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Indicator Displacement Assays based on Polyelectrolyte:Dye Complexes

Stephanie M. Amendola, Nikolas S. Hopkins, William P. Kabrich, Ashlynn M. Lawrence, and Rhett C. Smith*

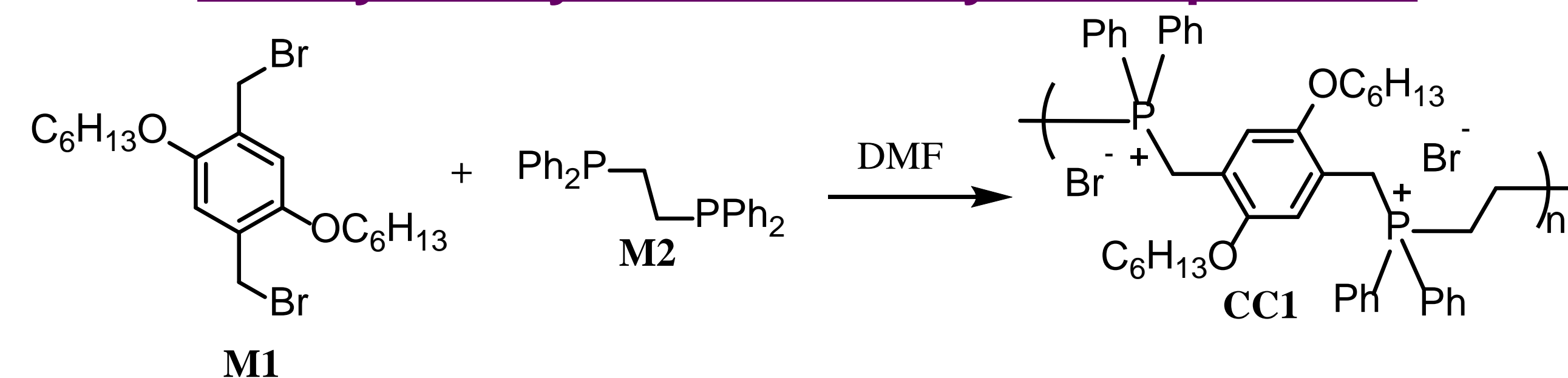
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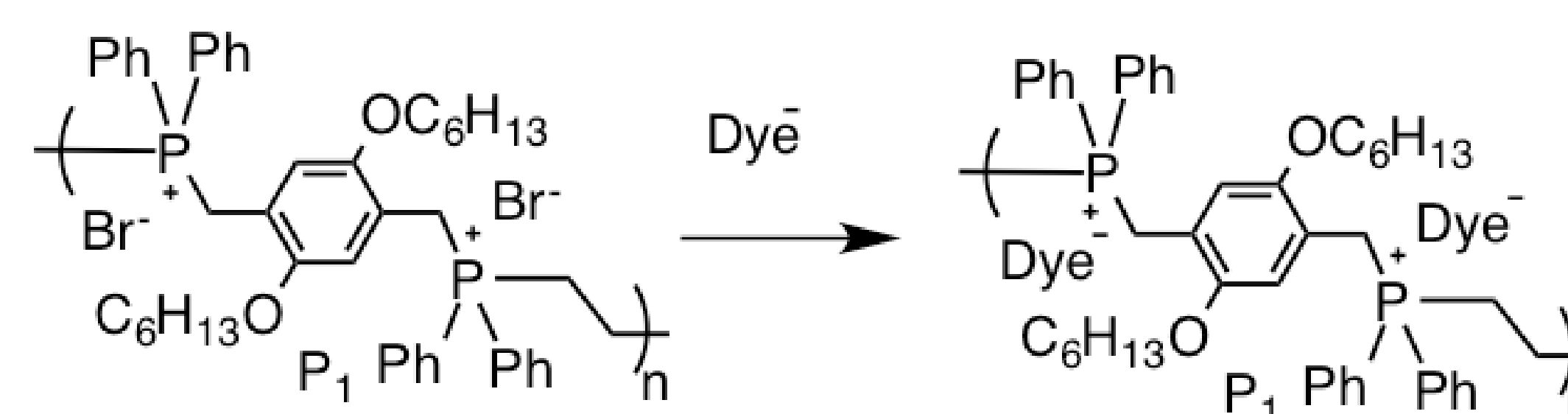
I. Introduction

A phosphonium polyelectrolyte (**CC1**) was readily prepared using a commercially-available diphosphine monomer. Exchange of the bromide ions in **CC1** for commercially-available anionic dyes such as magneson (**MG**) and alizarin red S (**ARS**) led to the formation of visible-absorbing polyelectrolytes (**CC1-MG** and **CC1-ARS**). The efficiency of anion exchange was readily assessed by integration of ¹H NMR spectra and ranged from ~60-100%. Spectral changes of **CC1-MG** and **CC1-ARS** in response to addition of anionic analytes was undertaken to assess the utility of these constructs in indicator displacement assays. The sensitivity and selectivity for target analytes, including the potential of phosphonium polymers to serve as receptors for colorimetric sensing of the anthrax biomarker dipicolinic acid (DPA), are discussed. The proof of principle study reported herein, along with the facile preparation **CC1-MG** and **CC1-ARS** and related polyelectrolytes from readily-available precursors, suggest that this type of dye displacement strategy holds promises for a versatile set of affordable anion detection platforms.

II. Polymer Synthesis and Dye Incorporation



Scheme 1: Polymer Synthesis



Scheme 2: Anion Exchange to incorporate anionic dyes

III. Dyes and Anions Studied

Acetate, Bromide, Chloride, Fluoride, Iodide, Hydroxide, Phosphate, Sulfate	
Adipic Acid	Isophthalic Acid
Alizarin Red S (ARS)	Magneson (MG)
Carbenicillin	Methyl Red (MR)
Dipicolinic Acid (DPA)	Phthalic Acid
Glutamic Acid	Picolinic Acid
Glutaric Acid	Terephthalic Acid

Table 1: Structures of dyes and anions examined in this study. The carboxylic acids are deprotonated to form carboxylates upon addition to neutral water or upon addition of equimolar base for studies in *N,N*-dimethylformamide (DMF).

IV. Dye Displacement by Anions

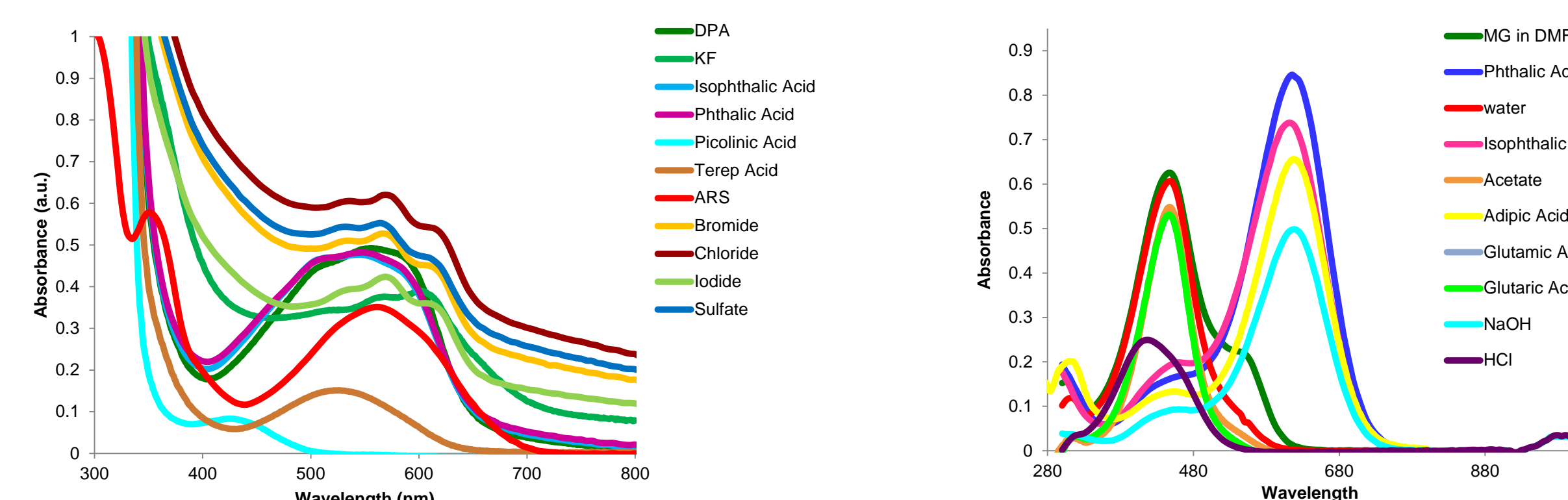


Figure 1. Spectroscopic response of **CC1-ARS** to different anions (10 equiv) in water.

Figure 2. Spectroscopic response of **CC1-MG** to different anions (10 equiv) in *N,N*-dimethylformamide.

V. Spectroscopic Response to Anions

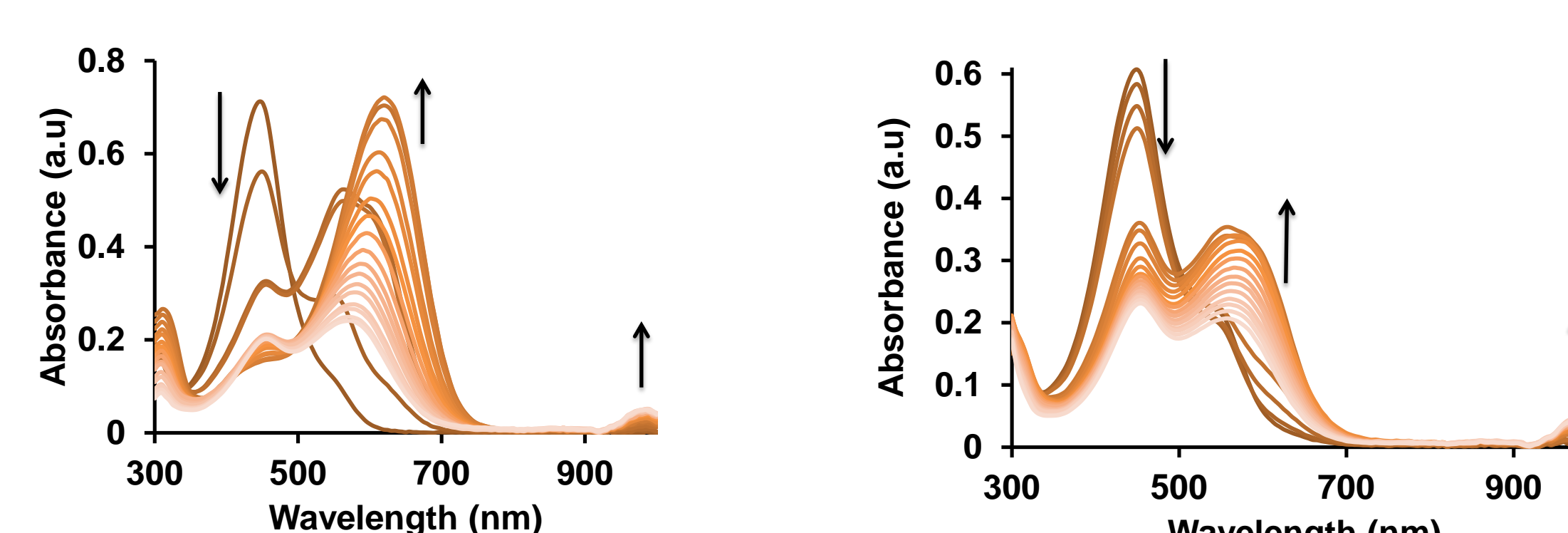


Figure 5. Titration of **CC1-MG** with phthalic acid

Figure 6. Titration of **CC1-MG** with DPA

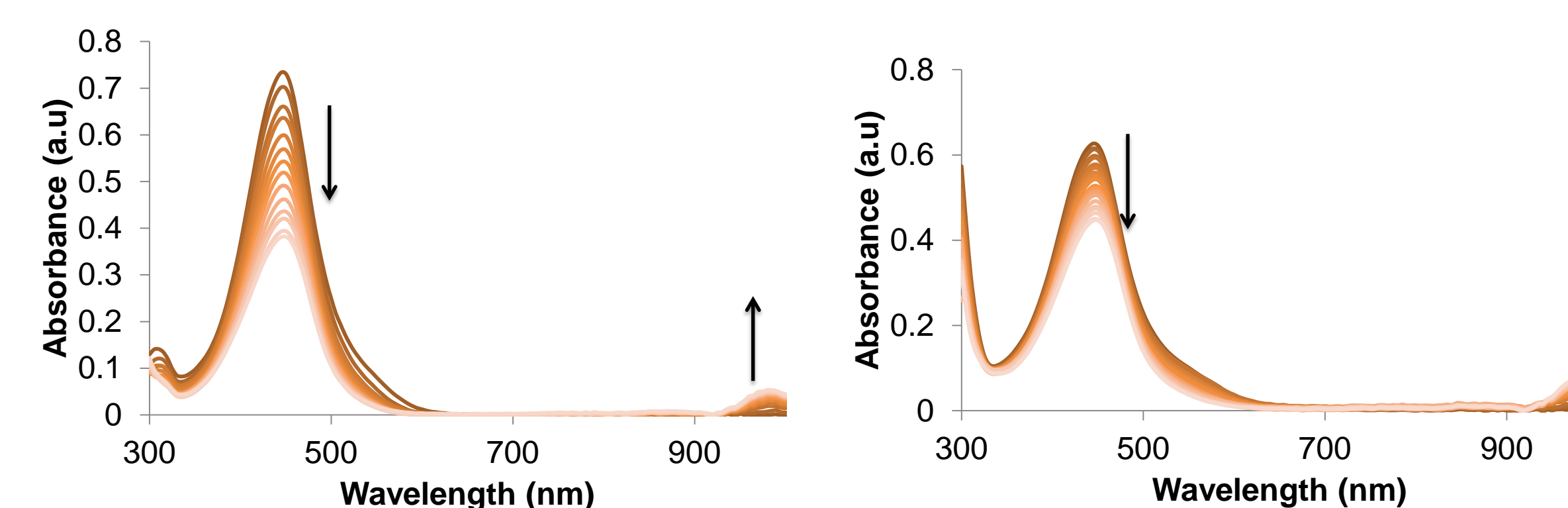


Figure 7. Titration of **CC1-MG** with picolinic acid

Figure 8. Titration of **CC1-MG** with carbenicillin

After titrating the **CC1-MG** complex with the various anions, the relative sensitivity, as measured by the ratio of the absorbance at 435 nm (which shrinks as anions are added) to the absorbance at 635 nm (which increases as anions are added) was assessed. Figure 9 reveals that the absorbance of the **CC1-MG** complex is most sensitive to the phthalic acid, with moderate selectivity for this anion versus the other aromatic carboxylates.

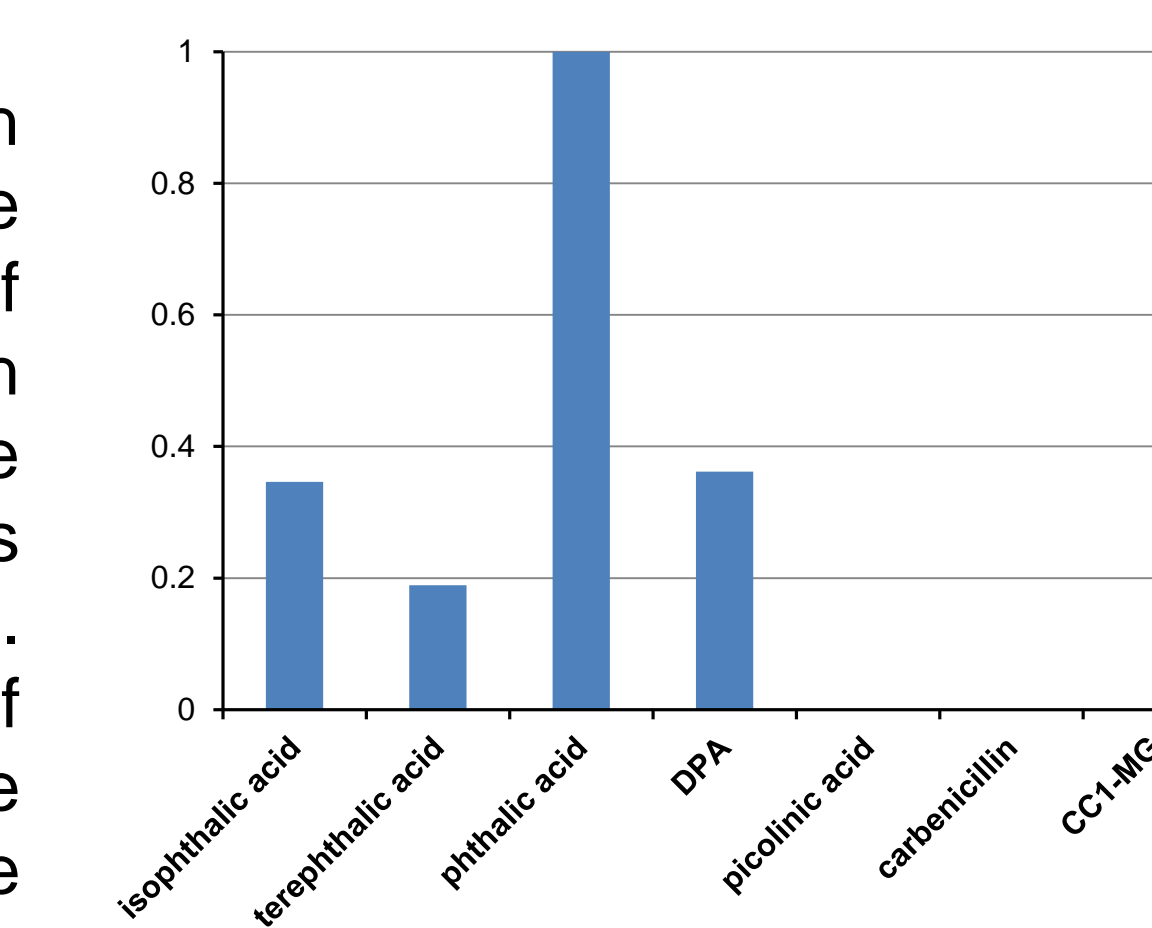


Figure 9. Relative change in absorbance ratio (635 nm/445 nm) upon addition of anions to **CC1-MG**

VI. Conclusions

The counteranions of phosphonium polyelectrolytes such as **CC1** can be effectively exchanged for chromophores such as the anionic dyes explored in this study. The phosphonium polymer-dye complex serves as an effective platform for the detection of various anions in aqueous or organic solutions via an indicator displacement with concomitant spectroscopic signal modulation. The specific dye-polymer complex (**CC1-MG**) studied in detail in this contribution showed particular response to aromatic carboxylic acids, with moderate selectivity for phthalic acid. This observation is rationalized by the fact that the anionic sites in the deprotonated phthalic acid might be expected to exhibit the best size match to pair the anionic charges with the cationic sites in the polymer.

VII. Acknowledgements and References

Research Team



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References

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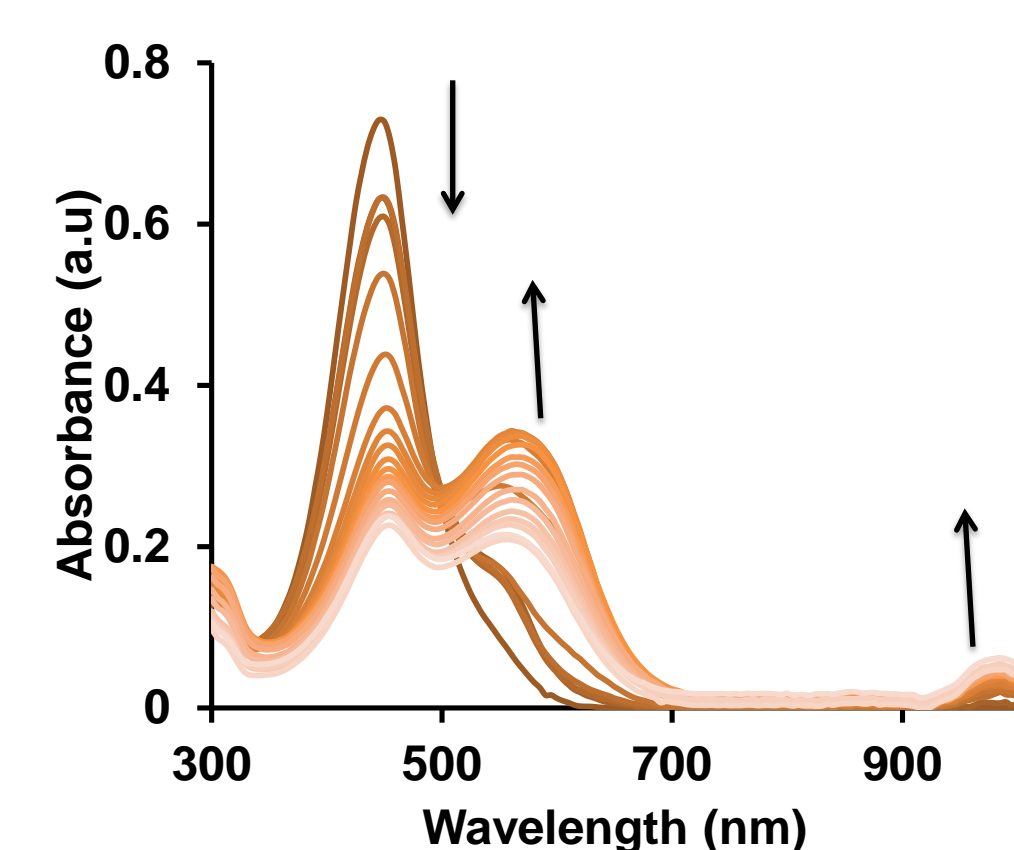


Figure 3. Titration of **CC1-MG** with isophthalic acid.

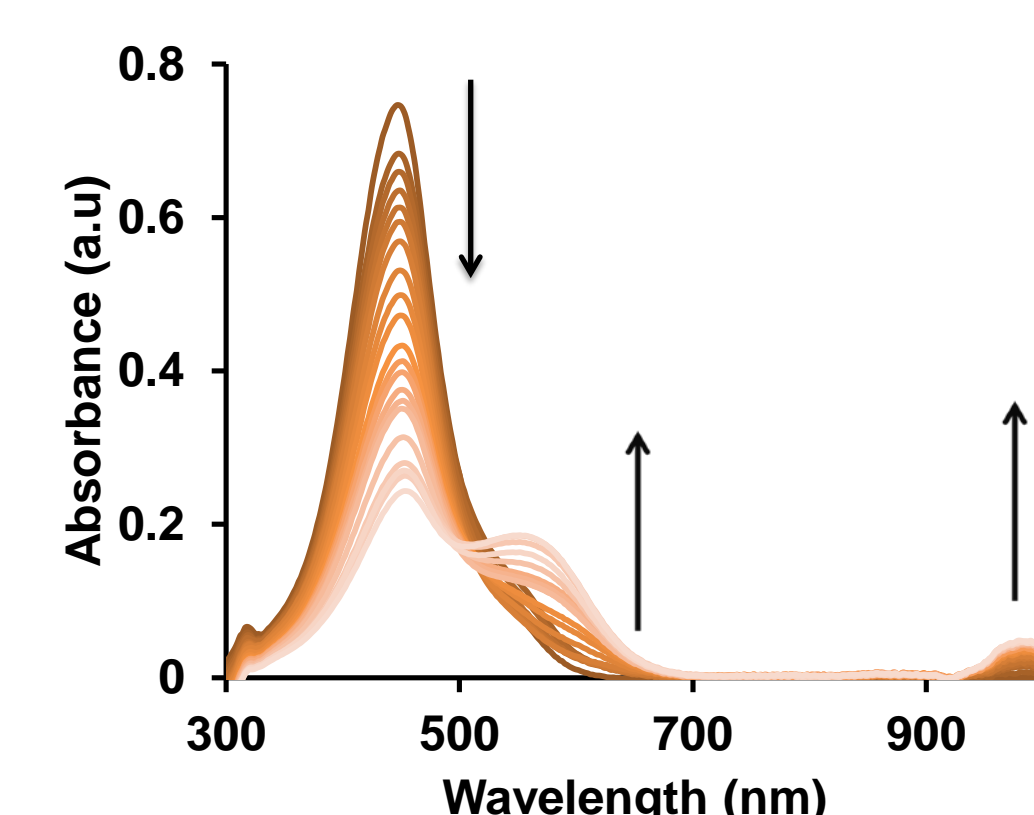


Figure 4. Titration of **CC1-MG** with terephthalic acid.