excited chromophore-TEMPO (CNO•, C = chromophore) dyads with a monomeric unit within the PMMA chain. Molecules shown in green are fluorescent.



**Fig. 3** Absorption (solid) and emission (dashed, Ex = 330 nm) spectra of the precipitated polymer obtained after 3 mL of a 30 mM solution of **1** in 5% PMMA/CH3CN was exposed to ultraviolet light for 120 min.

On the other hand, the supernatant recovered from the centrifugation of the polymer indicates the presence of the hydroxylamine product **2**, formed upon H abstraction from the PMMA matrix (note that for one equivalent of **1** successfully bound to the polymer, another equivalent produces the hydroxylamine **2** according to the stoichiometry described in Scheme 2). Indeed, the most prominent feature of the corresponding FTIR-ATR spectrum (Figure S15) is the strong O-H stretching vibration at 3330 cm-1 which alludes to the presence of **2**, and the spectrum is identical to that reported by another group.[32] This is consistent with what we suspected based on the experiments conducted under N2, especially in light of the fact that PMMA is a better H-donor than CH3CN. Based on these considerations, the progressive decrease in fluorescence at longer irradiation times observed in Figure 2 comes as no surprise, as the newly formed O-H bond in **2** will partially decompose in aerated conditions under prolonged illumination.

**Photochemistry of 1 in Polymer Films and Fluorescence Patterning**

To further validate the photochemistry of our antenna probe, we prepared polymer films of PMMA containing **1**. In order to avoid effects related to the presence of CH3CN, the films were oven-dried at 140°C for 10 minutes. Data (Figure 4) recorded upon exposure of these films to ultraviolet light mirror what was observed in a solution of PMMA in CH3CN: a vertical increase in fluorescence intensity during the first half of the irradiation period (indicating the formation of **2**) was followed by a subsequent intensity decrease and red-shift of the emission as **1** binds to the PMMA skeleton forming adduct **3**.

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**Fig. 4** Emission spectra of PMMA polymer films containing **1** (20°C, Ex = 330 nm) before and after UVA irradiation (365 nm, 0, 60 and 120 min, 0.4 mW cm–2) under air.

The activation of the fluorescence of **1** upon photoexcitation, and its addition to the PMMA matrix, can be exploited to imprint a desired pattern. We thus tested the ability of our probe to produce (‘write’) a patterned fluorescent image which can be subsequently detected (‘read’) under UV excitation. Owing to the thermoplastic properties of PMMA, which is known to become pliable at elevated temperatures and harden upon cooling, fluorophores that have been activated in a confined (patterned) space can then be thermally dispersed over the entire substrate area, causing the loss of the pattern (‘erase’). Indeed, irradiation of a PMMA film of **1** at 365 nm through a homemade stencil for 60 minutes encourages the activation of its fluorescence exclusively in the irradiated area, meanwhile producing a fluorescent image (**C** in Figure 5). The bright region in Figure 5C corresponds to the area where **1** has been photosensitized to abstract a hydrogen atom from and bind to the polymer, as discussed above. The patterned film was then heated at 150ºC for 60 minutes and cooled back to room temperature. While diffusion is usually considered undesirable in patterning applications, herein we actually used diffusion of the activated probes to ‘erase’ our image (**D** in Figure 5). Although the chemistry is not reversed, the fluorescent products are redispersed throughout the film upon heating above the glass transition temperature (Tg) of PMMA (105-140 °C).[58]



**Fig. 5** The writing-erasing approach. Photographs of PMMA films doped with **1** (0.5 mM) before (**B**) and after (**C**) exposure at 365 nm for 60 min through a patterned mask (**A**). (**D**) was recorded after heating the sample at 150ºC for 60 minutes.

**Conclusions**

A quinoline chromophore tethered to a nitroxide enables the photochemical sensitization of the latter via energy transfer upon mild excitation with ultraviolet light. The sensitized TEMPO undergoes hydrogen abstraction, thereby restoring fluorescence. In the presence of poly(methyl methacrylate), the hydrogen is abstracted from the polymer matrix, and subsequent linkage of the dye-nitroxide to the polymer skeleton occurs. In all cases, trapping of hydrogens or carbon-centered radicals by TEMPO converts the paramagnetic reagent into a diamagnetic product, thereby eliminating the intramolecular quenching pathway and resulting in the reactivation of the fluorescence of the quinoline dye, as well as the formation of a fluorescent polymer. Our results also provide an opportunity to reflect on electronic factors affecting the relative stability of the chromophore-TEMPO dyad and the photochemically generated *N*-hydroxylamines or *N*-alkoxyamines, as well as to provide insights on the intramolecular sensitization processes at work. The functionalization of PMMA with the probe can be exploited for the patterning (writing) of fluorescent images. The writing process can be ultimately reverted through thermal treatment of the polymer matrix, which disperses the activated molecule within the support and regenerates a clean surface.

**Supporting Information Summary**

Absorption and emission spectra of **1** in CH3CN irradiated at 365 nm; Emission spectra of **Q** and **1** in CH3CN; Absorption and emission spectra of **1** in C6H6 irradiated at 365 nm; Absorption spectra of **1** in CH3CN irradiated at 365 nm under N2 atmosphere; Emission spectra of **1** irradiated after 60 minutes under N2 and **4**; GC analysis of a 1.4 mg/mL solution of **1** before and after irradiation; MS analysis of the product obtained after irradiation of a 1.4 mg/mL solution of **1**; FTIR spectra of **1** before and after irradiation at 365 nm in CH3CN under N2; Emission spectra of **1** in C6H6 irradiated at 365 nm under N2; Emission spectra of absorption matched solutions of **4** in CH3CN or C6H6; Temporal evolution of the emission of **1** after photoactivation in CH3CN or C6H6; Absorption spectra of **1** in 5% PMMA in CH3CN irradiated at 365 nm; Emission spectra of **1** in 1% PMMA in CH3CN irradiated at 365 nm; Emission spectra of 5% PMMA in CH3CN before and after ultraviolet irradiation; FTIR spectra of the supernatant recovered after irradiation of **1** in 5% PMMA in CH3CN.

**Conflicts of Interest**

There are no conflicts to declare.

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**Keywords**

energy transfer • fluorescence activation • fluorescent probes • hydrogen abstraction • photochemistry

**References**

[1] N. J. Turro, V. Ramamurthy, J. C. Scaiano, *Principles of Molecular Photochemistry: An Introduction*, University Science Books, Herndon, **2009**.

[2] A. Albini, M. Fagnoni, Eds. , *Handbook of Synthetic Photochemistry*, Wiley‐VCH Verlag GmbH & Co. KGaA, Weinheim, **2009**.

[3] V. Balzani, P. Ceroni, A. Juris, *Photochemistry and Photophysics: Concepts, Research, Applications*, Wiley‐VCH, Weinheim, **2014**.

[4] D. Gust, T. A. Moore, A. L. Moore, *Acc. Chem. Res.* **2009**, *42*, 1890–1898.

[5] I. McConnell, G. Li, G. W. Brudvig, *Chem. Biol.* **2010**, *17*, 434–447.

[6] D. Gust, T. A. Moore, A. L. Moore, *Faraday Discuss.* **2012**, *155*, 9–26.

[7] S. Fukuzumi, K. Ohkubo, T. Suenobu, *Acc. Chem. Res.* **2014**, *47*, 1455–1464.

[8] M. E. El-Khouly, E. El-Mohsnawy, S. Fukuzumi, *J. Photochem. Photobiol. C* **2017**, *31*, 36–83.

[9] A. Facchetti, *Mater. Today* **2013**, *16*, 123–132.

[10] N. Kaur, M. Singh, D. Pathak, T. Wagner, J. M. Nunzi, *Synth. Met.* **2014**, *190*, 20–26.

[11] G. J. Hedley, A. Ruseckas, I. D. W. Samuel, *Chem. Rev.* **2017**, *117*, 796–837.

[12] S. Holliday, Y. Li, C. K. Luscombe, *Prog. Polym. Sci.* **2017**, *70*, 34–51.

[13] D. M. Schultz, T. P. Yoon, *Science* **2014**, *343*, 1239176–1239176.

[14] N. A. Romero, D. A. Nicewicz, *Chem. Rev.* **2016**, *116*, 10075–10166.

[15] M. H. Shaw, J. Twilton, D. W. C. MacMillan, *J. Org. Chem.* **2016**, *81*, 6898–6926.

[16] D. M. Arias-Rotondo, J. K. McCusker, *Chem. Soc. Rev.* **2016**, *45*, 5803–5820.

[17] J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Springer, New York, **2006**.

[18] V. Balzani, A. Credi, M. Venturi, *Molecular Devices and Machines–A Journey into the Nano World*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, **2003**.

[19] N. V. Blough, D. J. Simpson, *J. Am. Chem. Soc.* **1988**, *110*, 1915–1917.

[20] D. J. Kieber, N. V. Blough, *Anal. Chem.* **1990**, *62*, 2275–2283.

[21] G. I. Likhtenstein, K. Ishii, S. Nakatsuji, *Photochem. Photobiol.* **2007**, *83*, 871–881.

[22] G. I. Likhtenshtein, *Pure Appl. Chem.* **2008**, *80*, 2125–2139.

[23] C. Aliaga, A. Aspée, J. C. Scaiano, *Org. Lett.* **2003**, *5*, 4145–4148.

[24] C. Aliaga, E. A. Lissi, O. Augusto, E. Linares, *Free Radic. Res.* **2003**, *37*, 225–230.

[25] C. Aliaga, J. M. Juárez-Ruiz, J. C. Scaiano, A. Aspée, *Org. Lett.* **2008**, *10*, 2147–2150.

[26] G. G. Borisenko, I. Martin, Q. Zhao, A. A. Amoscato, V. E. Kagan, *J. Am. Chem. Soc.* **2004**, *126*, 9221–9232.

[27] S. Goldstein, A. Samuni, G. Merenyi, *J. Phys. Chem. A* **2008**, *112*, 8600–8605.

[28] L. J. Johnston, M. Tencer, J. C. Scaiano, *J. Org. Chem.* **1986**, *51*, 2806–2808.

[29] S. Impellizzeri, K. G. Stamplecoskie, J. C. Scaiano, *Phys. Chem. Chem. Phys.* **2013**, *15*, 14873–14878.

[30] A. Aspée, O. García, L. Maretti, R. Sastre, J. C. Scaiano, *Macromolecules* **2003**, *36*, 3550–3556.

[31] A. Goto, J. C. Scaiano, L. Maretti, *Photochem. Photobiol. Sci.* **2007**, *6*, 833–835.

[32] J. Su, X. Liu, M. Li, T. Zhang, Y. Cui, *Int. J. Polym. Sci.* **2016**, *2016*, 1–8.

[33] S. A. Green, D. J. Simpson, G. Zhou, P. S. Ho, N. V. Blough, *J. Am. Chem. Soc.* **1990**, *112*, 7337–7346.

[34] C. Bueno, L. Mikelsons, L. Maretti, J. C. Scaiano, A. Aspée, *Photochem. Photobiol.* **2008**, *84*, 1535–1542.

[35] S. Sato, M. Suzuki, T. Soma, M. Tsunoda, *Spectrochim. Acta A* **2008**, *70*, 799–804.

[36] S. Sato, M. Tsunoda, M. Suzuki, M. Kutsuna, K. Takido-uchi, M. Shindo, H. Mizuguchi, H. Obara, H. Ohya, *Spectrochim. Acta A* **2009**, *71*, 2030–2039.

[37] C. Aliaga, M. C. Rezende, C. Tirapegui, *Tetrahedron* **2009**, *65*, 6025–6028.

[38] Y. Liu, M. Zhu, J. Xu, H. Zhang, M. Tian, *Analyst* **2011**, *136*, 4316–4320.

[39] F. Mito, K. Kitagawa, T. Yamasaki, C. Shirahama, T. Oishi, Y. Ito, M. Yamato, K. I. Yamada, *Free Radic. Res.* **2011**, *45*, 1103–1110.

[40] N. B. Yapici, S. Jockusch, A. Moscatelli, S. R. Mandalapu, Y. Itagaki, D. K. Bates, S. Wiseman, K. M. Gibson, N. J. Turro, L. Bi, *Org. Lett.* **2012**, *14*, 50–53.

[41] L. Cao, Q. Wu, Q. Li, S. Shao, Y. Guo, *J. Fluoresc.* **2014**, *24*, 313–318.

[42] C. Aliaga, P. Fuentealba, M. C. Rezende, C. Cárdenas, *Chem. Phys. Lett.* **2014**, *593*, 89–92.

[43] C. Xu, L. Cai, *Luminescence* **2014**, *29*, 36–41.

[44] C. Aliaga, F. Celis, S. Lühr, R. Oñate, *J. Fluoresc.* **2015**, *25*, 979–983.

[45] S. E. Bottle, J. L. Clement, M. Fleige, E. M. Simpson, Y. Guillaneuf, K. E. Fairfull-Smith, D. Gigmes, J. P. Blinco, *RSC Adv.* **2016**, *6*, 80328–80333.

[46] A. Kaur, J. L. Kolanowski, E. J. New, *Angew. Chemi. Int. Ed.* **2016**, *55*, 1602–1613.

[47] S. E. Herbelin, N. V. Blough, *J. Phys. Chem. B* **1998**, *102*, 8170–8176.

[48] Z. Rappoport, J. F. Liebman, Eds. , *The Chemistry of Hydroxylamines, Oximes and Hydroxamic Acids*, John Wiley & Sons, Ltd., Chichester, United Kingdom, **2009**.

[49] S. A. F. Bon, G. Chambard, A. L. German, *Macromolecules* **1999**, *32*, 8269–8276.

[50] S. Marque, H. Fischer, E. Baier, A. Studer, *J. Org. Chem.* **2001**, *66*, 1146–1156.

[51] S. Marque, C. Le Mercier, P. Tordo, H. Fischer, *Macromolecules* **2000**, *33*, 4403–4410.

[52] A. Gaudel-Siri, D. Siri, P. Tordo, *ChemPhysChem* **2006**, *7*, 430–438.

[53] M. V. Ciriano, H. G. Korth, W. B. Van Scheppingen, P. Mulder, *J. Am. Chem. Soc.* **1999**, *121*, 6375–6381.

[54] P. Vasileva, B. Donkova, I. Karadjova, C. Dushkin, *Colloid. Surface. A* **2011**, *382*, 203–210.

[55] J. Rumble, Ed. , *CRC Handbook of Chemistry and Physics*, CRC Press, Taylor & Francis, Boca Raton, FL, **2020**.

[56] P. S. Billone, P. A. Johnson, S. Lin, J. C. Scaiano, G. A. Dilabio, K. U. Ingold, *J. Org. Chem.* **2011**, *76*, 631–636.

[57] S. Coiai, E. Passaglia, F. Cicogna, *Polym. Int.* **2019**, *68*, 27–63.

[58] The temperature range is determined using manufacturer information for bulk PMMA and the value for Tg of PMMA in films measured previously with differential scanning calorimetry (Ref 29).

**Entry for the Table of Contents**

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Under mild ultraviolet illumination, a quinoline dye acts as a molecular ‘antenna’ to promote the reactivity of chemically coupled TEMPO toward H abstraction to form the corresponding *N*-hydroxylamine. The hydrogen can also be abstracted from a polymer matrix (**R**), and subsequent linkage of the dye-nitroxide to the polymer skeleton can occur. In all cases, the intramolecular quenching pathway is suppressed and the fluorescence of the quinoline dye is restored.