

Electron Transfer Kinetics in a Series of Expanded Pyridiniums and its Correlation with Steric Constraints around N-pyridinio site.



Magdaléna Hromadová

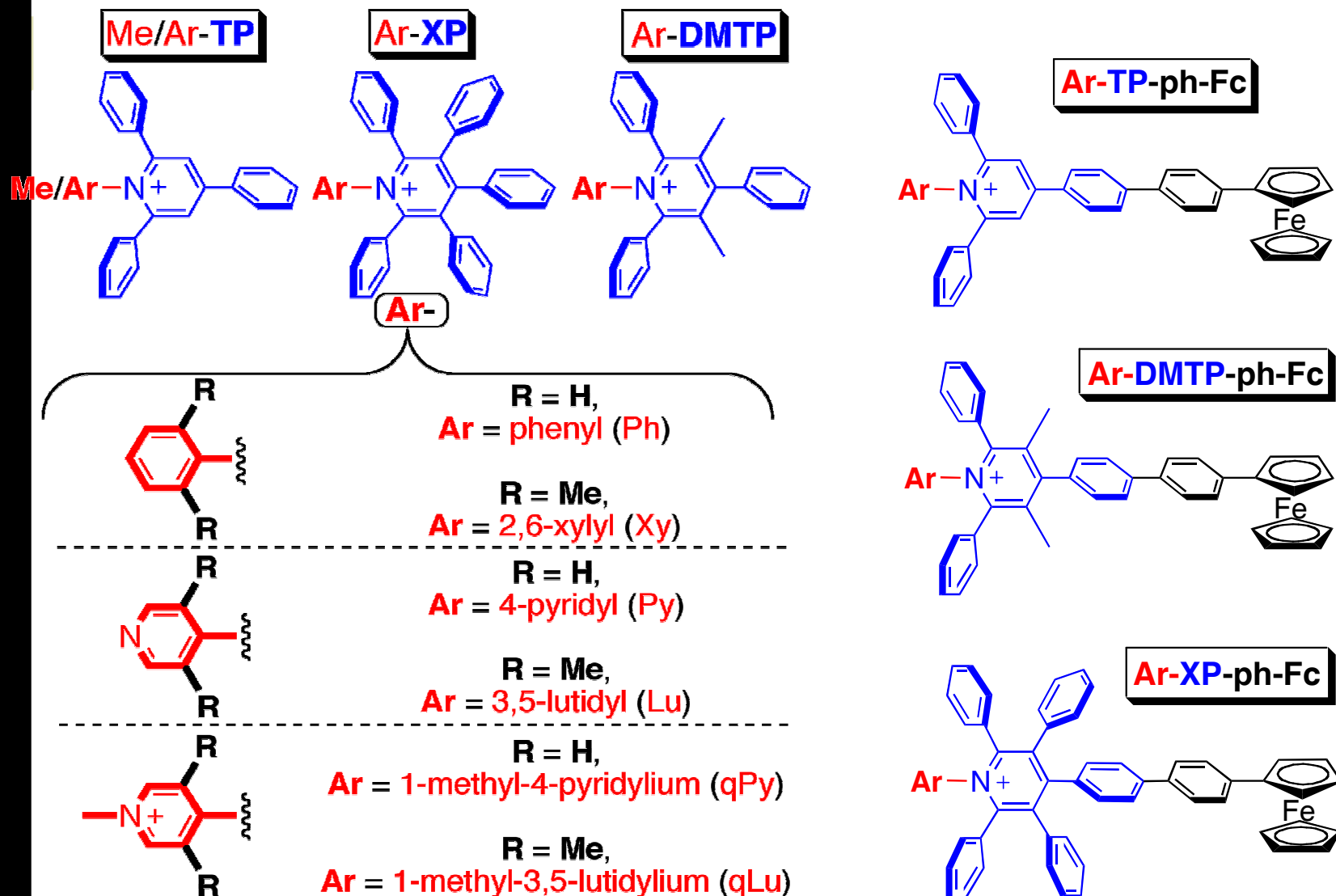
J. Heyrovský Institute of Physical Chemistry
Prague, Czech Republic

EIA10, Borovetz, Bulgaria, June 1 - 5, 2014



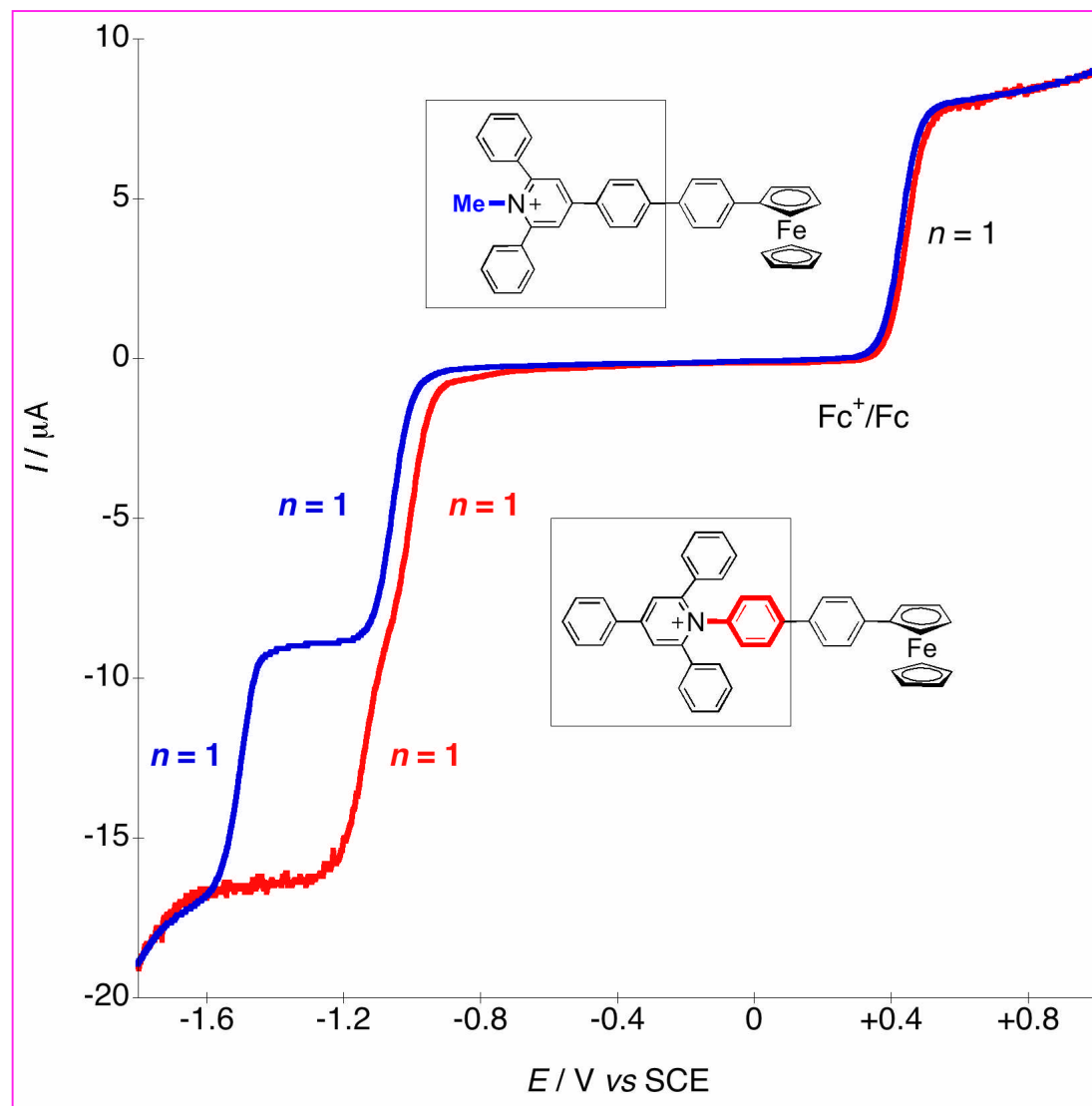
Two-electron Reduction: Insights from Experiment

« *Changing intramolecular steric constraints while counting the electrons* »

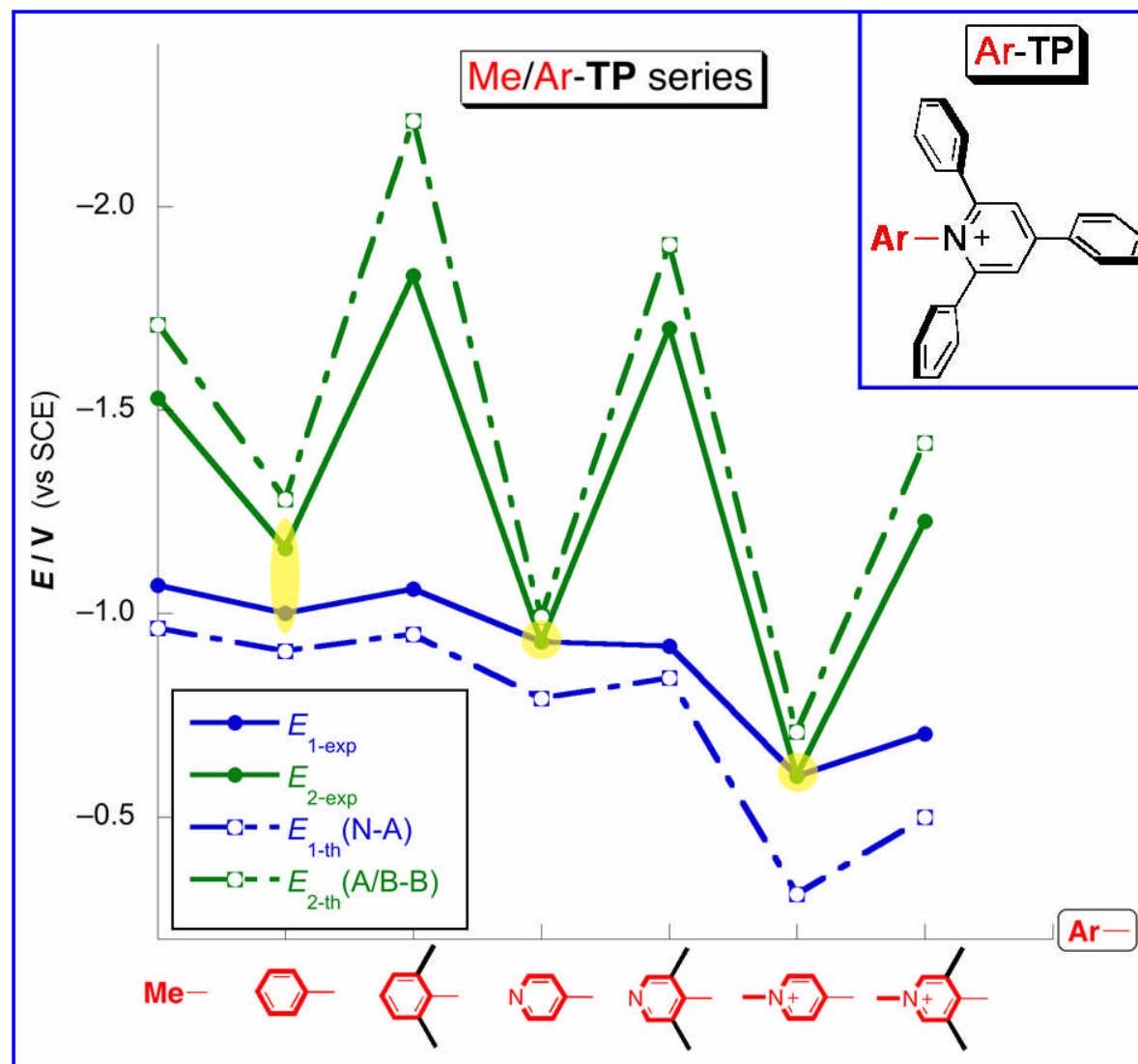


Two-electron Reduction: Insights from Experiment

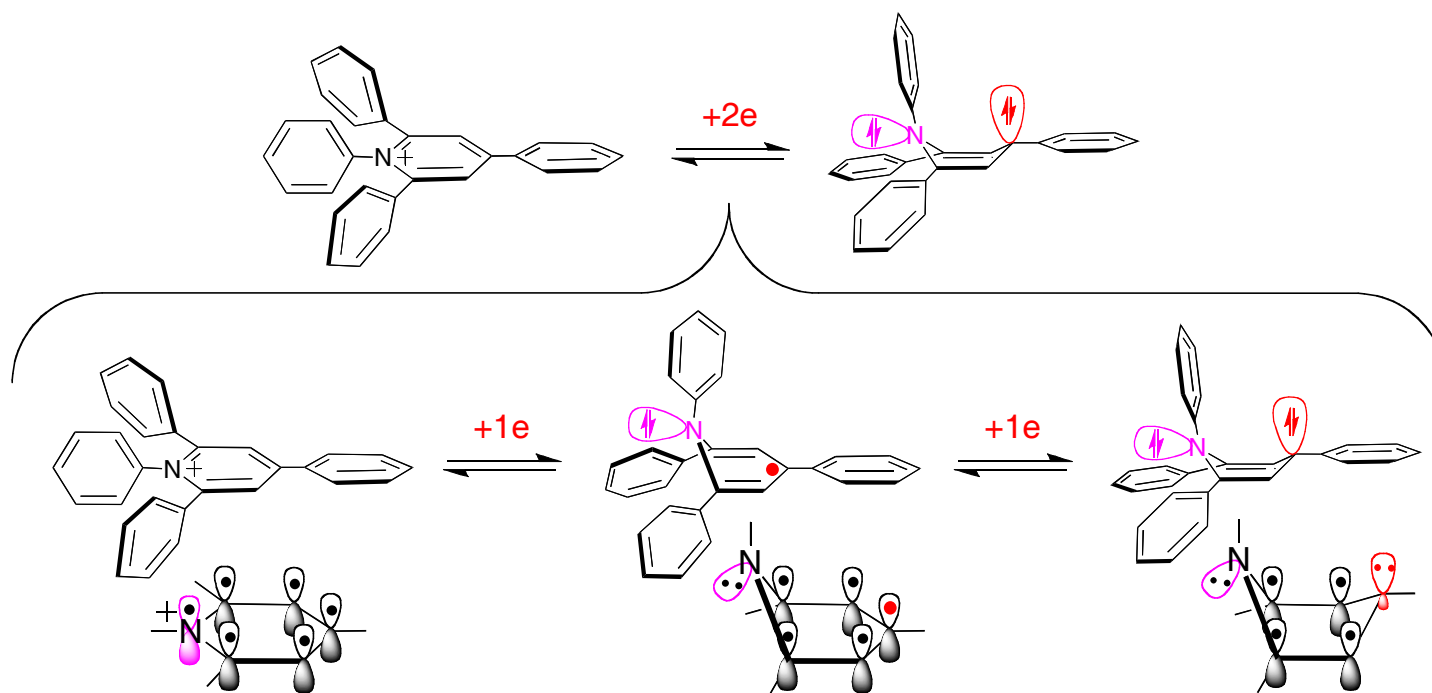
« Counting the electrons: *Rotating Disk Electrode experiments* »



Steric switching of the potential compression

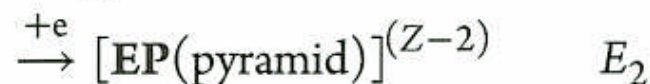
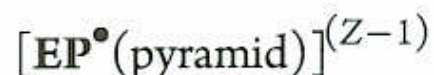


Pyramidalization of the N_{pyridinio} atom



J. Fortage, C. Peltier, C. Perruchot, Y. Takemoto, Y. Teki, F. Bedioui, V. Marvaud, G. Dupeyre, L. Pospisil, C. Adamo, M. Hromadova, I. Ciofini, P. P. Lainé *J. Am. Chem. Soc.* 2012, 134, 2691–2705.

Single Step Two Electron Transfer



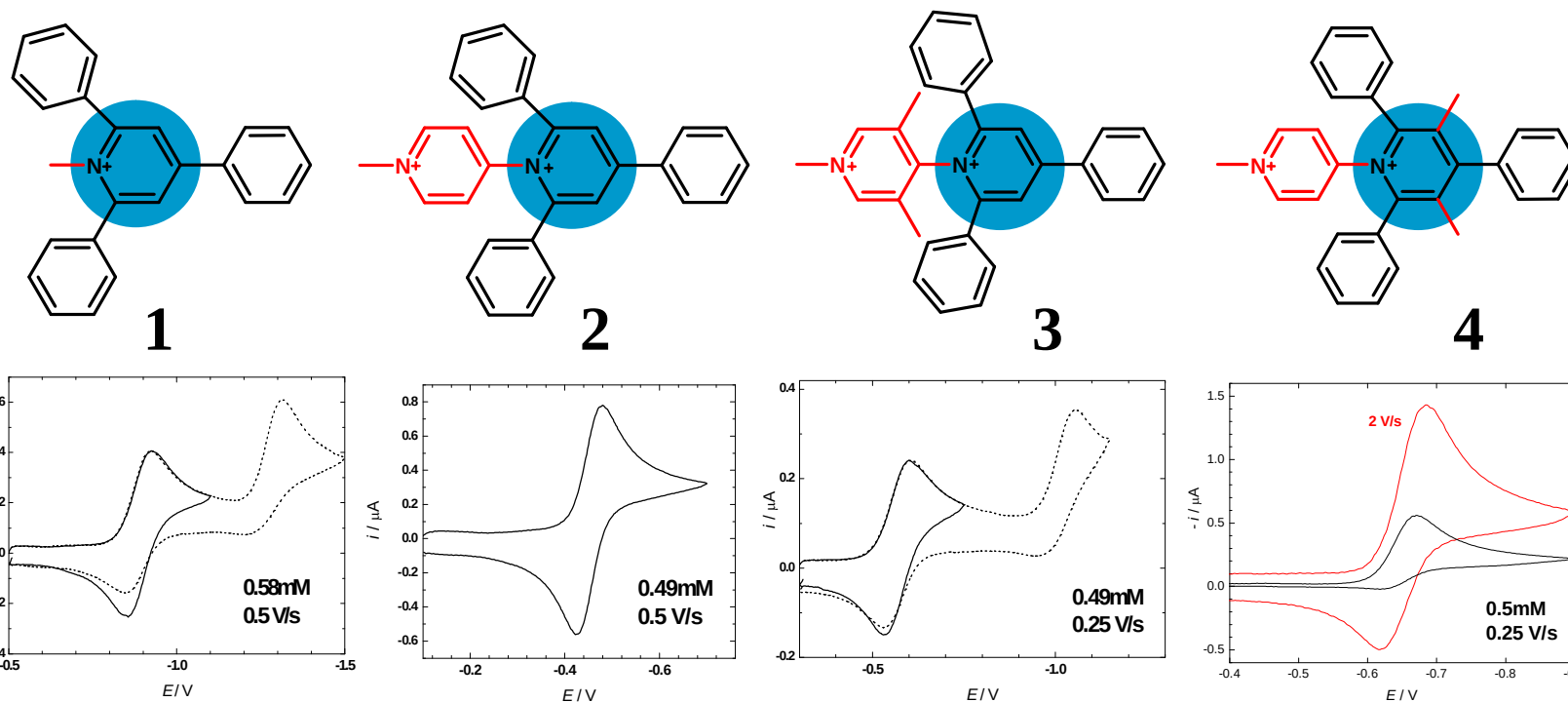
$$\Delta E \leq 0$$

Stepwise Two Electron Transfer

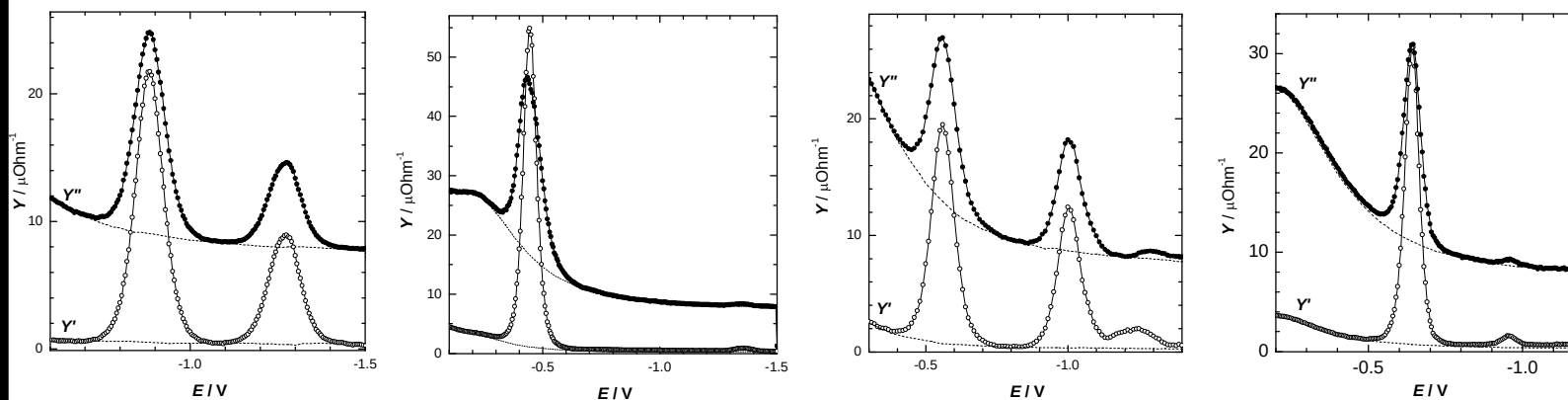


$$\Delta E > 0$$

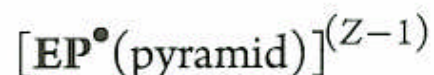
« Compression/Inversion of potentials within head-to-tail branched bipyridiniums ? »



AC polarograms in dimethylsulfoxide, $f = 160$ Hz



Single Step Two Electron Transfer



Stepwise Two Electron Transfer

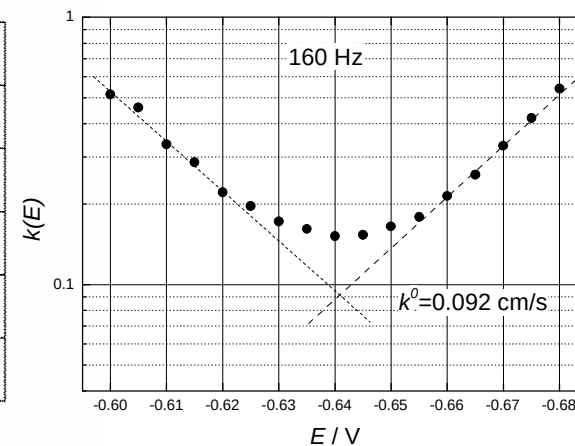
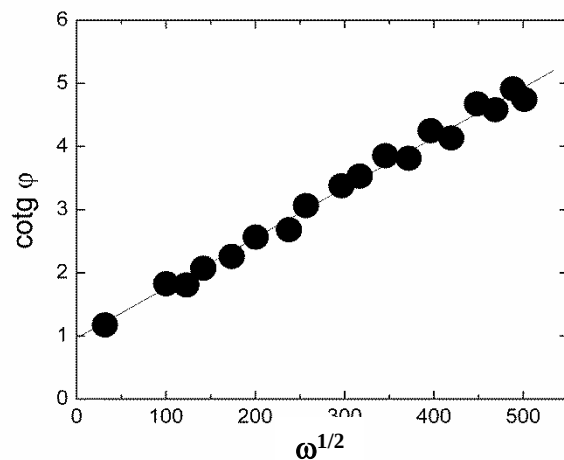


$$\Delta E > 0$$

Electron transfer kinetics

$$\tan \phi = \frac{Y_F''}{Y_F'}$$

$$\cotg \phi = 1 + \frac{\sqrt{2 \cdot \omega \cdot D}}{2 \cdot k_o}$$

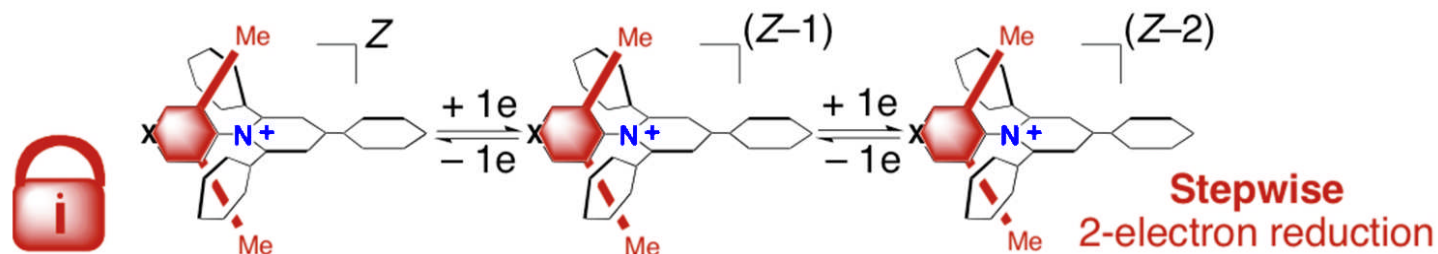


No.	E^0_1 / V	$k^0_1 / \text{cm} \cdot \text{s}^{-1}$	E^0_2 / V	$k^0_2 / \text{cm} \cdot \text{s}^{-1}$
1	- 0.883	1.4	- 1.283	0.85
2	- 0.450	0.23	-	-
3	- 0.567	1.0	- 1.004	0.68
4	- 0.627	0.10	-	-

Compound 3:

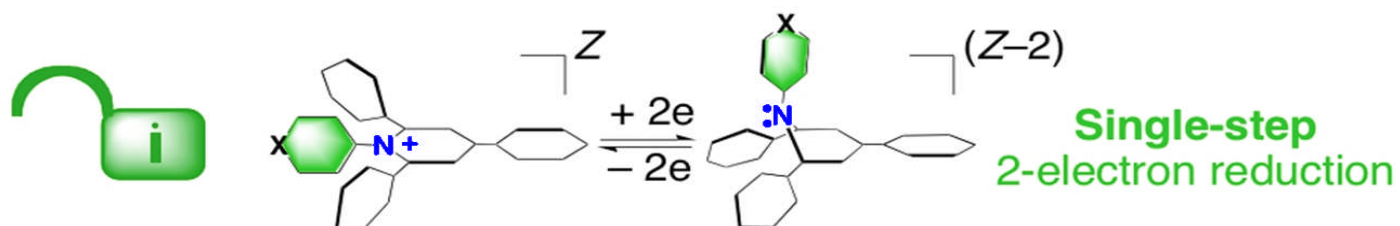
DFT (PBE0/EPR-II,
C-PCM for DMSO),
Gaussian'09

Entry	LUMO (native)	SOMO (singly reduced)	LUMO (singly reduced)	HOMO (doubly reduced)
Axial				
Prmd	Does not exist	Does not exist	Does not exist	

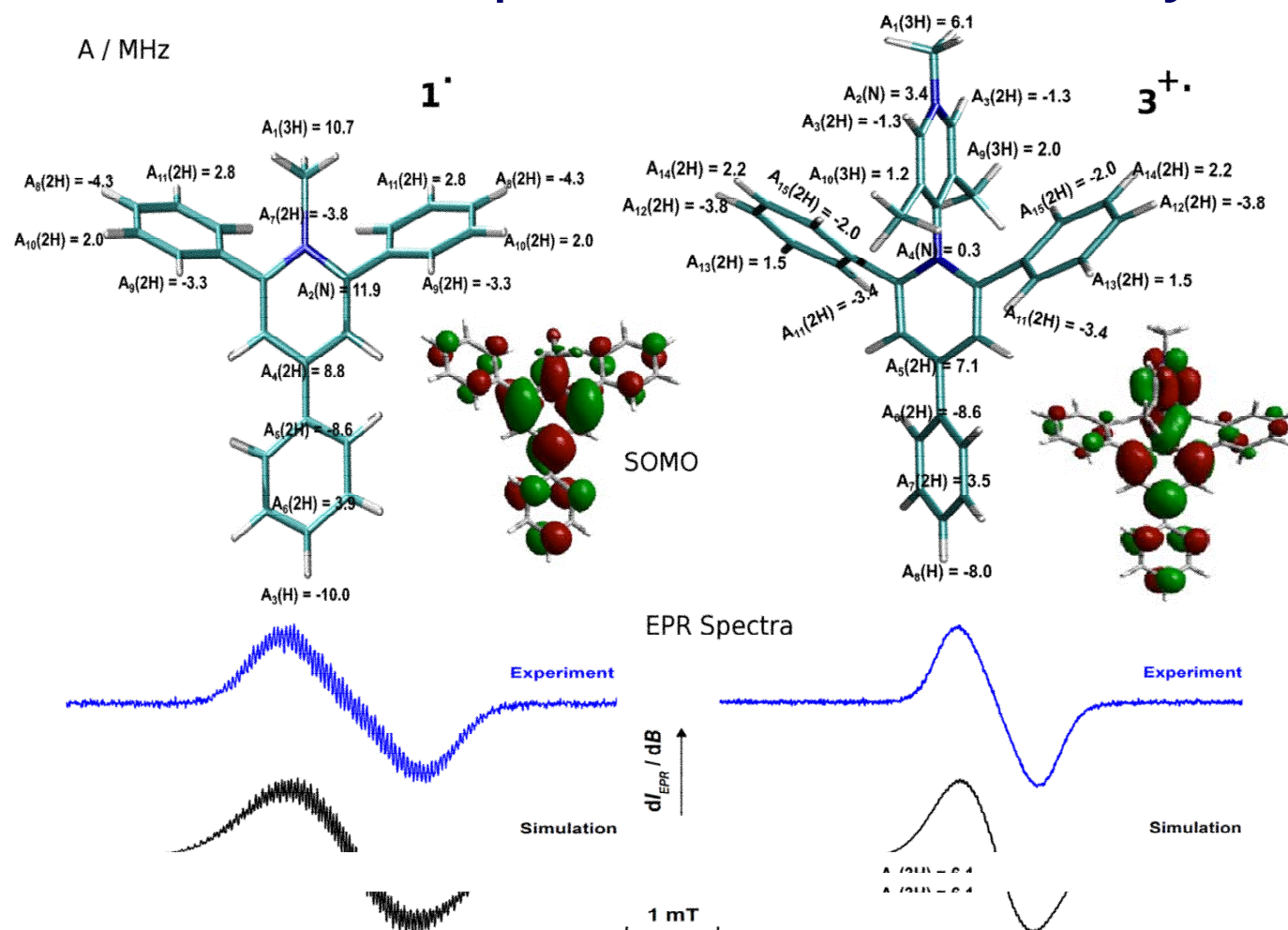


Compound 2 (and 4):

Entry	LUMO (native)	SOMO (singly reduced)	LUMO (singly reduced)	HOMO (doubly reduced)
Axial				
Pyramidal				



In-situ EPR spectroelectrochemistry

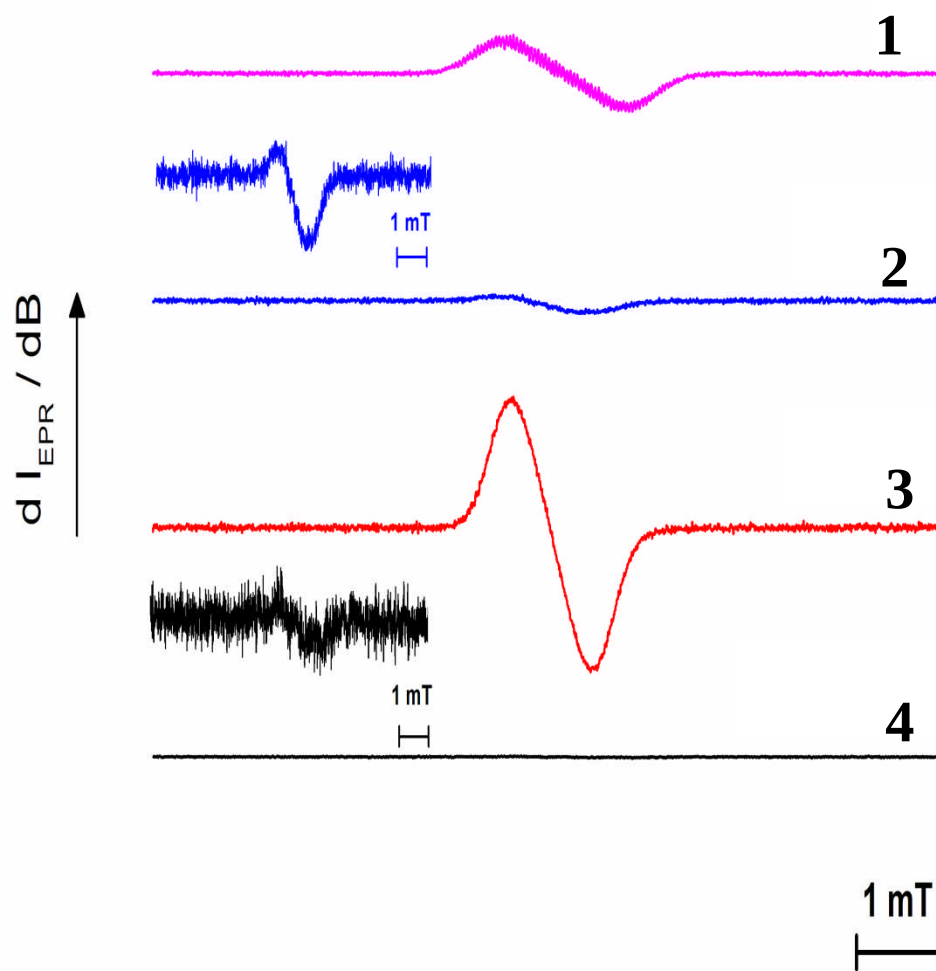


Hyperfine coupling constants point to spin density primarily delocalized over the central part of the molecule (including pyridinium sites)

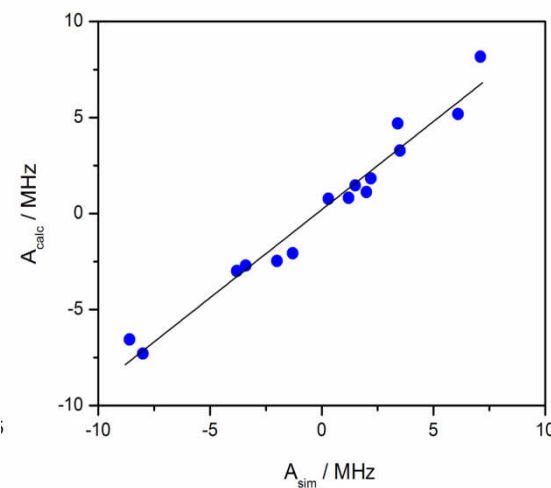
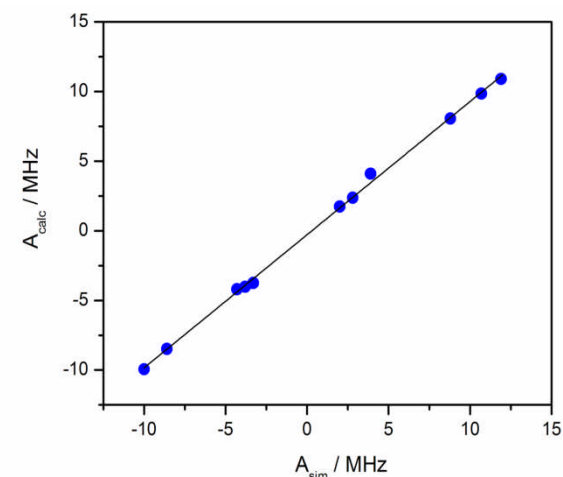
In-situ EPR spectroelectrochemistry

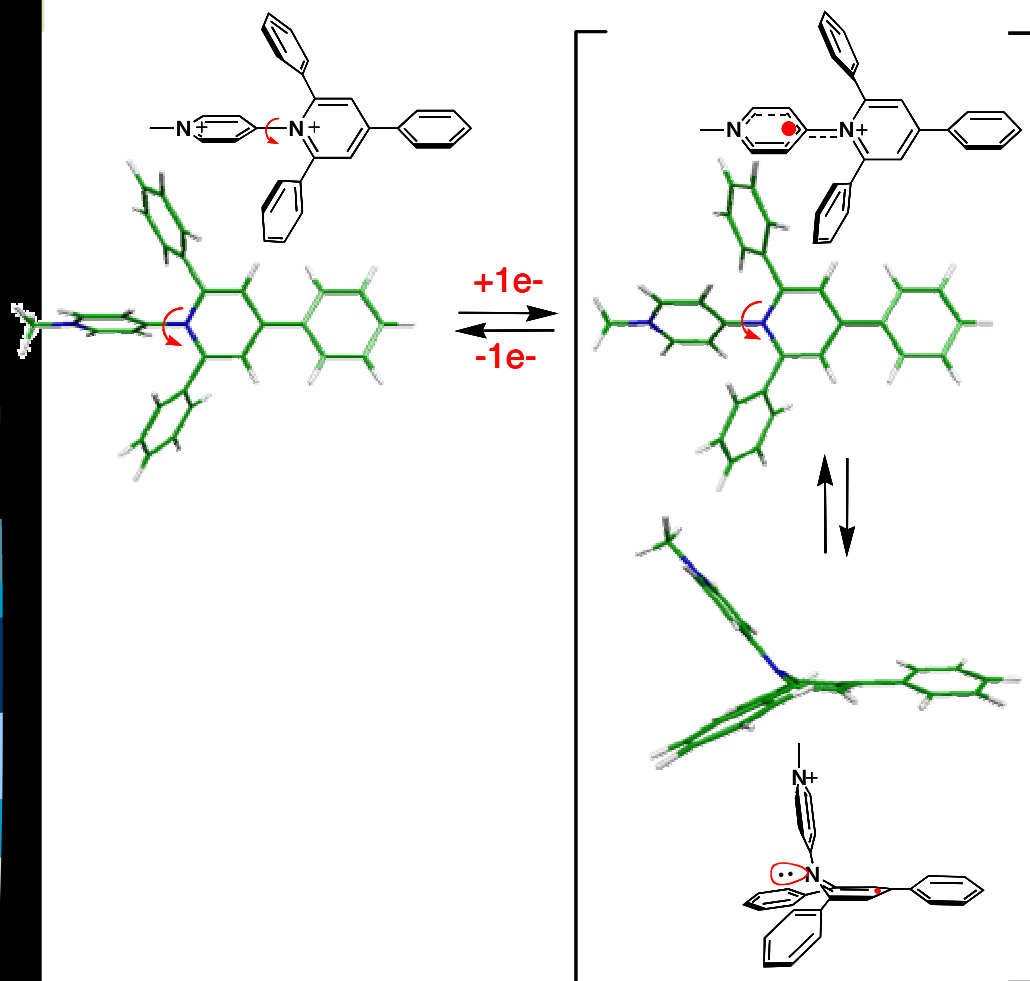
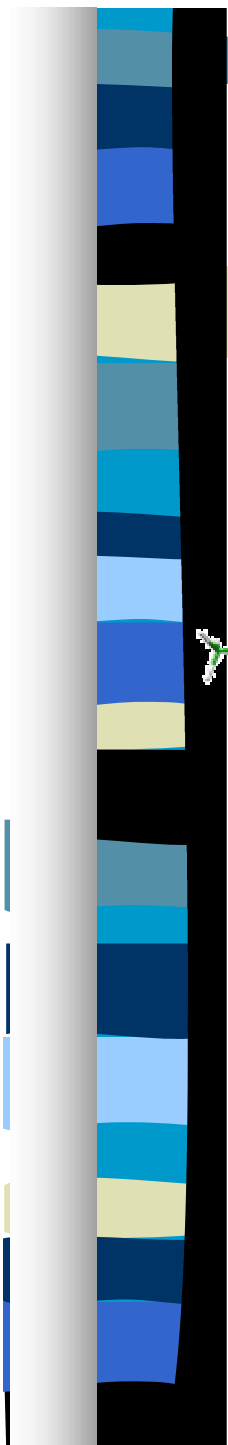
The EPR spectra of $2^{\cdot+}$ and $4^{\cdot+}$ under the same conditions exhibit broad ($\Delta B_{pp} = 1.2$ mT) lines without any hyperfine structure and low intensity.

Comparison of the EPR signal

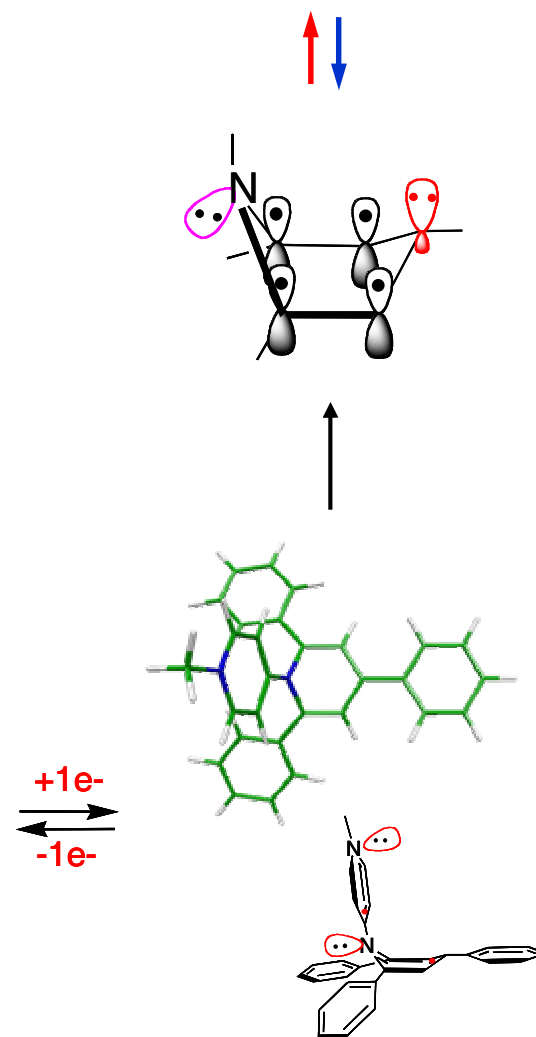


A_{calc} versus A_{exp}

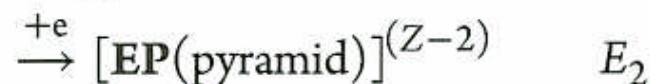
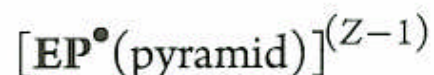




EPR result



Single Step Two Electron Transfer



$$\Delta E \leq 0$$

Stepwise Two Electron Transfer



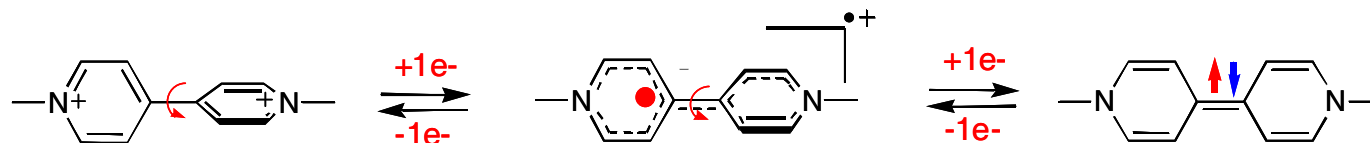
$$\Delta E > 0$$

Two kinetic ranges for electron transfer rates in head-to-tail branched bipyridiniums

$k^0 \geq 1.0 \text{ s}^{-1}$	$1.0 \text{ s}^{-1} > k^0 \geq 0.1 \text{ s}^{-1}$

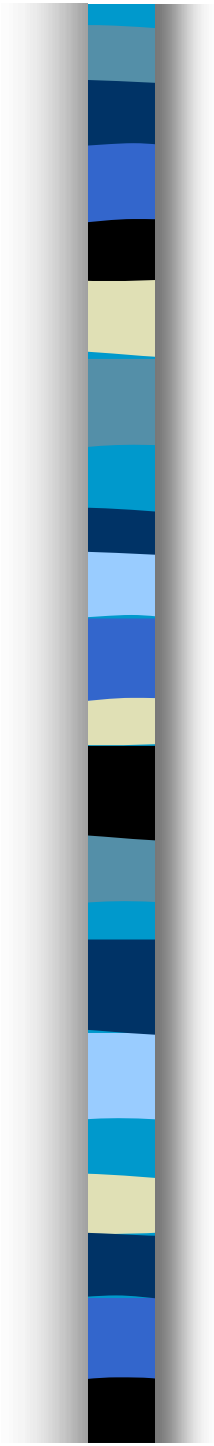
Dimethylviologen

$$k^0 < 0.1 \text{ s}^{-1}$$



$$E_1 = -0.44 \text{ V}$$

$$E_1 = -0.86 \text{ V}$$



Summary

- **Electron transfer is fast and reversible on CV timescale**
- First electron transfer in a stepwise process is very fast, whereas electron transfer in a single two-electron process with concomitant structural change (pyramidalization) is much slower
- EPR spectroelectrochemistry confirms the role of steric hindrance around the *N*-pyridinio site and that **pendant pyridinium serves as an electron acceptor (antenna)**
- **STERIC SWITCHING OF THE POTENTIAL COMPRESSION/INVERSION**

Thank you for your attention



2000



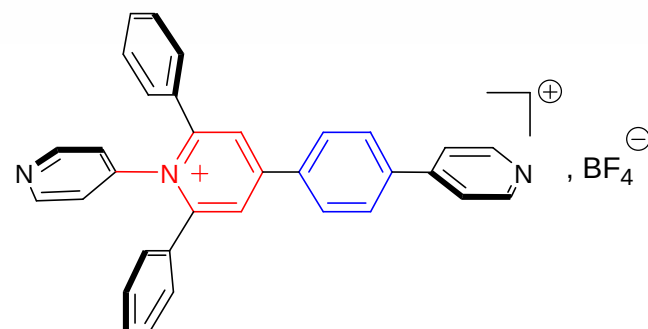
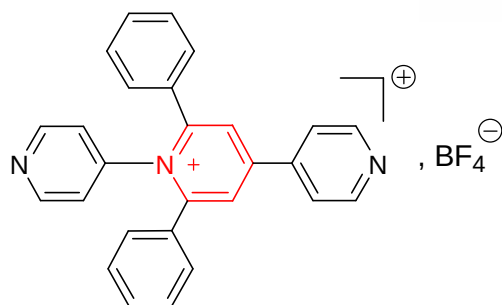
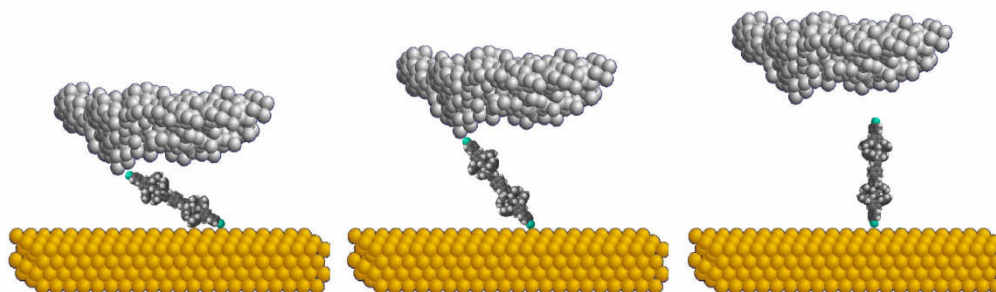
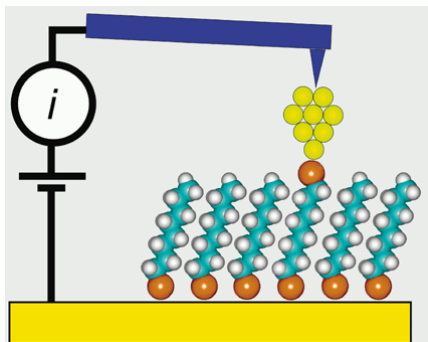
2010



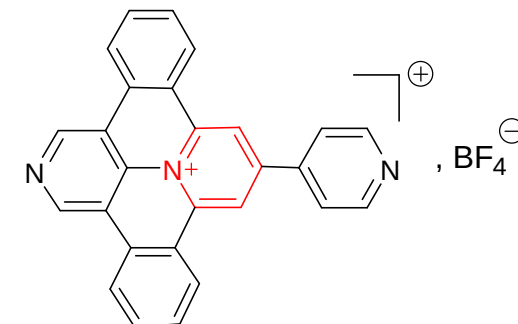
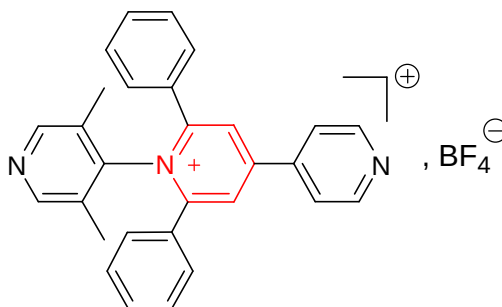
2020



Future prospects



1 wave



2 waves