

SUPPORTING INFORMATION

Visible Light-Mediated Photoclick Functionalization of a Conjugated Polymer Backbone

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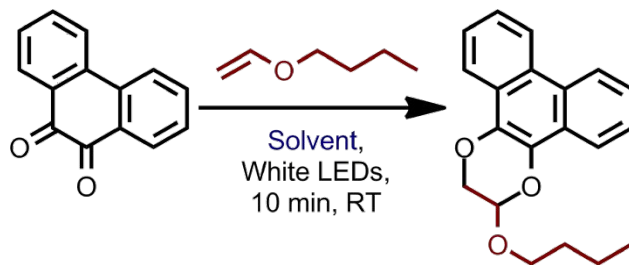
Experimental

General

Reagents were purchased from commercial suppliers and used as received. Flash chromatography was performed using an IntelliFlash 280 system from Analogix. Unless otherwise noted, compounds were monitored using a variable wavelength detector at 254 nm. Solvent amounts used for gradient or isocratic elution were reported in column volumes (CV). Columns were prepared in Sorbtech EZ Flash MT cartridges using 40 – 63 μm silica or 25 – 40 μm silica purchased from Silicycle. Photochemical reactions were performed using a Kessil A160WE Tuna Blue saltwater aquarium light, and reactions were cooled using an AC Infinity AXIAL 1238 Muffin Fan. Precision cuvettes made of Quartz SUPRASIL (Hellma Analytics; Macro Cell 111-QS, volume 3500 μL , light path 10 x 10 mm) were used for all optical spectroscopy experiments. Light intensities were measured using a LabMAX-Top equipped with a LM-2 VIS Sensor (Coherent Inc.) NMR was performed on a Bruker Avance 600 MHz or 700 MHz instrument and shift-referenced to the residual solvent resonance. Crude reaction mixtures or products were analyzed via HPLC using a Waters 2695 Separations Module equipped with a Waters 2487 dual λ absorbance detector (reactions monitored at 254 nm) and a Phenomenex Luna 3 μ (50 x 4.6 mm) phenyl-hexyl column. High-resolution (HR) electrospray ionization (ESI) MS measurements were carried out on the Micromass/Waters Quattro Ultima (ESI/APCI-LCMS Triple Quadrupole Mass Spectrometer). Infrared spectra were recorded using a Thermo Scientific Nicolet 6700 FT-IR spectrometer equipped with a Smart iTX attenuated total reflectance (ATR) sample analyzer. The boronic ester-containing fluorene monomer **1** was synthesized according to literature procedures.¹ Polymer molecular weights and dispersities were analyzed (relative to polystyrene standards) *via* GPC using a Waters 2695 Separations Module equipped with a Waters 2414 refractive index detector and a Jordi Fluorinated DVB mixed bed column in series with a Jordi Fluorinated DVB 10⁵ Å pore size column. THF with 2% acetonitrile was used as the eluent at a flow rate of 2.0 mL/min. Sonication was performed using a QSonica Q700 ultrasonicator. UV-Vis

spectra were recorded on a Cary 5000 spectrometer in dual beam mode, using matching 10 mm quartz cuvettes. Fluorescence spectra were measured on a Jobin-Yvon SPEX Fluorolog 3.22 equipped with a 450 W Xe arc lamp, digital photon counting photomultiplier, and an InGaAs detector, also using a 10 mm quartz cuvette. Slit widths for both excitation and emission were set to 2 nm band-pass, and correction factor files were applied to account for instrument variations. A commercially available two-part silicone kit (Gelest Optical Encapsulant, PP2-OE41) was used to prepare the polymer-silicone composites. Silicone mixtures were homogenized using a FlackTek Inc. DAC 150 FVZ-K Speed Mixer. 3D printed photomasks were prepared using an Objet 24 3D Printer with a VeroWhite RGD 835 resin (matte finish). Photomasks were made opaque to light by painting over the top face of the photomask using an oil-based fine point black paint marker (Sharpie). Confocal fluorescence microscopy was performed using a Nikon A1 Confocal Eclipse Ti microscope with Nikon A1 plus camera and Nikon Elements software (4×/0.2 NA objective lens). A z-stack of each sample was obtained (~300 μm slice with ~15 μm step size per sample) to ensure that the sample was homogenous throughout, and a representative image is shown in the respective figures.

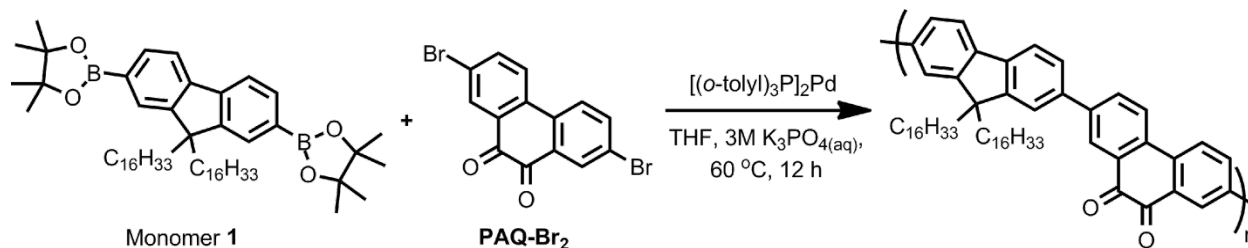
Synthetic Procedures



PAQ-BVE solvent screening. A glass vial equipped with a magnetic stir bar was charged with PAQ (10 mg, 48 μmol), solvent (1 mL), and BVE (48 mg, 480 μmol). The reaction mixture was irradiated with white LEDs and stirred at RT for 10 min (apparatus shown in Figure S1). The crude reaction mixtures were subjected to HPLC to determine the efficiency of the reaction. For the reaction in toluene, solvent

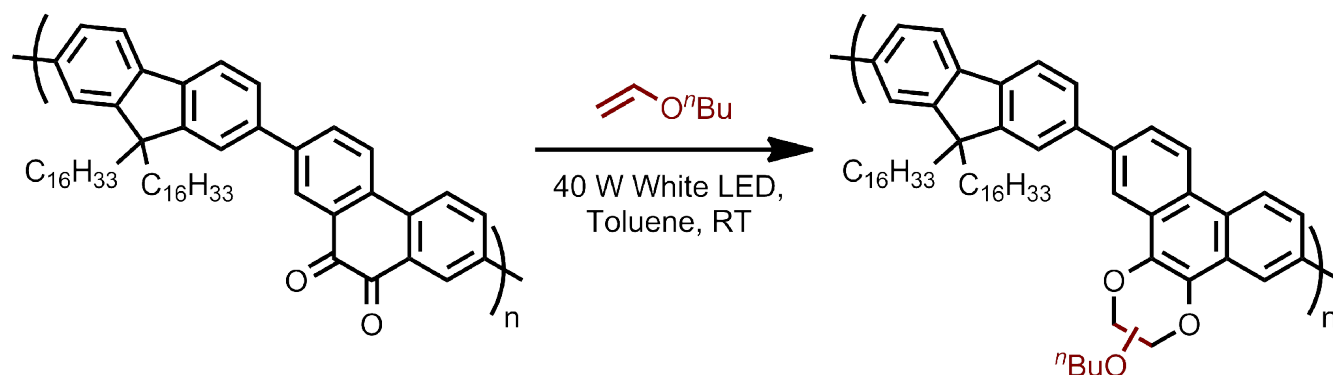
was removed *in vacuo* prior to HPLC analysis as the solvent appeared in the HPLC chromatogram. For the reaction in toluene, the reaction scale was increased to 100 mg of PAQ and the reaction mixture was purified by flash chromatography (12 g silica, 0 \rightarrow 50% CH₂Cl₂ in hexanes over 10 CV) to afford **PAQ-BVE** as a colourless solid (106 mg, 72% yield). ¹H-NMR (700 MHz; CDCl₃): δ 8.61 (t, J = 7.0 Hz, 2H), 8.19 (t, J = 8.2 Hz, 2H), 7.62-7.55 (m, 4H), 5.50 (dd, J = 2.5, 1.6 Hz, 1H), 4.43-4.34 (m, 2H), 4.02-3.98 (m, 1H), 3.77 (dt, J = 9.7, 6.7 Hz, 1H), 1.63-1.59 (m, 2H), 1.33 (q, J = 7.5 Hz, 2H), 0.86 (t, J = 7.4 Hz, 3H). ¹³C NMR (176 MHz; CDCl₃): δ 133.4, 130.8, 127.05, 126.87, 126.79, 126.77, 126.5, 126.2, 125.16, 125.05, 122.66, 122.51, 121.1, 120.6, 94.6, 69.1, 66.6, 31.7, 19.3, 13.9. HRMS (ESI+) (m/z) for C₂₀H₂₀O₃ [M+H]⁺ calculated: 309.1485, found: 309.1485.

PAQ-Br₂.² A round bottom flask equipped with a magnetic stir bar was charged with PAQ (1 g, 4.8 mmol) and conc. H₂SO₄ (24 mL). Upon addition of NBS (1.9 g, 10.6 mmol), the dark green mixture quickly turned dark red. The reaction mixture was stirred at RT for 12 h and then poured onto ice. The resulting dark orange slurry was vacuum filtered and washed with water and MeOH to afford **PAQ-Br₂** as an orange solid (1.68 g, 95%). ¹H-NMR (600 MHz; CDCl₃): δ 8.31 (dd, J = 1.5, 0.8 Hz, 2H), 7.85 (d, J = 1.7 Hz, 4H).

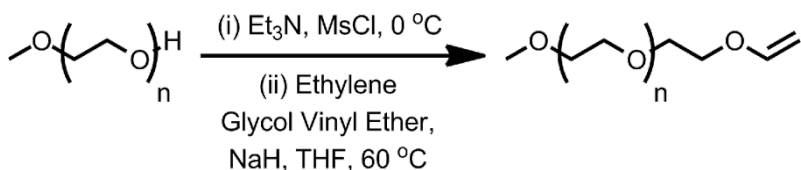


PF-PAQ. A Schlenk tube was charged with a magnetic stir bar and boronic ester monomer **1** (954.0 mg, 1.10 mmol), PAQ-Br₂ (402.7 mg, 1.10 mmol), THF (8 mL), and 3M K₃PO_{4(aq)} (8 mL). The biphasic mixture was degassed by three freeze-pump-thaw cycles, then, while frozen under liquid nitrogen, [(*o*-tol)₃P]₂Pd (18 mg, 2.5 μ mol) was added under a positive pressure of nitrogen. The Schlenk tube was evacuated and backfilled with nitrogen three times, and the reaction mixture was heated to 60 °C and

vigorously stirred for 12 h. The phases were allowed to separate, and the organic layer was isolated and filtered through a single plug of celite and neutral alumina. The plug was thoroughly washed with THF and the filtrate was concentrated *in vacuo*. The crude polymer was precipitated into MeOH (~150 mL) and then filtered to afford **PF-PAQ** as a red solid (782 mg, 87%). ¹H-NMR (600 MHz; CDCl₃): δ 8.58-8.53 (m, 2H), 8.18-8.04 (m, 4H), 7.88-7.85 (m, 2H), 7.75-7.67 (m, 4H), 2.16-2.09 (m, 4H), 1.25-1.09 (m, 48H), 0.85 (m, 10H), 0.76-0.70 (m, 4H). GPC: M_n = 4.6 kDa; Đ = 1.80. The above procedure was repeated on a 100 mg scale of PAQ-Br₂ (0.27 mmol), except the reaction mixture was stirred for 72 h to afford **PF-PAQ** as a dark red solid (132 mg, 60%). GPC: M_n = 12.2 kDa, Đ = 4.25.

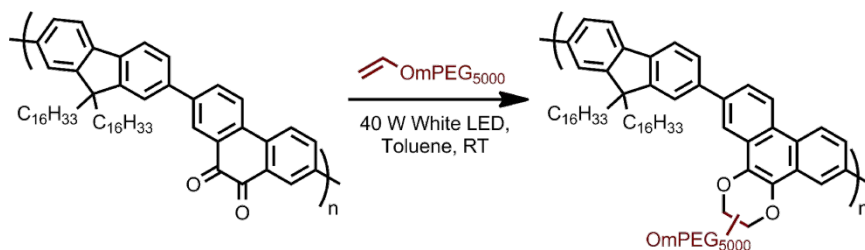


PF-PAQ photoclick reaction with BVE. A glass vial equipped with a magnetic stir bar was charged with **PF-PAQ** (10 mg, 12.2 μmol of PAQ units), BVE (1 – 10 eq, 12.2 – 122 μmol), and toluene (1 mL). The glass vial was irradiated with white LEDs for 30 min at RT, and then solvent was removed *in vacuo*. The crude solid was triturated with Et₂O to remove unreacted BVE and then the polymer was dried *in vacuo* and analyzed by ¹H NMR. ¹H-NMR (600 MHz; CDCl₃): δ 8.74-7.67 (m, 12H), 5.56 (m, 1H), 4.45 (m, 2H), 4.06 (m, 1H), 3.81 (m, 1H), 2.12 (m, 8H), 1.64 (m, 4H), 1.08 (m, 61H).



mPEG₅₀₀₀-OMs. A glass vial equipped with a magnetic stir bar was charged mPEG₅₀₀₀-OH (500 mg, 0.1 mmol), Et₃N (20 mg, 0.2 mmol), and CH₂Cl₂ (1 mL) then cooled to 0 °C. MsCl (57 mg, 0.5 mmol) was added dropwise to the colourless solution, and the reaction mixture was stirred at 0 °C for 2 h. The reaction mixture was filtered through an alumina plug and directly precipitated into Et₂O and vacuum filtered. The crude polymer was used directly in the next reaction.

mPEG₅₀₀₀-VE. A glass vial equipped with a magnetic stir bar was charged with mPEG₅₀₀₀-OMs (0.1 mmol), ethylene glycol vinyl ether (176 mg, 2 mmol), NaH (60 mg, 2.5 mmol), and THF (0.25 mL). The reaction mixture was heated to 60 °C (melting the mPEG₅₀₀₀-OMs to afford a homogenous solution) for 16 h. The resulting viscous orange reaction mixture was filtered through an alumina plug and then precipitated into Et₂O and vacuum filtered to afford **mPEG₅₀₀₀-VE** as a colourless solid (292 mg, 57%).
¹H-NMR (700 MHz; CDCl₃): δ 6.49 (dd, *J* = 14.4, 6.8 Hz, 1H), 4.17 (s, 1H), 4.00 (s, 1H), 3.83 (d, *J* = 24.7 Hz, 4H), 3.64 (s, 1H), 3.38 (s, 3H). ¹³C NMR (176 MHz; CDCl₃): δ 110.1, 86.8, 72.1, 70.87, 70.68, 70.62, 70.60, 69.8, 67.4, 59.2.



PF-PAQ photoclick reaction with mPEG₅₀₀₀-VE. A glass vial was charged with **PF-PAQ** (1 mg, 1.2 μmol), mPEG₅₀₀₀-VE (31.2 mg, 6.1 μmol), and toluene (1 mL). The glass vial was irradiated with white LEDs for 10 min at RT, and then solvent was removed *in vacuo*. The resulting clicked polymer could not be separated from the mPEG₅₀₀₀-VE starting material and was used without purification for the

subsequent study. The product was reconstituted in various solvents and interrogated for photophysical properties.

PF-PAQ silicone composites. The preparation process is illustrated in Figure S1. **PF-PAQ** (10 mg) was dissolved in toluene (1 mL) and added to part A (2.5 g) of the commercially available silicone elastomer kit. The ingredients were manually mixed together using a small wooden dowel, then toluene was removed *in vacuo* at 90 °C. Part B (2.5 g) of the silicone elastomer kit was added, and the components were homogenized using a speed mixer (3000 g, 30 sec). The silicone mixture was poured into a petri dish (circle-shaped with a diameter of 6 cm, for a total area of 28.3 cm²) and cured at 90 °C for 1 h. The solid silicone elastomer composite was removed from the petri dish and cut into smaller pieces using a razor blade for subsequent experiments.

PF-PAQ silicone composite functionalization. The **PF-PAQ-silicone** composite was soaked in a 50/50 v/v solution of BVE in toluene for 2 min and then removed from the mixture. The silicone composite was then irradiated with white LEDs for 5 min and analyzed using a confocal fluorescence microscope. As a control experiment, the same silicone composite was irradiated in an identical manner (*vide supra*) without soaking in the BVE solution. To functionalize only some of the silicone composite, a 3D printed mask was used to cover specific regions of the silicone composite during irradiation.

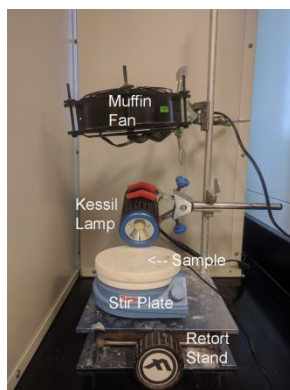


Figure S1. Photograph of the photochemical reaction setup (reaction sample not shown). The angle of the lamp was adjusted accordingly for the specific experiment using the clamp. For solution phase reactions, the lamp was placed side on while the sample was vigorously stirred. For the reactions with the solid silicone substrate, the lamp was placed directly overhead during irradiation. A Kessil A160WE

Blue Tuna saltwater aquarium light was used to irradiate the sample and an AC Infinity AXIAL 1238 muffin fan was used to keep the reaction mixture from overheating.

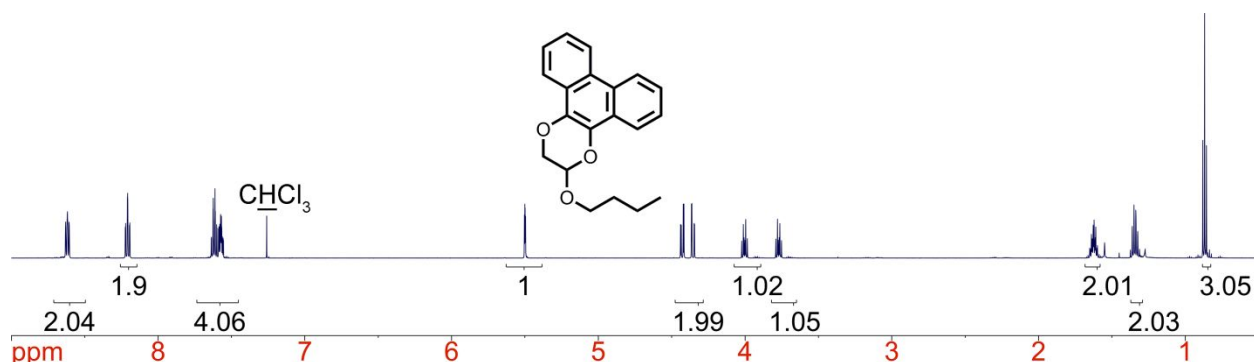


Figure S2. ¹H NMR spectrum of PAQ-BVE.

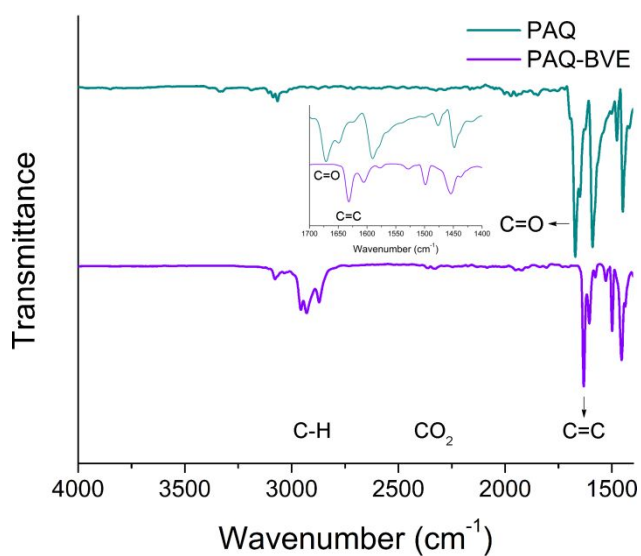


Figure S3. IR spectra of PAQ (teal) and PAQ-BVE (purple). Inset shows the zoomed in region around the C=O stretch.

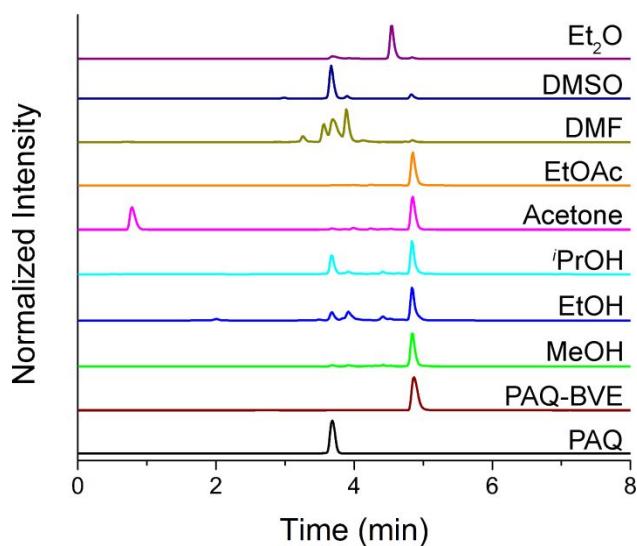


Figure S4. HPLC data of the crude reaction mixtures for the photoclick reaction between PAQ and BVE in various solvents. The bottom chromatograms correspond to PAQ starting material (black) and the isolated photoclick product PAQ-BVE (red), respectively.

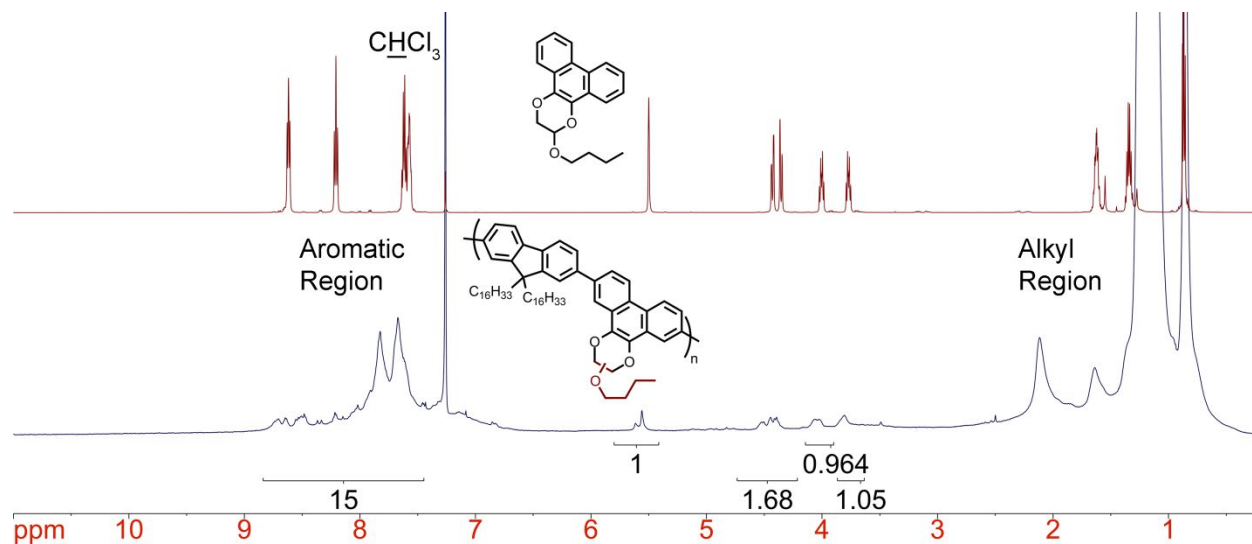


Figure S5. ¹H NMR spectra of PF-PAQ-BVE (blue) and PAQ-BVE (red).

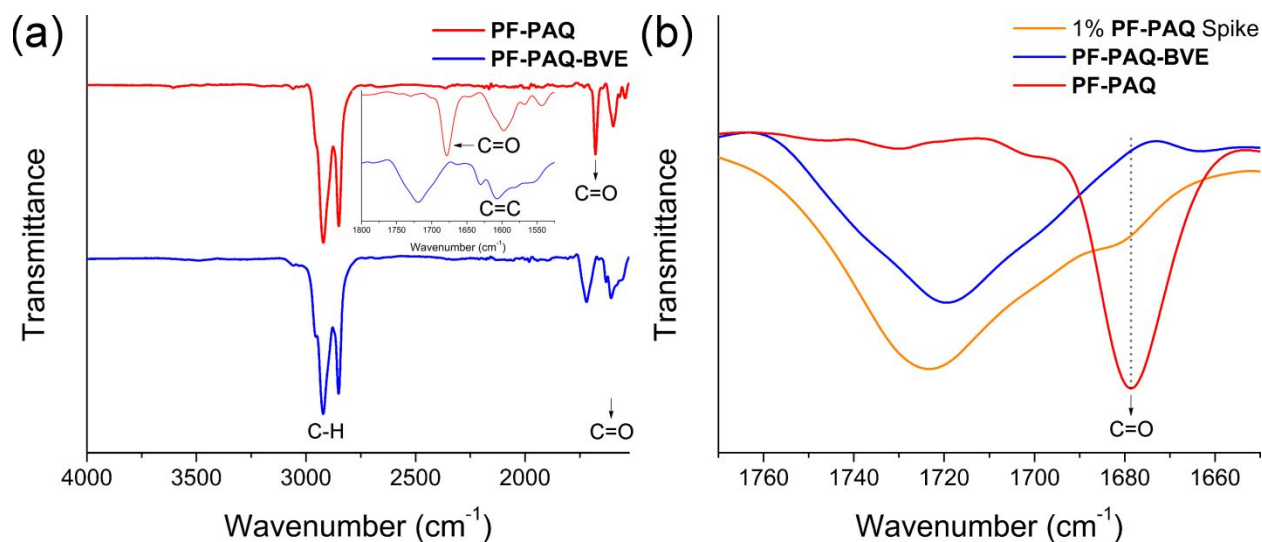
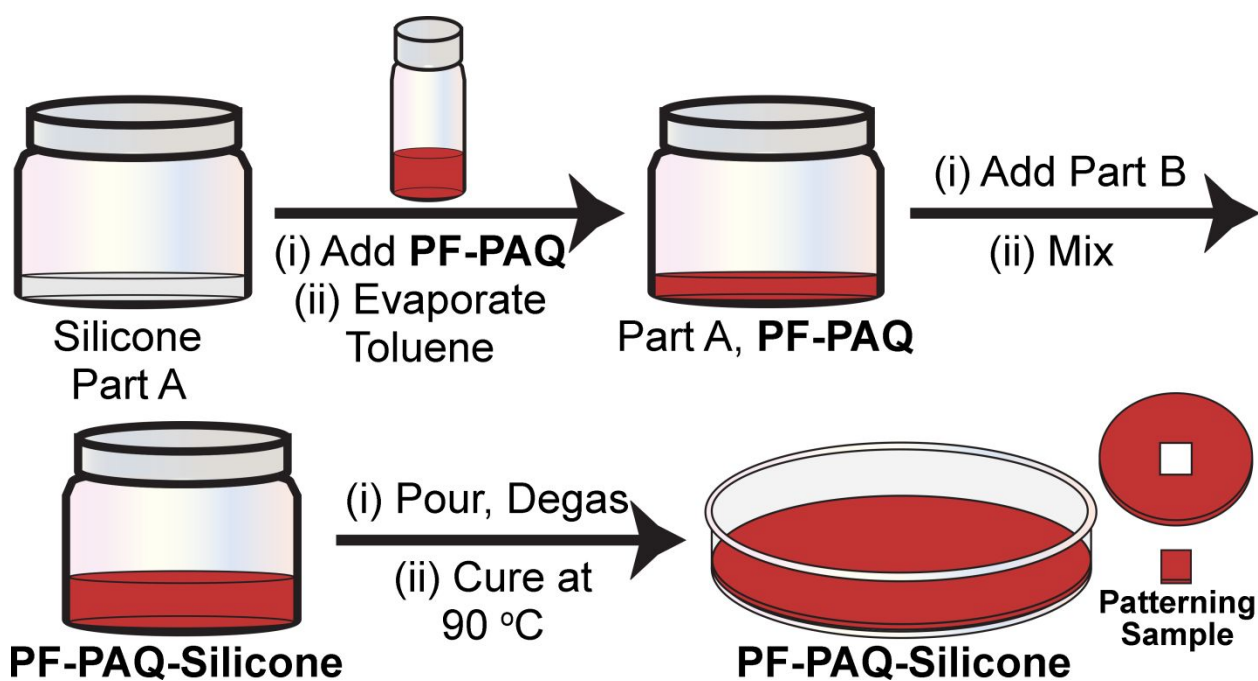


Figure S6. (a) IR spectra of PF-PAQ and PF-PAQ-BVE. Inset shows the zoomed in region around the C=O stretch. (b) Experiment where pristine PF-PAQ-BVE sample is spiked with 1% PF-PAQ to determine IR instrument sensitivity (orange trace).

Table S1. Fluorescence emission peaks of **PF-PAQ-mPEG₅₀₀₀** in various solvents

Solvent	Relative Polarity Index	λ_{em} (nm)
Toluene	2.4	415, 433, 548
CH ₂ Cl ₂	3.1	438
THF	4.0	415, 433, 543
EtOAc	4.4	415, 430, 543
Acetone	5.1	430, 548
EtOH	5.2	418, 540
MeCN	5.8	438, 558
Water	10.2	558



Scheme S1. Cartoon illustration of the **PF-PAQ-silicone** composite preparation process.

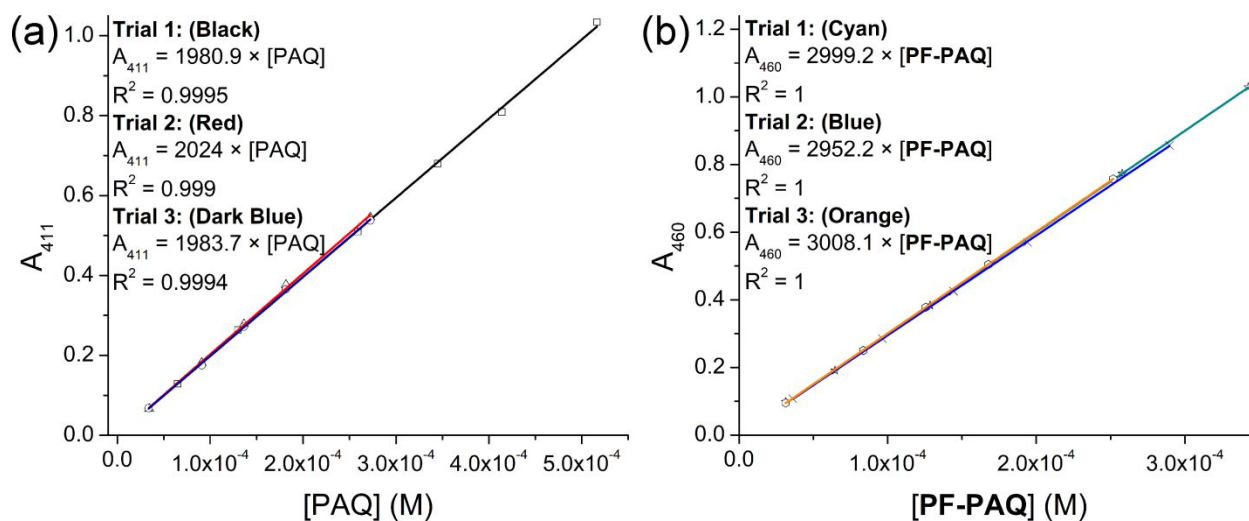


Figure S7. Plots of absorbance vs concentration (M) in toluene for (a) PAQ and (b) PF-PAQ.

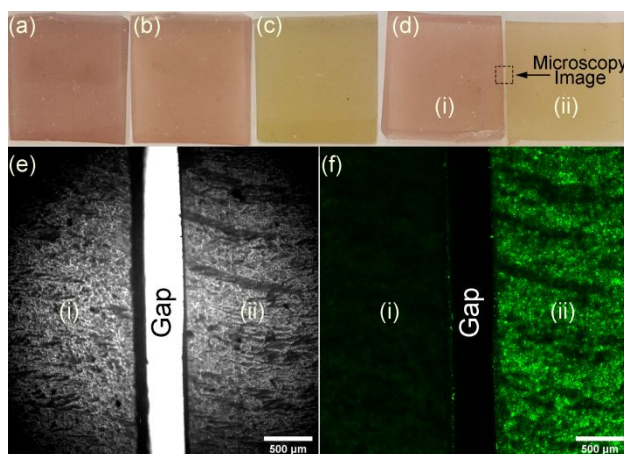


Figure S8. Photographs of **PF-PAQ-silicone** (a) pre-irradiation and post-irradiation with white LEDs (b) in the absence of BVE and (c) in the presence of BVE. (d) Photograph of the **PF-PAQ-silicone** samples used for microscopy post-irradiation with white LEDs (i) without or (ii) with BVE present. Representative (e) brightfield image and (f) confocal fluorescence image of **PF-PAQ-silicone** post-irradiation.

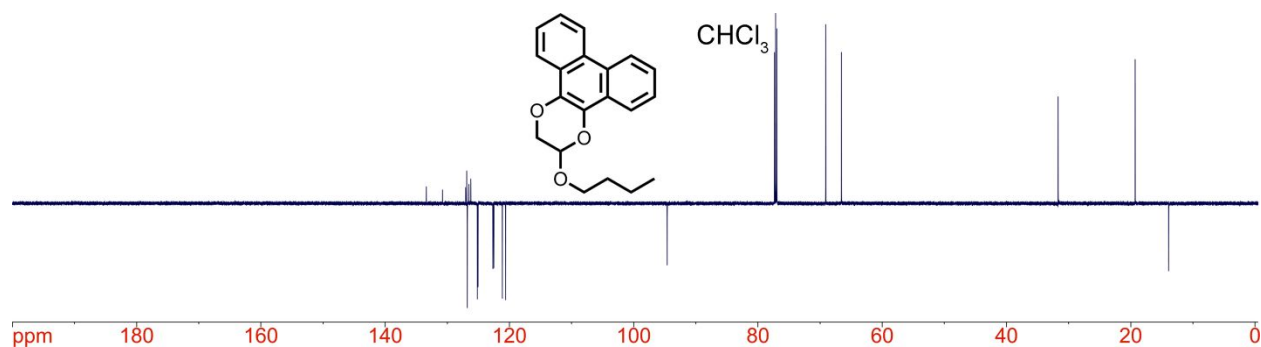
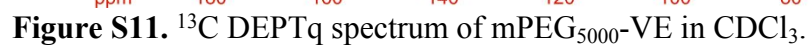
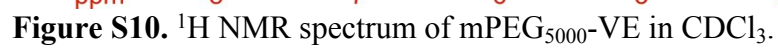


Figure S9. ^{13}C DEPTq spectrum of PAQ-BVE in CDCl_3 .



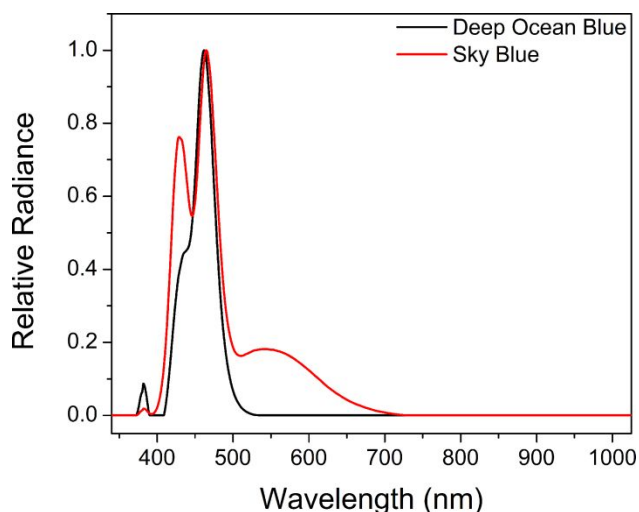


Figure S13. Emission spectrum of Kessil A160WE Tuna Blue saltwater aquarium light provided by commercial supplier.

References

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