SUPPLEMENTARY INFORMATION

Stern-Volmer Analysis of Photocatalyst Fluorescence Quenching within Hollow-Core Photonic Crystal Fibre Microreactors

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Methodology and Description of HC-PCF Microreactors

Materials
The 4CzIPN photosensitiser was synthesized via a procedure outlined by Engle et al. with inconsequential modifications [1]. All other chemicals and reagents were purchased from commercial suppliers and used as received unless otherwise noted. Laboratory-grade reagents were of the highest available purity. All stock solutions were made up using extra dry acetonitrile (MeCN; < 50 ppm water).

For Stern-Volmer experiments, 0.03 mM samples of 4CzIPN were prepared with five different quencher concentrations in MeCN and purged for with nitrogen for at least 15 minutes prior to fibre loading (more detailed description below). Cyclohexylamine and tetrabutylammonium azide were compared as fluorescence quenchers as they are two of the reagents utilised by Cresswell et al. in their newly-developed photoredox protocol for synthesising α-tertiary amines and their γ-lactam derivatives using a photocatalytic flow reactor [2].

 Fluorescence Spectroscopy Setup
A schematic of the optical layout for the fluorescence spectroscopy setup is shown in Figure S1a. As shown, a 365 nm UV LED source (HepatoChem EvoluChem 365PF), together with an optical diffuser (Thorlabs DG20-220-MD), was used to side-irradiate a 5 cm section of the HC-PCF. This ensured a homogenous excitation of 95 mW/cm² across a 36 nL volume within the fibre. A 365 nm excitation wavelength was chosen to match the absorption peak of 4CzIPN in acetonitrile (Fig. S3), proposed to correspond to a S₀ → S₃ transition (mainly HOMO → LUMO + 1 transition) [3]. A beamsplitter cube (BS – Fig. S1a) divides the guided fluorescent light over an imaging CCD (IDS UI-3240LE-NIR-GL) and a fibre-coupled spectrometer (Ocean Optics QE 65000). Spatial filtering through an aperture (A1 – Fig. S1a) was employed to selectively collect fluorescent counts from the core region of the HC-PCF (see Fig. 3 in manuscript). Fluorescence spectra were generated by integrating the spectrometer counts over a 1 s period and subtracting a background spectrum measured over the same integration period.

A 20 cm length of kagomé HC-PCF (fabricated at the Max Planck Institute for the Science of Light, Erlangan, Germany) was sealed using polyether ether ketone (PEEK) sleeves (IDEX F-240 Blue) and standard microfluidic fittings using home-built stainless steel pressure cells with sapphire windows (3D schematic of fluorescence collection stage – Fig. S1b; 3D-rendering of whole experimental setup – Fig. S1c). This enabled the HC-PCF to be loaded with a liquid solution whilst remaining optically accessible, as in previous work [4,5]. Samples were purged under nitrogen for at least 15 minutes prior to loading into the fiber, and were injected into the pressure cell using gas-tight syringes (Hamilton, 1 mL) and a syringe pump (Aladdin AL-1000). Fibres were thoroughly cleaned with acetonitrile before use, and a background fluorescence spectrum was taken. Samples were then inserted sequentially into the fibre.
References


Figure S1 | Optical setup of our fibre-based optofluidic microreactor for ultralow-volume fluorescence spectroscopy: (a) schematic of the optical layout that enables the fluorescence to be simultaneously analysed by a camera and an optical-fibre spectrometer using our setup (camera image of fluorescence and fluorescence spectrum shown in Fig. 3(c) in manuscript). BS - beamsplitter; MMF - multimode fibre; O1 - fluorescence out-coupling objective; O2 - objective lens used to fibre-couple the fluorescence to a MMF spectrometer; A1 - aperture used to spatially select the core region (green hexagon - Fig. 1(d)); and (c) 3D schematic showing the pressure cells used in these experiments that interface the optics with commercially-available PEEK microfluidics components. 3D-renderings of the optical setup used to perform fluorescence spectroscopy. Side view (left) and top view (right). Microfluidic tubing was omitted for clarity.
Figure S2 | Fluorescence spectrum of 4CzIPN (30 µM) in acetonitrile (CH$_3$CN) recorded in a cuvette using a conventional fluorometer (excitation wavelength was set to 365 nm).

Figure S3 | UV-Vis absorption spectra of 4CzIPN (30 µM), tetrabutylammonium azide (Bu$_4$NN$_3$, 0.6 mM) and cyclohexylamine (CHA, 12 mM). An Agilent Cary 300 UV-Vis Spectrophotometer was used to collect the absorption spectra. Absorbance is referenced to a 1 cm long cuvette of acetonitrile.
Figure S4 | Transmission properties of acetonitrile-filled fibre. (a) Mode intensity profiles taken at different wavelengths across the visible wavelength range. (b) Percentage of transmission (%T) through the 20 cm long acetonitrile-filled kagomé HC-PCF utilized in the fluorescence experiments, recorded at various wavelengths in the range of the 4CzIPN fluorescence spectrum. To experimentally confirm the guidance properties, a broadband light source (NKT Photonics SuperK Extreme EXR-15 supercontinuum source), was filtered using a tunable bandpass filter (NKT Varia) and coupled into the core of the acetonitrile-filled fibre using a 10x objective lens (Olympus PLN). A close to Gaussian intensity profile was observed over a broad 525-800 nm wavelength range (Figure S4a). We note that the numerical aperture of the focusing beam exceeds the acceptance angle of the HC-PCF modes, resulting in relatively low but very stable coupling efficiencies of around 3% (Figure S4b). The measured transmission window of the kagomé fibre covers the full fluorescence emission band of 4CzIPN (Figures S2 and 2c), making it highly suitable for our 4CzIPN fluorescence quenching investigations.
Figure S5 | Fluorometer-derived Stern-Volmer analysis on 4CzIPN with the fluorescence quencher tetrabutylammonium azide (Bu$_4$NN$_3$). Fluorescence spectra at different quencher concentrations (top) and Stern-Volmer plots (bottom) at three different excitation wavelengths (455 nm, 425 nm, and 365 nm). Error bars indicate the standard error of triplicate measurements. A Cary Eclipse Fluorescence Spectrophotometer was used to collect the fluorescence spectra, with Stern-Volmer analysis performed by the same method as the fibre-based measurements. Spectra were truncated to remove counts from the excitation source from the Stern-Volmer analysis where relevant.
**Figure S6** | Fluorometer-derived Stern-Volmer analysis on 4CzIPN with the fluorescence quencher tetrabutylammonium azide (Bu₄NN₃). Fluorescence profiles at each quencher concentration are shown in (a), with a Stern-Volmer plot presented in (b). A Cary Eclipse Fluorescence Spectrophotometer was used to collect the fluorescence spectra (λₑₓ = 365 nm), with Stern-Volmer analysis performed by the same method as the fibre-based measurements. Triplicate repeats gave a $k_q$ value of $(26.2 \pm 2.0) \times 10^9$ L mol⁻¹ s⁻¹.

**Figure S7** | Fluorescence profiles of 4CzIPN with and without 1.2 mM Bu₄NN₃. The 1.2mM Bu₄NN₃ profile is scaled by a factor 1.65 such that the spectral counts at low energies are equivalent. The resulting differences at higher energies, filled in red, correspond to the photons reabsorbed by either 4CzIPN or Bu₄NN₃. Each curve is integrated, and the difference in integrand gives the proportion of photons reabsorbed - 4%.
Figure S8 | Fluorometer-derived Stern-Volmer analysis on 4CzIPN with the fluorescence quencher cyclohexylamine (CHA). Fluorescence profiles at each quencher concentration are shown in (a), with a Stern-Volmer plot presented in (b). A Cary Eclipse Fluorescence Spectrophotometer was used to collect the fluorescence spectra ($\lambda_{\text{ex}} = 365$ nm), with Stern-Volmer analysis performed by the same method as the fibre-based measurements. Triplicate repeats gave a $k_q$ value of $(2.2 \pm 0.1) \times 10^9$ L mol$^{-1}$ s$^{-1}$.

Figure S9 | Proposed mechanism for the photoredox reaction cyclohexylamine (1) with methyl acrylate (2)