Supporting Information

Record Release of Tetramethylguanidine using a Green Light Activated Photocage for Rapid Synthesis of Soft Materials

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EXPERIMENTAL DETAILS

Materials

Chemicals. All reagents were used as received unless otherwise noted. Pyridine (99.0%) was purchased from Acros Organics. 4-(Dimethylamino)pyridine (99%) was purchased from Apollo Scientific. 2,4-Dimethyl-1*H*-pyrrole (98%) was purchased from Ark Pharm. *N*-Bromosuccinimide (>99%) was purchased from Chem-Impex. 4-Nitrophenyl chloroformate (97%) was purchased from Combi-Blocks. Methylmagnesium bromide 3 M in ether was purchased from Fischer Scientific. Boron trifluoride diethyl etherate (46%), pentaerythritol tetrakis(3-mercaptopropionate) (>95%), TEMPO, 1,4-butanediol diglycidyl ether (>=95%), and 2,2'-(ethylenedioxy)diethanethiol (95%) were purchased from Sigma-Aldrich. 2-Chloro-2-oxoethylacetate (>97%), 1,1,3,3-tetramethylguanidine (TMG), tetraethylene glycol diacrylate (stabilized with MEHQ) (90.0+%), and *N*,*N*-diisopropylethylamine (>99%) were purchased from TCI America.

Instrumentation

Nuclear Magnetic Resonance (NMR) Spectroscopy. NMR spectra were recorded using $CDCl_3$ and DMSO-d6 as solvents on an Agilent MR 400 MHz spectrometer. ^{1}H NMR spectra were recorded coupled and referenced to the $CDCl_3$ chemical shift at 7.26 ppm and DMSO-d6 at 2.05 ppm. ^{13}C NMR spectra were recorded decoupled and referenced to the $CDCl_3$ chemical shift at 77.16 ppm and DMSO-d6 at 39.52 ppm.

High Resolution Mass Spectrometry (HRMS). HRMS was performed on an Agilent Technologies 6530 Accurate-Mass Q-TOF LC/MS instrument using ESI. The resulting data was analyzed using Agilent MassHunter Qualitative Analysis Software.

High Performance Liquid Chromatography (HPLC). LC diagrams were recorded on an Agilent 1260 Infinity II Binary LC System equipped with a G7165A multiple wavelength detector. The detector recorded UV-Vis spectra ranging from 190 - 950 nm with a repetition rate of 120 Hz. The system used a C18 reversed phase column (InfinityLab Poroshell 120) as the stationary phase. The mobile phase consisted of a mixture of HPLC grade water and acetonitrile at a typical flow rate of 1 mL/min at room temperature. The injection volume ranged from 1 to 100 µL.

UV-Vis Spectroscopy. The UV-vis spectra were acquired using an Ocean Insight system. The system employed a balanced deuterium-tungsten halogen light source (DH-2000-BAL) with an average output of 194 µW (deuterium bulb) and 615 µW (tungsten bulb) through an SMA 905 connector. The range covered was 230 nm - 2.5 µm. Multimode fiber-optic cables with SMA connectors on both ends and a 600 µm core diameter (QP600-025-SR) were used to connect the light source to the sample holder. For dilute solutions, a qpod cuvette holder (QNW qpod 2eTM) with magnetic stirring and peltier-driven temperature control from -30 °C to 105 °C was utilized. The sample holder was connected to the spectrometer (QEPRO-ABS) through another multimode fiber, which had an entrance slit of 5 µm (INTSMA-005 Interchangeable Slit). The spectrometer measured in the range from 200-950 nm, at an optical resolution of 1.7 nm, using a back-thinned, TE cooled, 1024 × 58 element CCD array.

Fluorimeter. The photoluminescence data was recorded using a Fluorolog3 Fluorimeter. It was equipped with a 450 W ozone-free Xenon arc lamp as the light source and a photomultiplier tube with spectral resolution of 0.1 nm and detection range from 250 to 1050 nm. Time-correlated single

photon counting experiments were also carried out using the Fluorolog3 Fluorimeter. The Xenon lamp was replaced with NanoLEDs (482 nm) with a time resolution of 300 ps.

Nanosecond Transient Absorption. The nanosecond transient absorption measurements were conducted using the enVISion® system from MAGNITUDE INSTRUMENTS®. The spectrometer system was capable of measuring transient absorption spectra and photoluminescence spectra. The instrument could detect wavelengths from UV to visible to near-IR with a time resolution of ~5 ns.

Real-Time Fourier-Transform Infrared Spectroscopy (RT-FTIR). The RT-FTIR measurements were performed using an INVENIO-R FT-IR spectrometer manufactured by Bruker and controlled by the OPUS Spectroscopy Software. The spectra were detected using a liquid nitrogen cooled (LN-MCT Mid) detector. A modified GladiATR Illuminate ATR accessory provided by PIKE Technologies was utilized to investigate the chemical composition and monitor the photocuring of liquid resins upon exposure to light. The visible light exposure was carried out using collimated LED light sources (530 nm-P/N LCS-0530-15-22) from Mightex Systems, together with Lightguide Adapters. The LED Controller M/N SLC-MA02-U was employed, and a 3 mm liquid light guide (LLG-3- 4H) was used in the experiments.

Photorheology. Photorheology experiments were completed using a Discovery Hybrid Rheometer from TA Instruments (TA Instruments, DE, USA). The rheometer was equipped with a UV light guide assembly (TA Instruments, 546311.901), a 20 mm diameter acrylic bottom plate (TA Instruments, 403153.001), and a 20 mm diameter geometry upper aluminum parallel plate (TA Instruments, S6 513200.905). A liquid light guide (Thorlabs, LLG3-4Z) was used to illuminate the samples with a 530 nm LED (Mightex, LCS-0530-15-22) connected to the LED controller (Mightex, Model: SLC-MA02-U) from which light intensity could be controlled remotely through the SLC-series LED controller software (Mightex). The light intensity was measured on the acrylic plate using the thermal power sensor head (Thorlabs, Model: S401C) connected to a digital power and energy meter (Thorlabs, Model: PM100D). For sample loading, 40 µL of the sample was placed on the bottom acrylic plate and the aluminum plate was slowly lowered to 100 µm with a rotational speed set to 10 rad/s. For this study, the storage (G') and loss (G") moduli were monitored over time, the strain was set to 1%, and the oscillation frequency was set to 1 rad/s.

Light Emitting Diodes (LEDs). The LED emission profiles were collected using a spectrophotometer (QEPro, Ocean Insight), connected to an optical fiber (QP600-025-SR). Neutral density filters were used to reduce the emission intensity from the LEDs so as to avoid saturating the detector. The emission profiles for the LEDs used in this study are shown as below, **Figures S1-S4**.

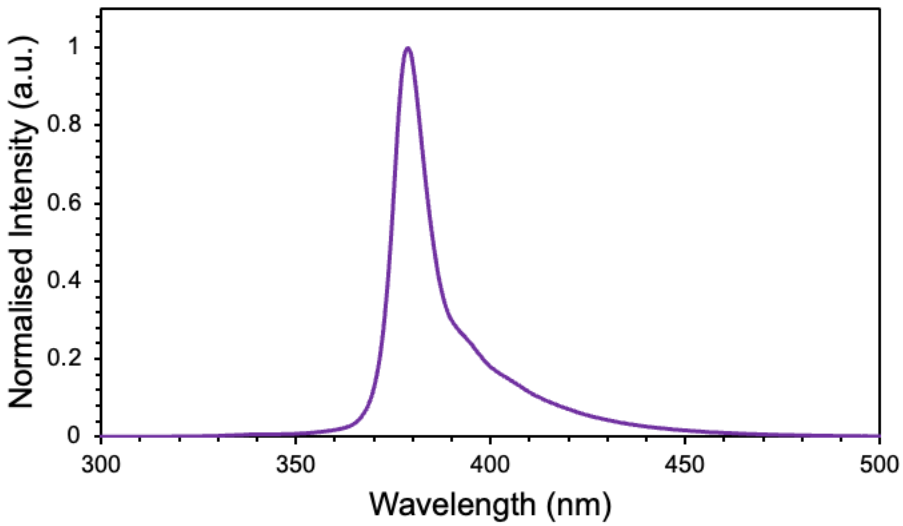


Figure S1. Emission profile of the UV LED (365 nm) used in these studies.

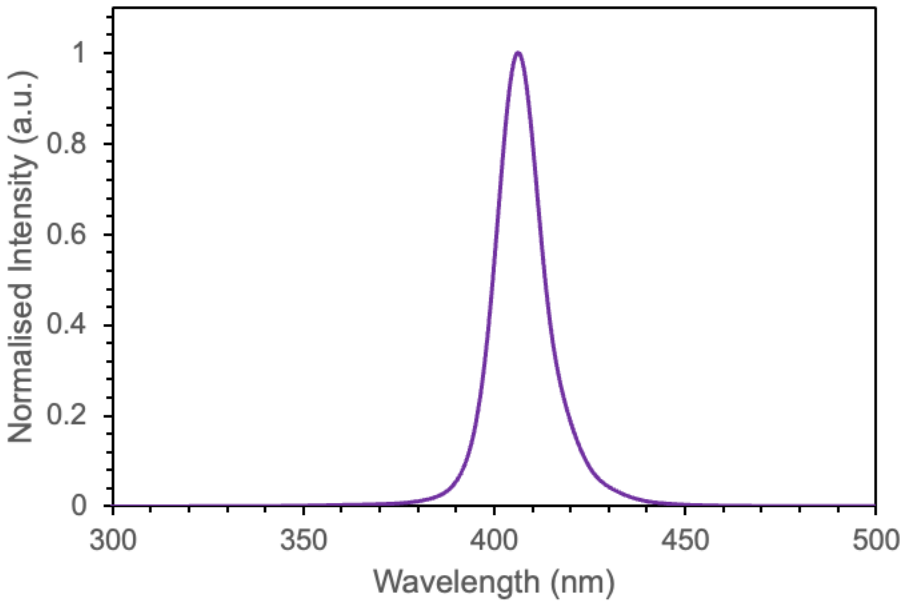


Figure S2. Emission profile of the violet LED (405 nm) used in these studies.

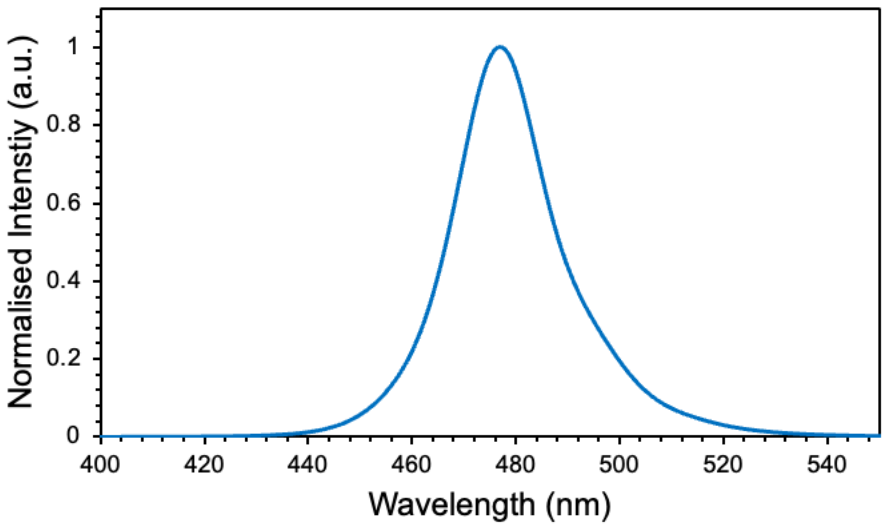


Figure S3. Emission profile of the blue LED (470 nm) used in these studies.

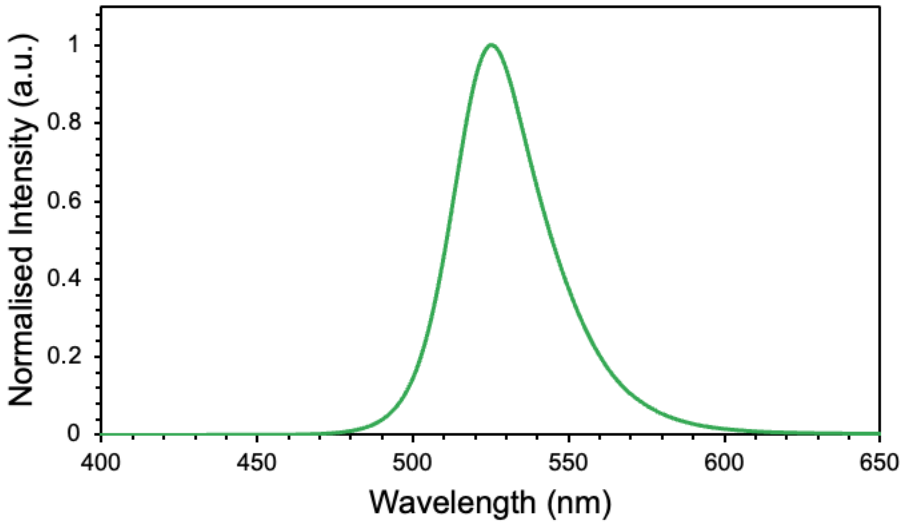
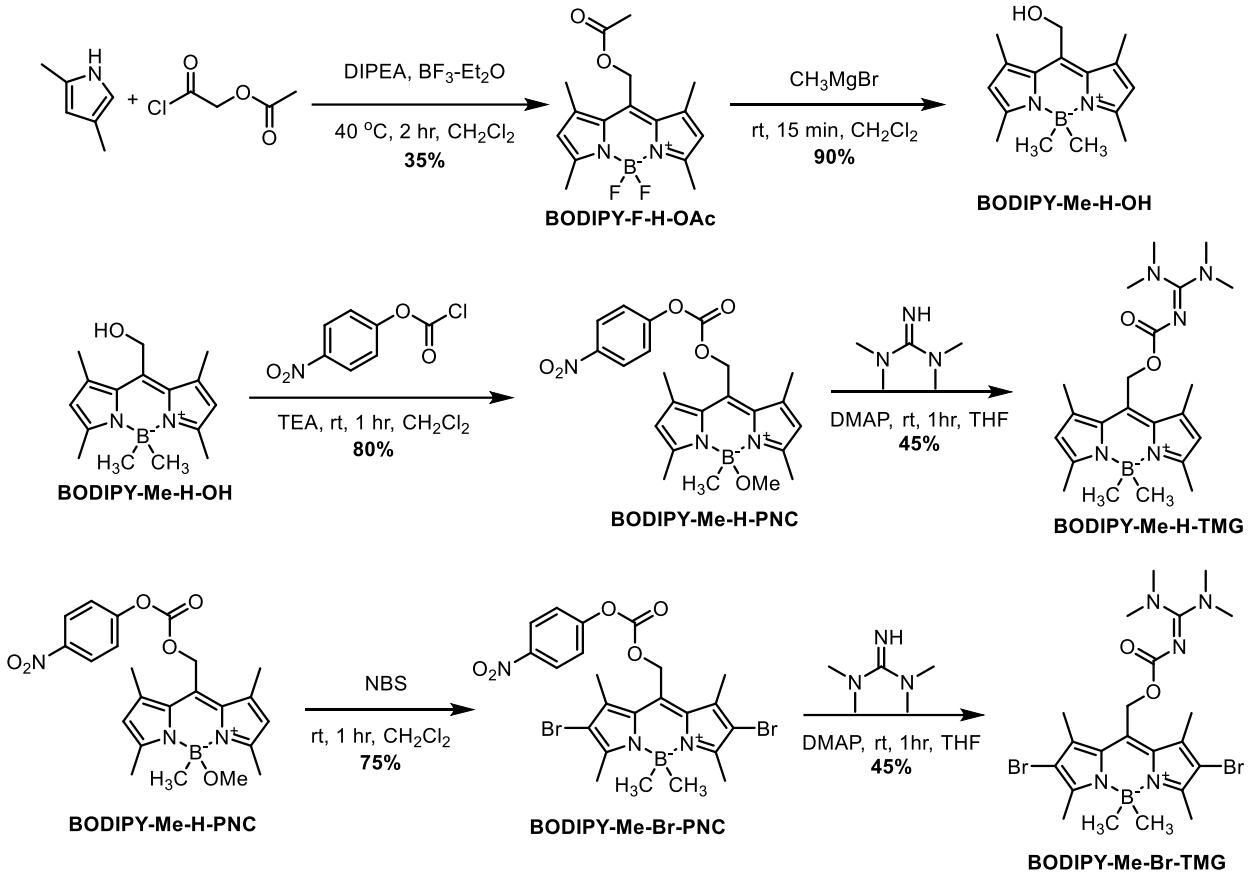


Figure S4. Emission profile of the green LED (530 nm) used in these studies.

Synthesis



Scheme S1. Synthetic route of the BODIPY-Me-H-TMG and -Br-TMG.

Synthesis of (5,5-difluoro-1,3,7,9-tetramethyl-5H-4 λ 4,5 λ 4-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-10-yl)methyl acetate (**BODIPY-F-H-OAc**). Compound **BODIPY-F-H-OAc** was synthesized following a modified protocol from literature.[S1] To a two-neck roundbottom flask equipped with a magnetic stir bar, inlet adapter, septum, and condenser was added 2,4-dimethyl-1*H*-pyrrole (4 g, 40 mmol, 2 eq.) and 2-chloro-2-oxoethyl acetate (3 g, 20 mmol, 1 eq.) under a nitrogen atmosphere. The mixture was then dissolved in dry dichloromethane (100 mL) and heated to reflux (40 °C) and stirred for 2 hours. After refluxing for 2 hours, the solution was cooled in an ice bath to ~0 °C followed by adding *N*,*N*-diisopropylethylamine (DIPEA, 10 g, 80 mmol, 20 mL, 4 eq) and boron trifluoride etherate (30 g, 200 mmol, 10 eq.) sequentially. The solution was then stirred for 30 minutes at 25 °C. The solution was then washed with water (3×) and brine (1×). The organic phase was dried over $MgSO_4$. Dichloromethane was then removed under reduced pressure and the crude product was purified by column chromatography with a mixture of hexanes and diethyl ether (gradient, *v*:*v* = 0:1 to 2:1, R_f = 0.5 with hexanes and diethyl ether *v*:*v* = 1:1), providing the desired product as an orange solid. Yield: 65%. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 6.07 (s, 2H), 5.07 (d, *J* = 1.1 Hz, 2H), 2.51 (s, 6H), 2.34 (s, 6H), 2.12 (d, *J* = 1.1 Hz, 3H). ^{13}C NMR: (126 MHz, $CDCl_3$) δ 170.62, 156.65, 141.48, 133.28, 132.66, 122.34, 77.29, 77.04, 76.78, 57.89, 29.73, 20.63, 15.66, 14.74, 14.72, 14.70, 1.05. HRMS (ESI): exact mass calculated for $C_{16}H_{19}BF_2N_2O_2$ $[M+Na]^+$ is 343.14, found $[M+Na]^+$ = 343.14.

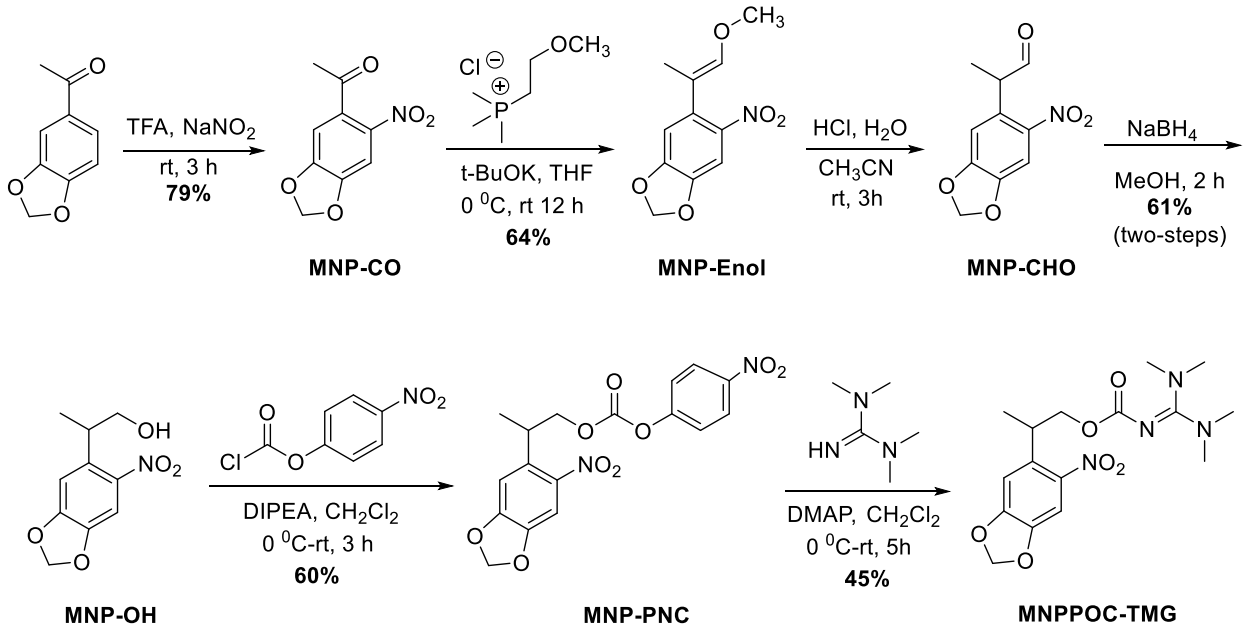
Synthesis of (1,3,5,5,7,9-hexamethyl-5H-4λ^4,5λ^4-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-10-yl)methanol (**BODIPY-Me-H-OH**). Compound **BODIPY-Me-H-OH** was synthesized following a modified protocol from literature.[S1] To a one-neck roundbottom flask equipped with a magnetic stir bar, inlet adapter and septum was added compound **1** (1 g, 3.6 mmol, 1 eq.) under a nitrogen atmosphere followed by anhydrous dichloromethane (100 mL). The mixture was placed in an ice bath to cool to 0 °C, followed by adding methylmagnesium bromide (3 M in diethyl ether, 12 mL, 72 mmol, 10 eq.) dropwise by syringe. After addition, the unreacted methylmagnesium bromide was quenched with dropwise addition of 1M $NH_4Cl_{(aq)}$ until bubble formation ceased. The organic and aqueous phases were separated. The aqueous phase was washed with dichloromethane (3×). The combined organic phase was dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using a gradient of hexanes:diethyl ether (*v:v* = 6:1 to 3:1). The desired band was collected (R_f = 0.6, dichloromethane) and concentrated under reduced pressure to provide the product as an orange solid. Yield: 60%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.07 (s, 2H), 4.89 (s, 2H), 2.52 – 2.46 (d, 12H), 0.05 (s, 6H). ^{13}C NMR: (126 MHz, $CDCl_3$) δ 152.86, 138.23, 136.99, 130.58, 122.53, 56.42, 20.63, 16.59, 15.95. HRMS (ESI): exact mass calculated for $C_{16}H_{23}BN_2O$ $[M+H]^+$ is 271.19, found $[M+H]^+$ =271.20.

Synthesis of (1,3,5,5,7,9-hexamethyl-5H-4λ^4,5λ^4-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-10-yl)methyl (4-nitrophenyl) carbonate (**BODIPY-Me-H-PNC**). Compound **BODIPY-Me-H-PNC** was synthesized following a modified protocol from literature.[S2] In a round bottom flask, **BODIPY-Me-H-OH** (100 mg, 0.4 mmol, 1 eq.) was dissolved in dichloromethane (100 mL) and pyridine (0.1 mL, 1 mmol, 3.5 eq.) was added. The flask was placed in an ice bath. 4-Nitrophenyl chloroformate (250 mg, 1 mmol, 3.5 eq.) and DIPEA (0.3 mL, 1 mmol, 4 eq.) were pre-dissolved in dichloromethane (50 mL) and added to the round bottom flask dropwise by syringe. After complete addition, the mixture was allowed to warm to room temperature and stirred for an additional 30 min. The solvent was then removed under reduced pressure, and the crude product was purified by silica gel chromatography with hexanes:dichloromethane (3:1, Rf = 0.4), yielding the desired product as an orange solid. Yield: 75%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.27 (d, *J* = 9.1, 4.3, 2.2 Hz, 2H), 7.39 (d, 2H), 6.10 (s, 2H), 5.60 (s, 2H), 2.46 (d, 12H), 0.18 (s, 6H). ^{13}C NMR: δ_C (126 MHz, DMSO) 155.56, 153.65, 152.28, 145.80, 137.93, 132.38, 131.05, 125.95, 123.54, 123.12, 71.73, 70.24, 62.67, 40.44, 40.27, 40.11, 39.94, 39.78, 39.61, 39.44, 16.76, 16.10. HRMS (ESI): exact mass calculated for $C_{23}H_{26}BN_3O_5$ is 435.29, found $[M+Na]^+$ = 458.19.

Synthesis of *10-((((bis(dimethylamino)methylene)carbamoyl)oxy)methyl)-1,3,5,5,7,9-hexamethyl-3H,5H-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-5-uide* (**BODIPY-Me-H-TMG**). To a two-neck round bottom flask, **BODIPY-Me-H-PNC** (200 mg, 0.46 mmol, 1 eq.) and 1,1,3,3-tetramethylguanidine (53 mg, 0.46 mmol, 1.0 eq.) were dissolved in anhydrous THF (30 mL) and *N*,*N*-dimethylaminopyridine (56 mg, 0.46 mmol, 1.0 eq.) was added to the reaction mixture under a N_2 atmosphere. After completion, THF was removed under reduced pressure and the residue was dissolved in dichloromethane. The solution was washed with deionized water (3×) and then brine (3×). The combined organic phase was dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The product was purified by column chromatography with hexanes:acetone (3:1, Rf = 0.5), yielding the desired product as a red solid Yield: 44%. δ_H (400 MHz, cdcl$_3$) 6.04, 5.39, 2.98, 2.47, 2.44, 1.61, 0.16. δ_C (126 MHz, MeOD) 166.68, 160.21, 152.49, 137.39, 134.97, 131.17, 122.06, 58.86, 38.89. HRMS (ESI): exact mass calculated for $C_{22}H_{34}BN_5O_2$ is 411.36, found $[M+Na]^+$ = 412.29.

Synthesis of (2,8-dibromo-1,3,5,5,7,9-hexamethyl-5H-4λ^4,5λ^4-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-10-yl)methyl (4-nitrophenyl) carbonate (**BODIPY-Me-Br-PNC**). Compound **BODIPY-Me-Br-PNC** was synthesized following a modified protocol from literature.[S2] In a round bottom flask, **BODIPY-Me-H-PNC** (200 mg, 0.46 mmol, 1 eq.) was dissolved in anhydrous dichloromethane (50 mL). While stirring, *N*-bromosuccinimide (200 mg, 1.15 mmol, 2.5 eq.) was added to the flask. After complete consumption of the starting material, dichloromethane was removed under reduced pressure, and the crude product was purified with silica gel column chromatography with hexanes:dichloromethane (4:1, Rf = 0.6), yielding the desired product as a deep red solid. Yield: 82%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 (d, 2H), 7.39 (d, 2H), 5.61 (s, 2H), 2.49 (d, *J* = 19.6 Hz, 12H), 0.06 (s, 12H). ^{13}C NMR: δ $_C$ (126 MHz, $CDCl_3$) 154.16, 151.11, 150.94, 144.54, 133.26, 129.93, 129.07, 126.87, 124.40, 120.56, 112.29, 61.55, 14.97, 14.15. HRMS (ESI): exact mass calculated for $C_{23}H_{24}BBr_2N_3O_5$ is 593.08, found $[M+H]^+$ = 594.02.

Synthesis of 10-((((bis(dimethylamino)methylene)carbamoyl)oxy)methyl)-2,8-dibromo-1,3,5,5,7,9-hexamethyl-3H,5H-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-5-uide (**BODIPY-Me-Br-TMG**). Compound **BODIPY-Me-Br-PNC** (200 mg, 0.34 mmol, 1 eq.) and 1,1,3,3-tetramethylguanidine (39 mg, 0.34 mmol, 1 eq.) were dissolved in anhydrous THF (30 mL) and *N*, *N*-dimethylaminopyridine (41 mg, 0.34 mmol, 1 eq.) was added to the reaction mixture. The reaction was left to stir for 30 mins until completion. After completion, THF was removed under reduced pressure and the residue was dissolved in dichloromethane. The solution was washed with deionized water (3×) and then brine (1×) to remove unreacted bases. The combined organic phase was dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The product was purified by column chromatography with hexanes:acetone (3:1, Rf = 0.4), yielding the desired product as a red solid Yield: 35%. δ $_H$ (400 MHz, cd_3od) 5.50, 4.86, 2.99, 2.98, 2.50, 2.49, 0.19. δ $_C$ (126 MHz, MeOD) 166.68, 159.81, 150.45, 136.00, 134.87, 130.14, 111.75, 58.97, 14.71. HRMS (ESI): exact mass calculated for $C_{22}H_{32}BBr_2N_5O_2$ is 569.15, found $[M+H]^+$ = 570.11.



Scheme S2. Synthetic of MNPPOC-TMG photocage.

Synthesis of 3,4-(methyIene dioxy)-6-nitroacetophenone (**MNP-CO**). To a one-neck roundbottom flask, equipped with a magnetic stir bar was added trifluoroacetic acid (300 mL), and $NaNO_2$ (6.42 g, 45.74 mmol) followed by cooling in an ice bath and slow addition of 3,4-(methylenedioxy)-acetophenone (10.0 g, 61.21 mmol) over 15 minutes. The reaction was stirred for 12 hours during which it was allowed to warm to room temperature. The reaction mixture was then slowly poured into cold saturated aqueous $NaHCO_3$ and the resultant precipitate was collected via filtration. The yellow solid was washed with water and dried under reduced pressure to afford the desired product, **MNP-CO** (10.27 g, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 6.74 (s, 1H), 6.17 (s, 2H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.32, 152.84, 148.99, 135.27, 120.02, 106.33, 104.96, 103.77, 30.35. HRMS (ESI): exact mass calculated for $C_9H_7NO_5$ $[M+Na]^+$ 232.0216, found 232.0218.

Synthesis of 2-(3,4-methylenedioxy-6-nitrophenyl) propyl enol methyl ether (**MNP-Enol**). To a two-neck roundbottom flask equipped with a magnetic stir bar, inlet adapter, and septum was added methoxymethyltriphenylphosphonium chloride (6.00 g 17.58 mmol) and THF (30 mL). The mixture was cooled in an ice bath and the atmosphere was purged with N_2. Then, potassium tert-butoxide (2.01 g, 17.63 mmol) was added slowly. The reaction was stirred for 30 minutes followed by adding **MNP-CO** (1.82 g, 8.80 mmol) in 10 mL of THF slowly over 30 minutes. The reaction was warmed to room temperature and stirred for an additional 12 hours, followed by pouring it into 200 mL of cold water. The crude product was then extracted with 3×100 mL of CH_2Cl_2. The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduce pressure. The crude product was purified by column chromatography with a 0-50% ethyl acetate gradient in hexanes, and the desired band was concentrated to provide the product as a yellows solid (cis/trans isomeric mixture), **MNP-Enol** (1.31 g, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 10.5 Hz, 1H), 6.57 (d, J = 7.9 Hz, 1H), 5.96 (d, J = 3.1 Hz, 2H), 5.83 (dd, J = 14.1,

1.5 Hz, 1H), 3.47 (d, J = 67.1 Hz, 3H), 1.75 (dd, J = 9.4, 1.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.06, 150.80, 146.44, 146.39, 145.09, 143.35, 132.99, 130.82, 112.75, 110.61, 109.54, 105.16, 102.61, 102.56, 59.73, 59.55, 18.13, 14.40. HRMS (ESI): exact mass calculated for $C_{11}H_{11}NO_5$ $[M+Na]^+$ 260.0529, found 260.0534.

Synthesis of 2-(3,4-methylenedioxy-6-nitrophenyl) propyl aldehyde (**MNP-CHO**). To a one-neck roundbottom flask, equipped with a magnetic stir bar was added **MNP-Enol** (1.00 g, 4.2 mmol) and acetonitrile (50 mL). The flask was cooled in an ice bath and 30 mL of 6N HCl was added slowly to the solution. The mixture was stirred at room temperature until the starting material was fully consumed as observed using thin layer chromatography. The mixture was slowly poured into saturated aqueous $NaHCO_3$ and extracted with 3×100 mL of CH_2Cl_2. The combined organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to afford the crude product, **MNP-CHO**, as a yellow oil. The crude product was used in the next step without further purification.

Synthesis of 2-(3,4-methylenedioxy-6-nitrophenyl) propanol (**MNP-OH**). To a two-neck roundbottom flask equipped with a magnetic stir bar, inlet adapter, and septum was added **MNP-CHO** (0.80 g, 3.57 mmol) and THF (50 mL). The atmosphere in the flask was replaced with N_2 and the mixture was cooled in an ice bath. Next, $NaBH_4$ (190 mg, 5.14 mmol) was added slowly to the flask and the reaction mixture was stirred overnight at room temperature. The reaction was then quenched with 20 mL of deionized water, poured into 50 mL of saturated NH_4Cl aqueous solution and extracted with 3×50 mL of CH_2Cl_2. The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduce pressure. The crude product was purified by column chromatography with a 0-3% methanol gradient in dichloromethane, and the product band was collected and concentrated to provide the desired product, **MNP-OH**, as a yellow solid (490 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (s, 1H), 6.89 (s, 1H), 6.08 (dd, J = 6.1, 1.3 Hz, 2H), 3.82 – 3.60 (m, 3H), 1.28 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.64, 146.22, 144.27, 135.29, 106.90, 105.33, 102.76, 67.91, 36.45, 17.65. HRMS (ESI): exact mass calculated for $C_{10}H_{11}NO_5$ $[M+Na]^+$ 248.0529, found 248.0531.

Synthesis of 2-(6-nitrobenzo[d][1,3]dioxol-5-yl)propyl (4-nitrophenyl) carbonate (**MNP-PNC**). To a two-neck roundbottom flask, equipped with a magnetic stir bar, inlet adapter, and septum was added **MNP-OH** (0.50 g, 2.24 mmol), diisopropylethylamine (1.90 mL, 11.20 mmol), and anhydrous CH_2Cl_2 (20 mL). The flask was purged with N_2 and cooled to 0 °C in an ice bath. Then 4-nitrophenyl-chloroformate (1.31 g, 6.65 mmol) in 5 mL of anhydrous CH_2Cl_2 was added dropwise to the solution. After complete addition, the reaction was brought to room temperature and the reaction was stirred for an additional 2 hours, after which it was poured into 50 mL of deionized water. The water was extracted with 3×50 mL of CH_2Cl_2 and the combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduce pressure. The crude product was purified by column chromatography with a gradient of 10-70% CH_2Cl_2 in hexanes (1:1, R_f = 0.6), and the desired band was collected and concentrated under reduced pressure to provide to provide the product, **MNP-PNC** as a yellow solid (520 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 – 8.24 (m, 2H), 7.38 – 7.33 (m, 3H), 6.88 (s, 1H), 4.49 – 4.32 (m, 2H), 4.01 – 3.90 (m, 1H), 1.38 (d, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.45, 152.32, 151.75, 146.70, 145.47, 144.01, 133.32, 125.31, 121.86, 106.89, 105.62, 102.97, 72.90, 33.23, 17.69. HRMS (ESI): exact mass calculated for $C_{17}H_{14}N_2O_9$ $[M+Na]^+$ 413.0592, found 413.0600.

Synthesis of 2-(3,4-methylenedioxy-6-nitrophenyl) propoxycarbonyl tetramethyl guanidine (**MNPPOC-TMG**). To a one-neck roundbottom flask equipped with a magnetic stir bar was added **MNP-PNC** (0.50 g, 1.29 mmol) and anhydrous CH_2Cl_2 (10 mL). Then 4-dimethylaminopyridine (235 mg, 1.93 mmol) was added into the solution, followed by dropwise addition of 1,1,3,3-tetramethylguanidine (217 mg, 1.93 mmol) in 20 mL of anhydrous CH_2Cl_2. The reaction was monitored by TLC (methanol:dichloromethane = 1:9, R_f = 0.5) until full conversion was achieved. The solution was then concentrated under reduced pressure. The crude product was purified by column chromatography with a gradient of 3-7% methanol in dichloromethane, and the desire band was concentrated to provide the product, **MNPPOC-TMG** as a yellow solid (210 mg, 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 1H), 6.95 (s, 1H), 6.05 (dd, J = 5.5, 1.3 Hz, 2H), 4.30 – 4.18 (m, 2H), 3.84 – 3.77 (m, 1H), 1.33 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.19, 160.10, 151.46, 146.03, 143.86, 135.51, 107.19, 105.27, 102.63, 68.32, 39.73, 34.04, 18.51. HRMS (ESI): exact mass calculated for $C_{16}H_{22}N_4O_6$ $[M+Na]^+$ 367.1612, found 367.1625.

Emission Quantum Yield Measurements

The emission quantum yields for all derivatives were calculated based on the equation **SE1**:

$$\Phi_{f,x} = \Phi_{f,R} \cdot \frac{A_R}{A_x} \cdot \frac{I_x}{I_R} \cdot \frac{n_x^2}{n_R^2} \qquad \textbf{(SE1)}$$

where the index R denotes the reference dye and x denotes the sample, Φ_f is the emission quantum yield, A is the absorption, I is the integrated emission intensity, and n is the refractive index of the solvent being used. For simplicity, absorption for all samples (in acetonitrile) including the reference dye, rhodamine 6G (Φ_f = 0.91 in ethanol) were measured under dilute conditions (abs. = 0.1) to prevent aggregation (**Figure S7**). After recording all the emission spectra for each sample and R6G, the area under the emission curve was integrated to calculate I. The refractive indices for acetonitrile and ethanol are 1.344 and 1.361, respectively. Following the equation, Φ_f was calculated for all samples.

Uncaging Quantum Yield Measurements

The uncaging quantum yields (Φ_{UC}) for all photocages were calculated based on equation **SE2**.[S3]

$$\Phi_{UC} = \text{(number of molecules)/(number of photons)} \qquad \textbf{(SE2)}$$

In a typical experiment, the photocage was dissolved in acetonitrile and water (v:v = 4:1). The solution was transferred to a cuvette with a stir-bar and then purged with argon for 15 min to remove oxygen. After degassing, the sample was brought to the LED setup, where the LED emission was collimated and focused into the cuvette. After irradiation, the sample was analyzed by HPLC and LCMS, and the concentration of target molecules were calculated from the calibration curves of TMG. From the concentration of products and the LED intensity at the sample (10 mWcm^{-2}), Φ_{UC} was calculated for all photocages.

The uncaging quantum yield (Φ_{UC}) was also determined using RT-FTIR-ATR by the ratio of decay flux (μ_{decay}) and photon flux (μ_{photon}) (**SE3**).[S4] The decay flux (μ_{decay}) was measured using RT-FTIR by monitoring the disappearance of stretches from the carbamate bond (~1550 cm^{-1}) during LED irradiation. The photon flux was calculated from the LED intensity used (**SE4**).

$$\Phi_{UC} = \mu_{decay}/\mu_{photon} \qquad \textbf{(SE3)}$$

$$\mu_{photon}\ (\text{cm}^{-2}\text{s}^{-1}) = \text{I (J cm}^{-2}\text{ s}^{-1}) \text{ / E (J)} \qquad \textbf{(SE4)}$$

FTIR Sample Preparation

For the samples with 100 μm thickness, resin was injected by needle and syringe between two microscope slides, separated by a 100 μm plastic shim stock. The conversions of acrylate and thiol were monitored at 3150 cm^{-1} and 2550 cm^{-1}, respectively.

For the samples with 12 μm thickness, resin was placed on one salt plate with a glass pipette and then covered by a second salt plate separated by 12 μm plastic shim stock. After each scan, the salt plates were soaked in CH_2Cl_2 for a few minutes so that they could be separated and reused. The conversions of acrylate and thiol were monitored at 780 cm^{-1} and 2550 cm^{-1}, respectively.

In the anionic thiol-epoxy experiments, the resin was placed on the ATR crystal with a glass pipette. The conversions of epoxide and thiol were monitored at 930 cm^{-1} and 2550 cm^{-1}, respectively.

Photon Flux Calculation

The total photon absorption flux for each photosystem was calculated based on the following supplemental equations. Equation **SE5** and **SE6** were used to convert the intensity output of the LED from (mW/cm^2·nm) into (# of photons/cm^2·s·nm). Transmission (*T*) of a sample was calculated using equation **SE7**, followed by the portion of photons flux absorption as (1-*T*). Multiplying the light intensity (# of photons/cm^2·s·nm) by (1-*T*) provided the total photon absorption flux at each wavelength (# of photons/cm^2·s·nm) by a particular sample. Finally, integrating the entire curve of (# of photons/cm^2·s·nm) × (1-*T*) provided the total photon absorption flux (# of photons/cm^2·s) for each sample.

$$E = hc/\lambda \quad \textbf{(SE5)}$$

where *E* is energy (mW), *h* is Plank's constant (= 6.626×10^{-34}J·s), *c* is the speed of light (3×10^8 m/s), and λ is wavelength (nm).

$$I_{LED} = n \times E/t \quad \textbf{(SE6)}$$

where I_{LED} is the LED intensity density in mW/cm^2, *n* is number of photons, *E* is energy density of photons (J), and *t* is the time in seconds.

$$-logT = A = \varepsilon cl \quad \textbf{(SE7)}$$

where *A* is absorption (AU), ε is molar absorptivity (M^{-1}·cm^{-1}), *c* is concentration (M), and *l* is path length (cm).

EXPERIMENTAL DATA

Photophysical and Photochemical Properties

The steady-state absorption and emission spectra (degassed) of the BOIDPY-TMGs and *ortho*-nitrobenzyl TMGs were taken in CH_3CN under dilute condition (10^{-5} M), as shown in **Table S1** and **Figures S5-S6** below. The uncaging yields of the photocages were determined using FTIR-ATR and HPLC-Abs, as shown in **Table S1**. The singlet excited state lifetime and triplet state lifetime of the BODIPY-TMGs were studied by TCSPC and nanosecond transient absorption, respectively (see **Table S1** and **Figures S8-S11**). **Table S2** shows the total photon absorption by each photocages under the irradiation of violet (405 nm) or green (530 nm) LEDs. The data was calculated from the extinction coefficients of each photocages.

Table S1. Summary of photophysical and photochemical characterizations.

TMG	λ_{abs} (nm)	λ_{em} (nm)	ε ($M^{-1}cm^{-1}$)	Φ_f	τ_f (ns)	τ_T (μs)	Φ_{UC} (%)[a]	Φ_{UC} (%)[b]
-Me-H	508	525	61 ± 3.0	0.37± 0.042	1.5	106	17 ± 0.73	16 ± 0.24
-Me-Br	528	553	59 ± 2.5	0.092 ± 0.010	0.61	52	11 ± 0.44	9.4 ± 0.12
MNPPOC	348	-	3.4 ± 0.18	-	-	-	14 ± 0.59	9.2 ± 0.18
NVOC	349	-	2.8 ± 0.17	-	-	-	4.9 ± 0.47[c]	5.7 ± 0.11[c]
CTMG	372	463	22 ± 1.8	0.33 ± 0.010	4.0	-	-	0.05 ± 0.012[c]

[a]Determined by HPLC-Abs; [b]Determined by FTIR-ATR; [c]Data obtained from the previous study [S4]

λ_{abs}, absorbance peak wavelength; λ_{em}, fluorescence peak wavelength; ε, extinction coefficient at peak absorption wavelength; Φ_f, fluorescence quantum yield; τ_T, fluorescence lifetime; τ_T, triplet excited state lifetime; Φ_{UC}, uncaging quantum yield.

Table S2. Summary of photon flux calculation.

	BODIPY-Me-H[a]	-Me-Br[a]	MNPPOC[b]	NVOC[b]	CTMG[b]
N	1.58×10^{17}	4.24×10^{17}	2.48×10^{15}	1.07×10^{15}	2.75×10^{16}
Φ_{abs}	0.37	1	0.0059	0.0025	0.065
Φ_{UC}	0.08	0.11	0.0481	0.057	0.0006
$N \times \Phi_{UC}$	1.27×10^{16}	4.66×10^{16}	1.19×10^{14}	6.10×10^{13}	1.65×10^{13}
$\Phi_{abs} \times \Phi_{UC}$	0.030	0.11	0.00028	0.00014	3.90×10^{-5}

[a]530 nm LED (10 mW/cm^2) was used in the calculation; [b]405 nm LED (10 mW/cm^2) was used in the calculation.

N, number of photons; Φ_{abs}, relative number of photons absorbed; Φ_{UC}, uncaging quantum yield.

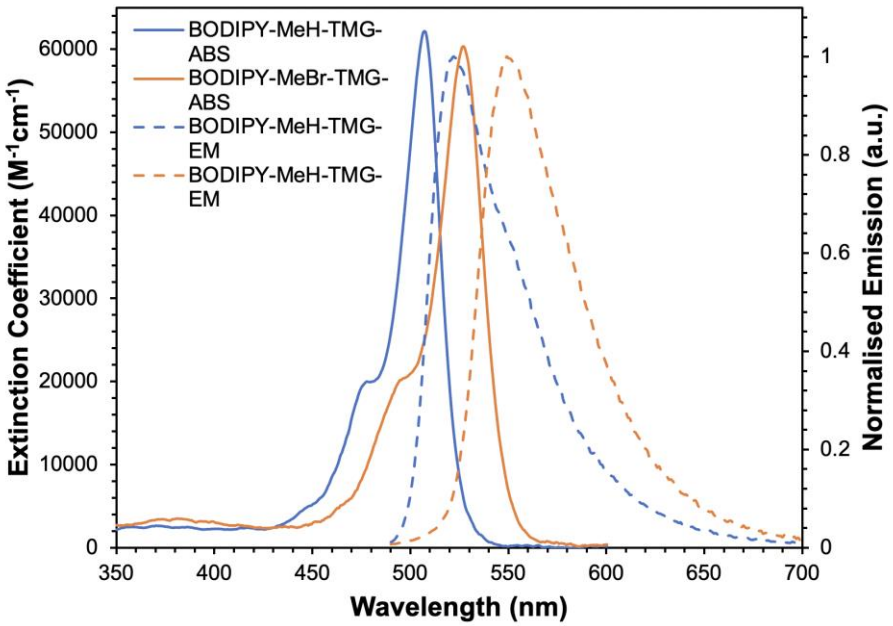


Figure S5. Steady-state absorption (solid line) and emission (dotted line) spectra of **BOIDPY-Me-H-TMG** (10^{-6} M) and **BODIPY-Me-Br-TMG** (10^{-6} M) in degassed acetonitrile.

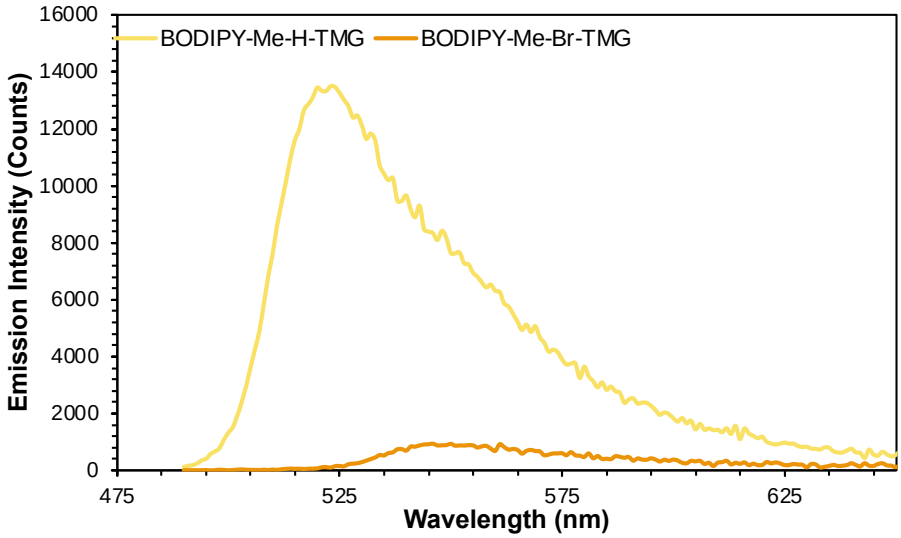


Figure S6. Steady-state emission spectra of **BOIDPY-Me-H-TMG** (10^{-6} M) and **BODIPY-Me-Br-TMG** (10^{-6} M) in degassed acetonitrile.

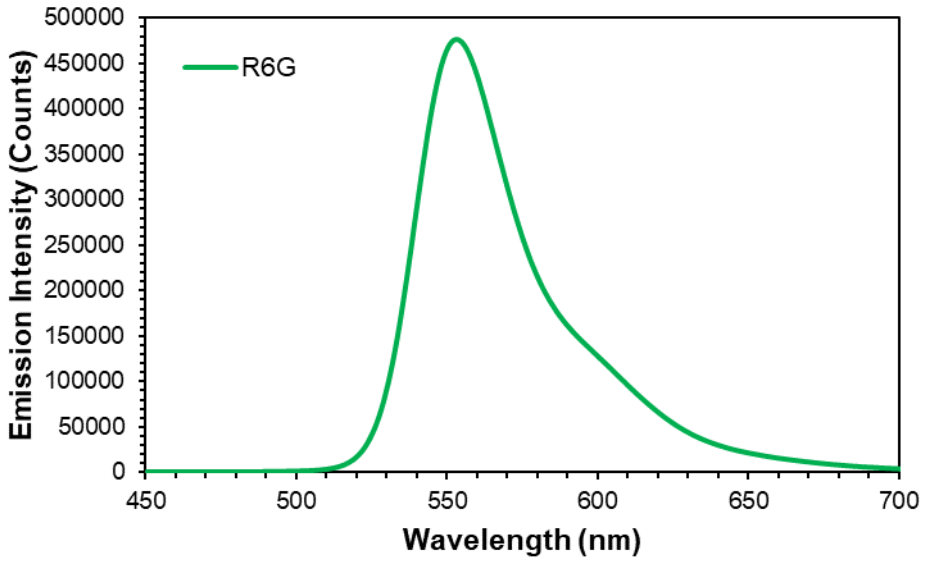


Figure S7. Emission spectrum of emission standard, R6G, in ethanol. Standard used to determine fluorescence quantum yield values provided in **Table S1**.

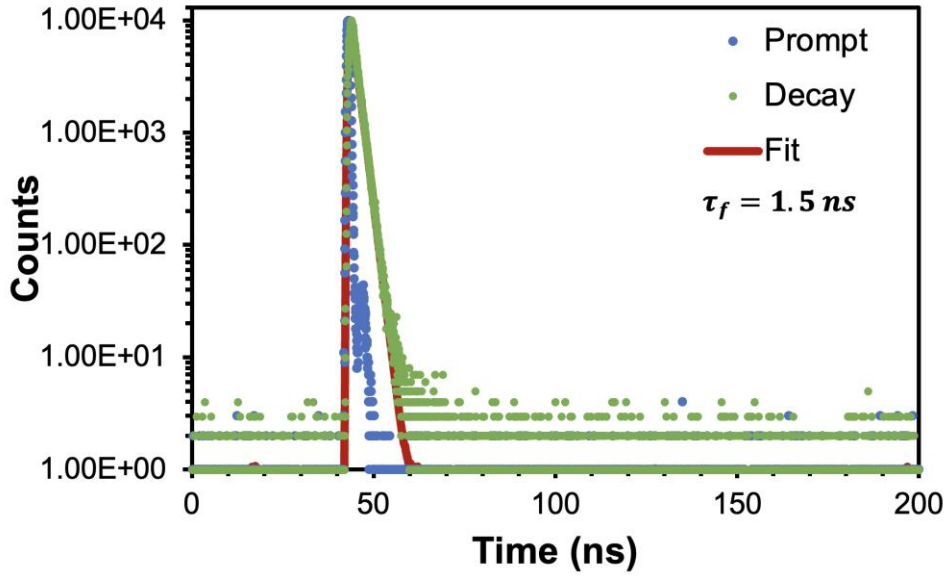


Figure S8. Singlet excited-state relaxation of **BODIPY-Me-H-TMG** (10^{-6} M) in degassed acetonitrile, measured using time-correlated single photon counting.

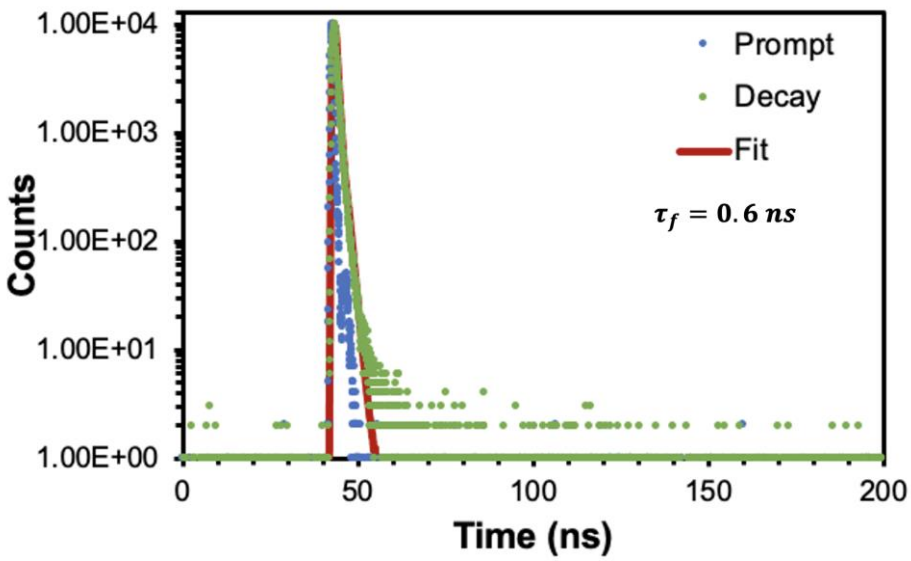


Figure S9. Singlet excited-state relaxation of **BODIPY-Me-Br-TMG** (10^{-6} M) in degassed acetonitrile, measured using time-correlated single photon counting.

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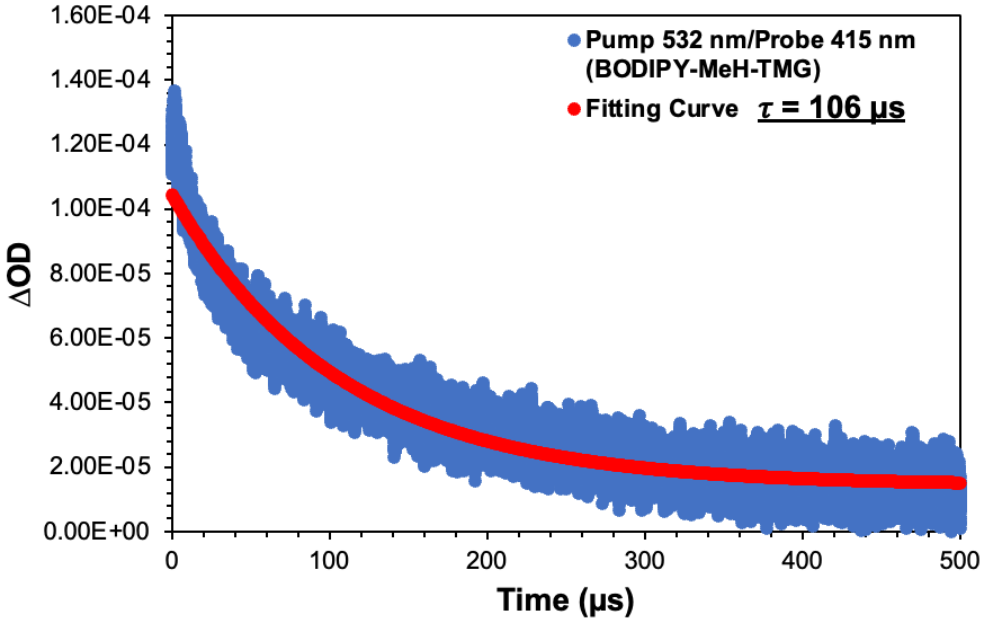


Figure S10. Nanosecond transient absorption data for **BODIPY-Me-H-TMG** collected in acetonitrile, excited at 532 nm, and monitored at 415 nm.

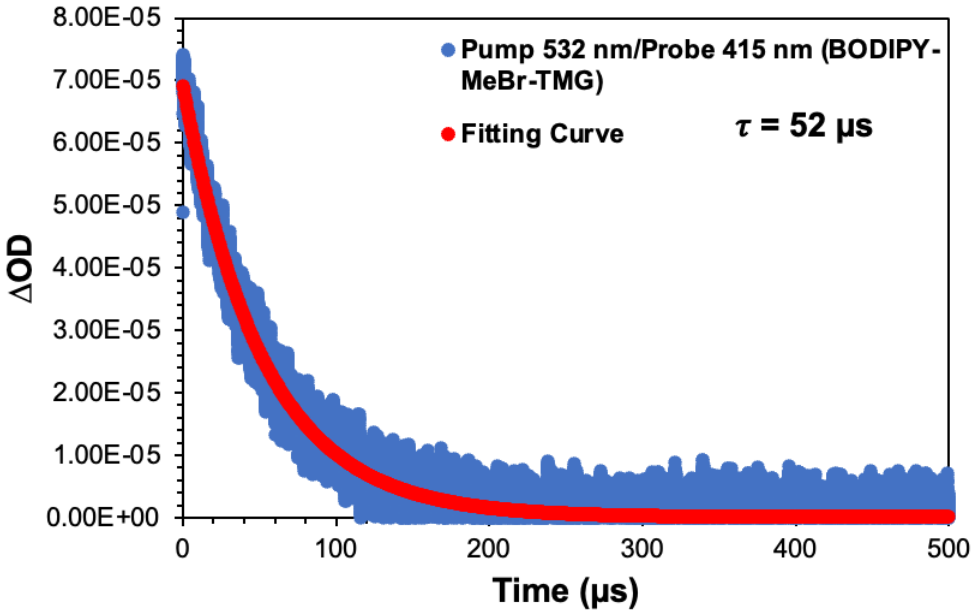


Figure S11. Nanosecond transient absorption data for **BODIPY-Me-Br-TMG** collected in acetonitrile, excited at 532 nm, and monitored at 415 nm.

Photopolymerization Kinetics

Photopolymerization of PETMP and TEGDA for **BODIPY-Me-H-TMG** and **-Me-Br-TMG** with addition of TEMPO (0-2 equivalents, eq.), as shown in **Figures S12-S14**. BODIPY-TMG (0.33 mol%) was dissolved in PETMP and TEGDA and placed between glass slides with a 100 μm spacer. The LED (530 nm, 40 mW/cm^2) was turned on 15s after the FTIR scans started. The conversion of C=C (3150 cm^{-1}) and S-H (2550 cm^{-1}) were calculated from **SE8**, where A_0 is the integration of C=C (3150 cm^{-1}) and S-H (2550 cm^{-1}) at T_0, and A_t is the integration at any given time.

$$\text{Conversion } (\rho) = (A_0 - A_t) / A_0 \qquad \textbf{(SE8)}$$

The photopolymerization kinetics of PETMP and TEGDA using MNPPOC-TMG is shown in **Figure S14 Tables S3-S5** provide summaries for the photopolymerization data of PETMP and TEGDA that is provided in **Figures 3B, 3C**, and **4A** in the main manuscript. The kinetics of anionic thiol-epoxy polymerization was summarized in **Figure S15** and **Table S4**.

Table S3. Summary of photopolymerization data in Figure 3B.

	BODIPY-Me-H-TMG			BODIPY-Me-Br-TMG		
LED on (s)	15	15	15	15	15	15
Conc. (mol%)	0.067	0.067	0.067	0.067	0.067	0.067
I_{LED} (mW/cm2)	10	5	1	10	5	1
$r_p^{C=C}$ (M/s)	1.03 ± 0.071	0.63± 0.054	0.17 ± 0.015	3.10 ±5 0.082	2.36 ± 0.034	0.92 ± 0.036
$r_p^{S–H}$ (M/s)	0.44 ± 0.016	0.24 ± 0.0087	0.06 ± 0.0066	1.27 ± 0.019	0.98 ± 0.014	0.32 ± 0.015
$\Delta\rho$	0.54 ± 0.0081	0.54 ± 0.011	0.55 ± 0.011	0.54 ± 0.0096	0.54 ± 0.013	0.56 ± 0.013
$\rho_{max}^{C=C}$	1	1	0.96	1	1	1
$\rho_{max}^{S–H}$	0.47	0.48	0.47	0.48	0.49	0.49

$r_p^{C=C}$, polymerization rate of acrylate (C=C); $r_p^{S–H}$, polymerization rate of thiol (S–H); $\Delta\rho$, difference between max conversions of acrylates and thiols; $\rho_{max}^{C=C}$, max conversion of acrylate (C=C); $\rho_{max}^{S–H}$, max conversion of thiol (S–H).

Table S4. Summary of photopolymerization data in Figure 3C.

	MNOPPC-TMG	NVOC-TMG	CTMG
LED on (s)	15	15	15
Conc. (mol%)	0.67	0.67	0.67
I (mW/cm2) @405 nm	100	100	100
$r_p^{C=C}$ (M/s)	0.11 ± 0.0056	0.0025 ± 0.00024	0.21 ± 0.0065
$r_p^{S–H}$ (M/s)	0.11 ± 0.020	0.0025 ± 0.00011	0.052 ± 0.0017
$\Delta\rho$	0.01 ± 0.00026	0.02 ± 0.00029	0.67 ± 0.0093
$\rho_{max}^{C=C}$	0.87	0.51	0.98
$\rho_{max}^{S–H}$	0.85	0.5	0.36

$r_p^{C=C}$, polymerization rate of acrylate (C=C); $r_p^{S–H}$, polymerization rate of thiol (S–H); $\Delta\rho$, difference between max conversions of acrylates and thiols; $\rho_{max}^{C=C}$, max conversion of acrylate (C=C); $\rho_{max}^{S–H}$, max conversion of thiol (S–H).

Table S5. Summary of photopolymerization data in Figure 4A.

	-Me-H-TMG		-Me-Br-TMG		MNPPOC-TMG	
LED on (s)	15	15	15	15	15	15
TEMPO eq	0	2	0	2	0	2
Conc. (mol%)	0.25	0.25	0.25	0.25	0.25	0.25
I (mW/cm^2)	40	40	40	40	40	40
$r_p^{C=C}$ (M/s)	1.47 ± 0.052	0.13 ± 0.0043	3.35 ± 0.11	0.078 ± 0.0022	0.0095 ± 0.00021	0.0096 ± 0.00032
$r_p^{S–H}$ (M/s)	0.69 ± 0.018	0.13 ± 0.0036	1.18 ± 0.034	0.078 ± 0.0017	0.0095 ± 0.00033	0.0096 ± 0.0003
$\Delta\rho$	0.47	0	0.5	0	0	0
$\rho_{max}^{C=C}$	0.99	0.83	1	0.65	0.63	0.63
$\rho_{max}^{S–H}$	0.52	0.83	0.5	0.65	0.63	0.63

$r_p^{C=C}$, polymerization rate of acrylate (C=C); $r_p^{S–H}$, polymerization rate of thiol (S–H); $\Delta\rho$, difference between max conversions of acrylates and thiols; $\rho_{max}^{C=C}$, max conversion of acrylate (C=C); $\rho_{max}^{S–H}$, max conversion of thiol (S–H).

Table S6. Summary of photopolymerization data in Figure 4C.

	TMG 1 eq.	TMG 0.3 eq.	TMG 0.2 eq.	TMG 0.1 eq.	-Me-H-TMG	-Me-Br-TMG
LED on (s)	15	15	15	15	15	15
Conc. (mol%)	2.6	0.78	0.52	0.26	2.6	2.6
I (mW/cm2)	40	40	40	40	40	40
r_p^{epox} (M/min)	0.319 ± 0.0080	0.156 ± 0.0036	0.082 ± 0.0018	0.008 ± 0.00020	0.095 ± 0.0018	0.040 ± 0.0011
$r_p^{S–H}$ (M/min)	0.3167 ± 0.011	0.1557 ± 0.0051	0.0819 ± 0.0030	0.0077 ± 0.00020	0.0947 ± 0.0030	0.0389 ± 0.0011

$r_p^{C=C}$, polymerization rate of acrylate (C=C); $r_p^{S–H}$, polymerization rate of thiol (S–H); $\Delta\rho$, difference between max conversions of acrylates and thiols; $\rho_{max}^{C=C}$, max conversion of acrylate (C=C); $\rho_{max}^{S–H}$, max conversion of thiol (S–H).

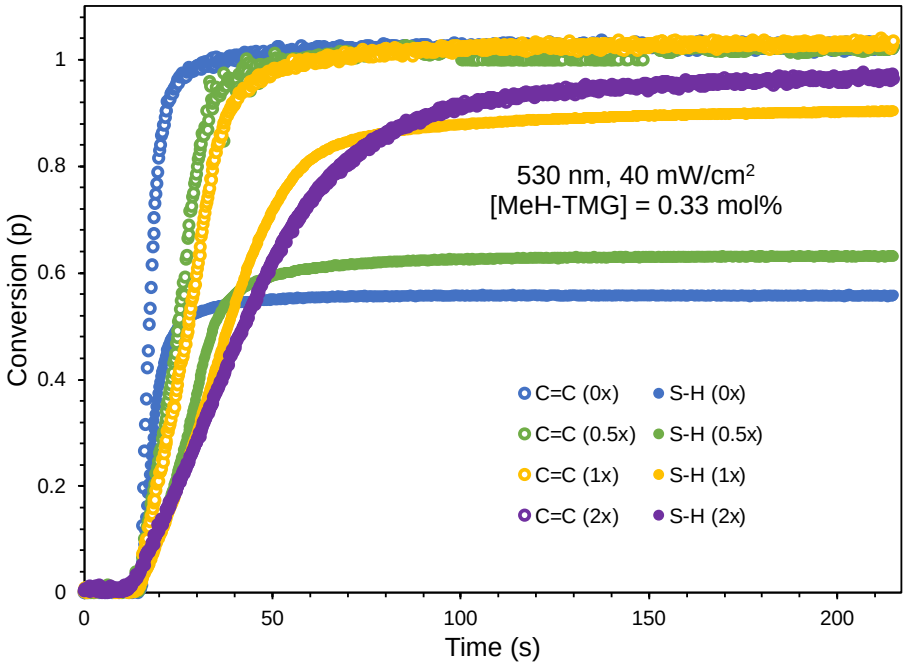


Figure S12. Photopolymerization of PETMP and TEGDA for **BODIPY-Me-H-TMG** (0.33 mol%) with TEMPO (0 - 2 eq) at a sample thickness of 100 µm.

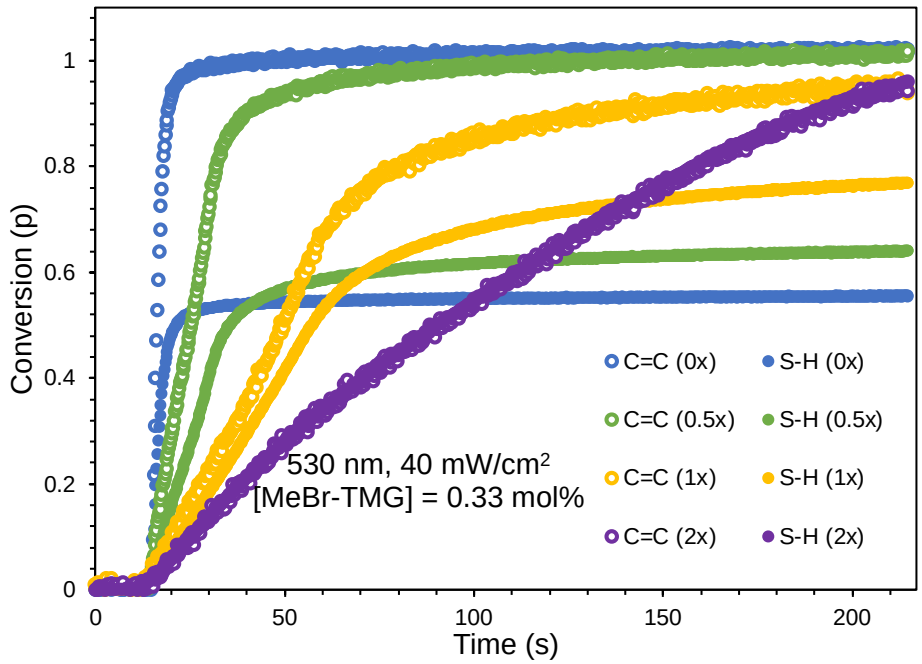


Figure S13. Photopolymerization of PETMP and TEGDA for **BODIPY-Me-Br-TMG** (0.33 mol%) with TEMPO (0 - 2 eq) at a sample thickness of 100 µm.

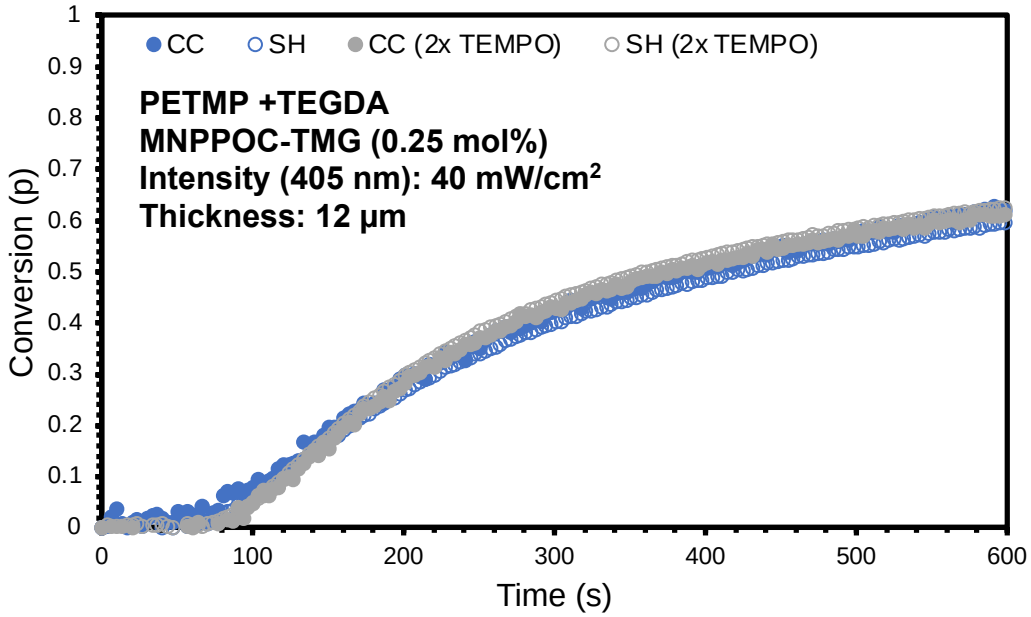


Figure S14. Photopolymerization kinetics for PETMP and TEGDA using **MNPPOC-TMG** with and without the presence of two equivalents of TEMPO as a radical scavenger.

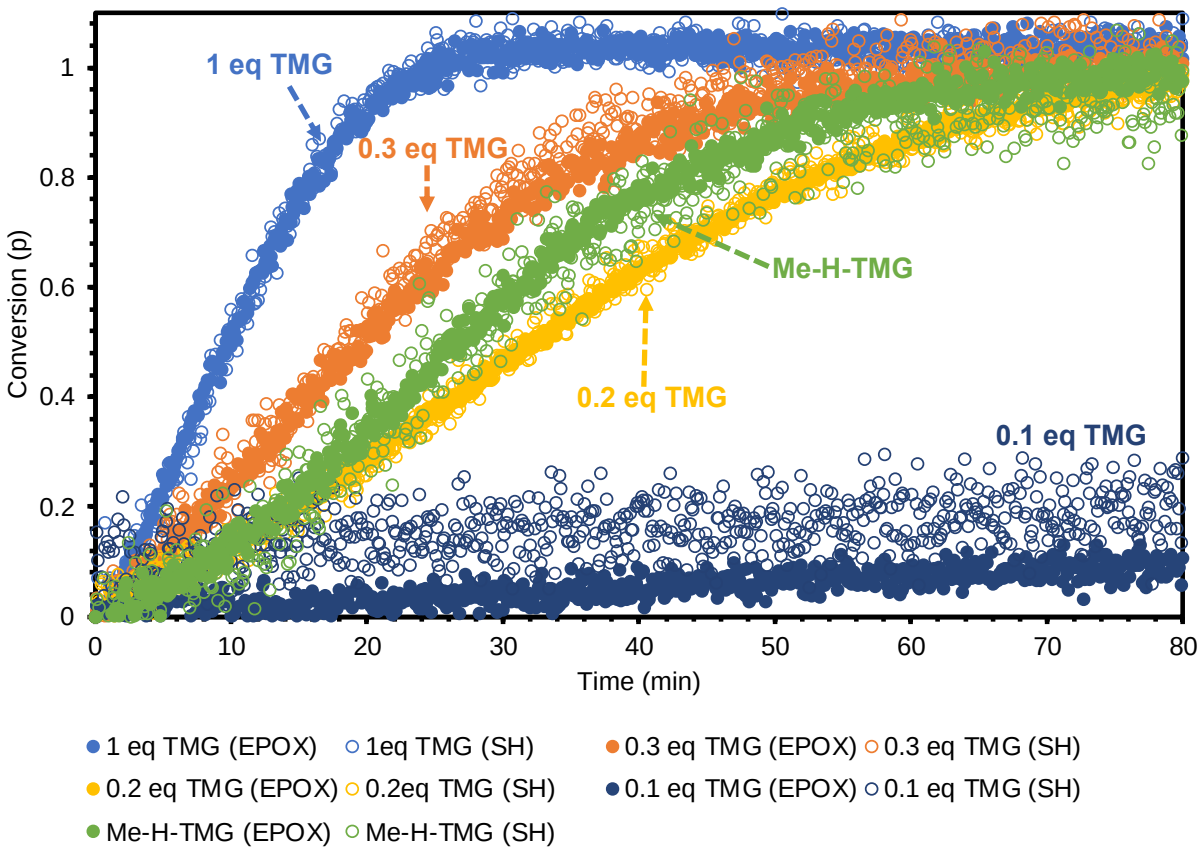


Figure S15. Kinetics of anionic thiol-epoxy ring-opening polymerizations using **BODIPY-Me-H-TMG** (2.6 mol%, 1 eq) and physical addition of TMG (0.26, 0.52, 0.78, 2.6 mol%) as control experiments. Measurements performed using an ATR RT-FTIR configuration.

Uncaging Quantum Yield (Φ_{UC}) Characterization

The uncaging yield of **BODIPY-Me-H-TMG**, **-Br-TMG**, and **MNPPOC-TMG** were determined using FTIR-ATR and HPLC-Abs. The decomposition kinetics of the carbamate bonding (1550 cm^{-1}) upon LED irradiation (365, 470, and 530 nm) is shown in **Figures S16-S18**. The calibration curve for TMG used in the HPLC-Abs measurements is shown in **Figure S19**. The photolysis of **BODIPY-Me-H-TMG** in solution is shown in **Figure S20**.

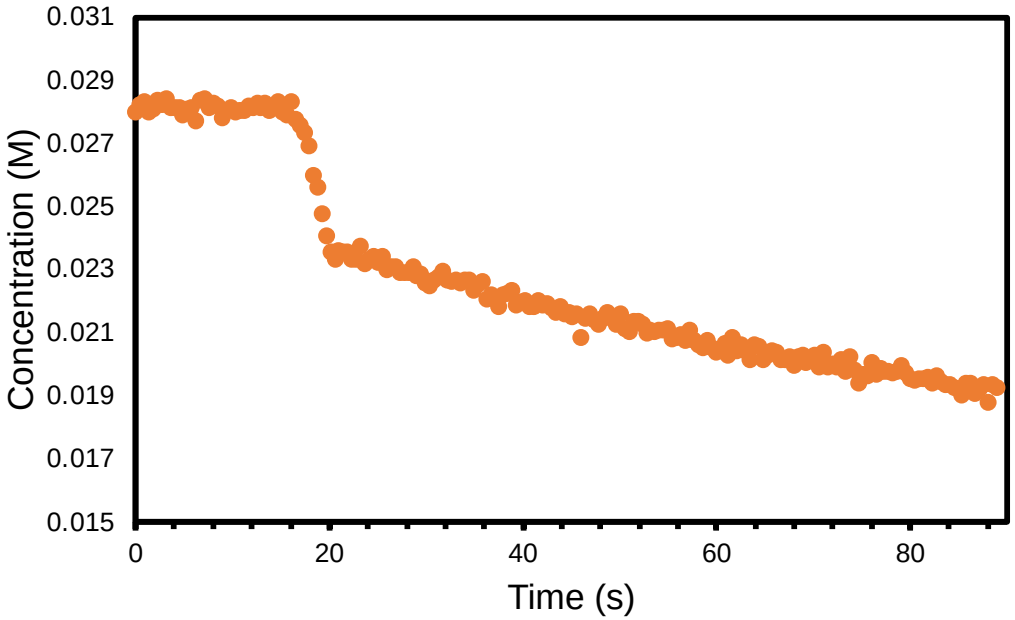


Figure S16. Analysis of the carbamate bond decomposition at 1550 cm^{-1} from real-time Fourier transform infrared spectroscopy for **BODIPY-Me-H-TMG** upon exposure to a 470 nm LED at an intensity of 4 mW/cm^2. **BODIPY-Me-H-TMG** (0.5 mol%) was dissolved in 3,6-dioxa-1,8-octanedithiol (DODT). LED was turned on 15 seconds after the measurement and the first 3 seconds (17 - 20s) after turning the LED 'on' were used to calculate the uncaging quantum yield (Φ_{UC}).

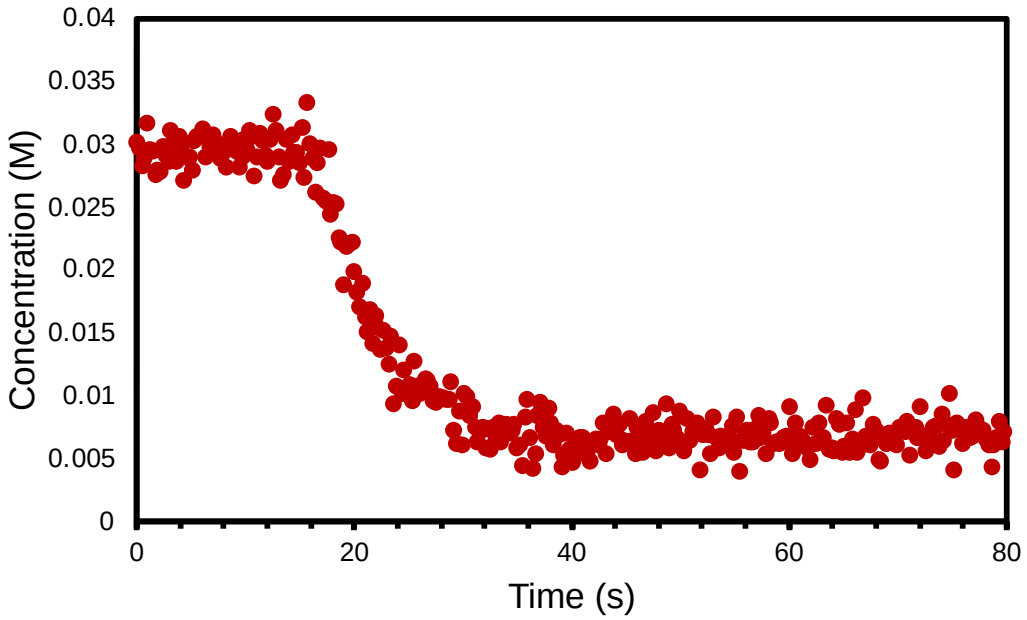


Figure S17. Analysis of the carbamate bond decomposition at 1550 cm^{-1} from real-time Fourier transform infrared spectroscopy for **BODIPY-Me-Br-TMG** upon exposure to a 530 nm LED at an intensity of 4 mW/cm^2. **BODIPY-Me-Br-TMG** (0.5 mol%) was dissolved in 3,6-dioxa-1,8-octanedithiol (DODT). LED was turned on 15 seconds after the measurement and the first 4 seconds (16 – 20s) after turning the LED 'on' were used to calculate the uncaging quantum yield (Φ_{UC}).

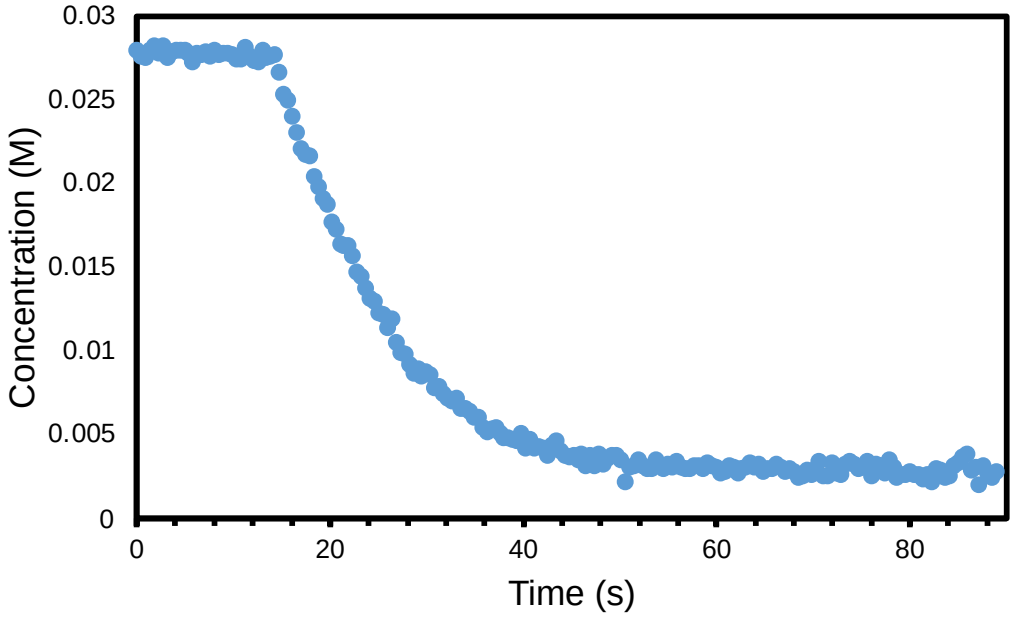


Figure S18. Analysis of the carbamate bond decomposition at 1550 cm^{-1} from real-time Fourier transform infrared spectroscopy for MNPPOC-TMG upon exposure to a 365 nm LED at an intensity of 40 mW/cm^2. MNPPOC-TMG (0.5 mol%) was dissolved in 3,6-dioxa-1,8-octanedithiol (DODT). LED was turned on 15 seconds after the measurement and the first 6 seconds (16 – 22s) after turning the LED 'on' were used to calculate the uncaging quantum yield (Φ_{UC})..

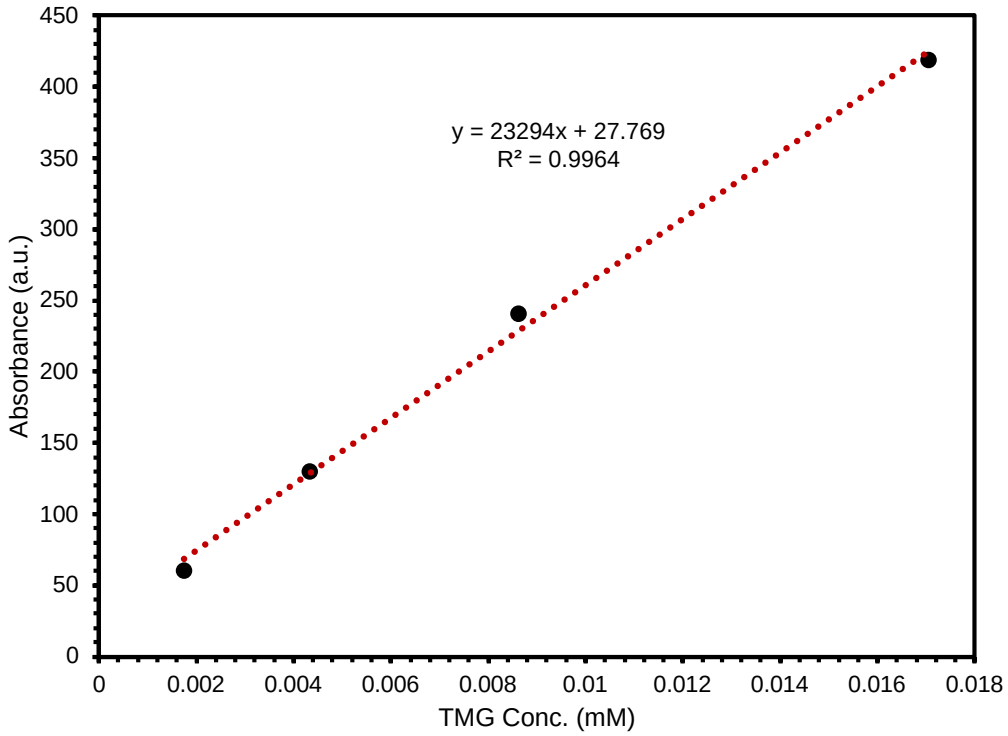


Figure S19. Calibration curve of TMG used in the calculation of Φ_{UC}.

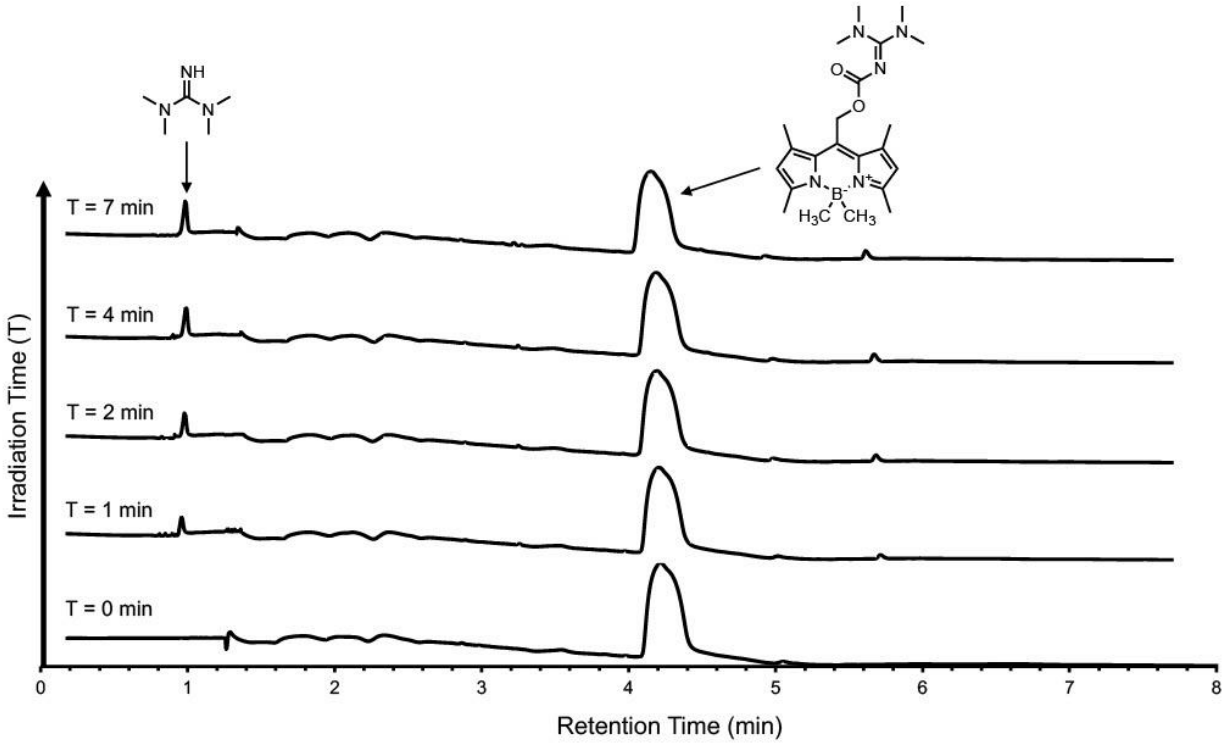


Figure S20. HPLC traces of **BODIPY-Me-H-TMG** (0.34 mM) irradiated with green LED (530 nm, 10 mW/cm^2) in CH_3CN:H_2O (*v*:*v* = 4:1). The signal was recorded with the HPLC UV-vis detector monitoring 220 nm.

Photorheology-FTIR

To demonstrate the influence of radical vs. anionic polymerization mechanism on mechanical properties, we employed photorheology to characterize the storage (*G'*) and loss (G)" moduli of a resin comprising bifunctional monomers, tetra(ethylene glycol) diacrylate (TEGDA) and 3,6-dioxa-1,8-octanedithiol (DODT), both with and without TEMPO using the same green LED for irradiation (17 mW/cm^2), as shown in **Figure 6** in the main manuscript. The photopolymerization kinetics of the resin was also monitored under identical conditions using RT-FTIR, showing faster kinetics in the absence of TEMPO along with a difference in maximum C=C and S–H conversion ($\Delta\rho \approx 0.2$), which is indicative of ene-ene chain-growth propagation. In contrast a $\Delta\rho \approx 0$ was observed when 2 equivalents of TEMPO relative to **BODIPY-Me-H-TMG** was present in the resin.

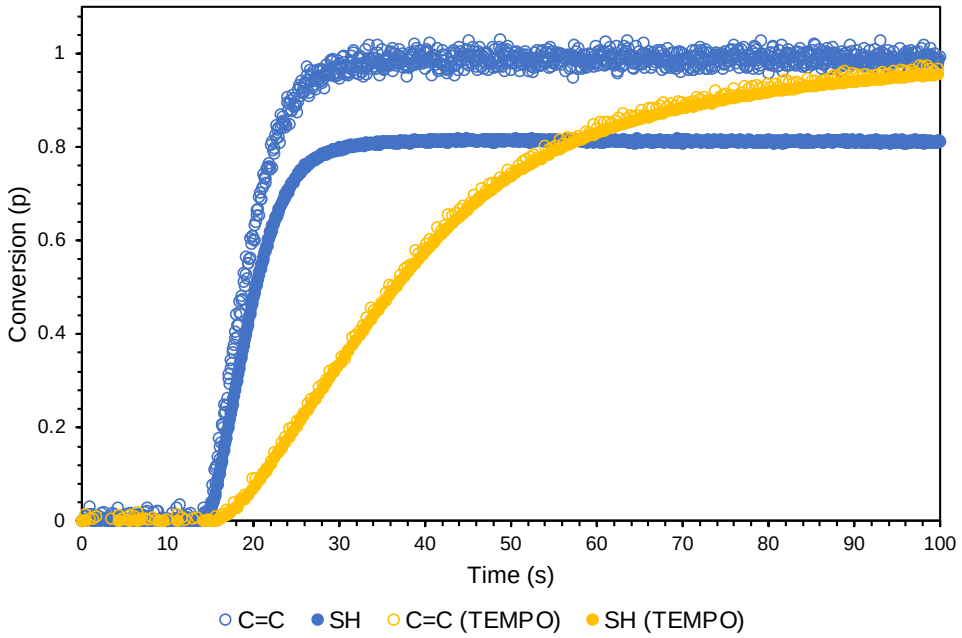


Figure S21. RT-FTIR monitoring of a photopolymerization comprising DODT, TEGDA, **BODIPY-Me-H-TMG** (0.25 mol%), and TEMPO (0 or 2 equivalents relative to BODIPY) at a sample thickness of 100 μm and a green LED intensity of 17 mW/cm^2.

CHARACTERIZATION

^{1}H & ^{13}C NMR and mass spectra

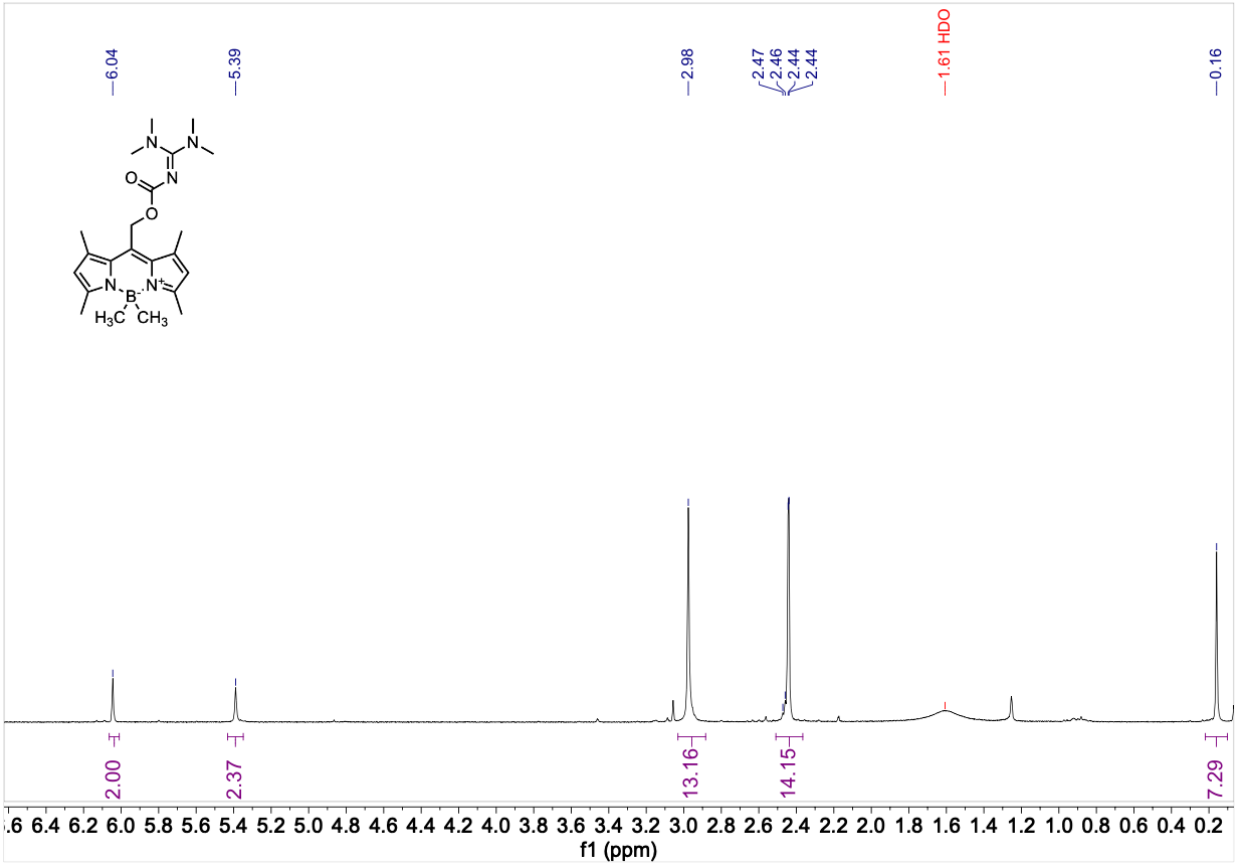


Figure S22. ^{1}H NMR of **BODIPY-Me-H-TMG** in d^{6}-DMSO.

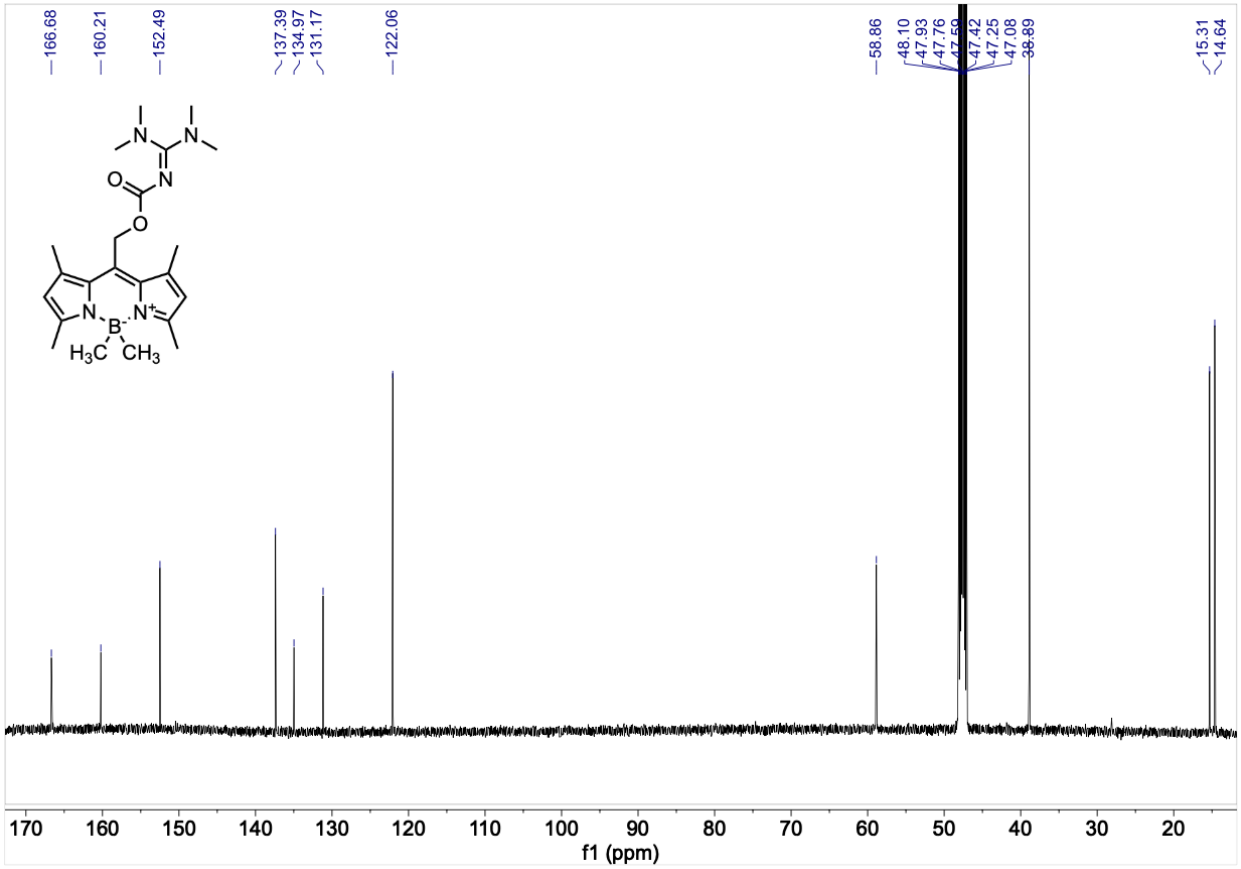


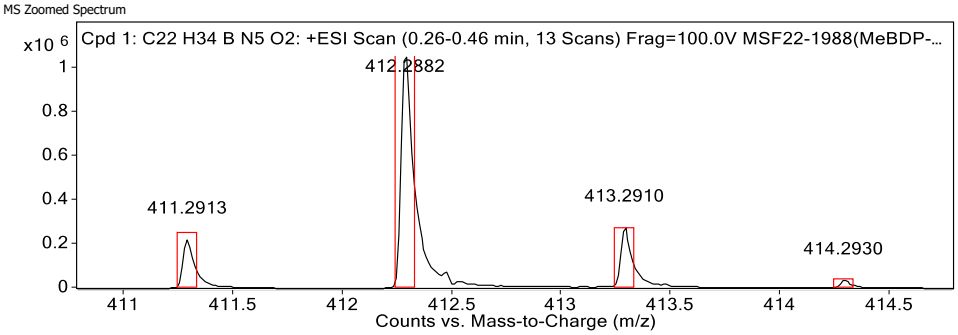
Figure S23. ^{13}C NMR of **BODIPY-Me-H-TMG** in d^6-DMSO.

Target Compound Screening Report

Results Acquired by The University of Texas at Austin Mass Spectrometry Facility

Data File	MSF22-1988(MeBDP-TMG)_hrESIpos1.d	**Sample Name**	1988(MeBDP-TMG)	**Comment**	1988(MeBDP-TMG)
Position	P1-E5	**Instrument Name**	Instrument 1	**User Name**	
Acq Method	FIA_pos.m	**Acquired Time**	11/30/2022 1:28:25 PM	**DA Method**	KS.m

MS Zoomed Spectrum



MS Spectrum Peak List

Obs. m/z	Calc. m/z	Charge	Abundance	Formula	Ion Species	Tgt Mass Error (ppm)
411.2913	411.2915	1	221112	C22H34BN5O2	(M+H)+	0.47
412.2882	412.2882	1	1072086	C22H34BN5O2	(M+H)+	0.04
413.2910	413.2910	1	275710	C22H34BN5O2	(M+H)+	0.02
414.2930	414.2937	1	35099	C22H34BN5O2	(M+H)+	1.66
415.2858	415.2963	1	4058	C22H34BN5O2	(M+H)+	25.3
416.3541	416.2989	1	1658	C22H34BN5O2	(M+H)+	-132.59

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Figure S24. HRMS (ESI) of **BODIPY-Me-H-TMG**.

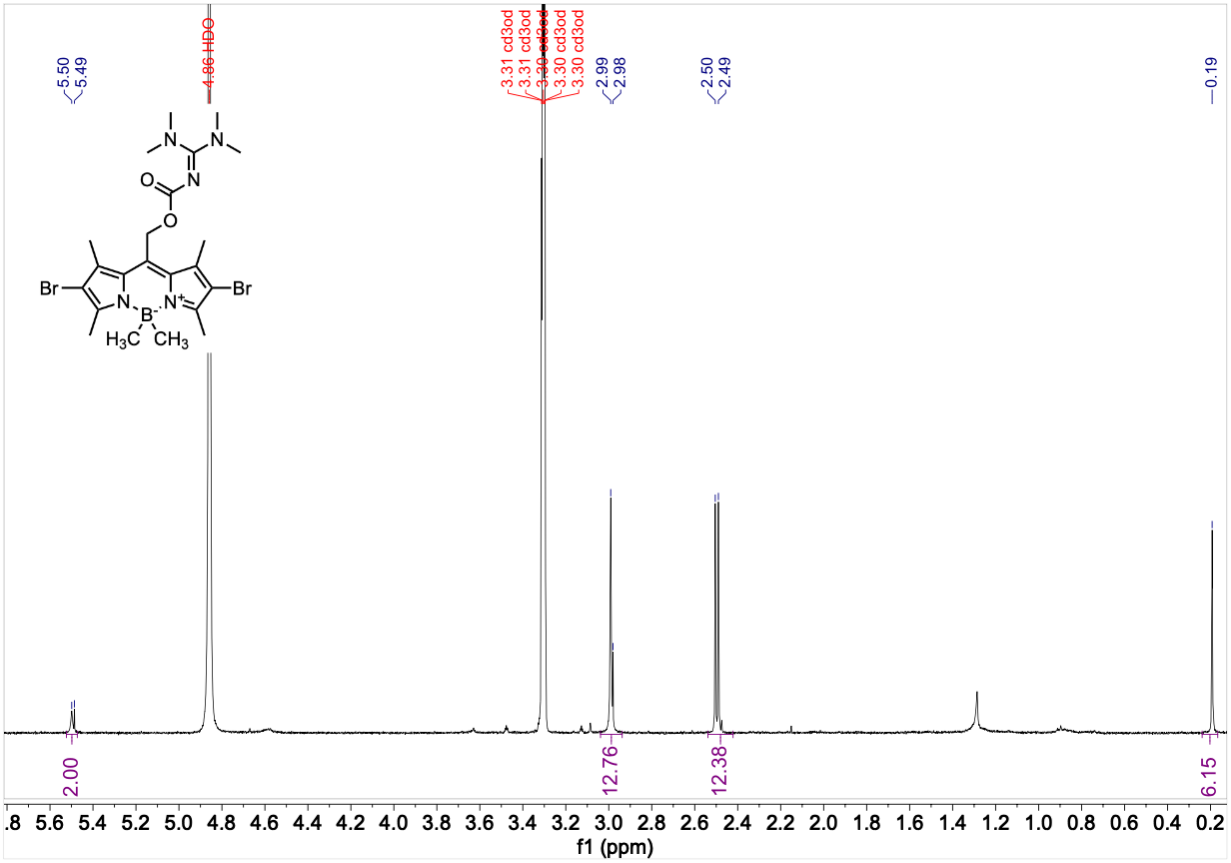


Figure S25. ^{1}H NMR of **BODIPY-Me-Br-TMG** in d^{6}-DMSO.

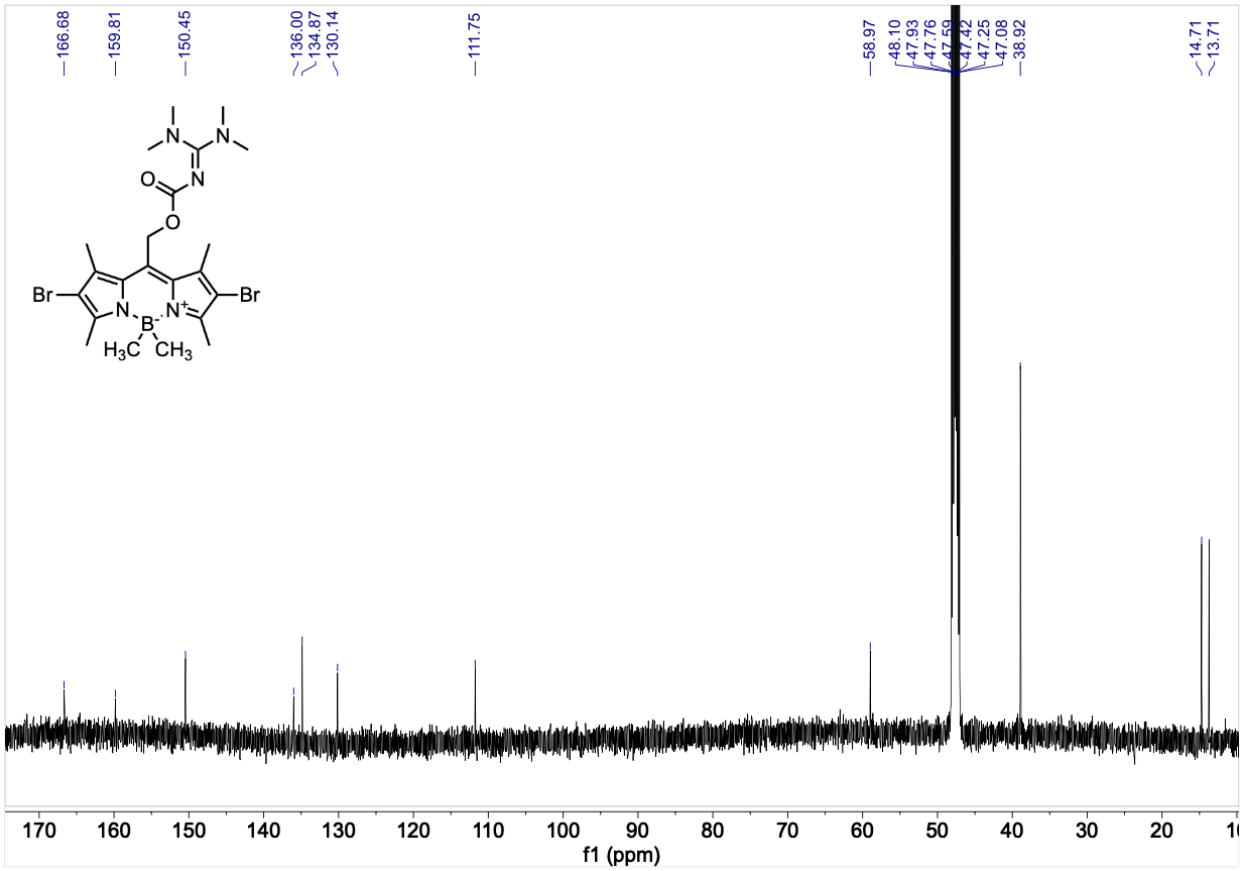


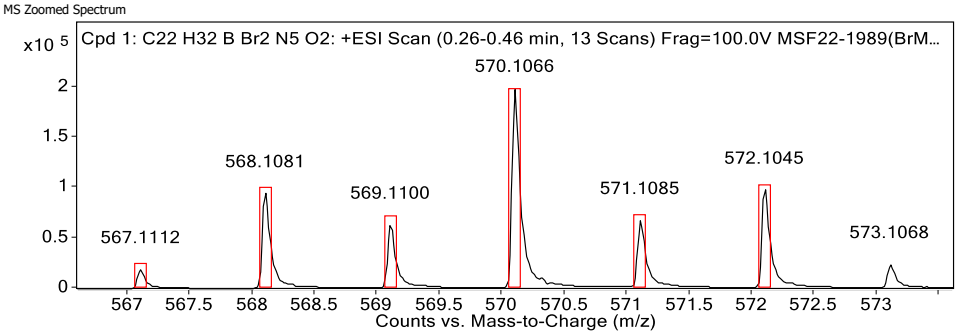
Figure S26. ^{13}C NMR of **BODIPY-Me-Br-TMG** in d^{6}-DMSO.

Target Compound Screening Report

Results Acquired by The University of Texas at Austin Mass Spectrometry Facility

Data File	MSF22-1989(BrMeBDP-TMG)_hrESIpos1.d	**Sample Name**	1989(BrMeBDP-TMG)	**Comment**	1989(BrMeBDP-TMG)
Position	P1-E6	**Instrument Name**	Instrument 1	**User Name**	
Acq Method	FIA_pos.m	**Acquired Time**	11/30/2022 1:30:29 PM	**DA Method**	KS.m

MS Zoomed Spectrum



MS Spectrum Peak List

Obs. m/z	Calc. m/z	Charge	Abundance	Formula	Ion Species	Tgt Mass Error (ppm)
567.1112	567.1125	1	18781	C22H32BBr2N5O2	(M+H)+	2.36
568.1081	568.1093	1	94150	C22H32BBr2N5O2	(M+H)+	2.01
569.1100	569.1110	1	62920	C22H32BBr2N5O2	(M+H)+	1.83
570.1066	570.1073	1	197393	C22H32BBr2N5O2	(M+H)+	1.29
571.1085	571.1095	1	67584	C22H32BBr2N5O2	(M+H)+	1.74
572.1045	572.1057	1	97620	C22H32BBr2N5O2	(M+H)+	2.05
573.1068	573.1081	1	23842	C22H32BBr2N5O2	(M+H)+	2.3
574.1099	574.1107	1	3078	C22H32BBr2N5O2	(M+H)+	1.46
575.1016	575.1133	1	534	C22H32BBr2N5O2	(M+H)+	20.27
943.9921			898194			

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Agilent Technologies

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Figure S27. HRMS (ESI) of **BODIPY-Me-Br-TMG**.

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