

A New Supramolecular Chemistry Motif:
Horizontally Linked Viologen Radical Dimers

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Supramolecular chemistry promises to bring great improvements to plastics and molecular recognition devices, which is why it is important to constantly develop new motifs that can be used for either. We report a set of experiments to explore the thermodynamic properties of horizontally linked viologens.

When reduced to their radical cationic form, methylviologens are known to pi dimerize in water. These pi dimers are known to favor an off center formation where the N-CH₃ axis of the two molecules are offset from one another at an angle that would be convenient for horizontal dimers based upon tetrahedral bonds.¹

The predicted thermodynamic changes of linking them together in horizontal arrays are that enthalpy of dimerization will increase linearly with increasing viologen moieties, and that entropy of dimerization will be less unfavorable with increasing viologen moieties. These will be tested by temperature-dependent spectroelectrochemical studies.

CV and spectroelectrochemical experiments performed at different concentrations and temperatures will determine the contributions of enthalpy and entropy to the equilibrium constants.

REFERENCES

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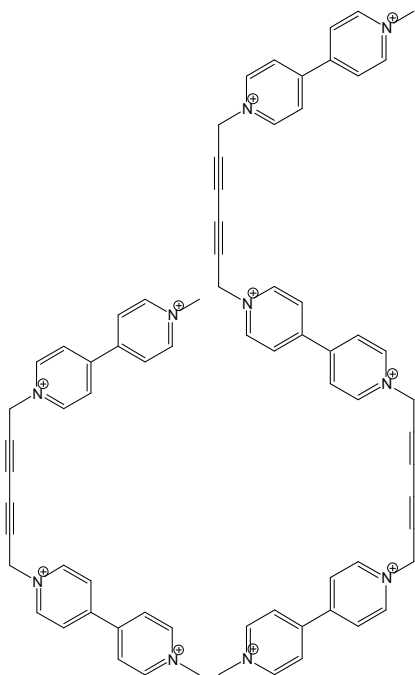


Figure 1. Examples of horizontally linked viologens to be studied.