

Electronic Supplementary Information

Two-phase photocatalytic oxidation of toluene derivatives by dioxygen with 3-cyano-1-decylquinolinium ion†

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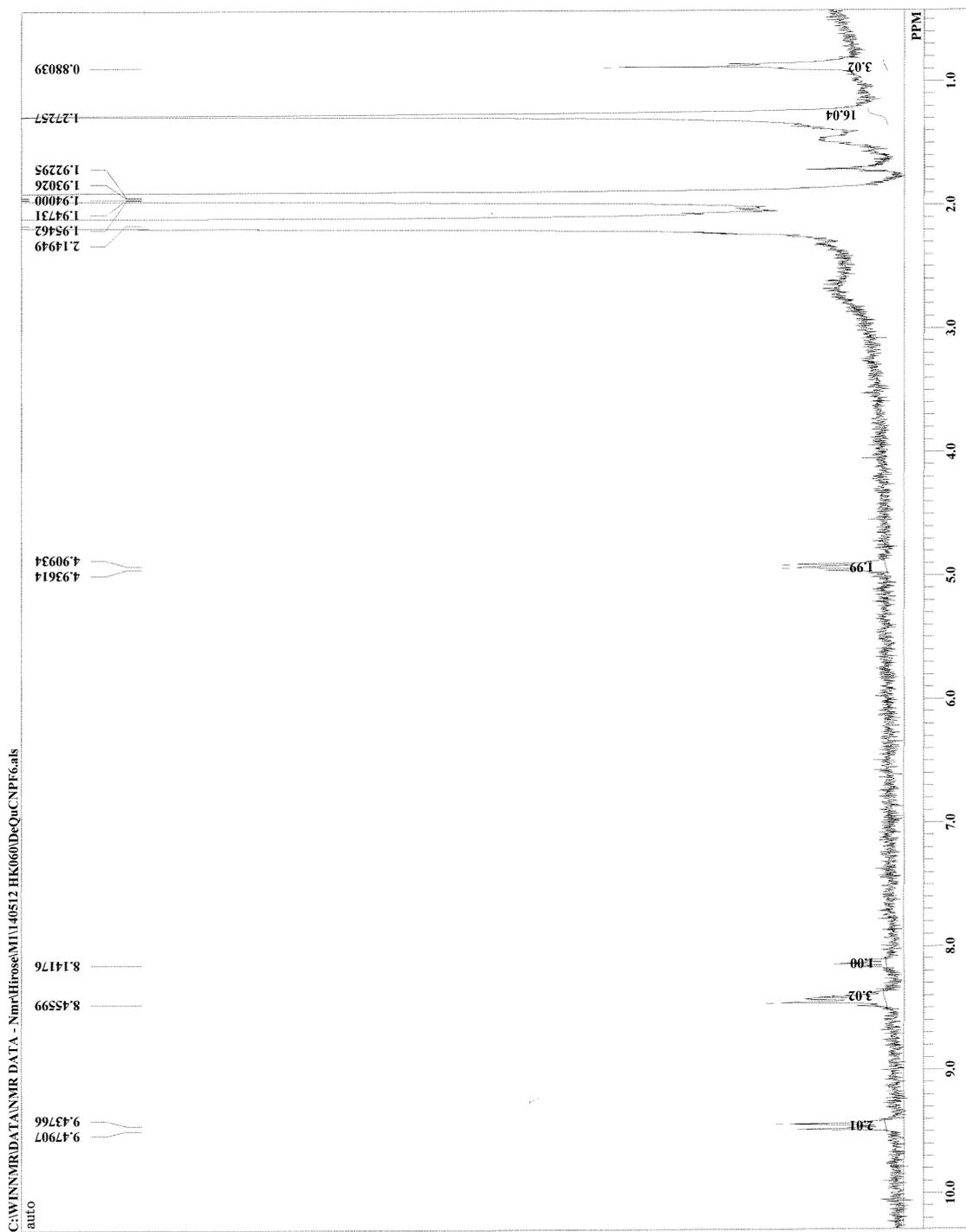


Fig. S1 ^1H NMR data for $\text{DeQuCN}^+\text{PF}_6^-$.

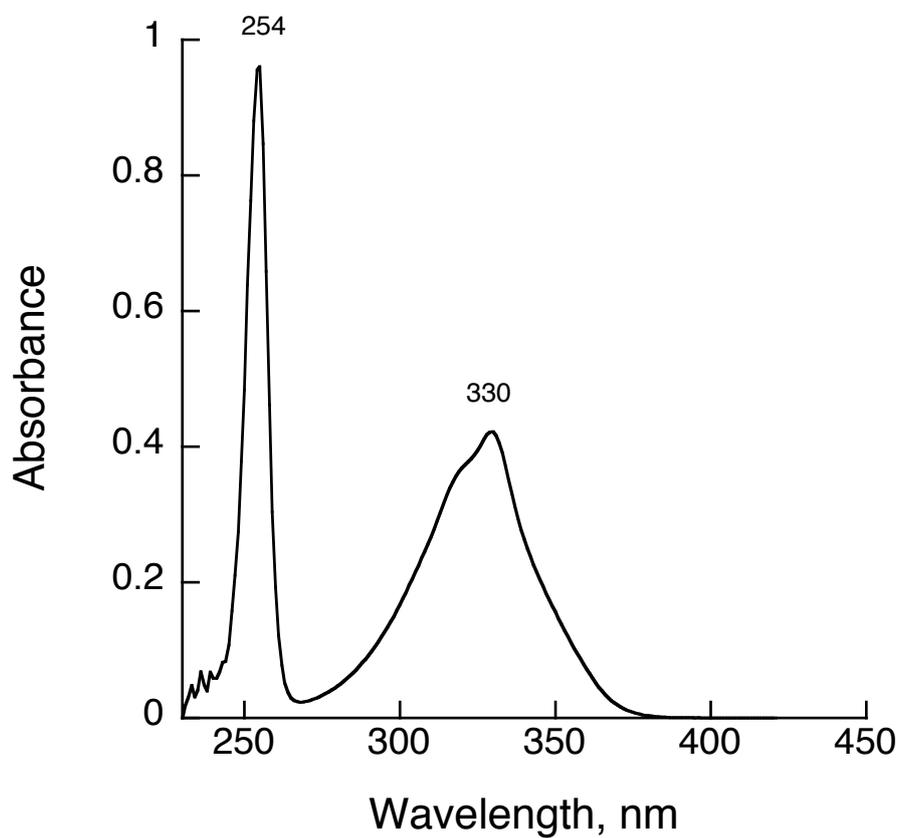


Fig. S2 UV-vis absorption spectrum of DeQuCN⁺PF₆⁻ in MeCN.

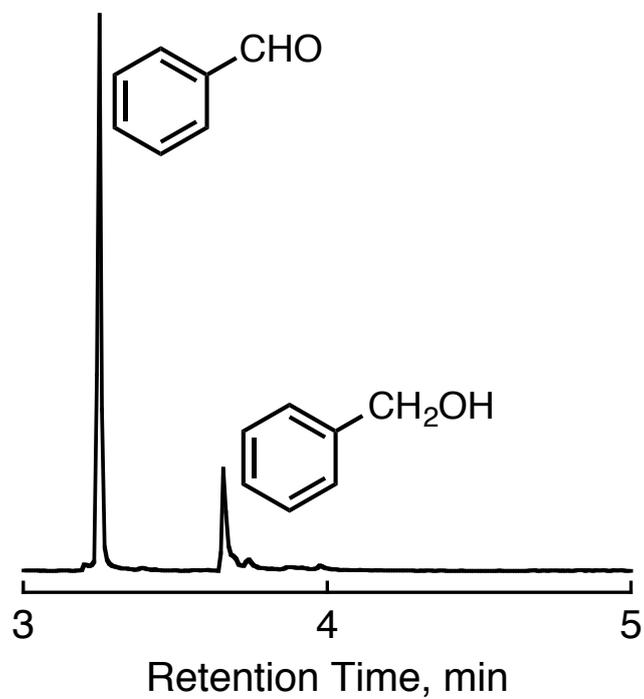


Fig. S3 GC charts of an oxygen-saturated toluene solution (36 cm³) containing DeQuCN⁺PF₆⁻ (50 μM) and H₂O (0.72 cm³) under photoirradiation ($\lambda > 310$ nm) at 298 K for 48 h.

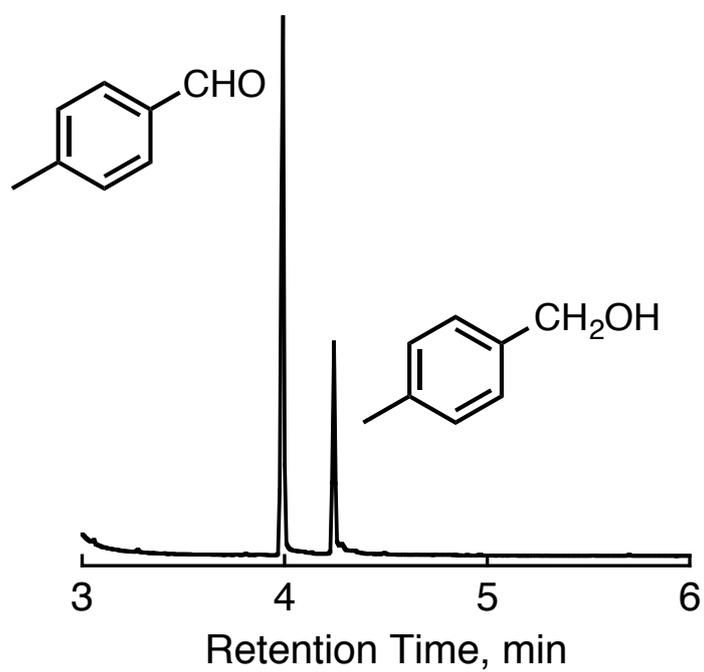


Fig. S4 GC charts of an oxygen-saturated *p*-xylene solution (5.0 cm³) containing DeQuCN⁺PF₆⁻ (50 μM) and H₂O (0.05 cm³) under photoirradiation ($\lambda > 310$ nm) at 298 K for 48 h.

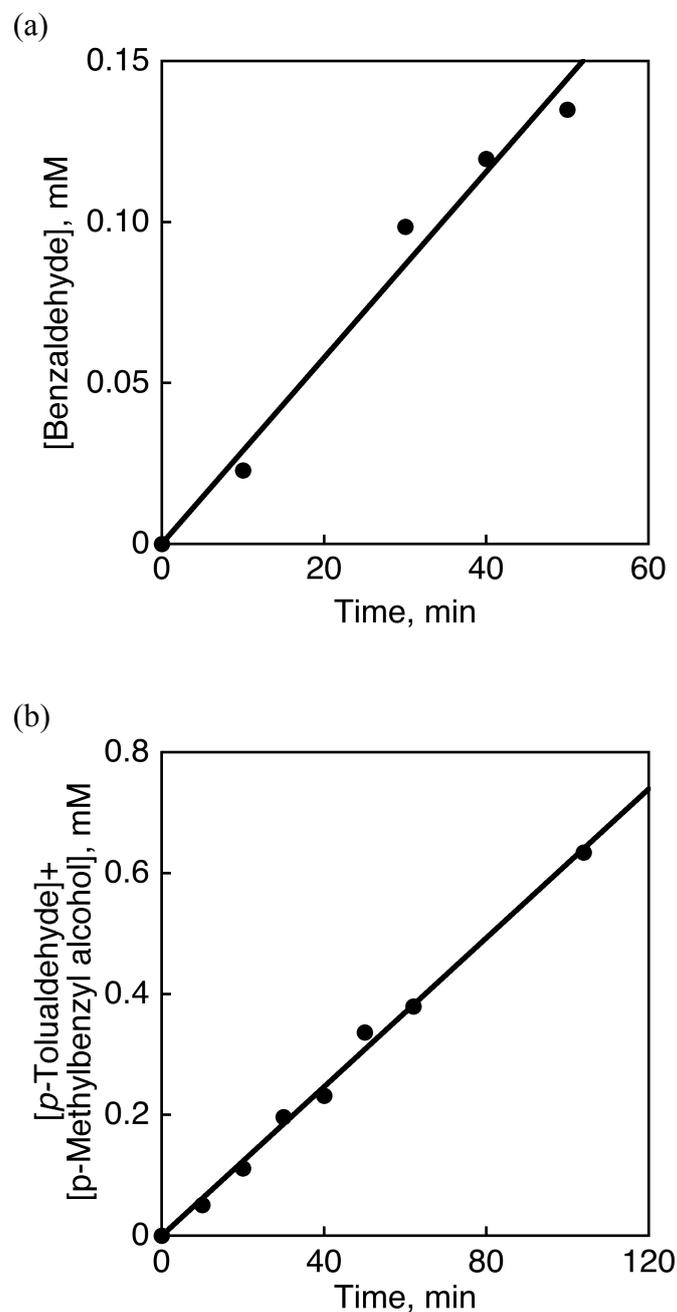


Fig. S5 Time courses of formation of (a) benzaldehyde in oxygen-saturated toluene and (b) *p*-methylbenzyl alcohol and *p*-tolualdehyde in oxygen-saturated *p*-xylene for the catalytic H₂O₂ generation with DeQuCN⁺PF₆⁻ (50 μM) under photoirradiation with monochromatized light of λ = 335 nm.

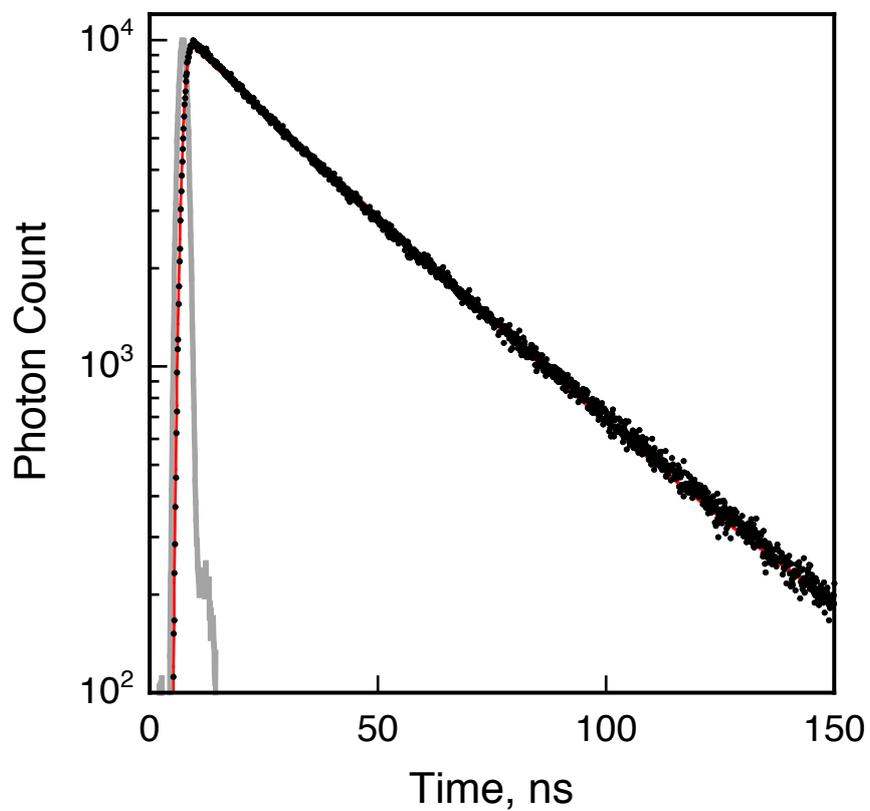


Fig. S6 Fluorescence decay of $\text{DeQuCN}^+\text{PF}_6^-$ at 432 nm in deaerated MeCN with a fitting curve ($\tau = 34$ ns). Excitation wavelength is 350 nm from an LED pulse. A gray line represents the prompt from the excitation pulse.

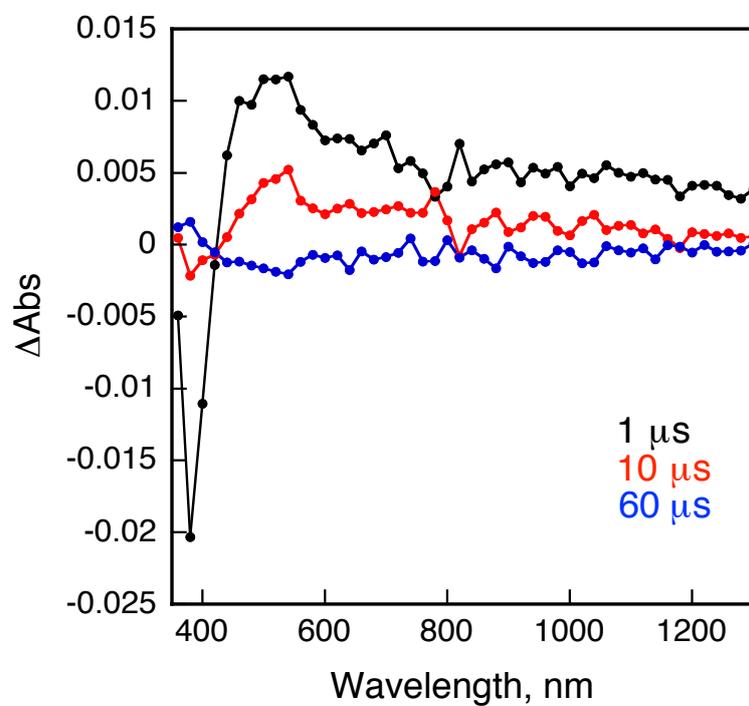


Fig. S7 Transient absorption spectra of DeQuCN⁺ (100 μM) in deaerated *p*-xylene at 298 K taken at 1, 10, 60 μs after nanosecond laser excitation at 355 nm.

Experimental section

Materials. Chemicals were purchased from commercial source and used without purification, unless otherwise noted. Potassium ferrioxalate used as an actinometer was prepared according to the literature and purified by recrystallisation from hot water.^{S1} Toluene and *p*-xylene were purified by the standard method.^{S2}

Synthesis of decyl triflate. Decyl triflate was prepared by the literature method.^{S3} Decyl iodide (2.0 g, 7.5 mmol) was reacted with 2.57 g (10 mmol) of silver triflate in 50 mL of benzene. The washed and dried benzene solution was filtered through silicic acid and stripped of solvent to give 1.7 g (78%) of decyl triflate, a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ ppm 4.54 (t, 2H, *J* = 6 Hz, CH₂O-), 1.83 (m, 2H, CH₂CH₂O-), 1.27 (m, 14H, CH₂), and 0.86 ppm (m, 3 H, CH₃).

Synthesis of 1-decyl-3-cyanoquinolinium hexafluorophosphate (DeQuCN⁺PF₆⁻). To a stirred solution of 3-quinolinecarbonitrile (154mg, 1.0 mmol) in acetonitrile (6 mL), decyl triflate (435 mg, 1.5 mmol) were added and the reaction mixture was refluxed for 24 h. After cooling to room temperature, the solvent was evaporated in vacuo and the resulting residue (yellow solid) was purified by column chromatography on SiO₂ (CH₂Cl₂ and methanol) to give 1-decyl-3-cyanoquinolinium triflate as a white solid (257 mg, 58% yield). Then, the counter ion exchange was performed by addition of KPF₆ (33 mg, 0.18 mmol) to the aqueous solution of 1-decyl-3-cyanoquinolinium triflate (40 mg, 0.090 mmol). The precipitate was filtered off and purified by crystallisation (diethyl ether) to afford the pure product as a white solid (20 mg, 50%). ¹H NMR (300 MHz, CD₃CN) δ ppm 9.46 (m, 2H), 8.44 (m, 3H), 8.14 (t, *J* = 8.0 Hz, 1H), 4.94 (t, *J* = 8.0 Hz, 2H), 1.27 (m, 16H), 0.88 (t, 3H, *J* = 7.3 Hz) (Fig. S6). HR-MS (MALDI-TOF-MS, dithranol used as a matrix) *m/z* calculated for C₂₀H₂₇N₂ [M+H]⁺ 296.22, found 296.22.

Reaction procedure. The oxygenation of toluene derivatives was carried out by the following procedure. A toluene solution (36 cm³) containing DeQuCN⁺PF₆⁻ (50 μM) and water (0.72 cm³) in pyrex® bottle glass sealed with a rubber septum was saturated with oxygen by bubbling oxygen through a stainless steel needle for 5 min. The solution was then irradiated with a high-pressure mercury lamp (1 kW) at room temperature. After photoirradiation, the corresponding oxygenated compounds were identified and quantified by comparison of the GC-MS analysis with that of an authentic sample. The reaction was monitored using a Shimadzu GC-17A gas chromatograph and Shimadzu MS-QP5000 GC-MS spectrometer.

Quantification of produced H₂O₂. From spectroscopic titration with an acidic solution of [TiO(tpypH₄)]⁴⁺ complex (Ti-TPyP reagent), the amount of produced H₂O₂ was determined.^{S4} The [TiO(tpyp)] complex (34 mg) was dissolved in 1.0 L of 50 mM hydrochloric acid and the solution was used as a Ti-TPyP reagent. An aliquot (e.g., 10 μL) of the reaction solution in water layer was diluted with water and 0.20 mL of the sample solution was mixed with 0.20 mL of 4.8 M perchloric acid and 0.20 mL of the Ti-TPyP reagent. After 5 min at room temperature, the mixture was diluted to 2.0 mL with water and used for the spectroscopic measurement. The absorbance at $\lambda = 434$ nm was measured by using a Hewlett Packard 8453 diode array spectrometer (A_S). In the similar manner, a blank solution was prepared by adding distilled water in place of the sample solution in the same volume with its absorbance designated as A_B . The difference in absorbance was determined by following the equation: $\Delta A_{434} = A_B - A_S$. Based on ΔA_{434} and the volume of the solution, the amount of hydrogen peroxide was determined according to the literature.^{S4}

Quantum yield determinations. A standard actinometer (potassium ferrioxalate) was used for the quantum yield determination of the DeQuCN⁺-photocatalysed oxygenation of toluene derivatives. An oxygen-saturated toluene solution (3.0 cm³) containing DeQuCN⁺PF₆⁻ (50 μM) and water (0.30 cm³) in a quartz cuvette (1.0 cm × 1.0 cm) was irradiated with monochromatized light of λ = 335 nm from a Shimadzu RF-5300PC fluorescence spectrophotometer. Under the conditions of actinometry experiments, DeQuCN⁺ absorbed essentially 50% incident light of λ = 335 nm (Abs₃₃₅ = 0.30). The light intensity of monochromatized light of λ = 335 nm was determined as 5.1 × 10⁻⁹ einstein s⁻¹. The photochemical reaction was monitored using a Shimadzu GC-17A gas chromatograph and Shimadzu MS-QP5000 GC-MS spectrometer. The quantum yields were determined from increase of benzaldehyde derivatives.

Fluorescence quenching. Quenching experiments of the fluorescence of DeQuCN⁺ by toluene derivatives were performed using a Shimadzu RF-5300PC fluorescence spectrophotometer. The excitation wavelength was 330 nm. The monitoring wavelength was the maxima of the emission band at 432 nm. The solutions were deoxygenated by argon purging for 3 min prior to the measurements. Relative emission intensities were measured for an acetonitrile solution containing DeQuCN⁺PF₆⁻ (20 μM) with toluene derivatives at various concentrations (0 – 5.0 mM). There was no change in shape but there was a change in the intensity of the fluorescence spectrum by the addition of a toluene derivative. The Stern-Volmer relationship (eqn 1) was obtained for the ratio of the emission intensities in the absence and presence of quenchers (I_0/I) and the concentrations of quenchers [D].

$$I_0/I = 1 + K_{SV}[D] \quad (1)$$

The fluorescence lifetime τ of DeQuCN⁺ in acetonitrile was determined by single photon counting using a Horiba NAES-1100 time resolved spectrofluorophotometer to be 34 ns. The quenching rate constant k_q ($=K_{SV}\tau^{-1}$) was determined from the Stern-Volmer constants K_{SV} and the emission lifetimes τ .

References for ESI

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(S3) C. D. Beard and K. Baum, *J. R. Org. Chem.*, 1974, **26**, 3875.

(S4) C. Matsubara, N. Kawamoto and K. Takamura, *Analyst*, 1992, **117**, 1781.