SUPPORTING INFORMATION

Single-molecule photoredox catalysis

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S1A. Experimental Section

Rh6G immobilisation

Standard 24×24 μm^2 glass cover slips were cleaned using 2% Hellmanex III (Hellma Analytics) solution, followed by rinsing with MilliQ water. Subsequently, the cover slips were transferred to a UV-ozone cleaner (Novascan, PSD Pro Series UV) to bleach residual fluorescent organic contaminants. A mixture of 5 mg to 1 mg per ml of bovine serum albumin (BSA, Sigma Aldrich) and BSA labelled with biotin (BSAbiotin, Sigma Aldrich) in standard PBS solution (tablets from Sigma Aldrich) was incubated on the glass surface for at least 6 hours. A solution of 0.1 mg/ml of streptavidin (streptavidin from streptomyces avidinii, Sigma Aldrich) in PBS was incubated on the surface for approximately 10 minutes to bind streptavidin to the biotinylated BSA. Customised double-strand DNA (dsDNA) was labelled with Rh6G on one single-strand (ssDNA) and with a biotin linker on the complementary ssDNA (IBA Lifesciences, sequence TAA TAT TCG ATT CCT TAC ACT TAT ATT GCA TAG CTA TAC G and complementary). In the final preparation step a solution of 0.5 nM of biotinylated dsDNA labelled with Rh6G in PBS was incubated on the surface while simultaneously taking confocal fluorescence scanning images of the sample. The final concentration of single fluorescent spots on the surface can therefore be monitored *in situ*. After approximately two minutes a concentration of order 15 spots per 10×10 μm^2 surface area was reached and the sample was subsequently washed with PBS to remove unbound ssDNA. Between each preparation step the sample was washed three times with PBS.

Sample preparation

Ascorbic acid (Sigma Aldrich) was dissolved to a stock solution of 100 mM concentration in PBS buffer. The stock solution concentration of 2-bromobenzonitrile (Sigma Aldrich) and benzonitrile (Sigma Aldrich) in PBS was set to 1 mM. The stock solution concentration of 4-

chloroanisole (Sigma Aldrich) in PBS was set to 0.2 mM. In the last preparation step, the compounds were diluted in PBS, so that the final ascorbic acid concentration was 20 mM and the final substrate concentration was 0.1 mM. The ascorbic acid concentration was chosen in such a way that the radical state is efficiently formed from the triplet as well as from the singlet state. The substrate concentration of 0.1 mM is ideal for the experiments performed here, since on the one hand the concentration is low enough so that all three compounds remain soluble in PBS and on the other hand it is sufficiently high to allow the observation of interactions relating to the excited radical state. The final sample solution was incubated in a custom-built reaction chamber, consisting of a glass slide with the immobilised Rh6G molecules and a sealable Teflon chamber of 1 ml volume. The Teflon chamber was prepared with hollow needles and connections to provide a constant nitrogen flow through the sample solution, which was adjusted to a rate of 50 sccm.

Microscope setup and data acquisition

An inverted microscope (Olympus IX73) was used to assemble a confocal fluorescence microscope. A white-light laser (NKT Photonics, SuperKExtreme with a SuperK Select Multi-Line Tunable Filter) was used at a repetition rate of 78 MHz and set to a wavelength of 530 nm for excitation of Rh6G. For the excitation of the radical a continuous-wave laser diode (PicoQuant, LDH-D-C-405) emitting at 405 nm was used in combination with an electrical shutter. The excitation intensity was adjusted to 2 kW/cm^2 for both wavelengths. The output of the two emission sources was overlaid by a dichroic beam splitter (AHF analysetechnik, F33-465 laser beam splitter) and coupled into an oil-immersion objective (Olympus, UPlanSApo 60×/1.35). The fluorescence signal was collected by the same objective and split equally by a 50/50 beam splitter onto two avalanche photodiodes (PicoQuant, τ-SPAD 25). The measured signals were subsequently cross-correlated by a PicoQuant software package (SymPhoTime 64).

Approximately 100 single-molecule fluorescence traces were recorded for each data set. The recording time for each molecule covered the entire photochemical lifetime of the molecule, which is between 10 to 60 s under the conditions used here. For each molecule the cross-correlation curve was calculated separately. The correlation curves were normalised and shifted to zero at a time lag of 100 ms. The data for each molecule was corrected for the measured signal-to-background level (S/B) by multiplying the $g^{(2)}(\Delta\tau)$ function with the prefactor $(1+\frac{B}{S})^2$. Finally, the median value for each set of correlation data points was calculated.

S2. GC chromatography of ensemble solution reactions

To demonstrate the reaction cycle of Fig. 1 we performed GC on reaction products under different reaction conditions, outlined in Fig. S1.

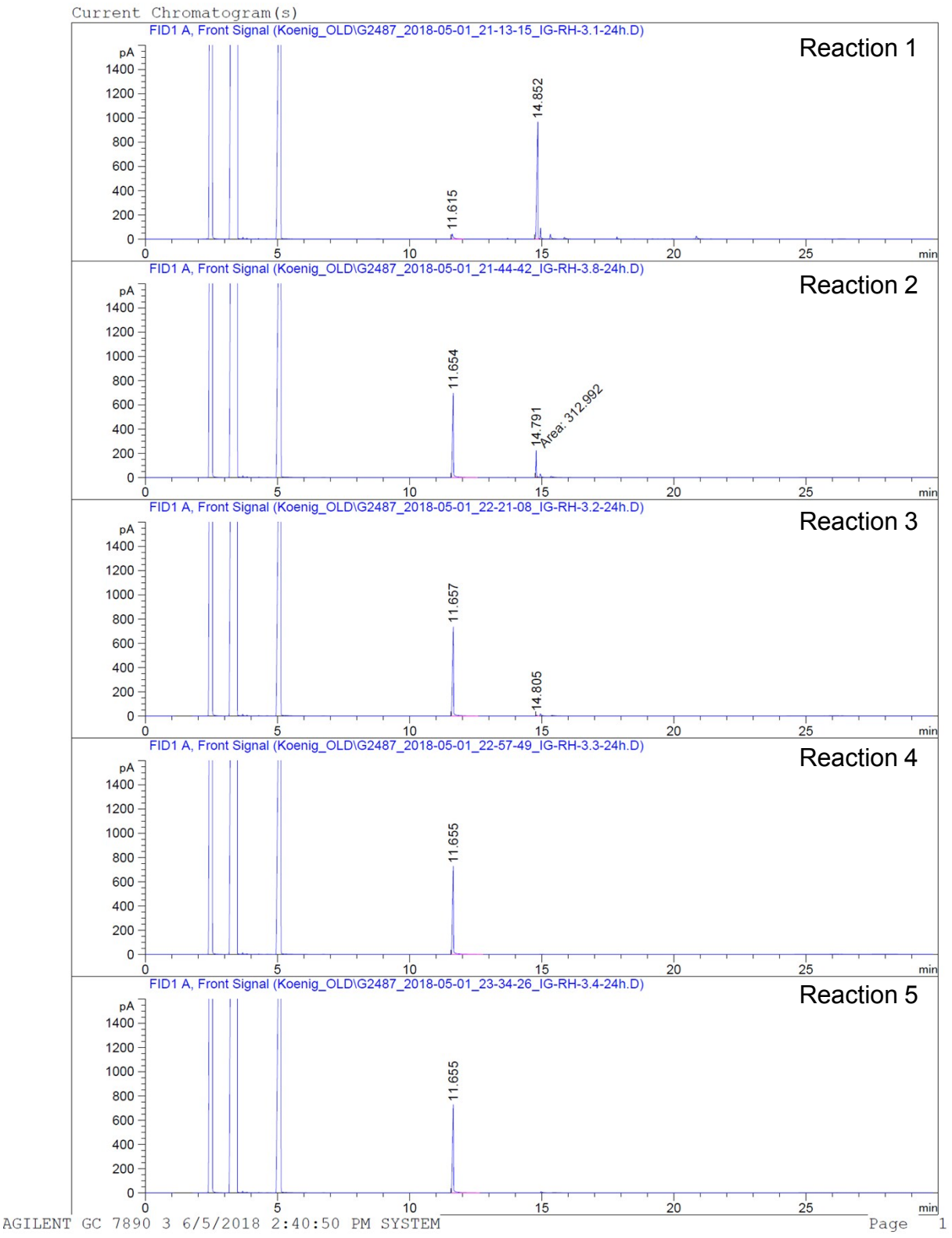

Figure S1. GC chromatograms of synthetic-scale C-H aromatic substitution reaction of 2-bromobenzonitrile with *N*-methylpyrrole in water. Reaction conditions and GC yields are stated below. The peak around 11.6 min. is associated with the substrate. The peak around 14.8 min. is associated with the C-H arylated product.

Conditions of Reaction 1: 2-bromobenzonitrile (0.1 mmol) + Rh6G (5.0 mg, 10 mol% w.r.t. to substrate) + ascorbic acid (1.4 equiv. w.r.t. substrate) + *N*-methylpyrrole (18 equiv. w.r.t. substrate) + 455 nm LED light + 530 nm LED light + reaction time 24 h in water. Yield: c. 94 %.

Conditions of control reactions:

Reaction 2: As Reaction 1, but only with 530 nm light. Yield: c. 14%.

Reaction 3: As Reaction 1, but without Rh6G: Yield: c. 1%.

Reaction 4: As Reaction 1, but without ascorbic acid: Yield: c. 0%.

Reaction 5: As Reaction 1, but without illumination: Yield: c. 0%.

The photodriven C-H arylation demonstrated here is of universal significance. Note that examples of C–H arylations of biologically important pyrrole derivatives are discussed in detail in Ref. 13.