

# **Supplementary Information: Substituent Effects in Iniferter PhotoPolymerization. Can Bond Homolysis Be Enhanced by Electronics?**

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## **Experimental**

### **Materials and Methods**

All reagents were purchased from commercial sources and used as received unless otherwise specified.

### **Nuclear Magnetic Spectroscopy**

All nuclear magnetic resonance (NMR) was performed on a Bruker 200, 300, or 500 MHz spectrometer.

### **UV-Vis Spectroscopy**

All UV-Vis spectroscopy was performed on a Perkin Elmer Lambda 35 UV/VIS Spectrometer.

### **Size Exclusion Chromatography with tetrahydrofuran (THF) as the eluent**

All size exclusion chromatography (SEC) was performed on an Agilent 1260 gel permeation chromatography system (GPC) equipped with an isocratic pump, a degasser, an auto-sampler, a guard and 2 x PL Gel Mixed B columns, and a refractive index detector and viscometer. The eluent was THF running at 1mL/min at 30 °C. The system was calibrated with poly(methyl methacrylate) (PMMA) standards in the range of 617,000 to 1,010.

### **Size Exclusion Chromatography with N,N-dimethylformamide (DMF) as the eluent**

All size exclusion chromatography (SEC) was performed on an Agilent 1260 gel permeation chromatography system (GPC) equipped with an isocratic pump, a degasser, an auto-sampler, a guard and 2 x PL Gel Mixed B columns, and a refractive index detector and viscometer. The eluent was DMF running at 1mL/min at 50 °C. The system was calibrated with poly(methyl methacrylate) (PMMA) standards in the range of 617,000 to 1,010.

### **Cyclic Voltammetry**

Cyclic voltammetry was used to estimate the redox potential of the compounds, which was performed using a CHI 700E potentiostat (CH Instruments, Austin, TX). A three-electrode setup was used for the voltammetric experiment, with a 3 mm diameter glassy carbon electrode as the working electrode, Ag/AgCl (3 M Ag/AgCl) as the reference electrode, and Pt wire as the counter electrode. The compound of interest was dissolved in acetonitrile containing 0.1 M

TBAPF<sub>6</sub>. The solution was degassed by bubbling N<sub>2</sub> for 20 min before each voltammetric experiment. To minimize the error from the junction potential, the potential of the reference electrode was calibrated by running a voltammetry with ferrocene spiked into the solution at the end of each experiment. The half-wave potential of the reversible wave for ferrocene, corresponding to  $E^0 = 0.4$  V vs SHE, was used for the calibration<sup>23</sup>.

### Construction of Photoreactors

Custom built photoreactors were made by wrapping and attaching a 5 m LED strip (Lighting Ever brand Blue LED) in a helical pattern inside a metal cylinder of diameter 15 cm.

### Characterization of Photoreactors

The emission spectra of the LED photoreactors were characterized using a Princeton Instruments SP2300 300 mm spectrograph equipped with a 300 groove per mm grating blazed at 500 nm and a SpectraPro 512 × 512 BUUV electron-multiplying CCD. The power intensity of each LED based photoreactor was determined using a wavelength-tunable Thorlabs PM100A meter with a S120VC silicon photodiode. The blue LED photoreactor had a peak at 440 ± 20 nm and intensity of 11.6 ± 0.3 mW/cm<sup>2</sup>. The green LED photoreactor had a peak at 520 ± 30 nm and intensity of 5.9 ± 0.3 mW/cm<sup>2</sup>. The red LED photoreactor had a peak at 630 ± 20 nm and intensity of 4.7 ± 0.3 mW/cm<sup>2</sup>.

### 2-Cyanopropyl-2-yl(4-methoxy) Dithiobenzoate

A mixture of Mg (0.25 g) in dry THF (40 mL) and a pinch of iodine was deoxygenated for 20 minutes in a 150 mL two neck round bottom flask equipped with a condenser and a magnetic stirrer bar. A solution of 4-bromoanisole (1.25 mL, 10 mmol) in 10 mL of dry THF was added to the deoxygenated system while purging nitrogen. The reaction mixture was heated gently to initiate the reaction and let stirred for 3 h. After 3 hours, carbon disulfide (1 mL, 16.7 mmol) was added dropwise to the solution and stirred for further 3 hrs. The excess solvent was removed under vacuum and resulting deep red viscous liquid was dissolved in 0.1 M K<sub>2</sub>CO<sub>3</sub> solution (100 mL). Dissolved red color solvent was then filtered and washed with ethyl ether (2 x 50 mL) to remove unreacted materials and dissolved I<sub>2</sub> and poured into a flask equipped with a magnetic stirrer. An aqueous solution of 1 N iodine ( 2 g of KI and 1.27 g of I<sub>2</sub> crystals in 10 mL of distilled water) was added to the reaction mixture until the solution started to change color from dark red to pink as the formed disulfide get precipitated. To quench the excess I<sub>2</sub> few crystals of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> was added. The resultant aqueous solution was extracted with methylene chloride and dried over anhydrous sodium sulfate. The excess solvent was evaporated under vacuum to obtain the disulfide bridge compound as a red solid.

The resultant bridge compound (0.65 g, 1.8 mmol) and AIBN (0.34 g, 2.1 mmol) was dissolved in 120 mL of ethyl acetate in a 250 mL two neck round bottom flask equipped with a condenser and a magnetic stirrer. The solution was degassed for 20 minutes and refluxed (100 °C) under nitrogen atmosphere for 24 h. The reaction was monitored with TLC and once all the bridge compounds converted to product the reaction was stopped and the excess solvent was removed under vacuum. The crude product was purified by a flash chromatography (hexane/ethyl ether=7:3) obtaining reddish pink color crystalline solid (yield 86%)

## **Methyl Derivative**

Following the procedure for compound CPMODP, the disulfide bridge compound was synthesized using 4-bromoanisole (1.23 mL) as starting material.

The CPMDP product was obtained using the disulfide bridged compound (0.54 g, 1.6 mmol) and AIBN (0.32 g, 2.0 mmol) after a flash chromatography (hexane/ethyl ether=7:3) as a reddish pink color crystalline solid (yield 88%)

## **Trifluoromethoxy Derivative**

Following the procedure for compound CPMODP, the disulfide bridge compound was synthesized using 4-bromoanisole (1.49 mL) as starting material.

The CPMDP product was obtained using the disulfide bridged compound (0.82 g, 1.2 mmol) and AIBN (0.32 g, 1.9 mmol) after a flash chromatography (hexane/ethyl ether=7:3) as a reddish pink color crystalline solid (yield 77%)

## **Polymerization of methyl methacrylate (MMA)**

MMA (15.3mmol, 1.53g), and the chain transfer agent of choice (0.076 mmol) were dissolved into 50% by weight DMSO. The solutions were purged with nitrogen gas and left to stir under blue light irradiation. At various time intervals, small samples were removed from the reaction vessel to monitor the progression of the reaction by use of NMR and GPC using THF as the eluent.

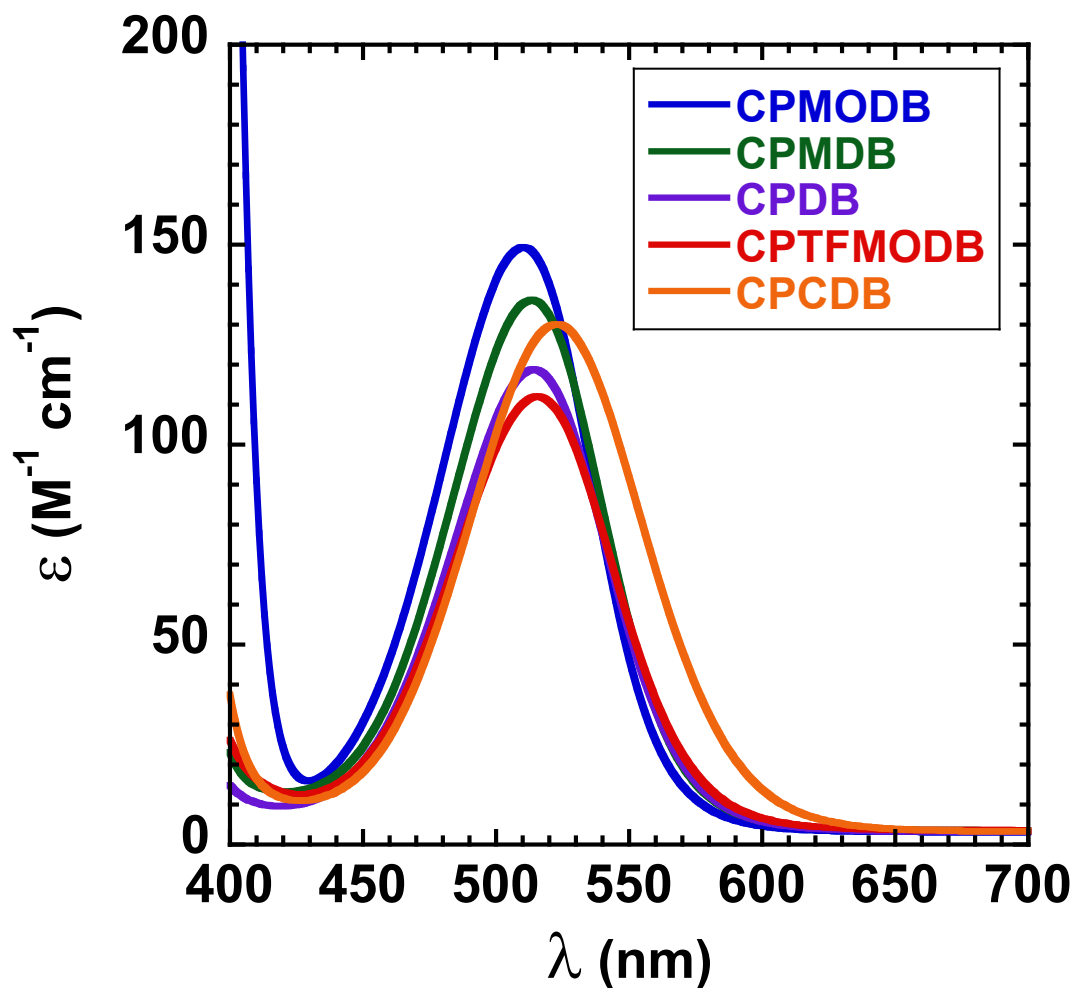
## **PET-RAFT Polymerization of methyl methacrylate (MMA)**

MMA (15.3 mmol, 1.53 g) and CPDB (0.076 mmol, 0.0169 g) were dissolved into 50% by weight DMSO. A 1000 ppm stock solution of tris[2-phenylpyridinato-C2,N]iridium(III) (Ir(ppy)<sub>3</sub>) in DMSO was made. 0.1mL of the stock Ir(ppy)<sub>3</sub> solution were added to the reaction flask The solutions were purged with nitrogen gas and left to stir under blue light irradiation for 11 hours. The progression of the reaction by use of NMR and GPC using THF as the eluent.

## **Synthesis of PMMA-HEMA Copolymer**

Macro CTA was synthesized from the above procedure using MMA:CPMODB in a 50:1 molar ratio. After reaching 85% conversion, hydroxyethyl methacrylate was added to the solution in addition to DMSO (1:200 molar ratio). The Flask was then purged with nitrogen gas and stirred under blue light irradiation for 4 hours. The initial macro-CTA and HEMA extended polymer conversion was determined by NMR and molecular weight data was gathered using GPC using DMF as an eluent.

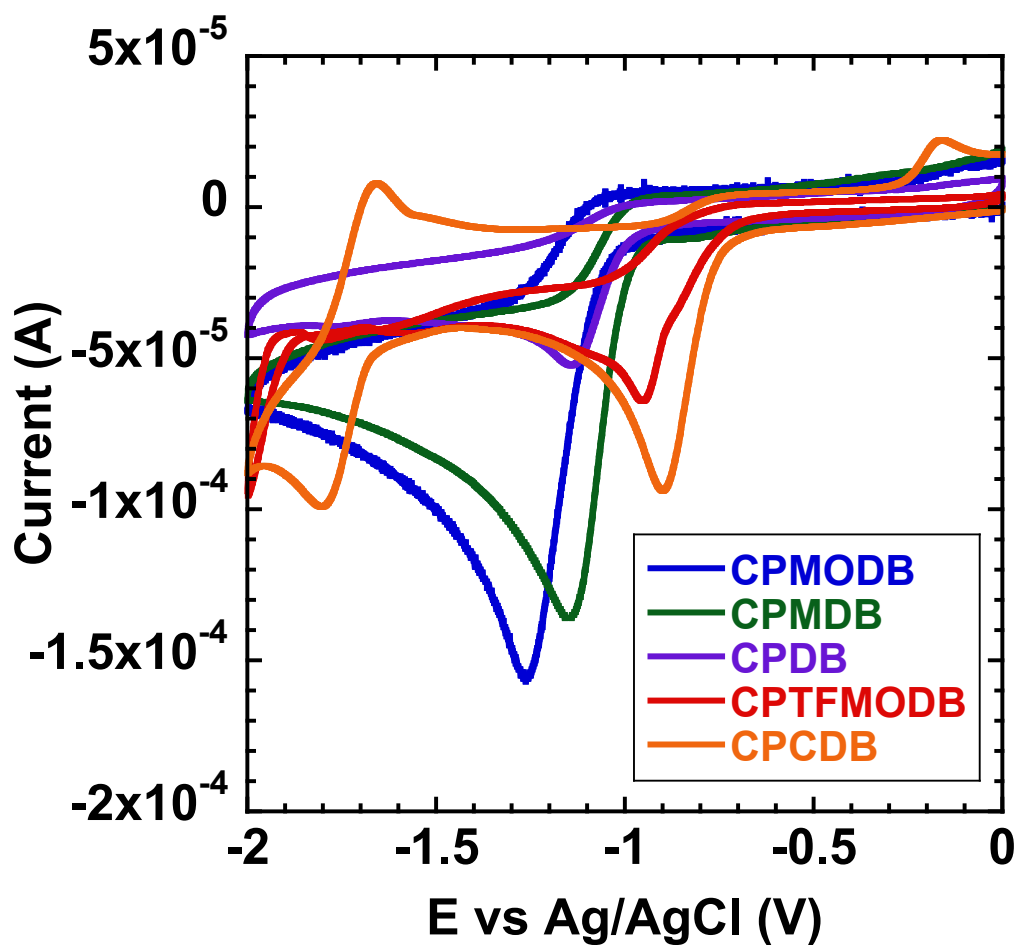
## Supplementary Data



**Figure S1:** The UV-Vis absorbance spectrum of each chain transfer agent.

**Table S1:** Calculated peak absorbance wavelength in the visible region for each transfer agent.

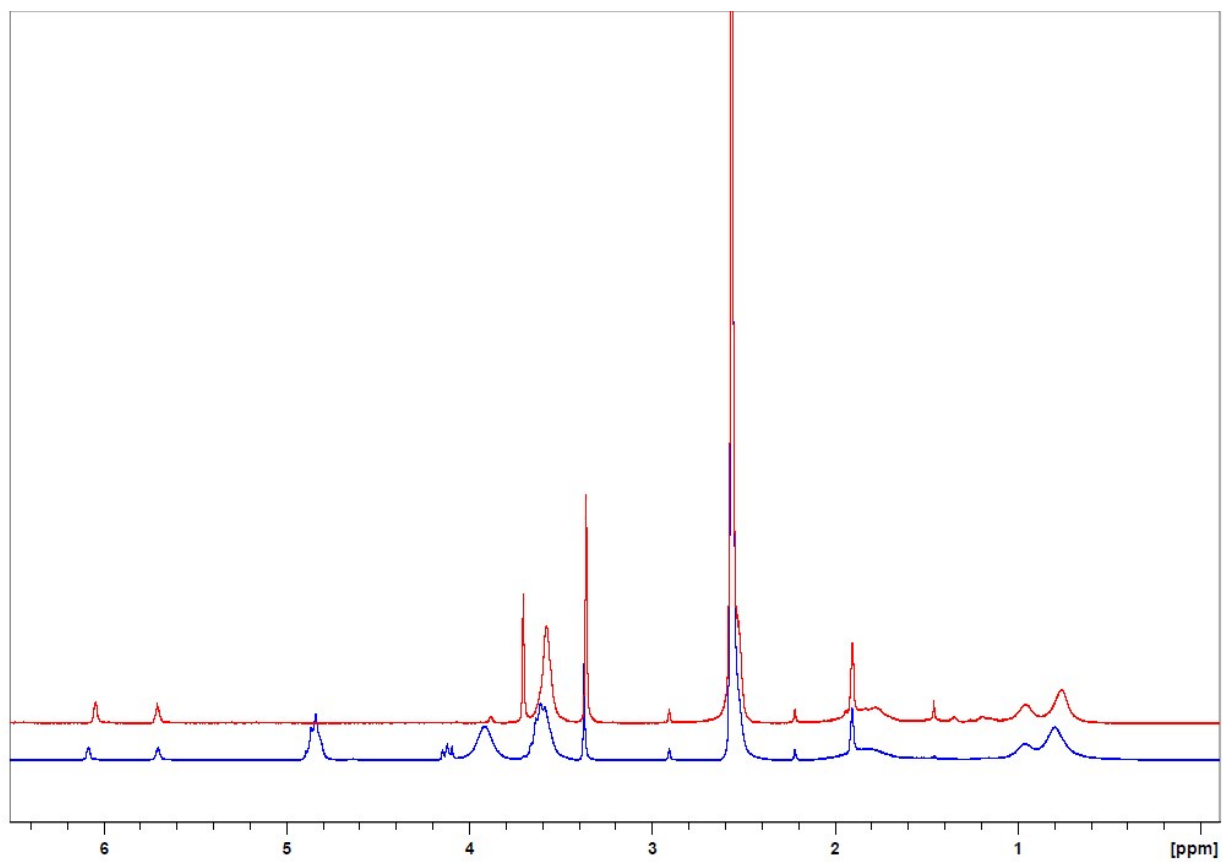
CTA	Peak Wavelength (nm)	$\epsilon$ at Peak ( $M^{-1} cm^{-1}$ )
CPMODB	510	149
CPMDB	514	136
CPDB	514	119
CPTFMOB	516	112
CPCDB	523	130



**Figure S2:** The cyclic voltammetry data of each chain transfer agent in 0.1 M TBAPF<sub>6</sub> and acetonitrile. The Scan rate was 0.5 V/s.

**Table S2:** Kinetic and molecular weight data for MMA polymerization using various concentrations of CPMODB as CTA under blue light irradiation

MMA:CPMODB	Time(h)	Conversion	M <sub>n</sub> (g/mol)
100:1	11	0.84	10249
200:1	11	0.85	20884
400:1	11	0.84	52435



**Figure S3:** NMR of PMMA macroCTA mixture (top) and HEMA extension of the macroCTA after 10h (bottom)