Supplementary Information

Light-active azaphenalene alkoxyamines: Fast and efficient mediators of a photo-induced persistent radical effect

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Experimental Section

1. **General.** All air-sensitive reactions were carried out under ultra-high purity argon. Diethyl ether and xylene were dried by storage over sodium wire. Synthesis of precursor azaphenalenone nitroxide 1,1,3,3-tetramethyl-2,3-dihydro-2-azaphenalene-2-yloxyl was achieved in 3 steps from 1,8-naphthalic anhydride using the established literature procedure. All other reagents were purchased from commercial suppliers and used without further purification. 

1H and 13C NMR spectra were recorded with a Varian 400 MHz spectrometer and referenced to the relevant solvent peak. HRMS were recorded on an Agilent accurate mass QTOF LC-MS. Melting points were measured with a Gallenkamp Variable Temperature Apparatus by the capillary method and are uncorrected. Fluorescence Spectrofluorimetry was undertaken on a Agilent Cary Eclipse Fluorescence Spectrophotometer. Offline photolysis experiments were carried out by irradiation in Rayonet Photoreactor with 300 nm lamps (4 x 8W) with EPR spectra recorded on a MiniScope MS400 Spectrometer at room temperature. Online photolysis and thermolysis experiments were carried out in a Bruker ESP 300 ESR spectrometer at 9.5 GHz (X-band) employing 100 kHz field modulation and a microwave power of 10 mW, equipped with a variable temperature unit Bruker ER 4111 VT. The magnetic field strength and microwave frequency were measured with a Bruker ER 035 M NMR gaussmeter and a Hewlett-Packard 5350B frequency counter, respectively. The UV irradiations were performed with a tunable Hg-Xe lamp (Hamamatsu, L8252, 150 W) set at 1% overall power.

2. **Synthesis of 2-phenylethoxy-1,1,3,3-tetramethyl-2,3-dihydro-2-azaphenalene.**

    ![Chemical Structure](image)

    The nitroxide 1,1,3,3-tetramethyl-2,3-dihydro-2-azaphenalene-2-yloxyl (50.0 mg, 0.21 mmol, 1.0 eq.) and 1-bromoethylbenzene (57 µL, 0.42 mmol, 2.0 eq.) were dissolved in MeCN (2 mL). Copper (13.3 mg, 0.21 mmol, 1.0 eq.) was added and the solution was degased by bubbling with argon for 15 min. Then N,N,N',N'-pentamethyldiethylenetriamine (52.0 µL, 0.25 mmol, 1.2 eq.) was added. The orange solution turned over green to blue. After the reaction was stirred for 16 h the solution was filtered with Et₂O through
Celite®. The crude product was purified by chromatography (n-Hexane:Ethyl acetate 95:5, v:v) and the product was yielded in 62 % (43.8 mg, 0.13 mmol) as a light yellow solid.

$R_f = 0.45$ (n-Hexane:EtOAc 95:5, v:v).

$\textit{mp} = 75-76 \degree \text{C}$

$^1H \text{ NMR}$ (400 MHz, CDCl$_3$, 300 K, ppm): $\delta = 7.72-7.68$ (m, 2H, Naph-$CH$), 7.53-7.45 (m, 2H, Naph-$CH$), 7.44-7.34 (m, 6H, Naph-$CH$, Ph-$CH_{ortho}$, Ph-$CH_{meta}$), 7.34-7.27 (m, 1H, Ph-$CH_{para}$), 5.02 (q, $^3J_{HH} = 6.7$ Hz, 1H, OCHCH$_3$), 1.93 (s, 3H, CH$_3$) 1.65-1.64 (m, 6H, CH$_3$, OCHCH$_3$), 1.49 (s, 3H, CH$_3$), 1.27 (s, 3H, CH$_3$).

$^{13}C(^1H) \text{ NMR}$ (100 MHz, CDCl$_3$, ppm): (Isomer 1) $\delta = 145.1$ (Naph-$C_i$), 142.7 (Ph-$C_{ipso}$), 133.2 (Naph-$C_d$), 128.2 (Naph-$C_b$), 127.2 (Naph-$C_c$), 126.9 (Naph-$C_a$), 126.1 (Ph-$C_{para}$), 125.61 (Ph-$C_{meta}$), 124.9 (Naph-$C_e$), 121.5 (Ph-$C_{ortho}$), 84.1 (CHCH$_3$), 63.6 (C$_q$), 32.0 (CHCH$_3$), 26.9 (CH$_3$), 23.3 (CH$_3$); (Isomer 2) $\delta = 145.1$ (Naph-$C_i$), 142.6 (Ph-$C_{ipso}$), 133.2 (Naph-$C_d$), 128.2 (Naph-$C_b$), 127.2 (Naph-$C_c$), 126.9 (Naph-$C_a$), 126.0 (Ph-$C_{para}$), 125.59 (Ph-$C_{meta}$), 124.9 (Naph-$C_e$), 121.3 (Ph-$C_{ortho}$), 84.1 (CHCH$_3$), 63.4 (C$_q$), 31.7 (CHCH$_3$), 26.9 (CH$_3$), 23.3 (CH$_3$).

HRMS (ESI): calc. for $[C_{24}H_{28}NO]^+$: m/z = 346.2165; found: m/z = 346.2166.
Figure S1. EPR Spectrum of TMAO

Figure S2. EPR Spectrum present of radical present after thermolysis of TMAO-Alkoxyamine at 92.5 °C for 1020 minutes. (4 mM solution in tBuBenz)
Figure S3. EPR Spectrum present of radical present after photolysis of TMAO-Alkoxyamine under UV irradiation for 120 seconds.

Figure S4. Comparison between experimental and calculated rate of decomposition of TMAO-Alkoxyamine at 92.5 °C. From this a $k_d = 7.733 \times 10^{-5}$ s$^{-1}$ was found giving a BDE of 129.6 kJ.mol$^{-1}$. 
Figure S5. Comparison of nitroxide generation (concentrations calculated by double integration of EPR spectra) between irradiation of azaphenalene-alkoxyamine under normal atmosphere (blue) and in a deoxygenated environment (black).

Figure S6. Comparison of nitroxide generation (concentrations calculated by double integration of EPR spectra) between irradiation of azaphenalene-nitroxide under normal atmosphere
(black) and in a deoxygenated environment (solid blue). Dotted line represents the true nitroxide concentration as under equivalent deoxygenated conditions at 0.4 mM starting concentration the signal saturated the detector.

Figure S7. $^1$H NMR Spectrum of azaphenalene-alkoxyamine.
Figure S8. $^{13}$C NMR Spectrum of azaphenalene-alkoxyamine.
Figure S9. $^1$H NMR spectrum of precipitated polymer from the reaction of a well stirred, degassed solution of the azaphenalene-alkoxyamine in styrene (ratio of 1:250) after 10 hours irradiation. Estimation of $M_n$ based on protons related to the 1,3,5,8 protons from the naphthalene moiety visible between 7.5 and 7.8 ppm give $M_{n\text{NMR}} = 3,150$.

Reference