Electronic Supplementary Information

Fluorescence Activation, Patterning and Enhancement with Photogenerated Radicals, a Prefluorescent Probe and Silver Nanostructures

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Synthetic Schemes







Fig. S1 Emission spectra (1 μ M, 20°C, λ_{Ex} = 470 nm, CH₃CN) of 1 and 10.



Fig. S2 Gas chromatogram and MS analysis of a solution (1 mg/mL) of 4-Hydroxy-TEMPO and **I-2959** before UVA illumination.



Fig. S3 Gas chromatogram and MS analysis of a solution (1 mg/mL) of 4-Hydroxy-TEMPO and **I-2959** after UVA illumination (365 nm, 180 min, 0.4 mW cm⁻²) under air.

GC-MS Analysis

The gas chromatograph of a solution of the model radical trap 4-Hydroxy-TEMPO and **I-2959** after UVA illumination (Fig. S3) shows two peaks at ~11 and 18 min, attributable to the starting materials. Upon irradiation with ultraviolet light of the same solution we observe the formation of two prominent products with peaks at 8.3 and 11.2 min, respectively.

MS analysis revealed the peak at 11.2 min to be 4-Hydroxy-TEMPO-H. It is known that free radicals (\mathbb{R} •), such as those produced by the photoinduced decomposition of **I-2959**, can be trapped by TEMPO• to provide the cross-coupling product TEMPO-R. Nonetheless, if the product radical bears a weak C-H bond next to the radical site (or if trapping is sterically hindered) disproportionation to form TEMPO-H and a product alkene is also likely to occur.



We attribute the peak at 8.3 min to 2,2,6,6-tetramethyl-4-piperidinol (Fig. S3) formed upon fragmentation in positive mode of a TEMPO-R species obtained by radical trapping of ketyl radical from **I-2959** (Scheme 1, main article) by 4-Hydroxy-TEMPO, and according to the typical fragmentation pattern of TEMPO-R.^{S1}





Fig. S4 Absorption spectra of a CH₃CN solution of I-2959 (10 μ M, 20°C) before and after ultraviolet irradiation (365 nm, 0-15 min, 0.4 mW cm⁻²).



Fig. S5 Absorption (*a*, close-up of the visible region) and emission (*b*, $\lambda_{Ex} = 470$ nm) spectra of a CH₃CN solution of **1** (1 μ M, 20°C) before and after ultraviolet irradiation (365 nm, 0-15 min, 0.4 mW cm⁻²).



Fig. S6 Temporal evolution of the emission spectra of an aerated CH₃CN solution of **1** (1 μ M, 20°C, λ_{Ex} = 470 nm) and **I-2959** (10 μ M) after ultraviolet irradiation (365 nm, 0.4 mW cm⁻²).



Fig. S7 Emission spectra of a CH₃CN solution of **1** (1 μ M, 20°C, $\lambda_{Ex} = 470$ nm) and **I-2959** (10 μ M) exposed to visible light (505 nm, 30 min) after being previously 'activated' with UVA illumination.



Fig. S8 Absorption (*a*) and emission (*b*, $\lambda_{Ex} = 470$ nm) spectra of a CH₃CN solution of **1** (1 μ M, 20°C) and **I-2959** (10 μ M) before and after ultraviolet irradiation (365 nm, 0-15 min, 0.4 mW cm⁻²) under N₂ atmosphere.



Fig. S9 Temporal evolution of the emission spectra of a degassed CH₃CN solution of **1** (1 μ M, 20°C, $\lambda_{Ex} = 470 \text{ nm}$) and **I-2959** (10 μ M) after ultraviolet irradiation (365 nm, 0.4 mW cm⁻²).



Fig. S10 Absorption (*a*) and emission (*b*, $\lambda_{Ex} = 470$ nm) spectra of a 1% PMMA/CH₃CN solution of **1** (1 μ M, 20°C) and **I-2959** (10 μ M) before and after ultraviolet irradiation (365 nm, 0-15 min, 0.4 mW cm⁻²) under air.



Fig. S11 (a) Absorption spectrum of a PMMA (10% w/v in MeCN) film containing 1 (0.5 mM) and I-2959 (5 mM). (b) Emission ($\lambda_{Ex} = 470$ nm) spectra of the same film before and after ultraviolet irradiation (LED₃₆₅, 0-15 min).



Fig. S12 Emission spectra of a PMMA (10% w/v in MeCN) film containing **1** (0.5 mM, $\lambda_{Ex} = 470$ nm) before and after ultraviolet irradiation (LED₃₆₅, 0-15 min).



Fig. S13 Photographs of PMMA films doped with 1 (0.5 mM) before (a) and immediately after (b) exposure at 365 nm for 3 min through a RU-shaped 3D printed mask.

Thin Film Thickness and Maximum AgNP-Fluorophore Distance

The thickness *d* of a thin PMMA film spin-coated onto a glass microscope slide was estimated using a previously reported procedure (ref. 26 main article) which utilizes the principles of thin film interference.^{S2} A portion of light incident normal to the sample surface experiences a phase shift φ_I equivalent to one half wavelength upon specular reflection at the air/polymer interface, where the index of refraction of air *n*_{air} (1.00) is less than that of the polymer *n*_{PMMA} (1.49).^{S3} The remaining light penetrates the film and slows down as it moves through the polymer. It is reflected at the polymer/glass interface and emerges from the material having traveled an extra distance 2*d*, equal to twice the film thickness, relative to the light reflected at the air/polymer surface. Since *n*_{PMMA} is less than *n*_{glass} (1.50), specular reflection at the polymer/glass interface induces a phase shift φ_2 of $2d + \lambda/2$. The relative phase shift Φ between the two spectrally reflected waves can therefore be computed as follows.

$$\Phi = \varphi_2 - \varphi_1$$
$$\Phi = 2d + \frac{\lambda_{PVP}}{2} - \frac{\lambda_{PVP}}{2} = 2d$$

The two traveling waves are moving in the same direction and can interfere constructively or destructively with one another. To determine which type of interference occurs, UV-visible spectroscopy was used to obtain the specular reflectance of the sample as a function of wavelength (Figure S14). This was done by subtracting the diffuse reflectance spectrum of the sample from its total reflectance spectrum, assuming a flat sample of uniform thickness. As shown in Figure S14 below, specular reflection is lower for the PMMA film relative to the glass substrate all across the UV-visible region, indicative of partial destructive interference between the two waves. The relative phase shift Φ can therefore be set equal to the condition for destructive interference as follows;

$$(m+\frac{1}{2})\lambda_{PVP} = \Phi = 2d$$

where m is an integer (0, 1, 2...) corresponding to the periodic nature of interference patterns. Since the dominant interference fringe is of the zeroth order, m is set equal to zero here. The relationship between wavelength in the polymer (where the difference in path length occurs) and wavelength measured in air by UV-visible spectroscopy is;

$$\lambda_{PVP} = \frac{\lambda_{air}}{n_{PMMA}}$$

Substituting for λ_{PMMA} and isolating the film thickness *d*, we arrive at;

$$d = \frac{\lambda_{air}}{4n_{PMMA}}$$

As shown in Figure S14, the dominant wavelengths of specular reflectance are 350, 500 and 620 nm.



Fig. S14 Specular reflectance as a function of wavelength for (*a*) a thin PMMA film and (*b*) the bare glass substrate.

The PMMA film thickness range can therefore be estimated as follows;

Using 350 nm;

$$d = \frac{\lambda_{air}}{4n_{PVP}} = \frac{350 \text{ nm}}{4(1.49)} = 58.7 = 59 \text{ nm}$$

Using 500 nm;

$$d = \frac{\lambda_{air}}{4n_{PVP}} = \frac{500 \text{ nm}}{4(1.49)} = 83.9 = 84 \text{ nm}$$

Using 620 nm;

$$d = \frac{\lambda_{air}}{4n_{PVP}} = \frac{620 \text{ nm}}{4(1.49)} = 104 \text{ nm}$$

It follows that the PMMA film thickness is approximately between 59 and 104 nm when prepared according to the reported spin coating conditions in the absence of AgNP. Not only would the presence of AgNP have impacted specular reflectance measurements, the thickness of the PMMA layer is more important than the total sample thickness because we are more interested in determining the maximum possible distance between AgNP and fluorophores distributed throughout the PMMA matrix, which can evidently be as high as about 82 nm. Previous research has shown that preparing such films atop glass slides coated with these same AgNP caused the total sample thickness to increase by 22 ± 5 nm, for a total sample thickness in the range of 81-126 nm.^{S4}



Fig. S15 (*a*) Extinction spectrum of AgNP in Milli Ω H₂O. Absorption spectrum of a single coated PMMA film containing **1** (0.5 mM) and **I-2959** (50 mM) atop AgNP (*b*), compared with the absorption spectrum of a glass slide functionalized with AgNP (*c*).

References

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