Influencing Inclusion: Solvent and Guest Redox State Dependence on the Host-Guest Equilibrium Between Pillar[5]arene Hosts and Viologen Guests

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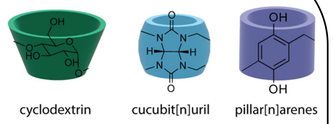
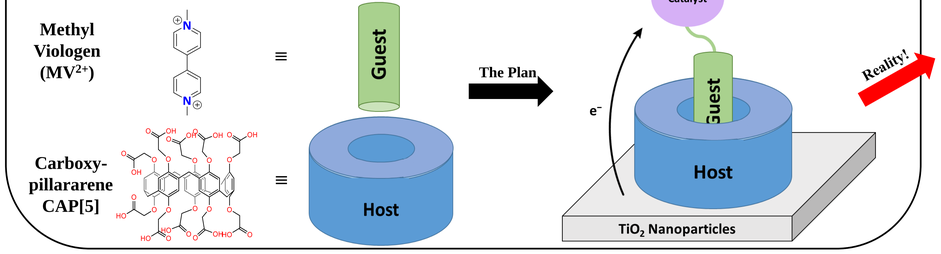
Introduction & Motivation

- Host-Guest (non-covalent) binding is a rising strategy for developing **sensitive** and **selective** electrochemical devices.
- Non-covalent systems are often renewable but suffer from poor/ill-defined binding and aggregation.
- Host-Guest anchoring provides a route to renewability with well-defined and tunable binding.
- Pillararenes are a new, exciting class of molecular host, but their electrochemical behavior is underexplored.

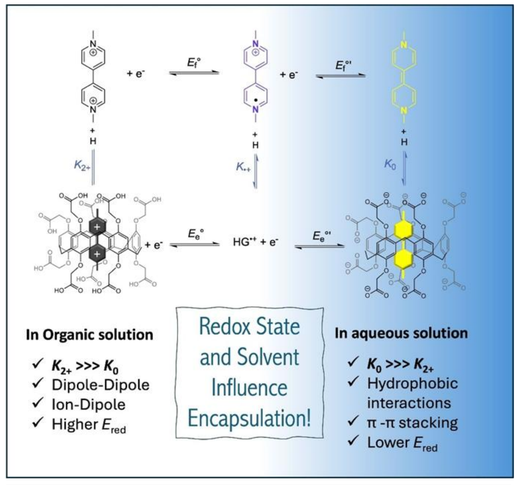
Molecular Hosts



Host-Guest Chemistry

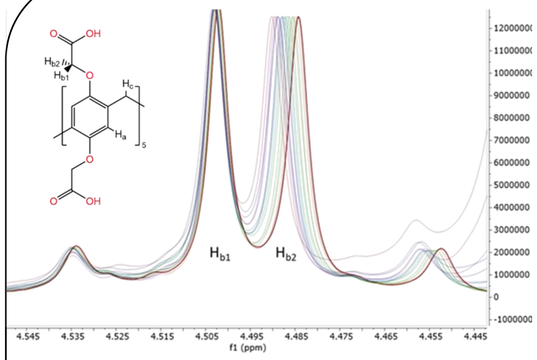


Expectation



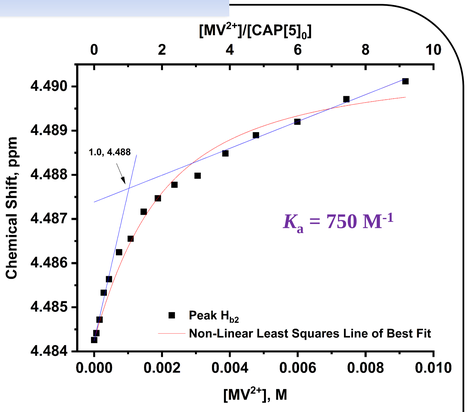
"Reality is not neat, not obvious, not what you expect."
-C.S. Lewis

Determination of K_a – Organic Solvent



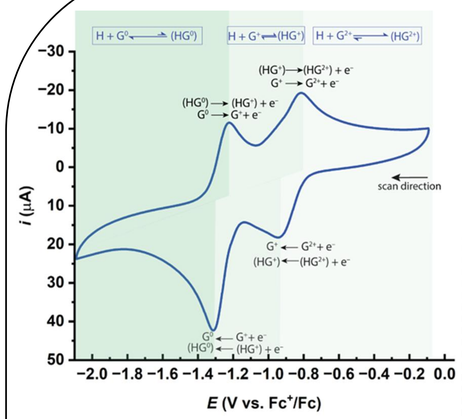
- The Δδ signal of the inner methylene protons of **CAP[5]** was used to quantify K_a.

$$\delta_{obs} - \delta_{initial} = \frac{\delta_{\Delta HG}}{2[H]_0}\left([G]_0 - [H]_0 + \frac{1}{K_a}\right) - \sqrt{\left([G]_0 + [H]_0 + \frac{1}{K_a}\right)^2 + 4[G]_0[H]_0}$$

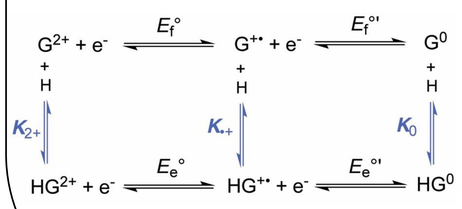


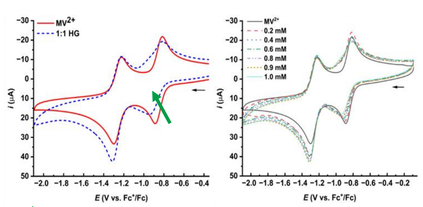
- The breakpoint at 1.0 Host:Guest confirms a 1:1 stoichiometry for the inclusion complex.

Thermodynamic Analysis



Solvent Condition	E_{pc1} (MV^{2+})	E_{pc1} (1:1 HG)	$\Delta E°'$	$E°'$ (MV^{2+})	$E°'$ (1:1 HG)	$\Delta E°'$
Organic	-0.886	-0.944	-0.058	-0.886	-0.879	-0.028
Aqueous	-0.635	-0.615	0.020	-0.597	-0.563	0.034

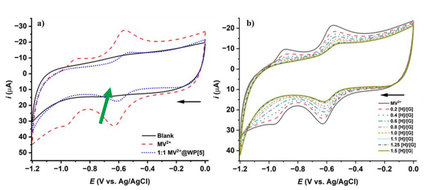




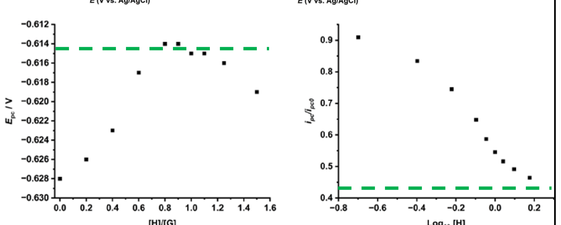
Organic

Under **organic** conditions, **MV^{2+}@CAP[5]** is 58 mV **harder** to reduce.

Under **aqueous** conditions, **MV^{2+}@CAP[5]** is 20 mV **easier** to reduce.



Aqueous



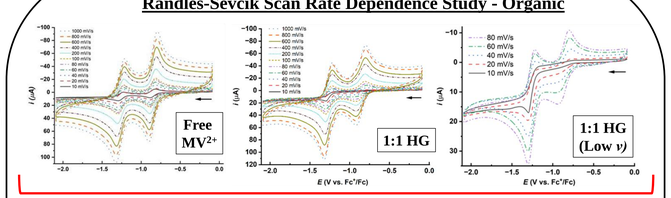
- The leveling off of i_{pc}/i_{pc0} allows for estimation of K_a'

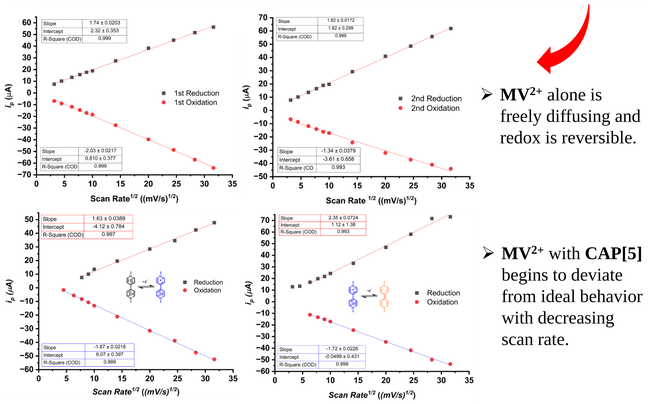
$E°'$ (MV^{2+})	$E°'$ (MV^{2+}@WP[5])	K_a/K_a'	K_a (M^{-1})	K_a' (M^{-1})
-0.597	-0.552	0.17	82,000	**480,000**

6-fold increase in K_a!

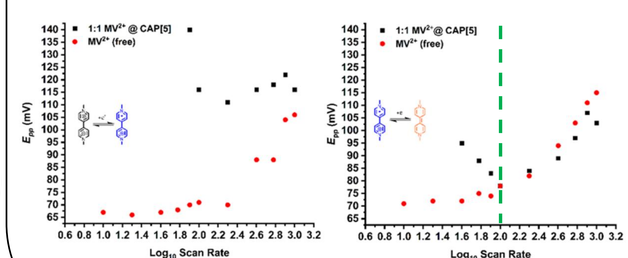
Diffusion and Kinetics

Randles-Sevcik Scan Rate Dependence Study - Organic





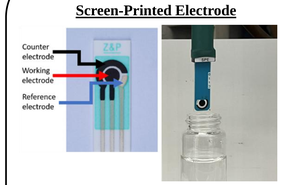
- MV^{2+} alone is freely diffusing and redox is reversible.
- MV^{2+} with **CAP[5]** begins to deviate from ideal behavior with decreasing scan rate.

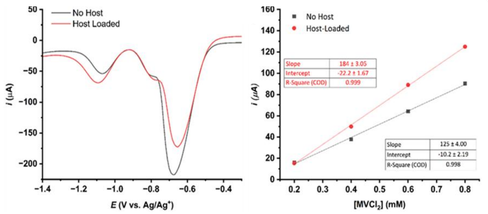


- Free guest and 1:1 host:guest show identical ΔE_{pp} until ~100 mV/s. Then threading kinetics begin to interfere.

Host-Modified Electrode

Screen-Printed Electrode





- **CAP[5]** dropcast onto inexpensive, C110 screen-printed electrode (SPE).
- **CAP[5]** increases sensitivity towards **MV^{2+}** by 55%.

Summary and Future Work

- **MV^{2+}** exhibits solvent and redox state dependent threading with **CAP[5]**.
  - In organic solvent: **MV^{2+}@CAP[5]** is 58 mV **harder** to reduce.
  - In aqueous solvent: **MV^{2+}@CAP[5]** is 20 mV **easier** to reduce.
- Even electrochemically silent hosts like pillararene are not innocent towards electron transfer reactions!

Acknowledgements

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References

(1) Wilson, C.E., Zhao, P., Caputo, C. A., Solvent and Guest Redox State Dependence on the Host-Guest Equilibrium Between Pillar[5]arene Hosts and Viologen Guests. In *ACS Electrochemistry*; 2025; In peer-review.
(2) Kaifer, A. E. Molecular Encapsulation of Redox-Active Guests. In *Electrochemistry of Functional Supramolecular Systems*; 2009; pp 59–85. https://doi.org/https://doi.org/10.1002/9780470583463.ch3.
(3) Kaifer, A. E. Interplay between Molecular Recognition and Redox Chemistry. *Acc. Chem. Res.* **1999**, *32* (1), 62–71. https://doi.org/10.1021/ar970335u.
(4) d'Astous, É. V; Dauphin-Ducharme, P. Harnessing Host–Guest Chemistry for Electrochemical Sensing in Complex Matrices. *Curr. Opin. Electrochem.* **2022**, *34*, 101029. https://doi.org/https://doi.org/10.1016/j.coelec.2022.101029.