

Supporting Information

**Polymer Chain Length Dependence of Amplified Quenching in Conjugated  
Polyelectrolytes**

*Xiaoyong Zhao, Hui Jiang, and Kirk S. Schanze\**

*Department of Chemistry, University of Florida, PO Box 117200*

*Gainesville, Florida 32611-7200*

## Monomer Synthesis

**2,2'-(1,4-Phenylenebis(oxy))diacetic acid (1a).** A solution of 5.0 g (125 mmol) of sodium hydroxide in 20 ml of water was added drop-wise to a stirred solution of 3.3 g (30 mmol) of hydroquinone and 9.2 g (66 mmol) of bromoacetic acid in 30 ml water. The resulting solution was refluxed for 4 hr, then cooled to 2-5 °C whereupon the sodium salt of **1a** settled at the bottom of the flask. The white solid was collected on a Büchner funnel, washed with 60 ml of water, 60 ml of methanol, dried and dissolved in 30 ml of hot water, then acidified with 6 N HCl. The white precipitate was collected by vacuum filtration, rinsed with cold water and dried under vacuum. Yield: 4.5 g, 67%. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, δ<sub>ppm</sub>): 12.94 (s, br, 2H), 6.83 (s, 4H), 4.60 (s, 4H). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, δ<sub>ppm</sub>): 140.32, 122.06, 85.25, 34.96.

**Didodecyl 2,2'-(1,4-phenylenebis(oxy))diacetate (1b).** A mixture of 1.5 g (6.6 mol) of **1a**, 25 g (134 mmol) of dodecyl alcohol and 1 ml of 85% phosphoric acid was heated at 150 °C in a two-necked round bottom flask with a magnetic stirring bar. The water formed during the esterification was removed by flowing nitrogen slowly through the top of the reaction flask. After 6 hr, the clear solution was poured into 300 ml of hot hexane. The resulting mixture was cooled in a refrigerator overnight. The obtained white solid was collected by vacuum filtration. Further recrystallization from isopropanol affords a white crystalline product (yield: 3.1 g, 84%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ<sub>ppm</sub>): 6.86 (s, 4H), 4.57 (s, 4H), 4.20 (t, 4H), 1.65 (m, 4H), 1.27 (m, 36H), 0.89 (t, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ<sub>ppm</sub>): 169.12, 115.80, 66.17, 65.46, 31.93, 29.65, 29.36, 19.21, 28.54, 25.80, 22.71, 14.14.

**Didodecyl 2,2'-(2,5-diiodo-1,4-phenylene)bis(oxy)diacetate (1).**<sup>1</sup> Compound **1b** (5.2 g, 9.2 mmol), iodine (2.3 g, 9.2 mmol) and bis(trifluoroacetoxy)phenyliodine (4.3 g, 9.0 mmol) were mixed in 25 ml CCl<sub>4</sub>. The purple suspension was stirred at room temperature for 6 h, and then diluted with 75 ml CH<sub>2</sub>Cl<sub>2</sub>, washed with 5% NaHSO<sub>3</sub> till the purple color disappeared. The

solution was then dried with anhydrous  $\text{MgSO}_4$  and the solvent was removed under reduced pressure. The obtained yellow solid was further purified by recrystallization from 25 ml isopropanol, and white crystal product was obtained (yield: 6.8 g, 90%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta_{\text{ppm}}$ ): 7.16 (s, 2H); 4.62 (s, 4 H); 4.22 (t, 4H); 1.67 (m, 4H), 1.27 (m, 36 H); 0.89 (t, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta_{\text{ppm}}$ ): 168.53, 153.23, 124.03, 86.61, 67.75, 32.37, 30.09, 29.97, 29.81, 29.67, 28.99, 26.28, 23.15, 14.59.

**1,4-Bis((trimethylsilyl)ethynyl)benzene (2a).** 1,4-Diiodobenzene (18.0 g, 54.6 mmol) was dissolved in 200 ml of THF/ $\text{HN}(\text{i-Pr})_2$  (4/1) in a Schlenk flask and degassed with argon for 30 minutes. The solution was cooled down to  $5^\circ\text{C}$  using an ice/water bath. Then 400 mg of  $\text{Pd}(\text{PPh})_2\text{Cl}_2$  (0.57 mmol) and 100 mg of CuI (0.53 mmol) were added, followed by the addition of 20 ml of trimethylsilylacetylene (141.8 mmol) via a syringe. A thick precipitate formed immediately (ensure efficient stirring!). After half an hour, the reaction mixture was allowed to warm to room temperature and stirred overnight. After filtering through a bed of celite, the solvent was removed *in vacuo*. The brown crude product was dissolved in a large amount of hexane and filtered through a short plug of silica. Recrystallization from ethanol afforded a white flake crystalline product (yield: 10.4 g, 74%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta_{\text{ppm}}$ ): 7.40 (s, 4H), 0.25 (s, 18H).

**1,4-Diethynylbenzene (2).** Compound **2a** (2.0 g, 7.4 mmol) was dissolved in a minimum of dioxane (~ 20 ml) in a 250 ml beaker and acidified with 1 ml acetic acid. Then 18 ml of tetrabutylammonium fluoride (18 mmol) was added drop-wise. After 30 minutes, the volume of the solution was reduced to around 20 ml by flowing nitrogen above the surface. Then 200 ml of  $\text{H}_2\text{O}/\text{MeOH}$  (9/1) was added to the reaction mixture. The product precipitated as a white solid and was collected on a Büchner funnel, washed with 50 ml of  $\text{H}_2\text{O}/\text{MeOH}$  (v/v = 9/1), dried in a

desiccator loaded with 10 g of anhydrous  $\text{CaCl}_2$ . The dry product was typically sufficiently pure for polymerization; however, in some cases it was necessary to effect purification by dissolving the material in hexane and passing the solution through a short plug of silica.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta_{\text{ppm}}$ ): 7.45 (s, 4H), 3.18 (s, 2H).

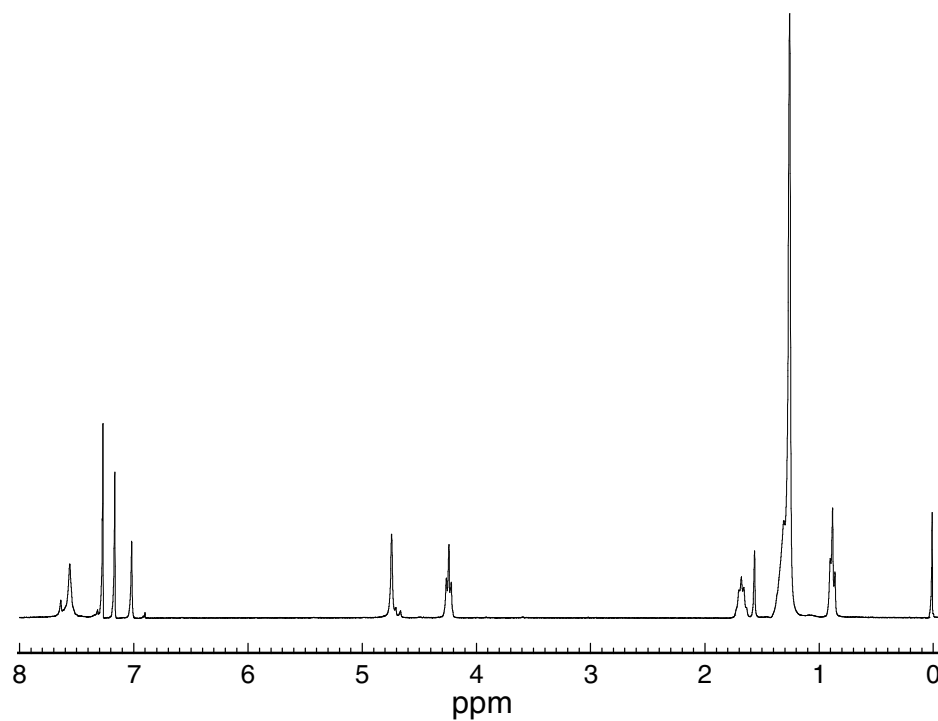


Figure S1.  $^1\text{H}$  NMR spectrum of PPE-CO<sub>2</sub>R-13 in CDCl<sub>3</sub>.

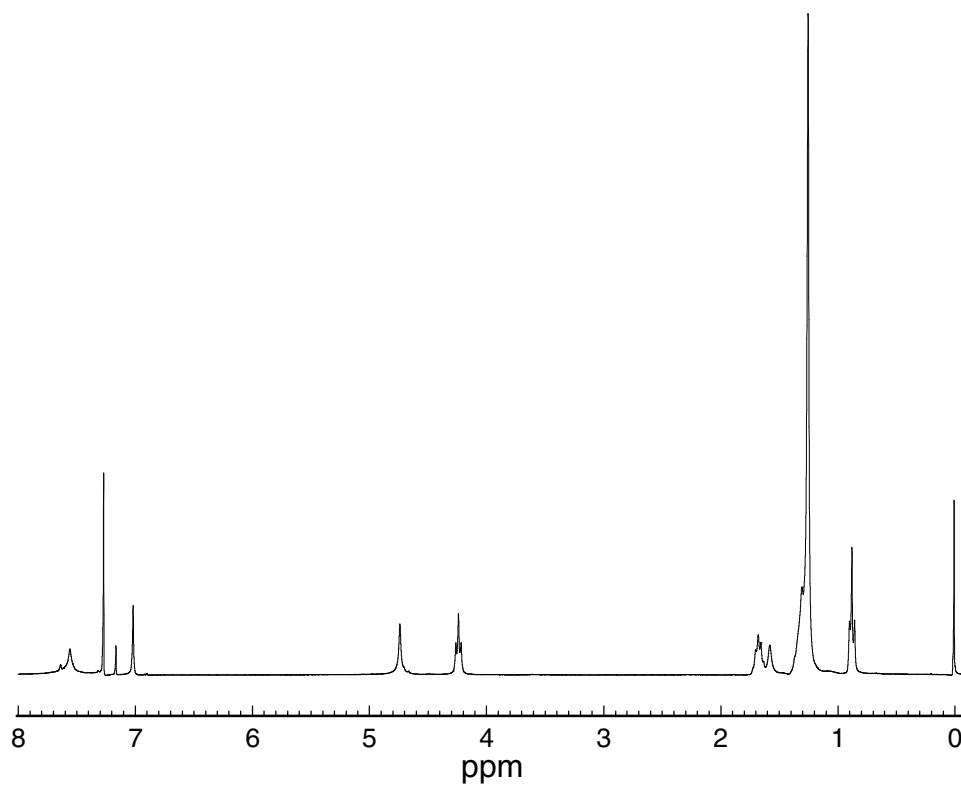


Figure S2.  $^1\text{H}$  NMR spectrum of PPE-CO<sub>2</sub>R-35 in CDCl<sub>3</sub>.

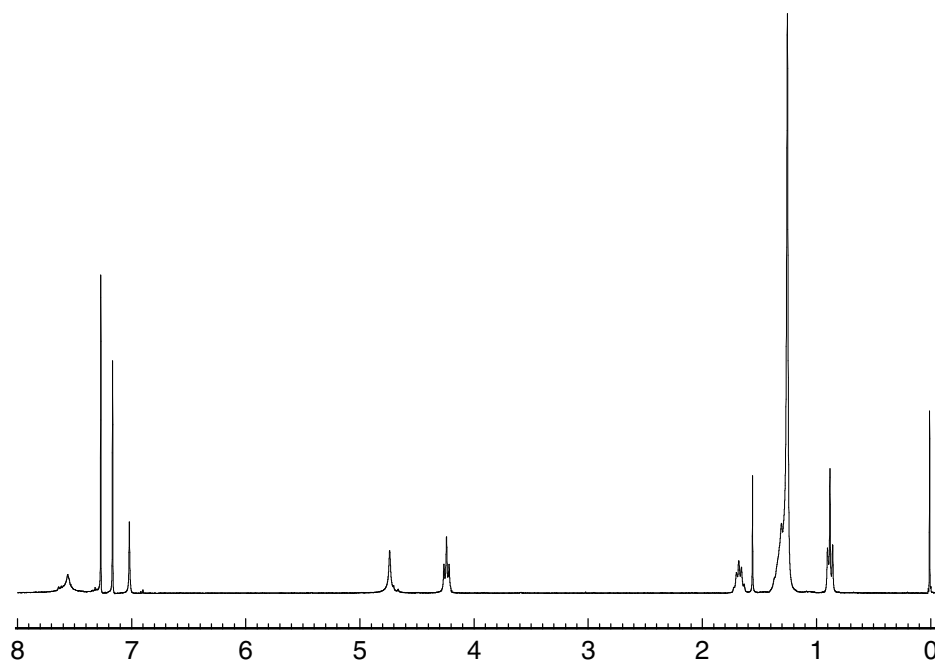


Figure S3.  $^1\text{H}$  NMR spectrum of PPE- $\text{CO}_2\text{R}$ -49 in  $\text{CDCl}_3$ .

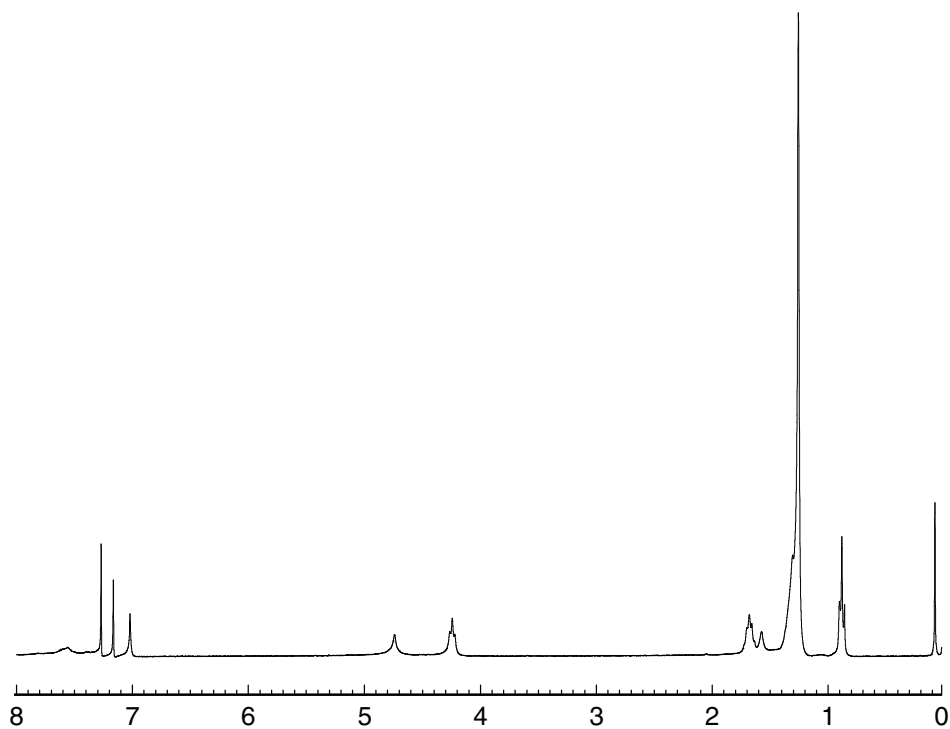


Figure S4.  $^1\text{H}$  NMR spectrum of PPE- $\text{CO}_2\text{R}$ -108 in  $\text{CDCl}_3$ .

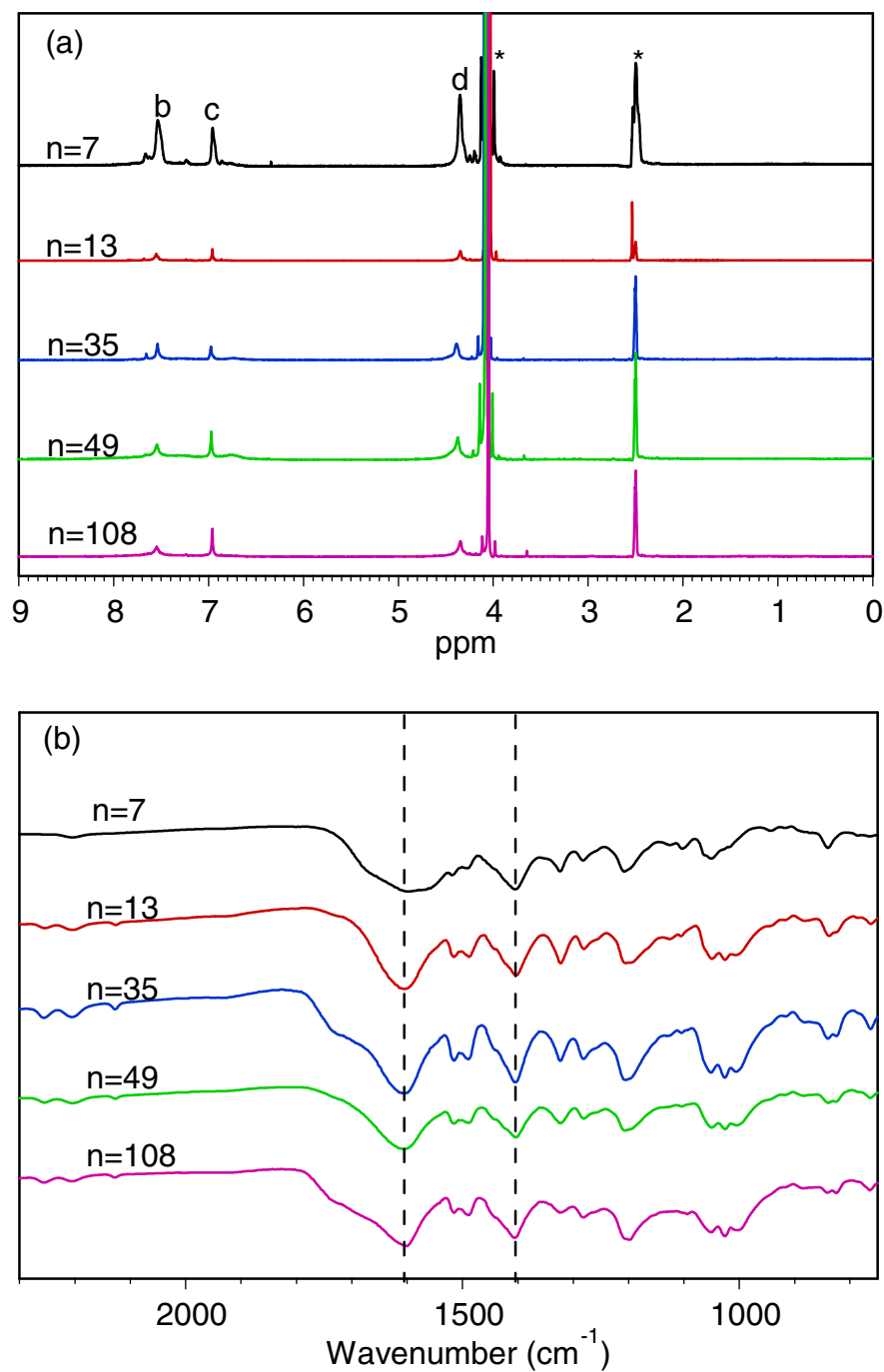


Figure S5.  $^1\text{H}$  NMR (a) and IR (b) spectra of the PPE- $\text{CO}_2\text{Na}$  series. The starred signals at 4.05 ppm and 2.50 ppm in the  $^1\text{H}$  NMR spectra are due to DMSO- $\text{d}_6$  and  $\text{D}_2\text{O}$ , respectively.

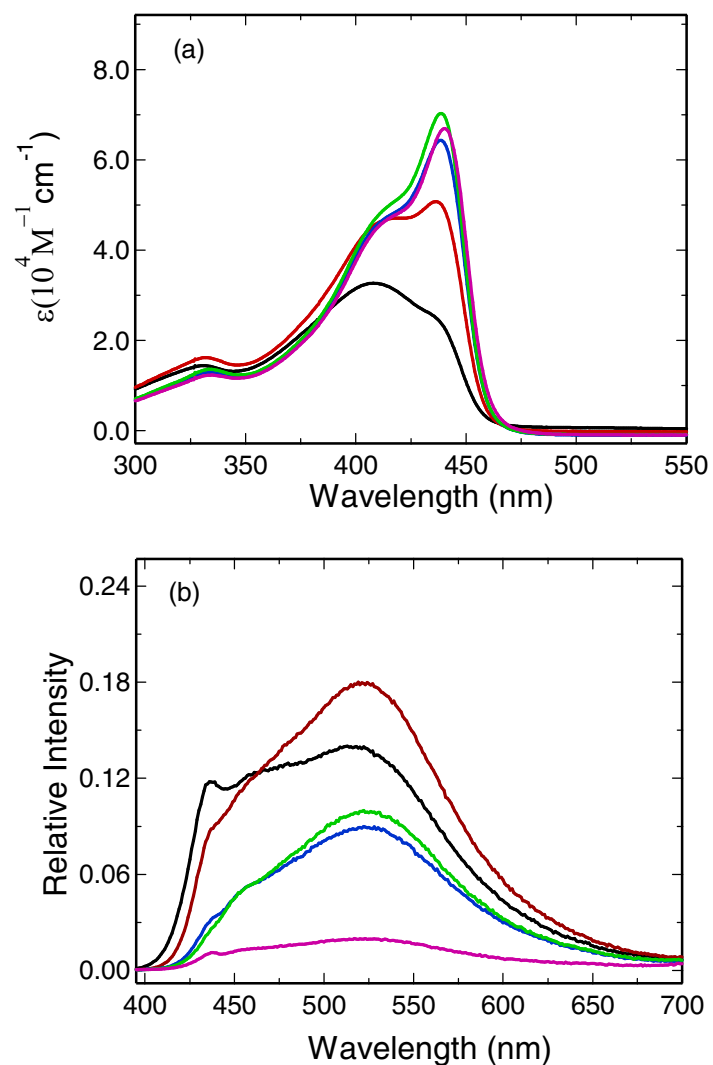


Figure S6. (a) Absorption and (b) emission spectra of the PPE-CO<sub>2</sub>Na series in water. black: PPE-CO<sub>2</sub>Na-7, red: PPE-CO<sub>2</sub>Na-13, blue: PPE-CO<sub>2</sub>Na-35, green: PPE-CO<sub>2</sub>Na-49, purple: PPE-CO<sub>2</sub>Na-108. [PRU] = 5  $\mu\text{M}$ , the emission spectra were acquired by exciting at 380 nm for all the CPEs.



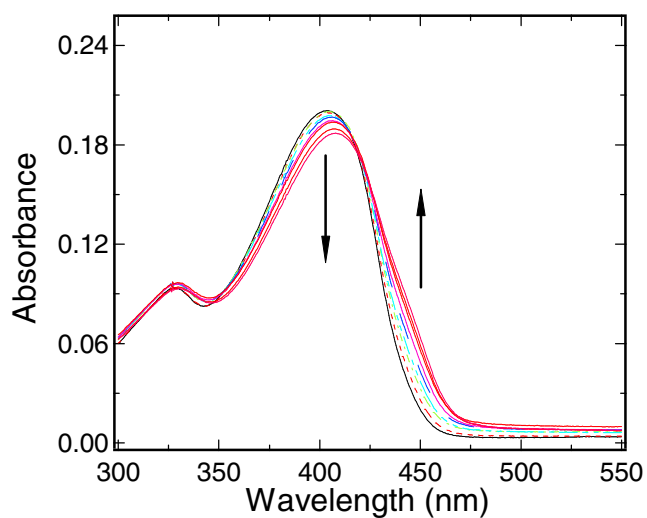


Figure S7. Absorption spectra of PPE-CO<sub>2</sub>Na-7 with the addition of MV<sup>2+</sup>, [PPE-CO<sub>2</sub>Na-7] = 5  $\mu$ M. [MV<sup>2+</sup>] ranges from 0.1  $\mu$ M to 0.8  $\mu$ M. Arrows show the direction of change.

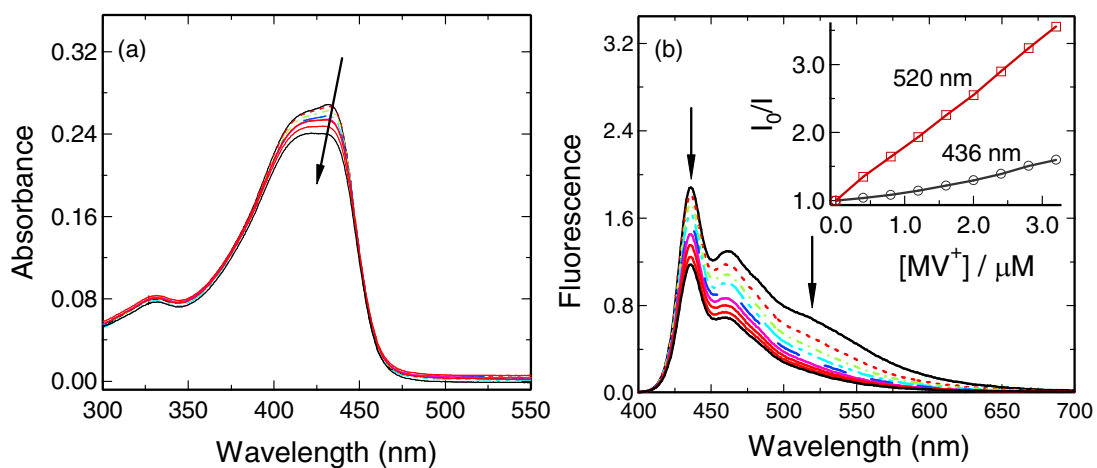


Figure S8. Absorption (a) and emission (b) spectra of PPE-CO<sub>2</sub>Na-108 in MeOH with the addition of MV<sup>+</sup>. [PPE-CO<sub>2</sub>Na-108] = 5  $\mu$ M. MV<sup>+</sup> was added in 0.4  $\mu$ M aliquots, [MV<sup>+</sup>] ranges from 0  $\mu$ M – 3.2  $\mu$ M. The inset of b shows the SV-plots and the linear fits. Arrows show the direction of change with the addition of quenchers.

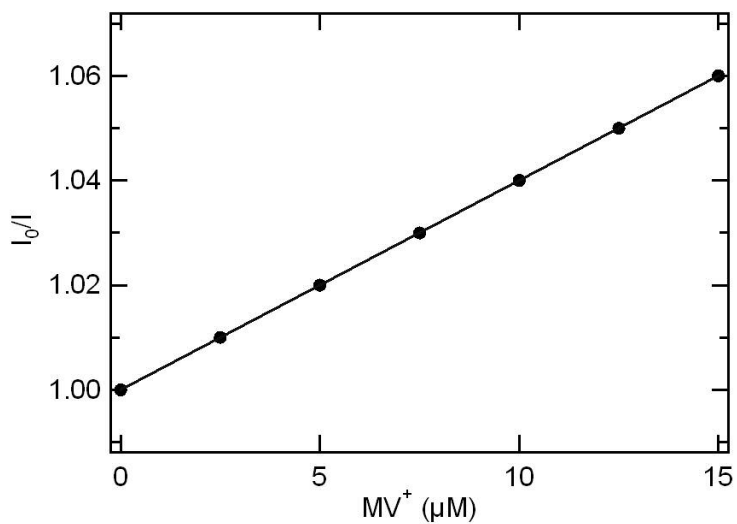


Figure S9. Stern-Volmer (SV) plot for the quenching of model compound (PE-CO<sub>2</sub>Na) in MeOH by MV<sup>+</sup>. MV<sup>+</sup> was added in 2.5  $\mu M$  aliquots, [MV<sup>+</sup>] ranges from 0  $\mu M$  – 15.0  $\mu M$ .

## References

1. Haskins-Glusac, K.; Pinto, M. R.; Tan, C. Y.; Schanze, K. S. *J. Am. Chem. Soc.* **2004**, *126*, 14964-14971.