Center for Exploitation of Solar Energy &

Department of Chemistry, University of Copenhagen

Tetrathiafulvalene-Fused Radiaannulenes and π-Extended Tetrathiafulvalenes – Towards New Electrochromic Materials

OMICS International

Mogens Brøndsted Nielsen

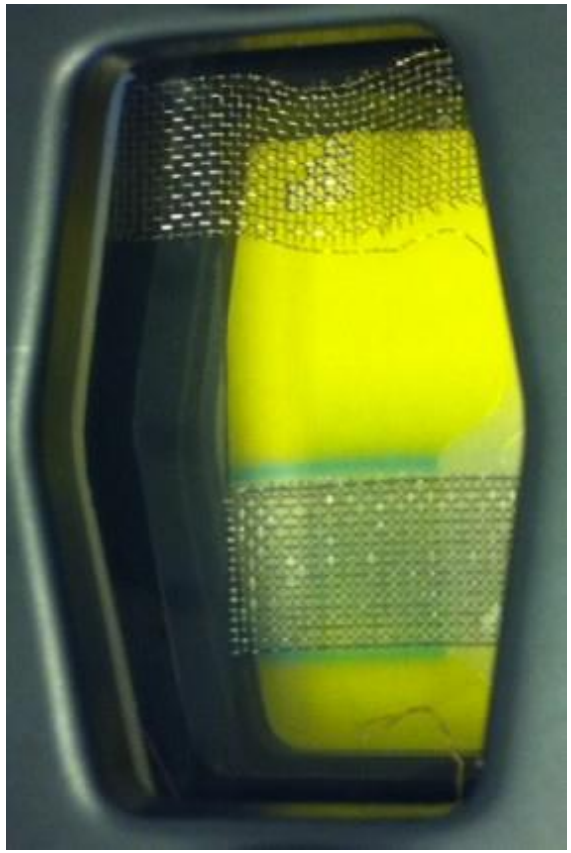


Smart Materials & Structures, Las vegas, 15-17.6.2015

Electrochromic Materials

- Reversibly changing color by electrochemical redox reactions





nature

THE INTERNATIONAL WEEKLY JOURNAL OF SCIENCE



Windows upgrade

Smart nanocrystal-in-glass composites regulate light and heat transmission

PAGES 278 & 323

PSYCHOLOGY

UNRELIABLE EVIDENCE

The vagaries of eyewitness testimony

PAGE 268

ECOLOGY

CARBON SINKS FEEL THE HEAT

Climate extremes could raise atmospheric CO_2

PAGE 287

QUANTUM INFORMATION

BRIDGING THE GAP

Two new approaches to on-demand teleportation

PAGES 282, 315 & 319

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Electrochromic Materials

- **On/off switching of NIR absorptions?**

Optical attenuator: device used to reduce the power level of an optical signal, usually working by absorbing the light

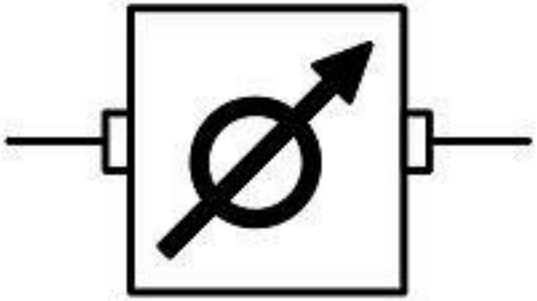
Telecommunication industry: wavelengths of 1300 and 1550 nm

Both anodically and cathodically **NIR-coloring materials** are ideally needed

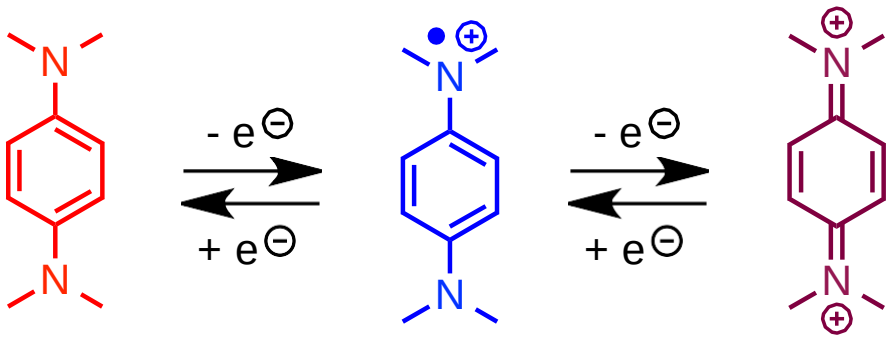
π-Conjugated organic molecules



…. Redox-active molecules



Wurster's Blue



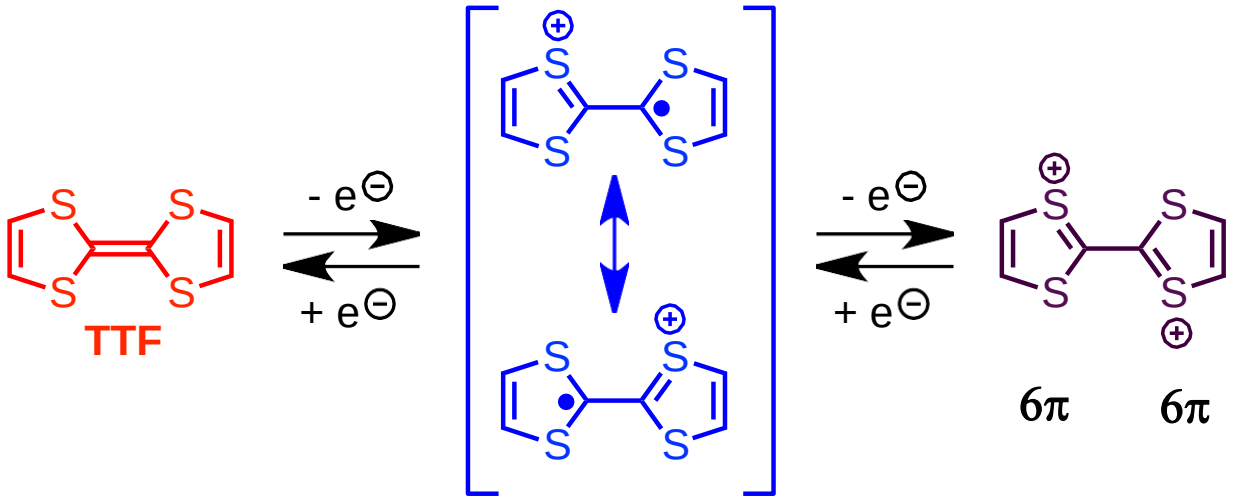
Mixed Valence (MV)

fully delocalized

Blue color

Wurster redox system: aromatic in reduced form

Tetrathiafulvalene (TTF)

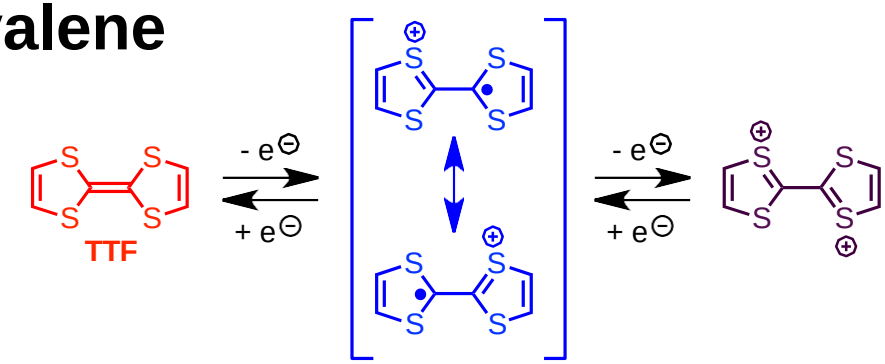


Mixed Valence (MV)

fully delocalized

Weitz redox system: aromatic in oxidized form

Tetrathiafulvalene

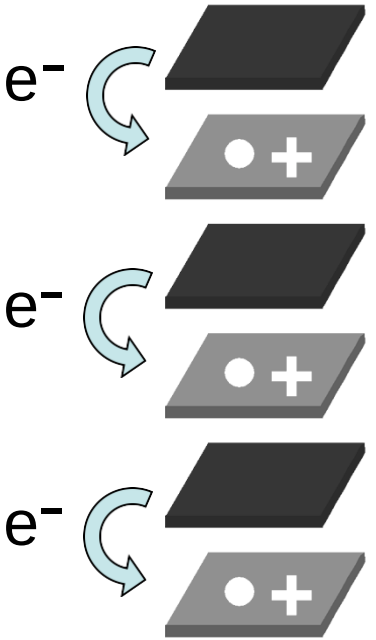


Mixed Valence (MV)
fully delocalized



Properties can be tuned by introduction of π-spacer or substituents R

Mixed valence conduction

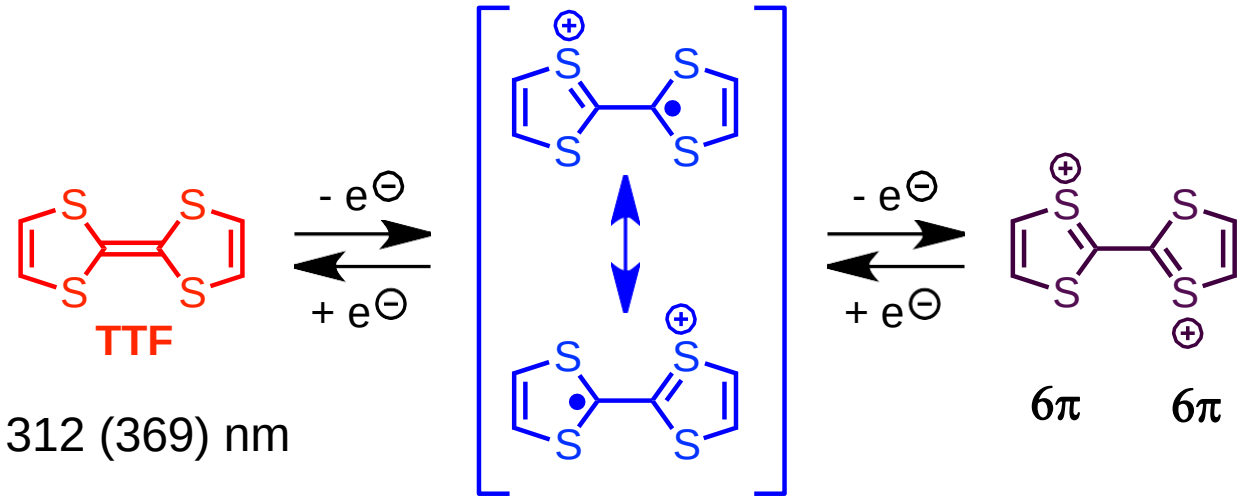


TTF / $TTF^{\bullet+}$

Some applications of TTF:

- **Redox-active unit in supramolecular chemistry … molecular sensors, switches, and devices**
- **Redox-active unit in molecular electronics**
- **Mixed valence ($TTF/TTF^{\bullet+}$) organic conductors**
- **Electrochromic materials**

Tetrathiafulvalene (TTF)



312 (369) nm

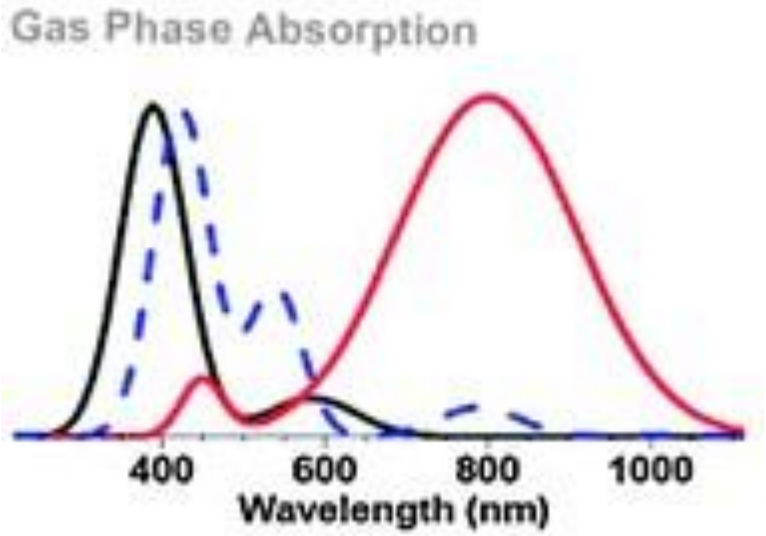
390 nm

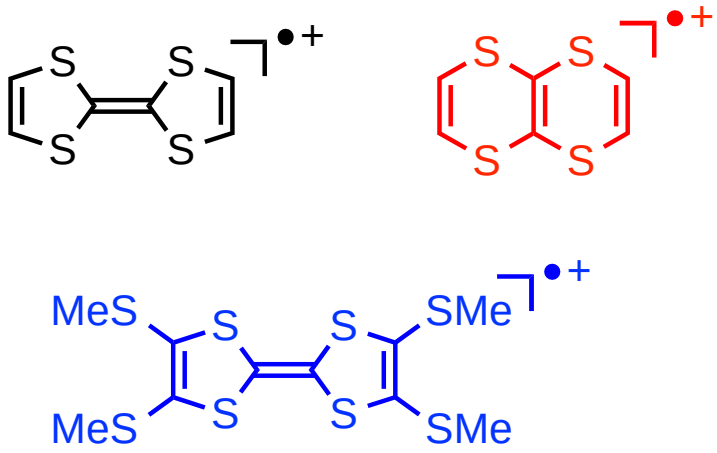
Mixed Valence (MV)

fully delocalized

580 nm

Radical Cation Absorptions





M.-B.S. Kirketerp, L.A.E. Leal, D. Varsano, A. Rubio, T.J.D. Jørgensen, K. Kilså, M.B. Nielsen, S.B. Nielsen, *Chem. Commun.* **2011**, *47*, 6900-6902.

Robin and Day Classification of Two-Center Redox Systems

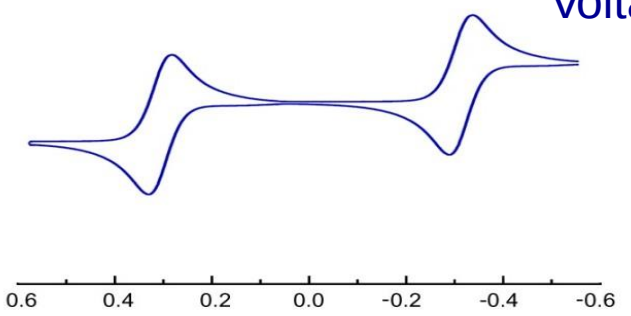
Class III: $D_\pi_D \underset{+\,e^-}{\overset{-\,e^-}{\rightleftharpoons}} [D-\pi-D]^{+} \underset{+\,e^-}{\overset{-\,e^-}{\rightleftharpoons}} [D-\pi-D]^{2+}$ $\Delta E_{ox} > 0.2$ V

fully delocalized

Mixed Valence (MV)

Class III

Cyclic Voltammogram



Robin and Day Classification of Two-Center Redox Systems

$\Delta E_{ox} = E_{ox2} - E_{ox1}$

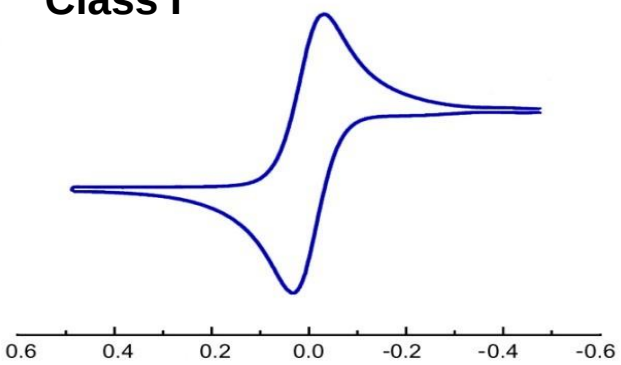
Class I: $D-\pi-D \underset{+\,2e^-}{\overset{-\,2e^-}{\rightleftharpoons}} [D-\pi-D]^{2+}$ $\quad \Delta E_{ox} \approx 0$ V (35 mV)

Class III: $D_\pi_D \underset{+\,e^-}{\overset{-\,e^-}{\rightleftharpoons}} [D-\pi-D]^{+} \underset{+\,e^-}{\overset{-\,e^-}{\rightleftharpoons}} [D-\pi-D]^{2+}$ $\quad \Delta E_{ox} > 0.2$ V

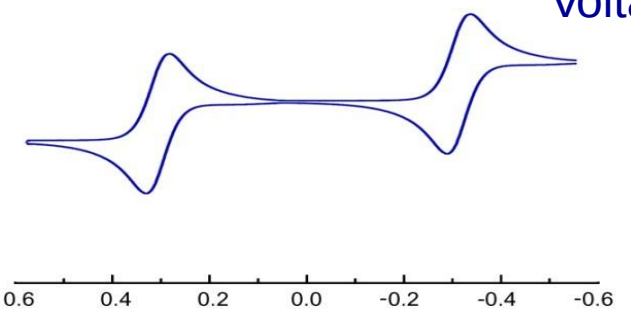
fully delocalized

Mixed Valence (MV)

Class I



Class III



Cyclic Voltammogram

Robin and Day Classification of Two-Center Redox Systems

$\Delta E_{ox} = E_{ox2} - E_{ox1}$

Class I: $D-\pi-D \underset{+\,2e^-}{\overset{-\,2e^-}{\rightleftharpoons}} [D-\pi-D]^{2+}$ $\quad \Delta E_{ox} \approx 0$ V (35 mV)

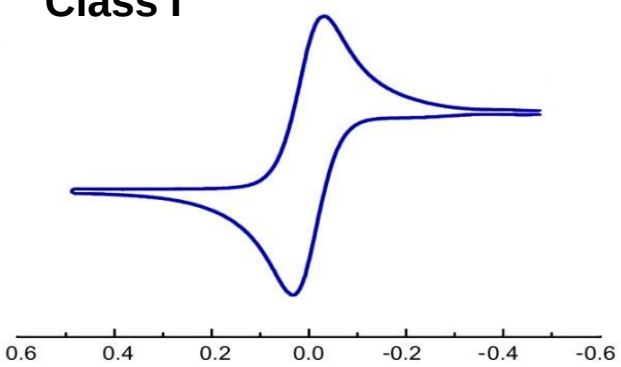
Class II: $D_\pi_D \underset{+\,e^-}{\overset{-\,e^-}{\rightleftharpoons}} D^{+}\text{-}\pi\text{-}D \underset{+\,e^-}{\overset{-\,e^-}{\rightleftharpoons}} [D-\pi-D]^{2+}$ $\quad \Delta E_{ox} \approx 0$ - 0.2 V

Class III: $D_\pi_D \underset{+\,e^-}{\overset{-\,e^-}{\rightleftharpoons}} [D-\pi-D]^{+} \underset{+\,e^-}{\overset{-\,e^-}{\rightleftharpoons}} [D-\pi-D]^{2+}$ $\quad \Delta E_{ox} > 0.2$ V

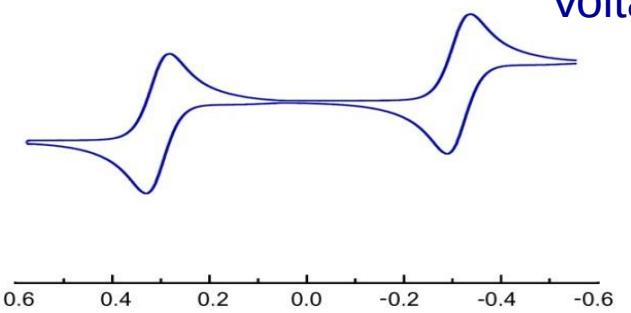
fully delocalized

Mixed Valence (MV)

Class I

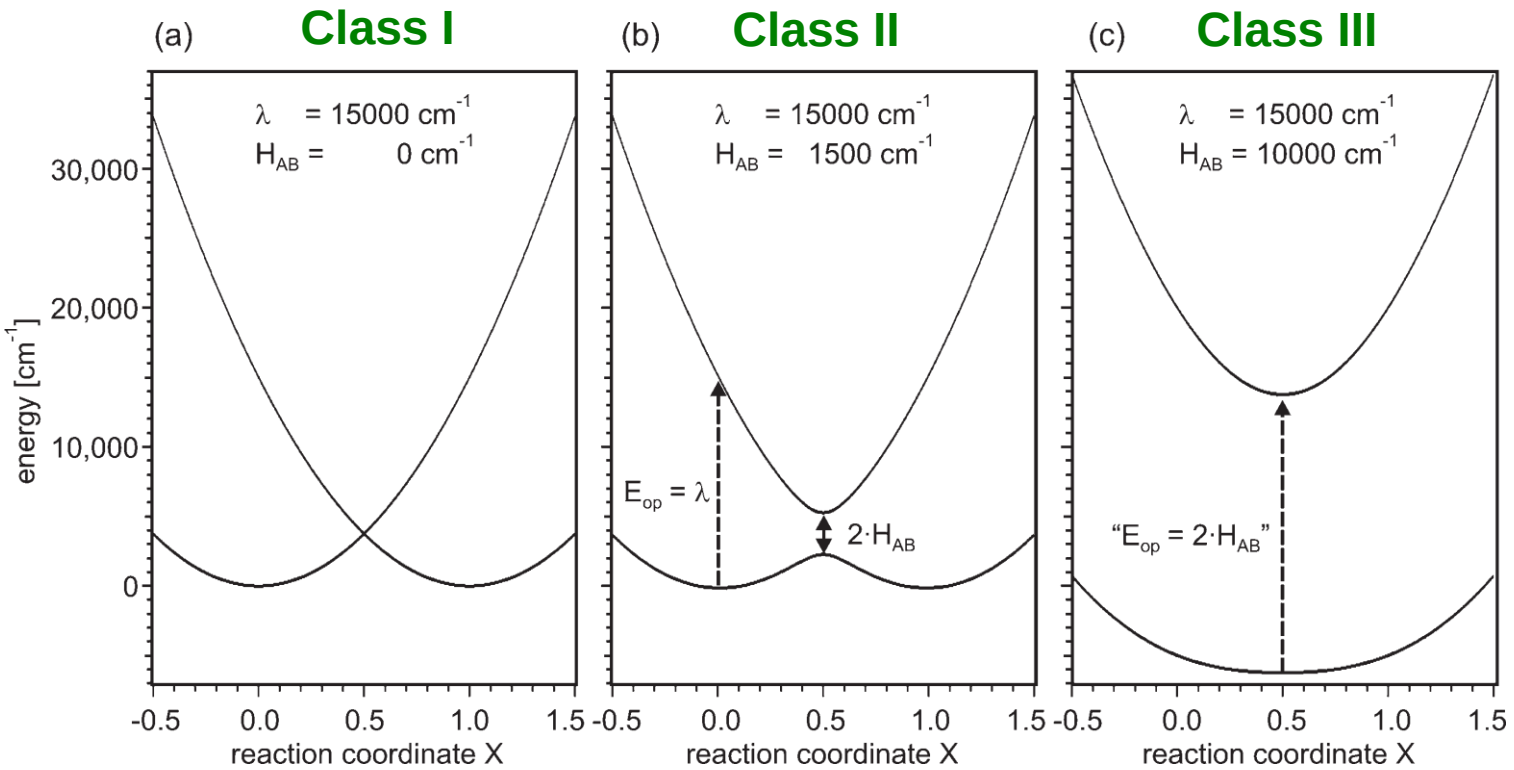


Class III



Cyclic Voltammogram

Potential Energy Surfaces for Electron Transfer in MV Systems

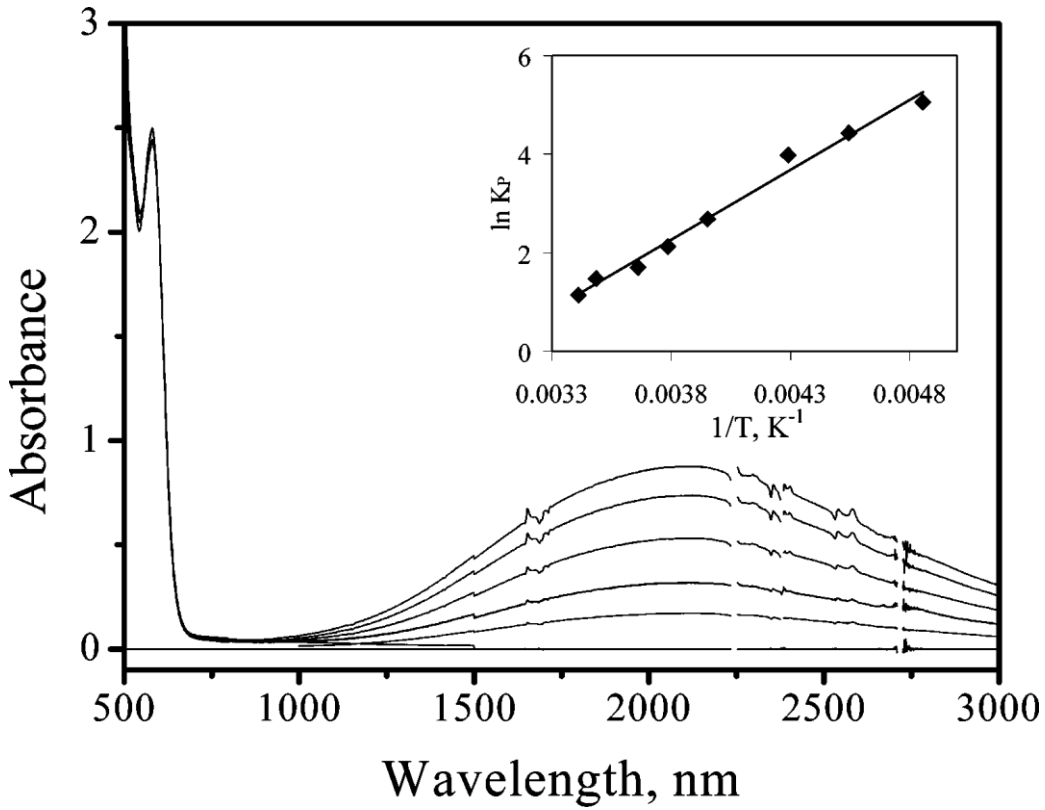


Electronic coupling: **None** **Weak** **Strong**

Broad NIR absorption *Narrow NIR absorption*

J. Hankache, O. S. Wenger, *Chem. Rev.* **2011**, *111*, 5138-5178.

Intermolecular MV Species – TTF•TTF^{+}



[TTF•TTF^{+}]:

K_{as} = 6.0 M^{-1}

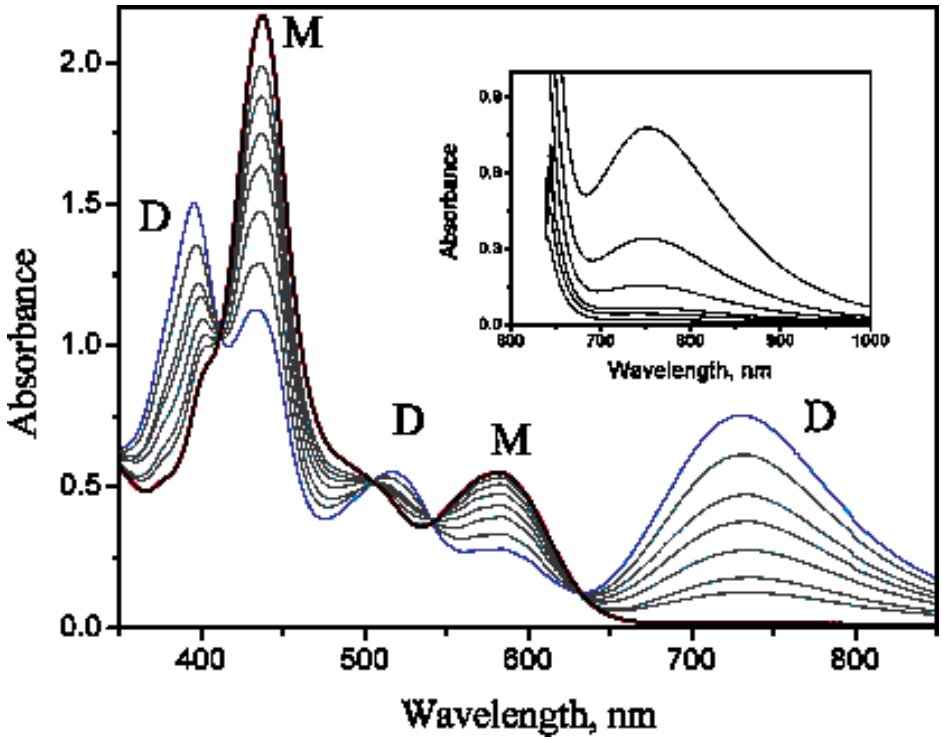
Class II:

(2310 x ν_{max})$^{1/2}$ = FWHM

Figure 4. Spectral changes attendant upon the addition of neutral **TTF** to the 5.8 mM solution of **TTF**$^{+}$•CB^{-} in CH_2Cl_2 at 22 °C. **TTF** concentration (bottom to top): 0, 44, 88, 141, 200, and 250 mM. Inset: Linear dependence of ln K_{CT} on 1/T.

S. V. Rosokha, J. K. Kochi, *J. Am. Chem. Soc.* **2007**, *129*, 828-838.

π-Dimer of Two TTF Radical Cations



[TTF⁺•TTF⁺]:

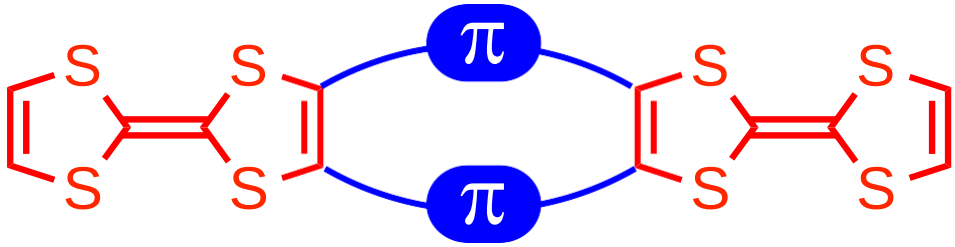
K_{as} = 0.6 M^{-1}

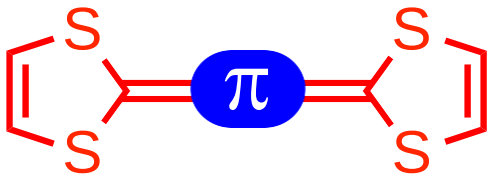
Figure 2. Temperature-dependent absorption of 1.3 mM solutions of **TTF**$^{+\bullet}$CB^{-} in acetone, showing reversible interconversion between the electronic spectrum of the monomer M (prevailing at room temperature) and the dimer D (at low temperature). Temperature (in °C, from bottom to top at 740 nm): 22, - 40, - 55, - 63, - 70, - 78, - 85, and - 90. Inset: Low-energy range of the absorption at high concentrations of **TTF**$^{+\cdot}$CB^{-} (λ) 2 mm, 22 °C). Concentration of **TTF**$^{+\bullet}$CB^{-} (in mM, bottom to top): 0, 4.7, 6.2, 9.3, 13, and 19.

S. V. Rosokha, J. K. Kochi, *J. Am. Chem. Soc.* **2007**, *129*, 828-838.

Outline



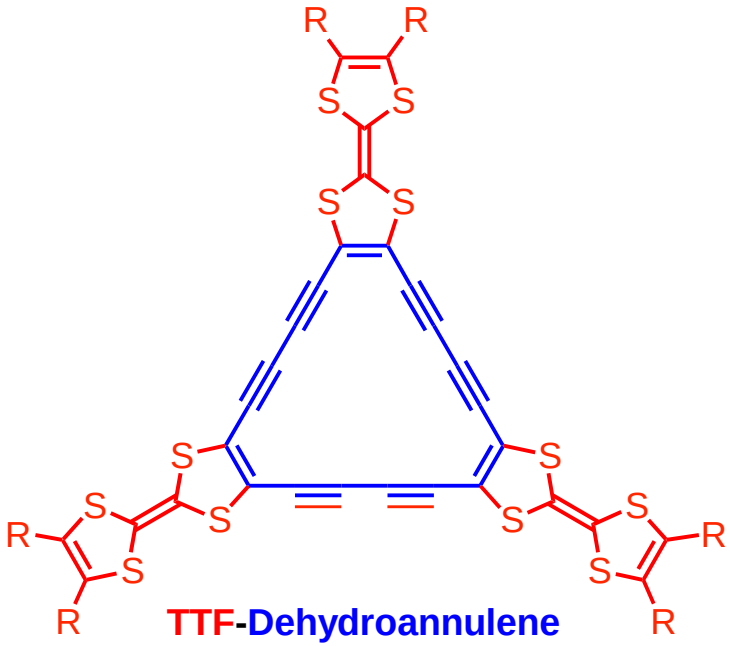




- **Redox properties?**
- **Optical properties of oxidized species?**
- **Interactions between redox centers?**

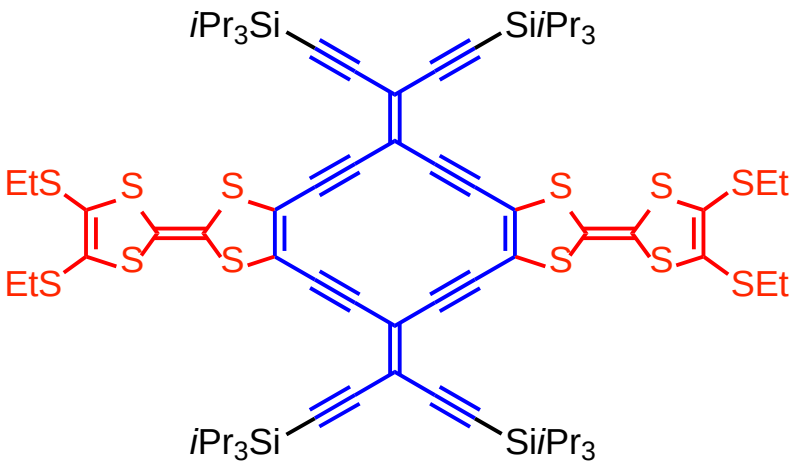
Tetrathiafulvalene (TTF) – Acetylene Macrocycles

How do the TTFs interact?



TTF-Dehydroannulene

Linearly conjugated cyclic core

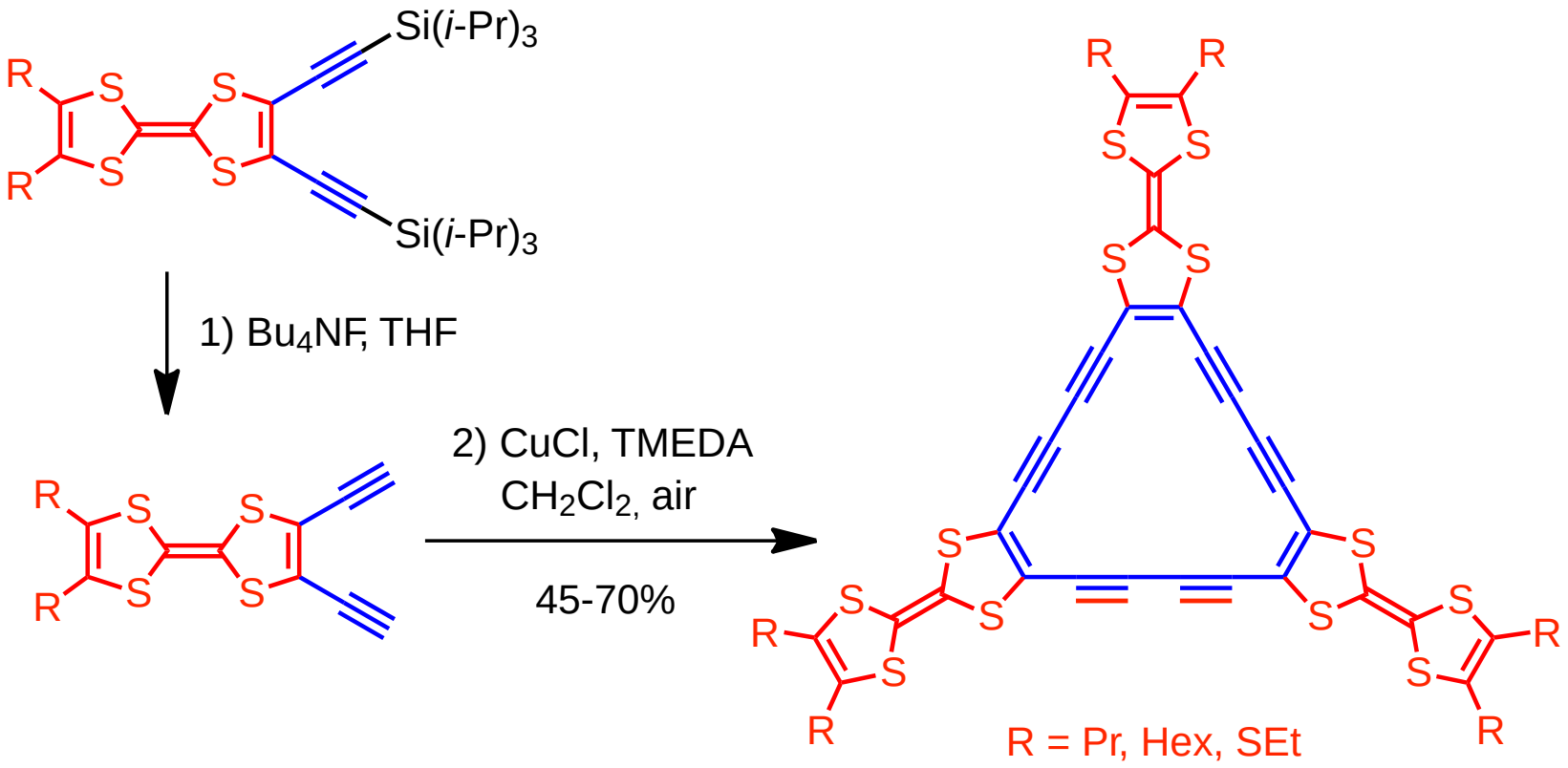


TTF-Radiaannulene

Cross-conjugated cyclic core

Synthesis of TTF-Dehydroannulenes

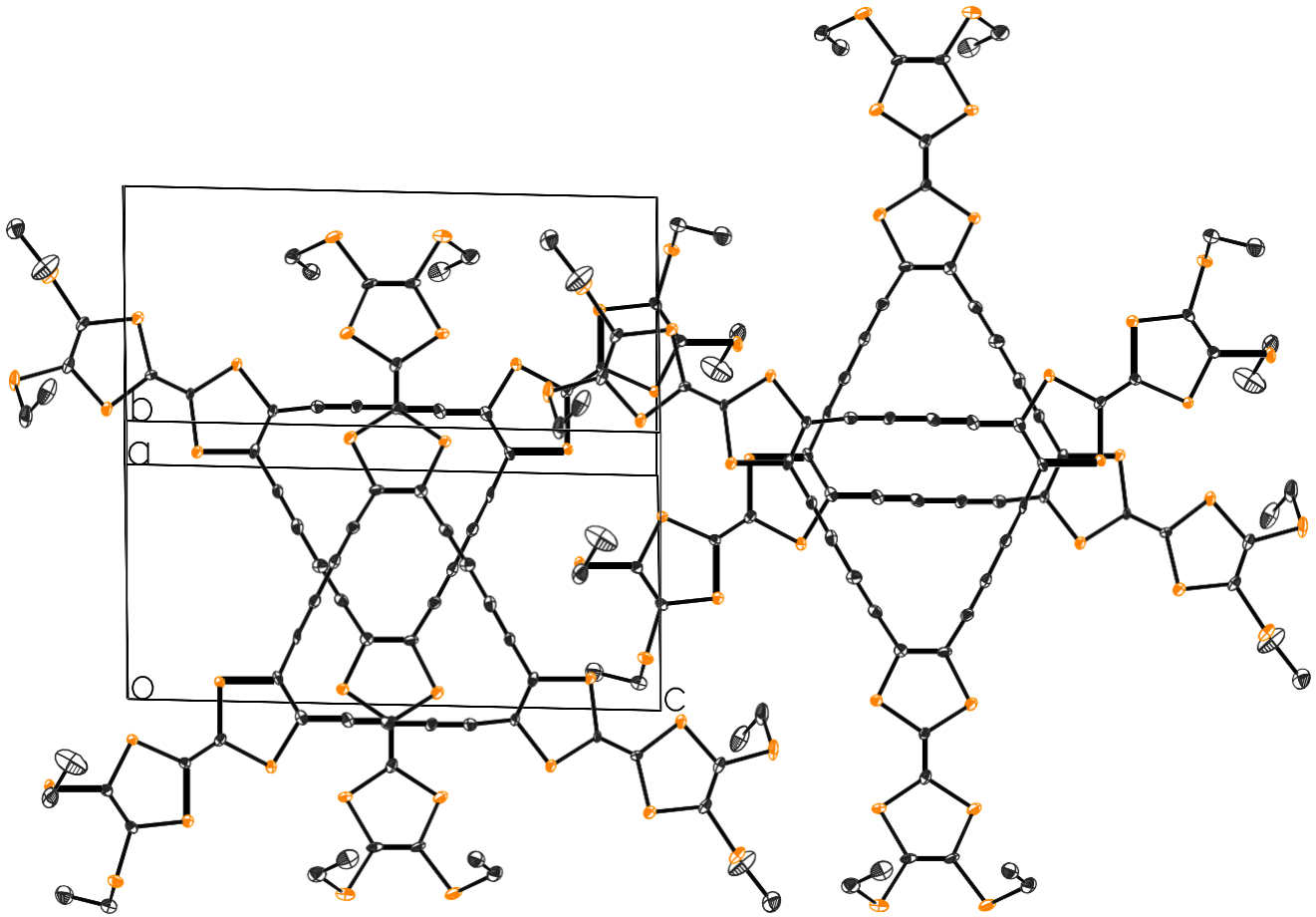
by Hay Couplings



A. S. Andersson, K. Kilså, T. Hassenkam, J.-P. Gisselbrecht, C. Boudon, M. Gross, M. B. Nielsen, F. Diederich, *Chem. Eur. J.* **2006**, *12*, 8451.

K. Lincke, M. A. Christensen, F. Diederich, M. B. Nielsen, *Helv. Chim. Acta* **2011**, *94*, 1743-1753.

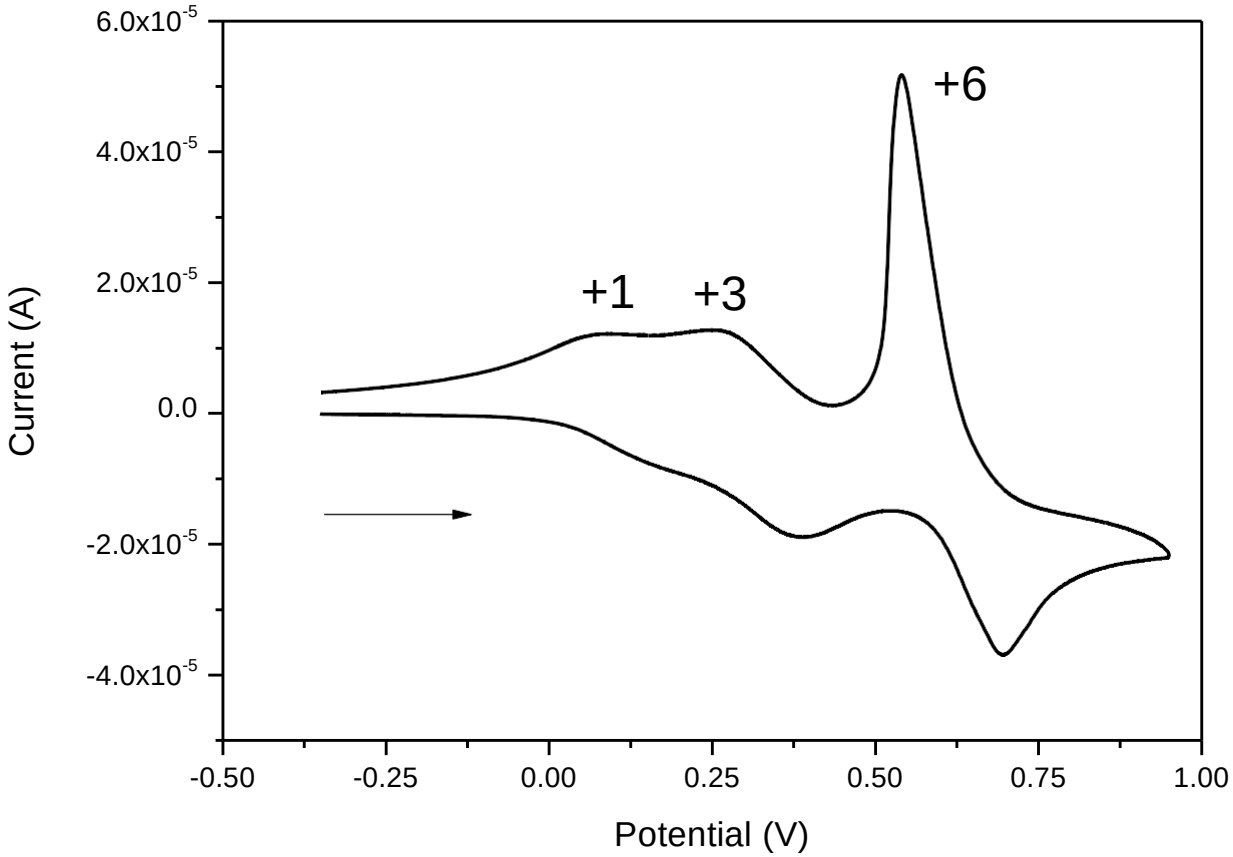
X-Ray Crystal Structure

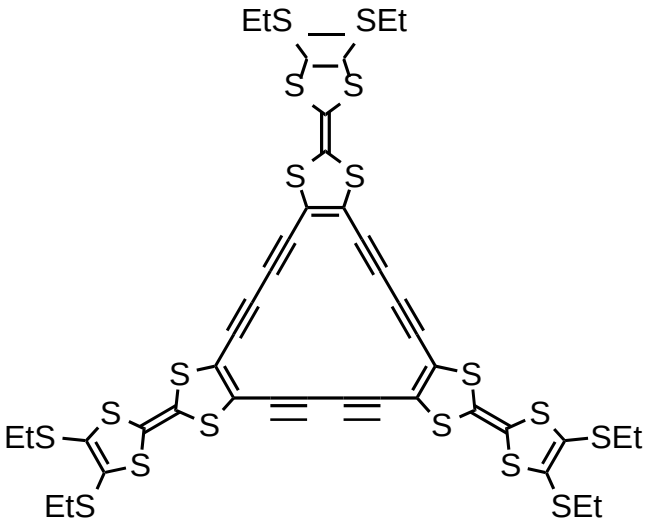


No π–π stacking interactions

The molecule does not seem either to associate in solution

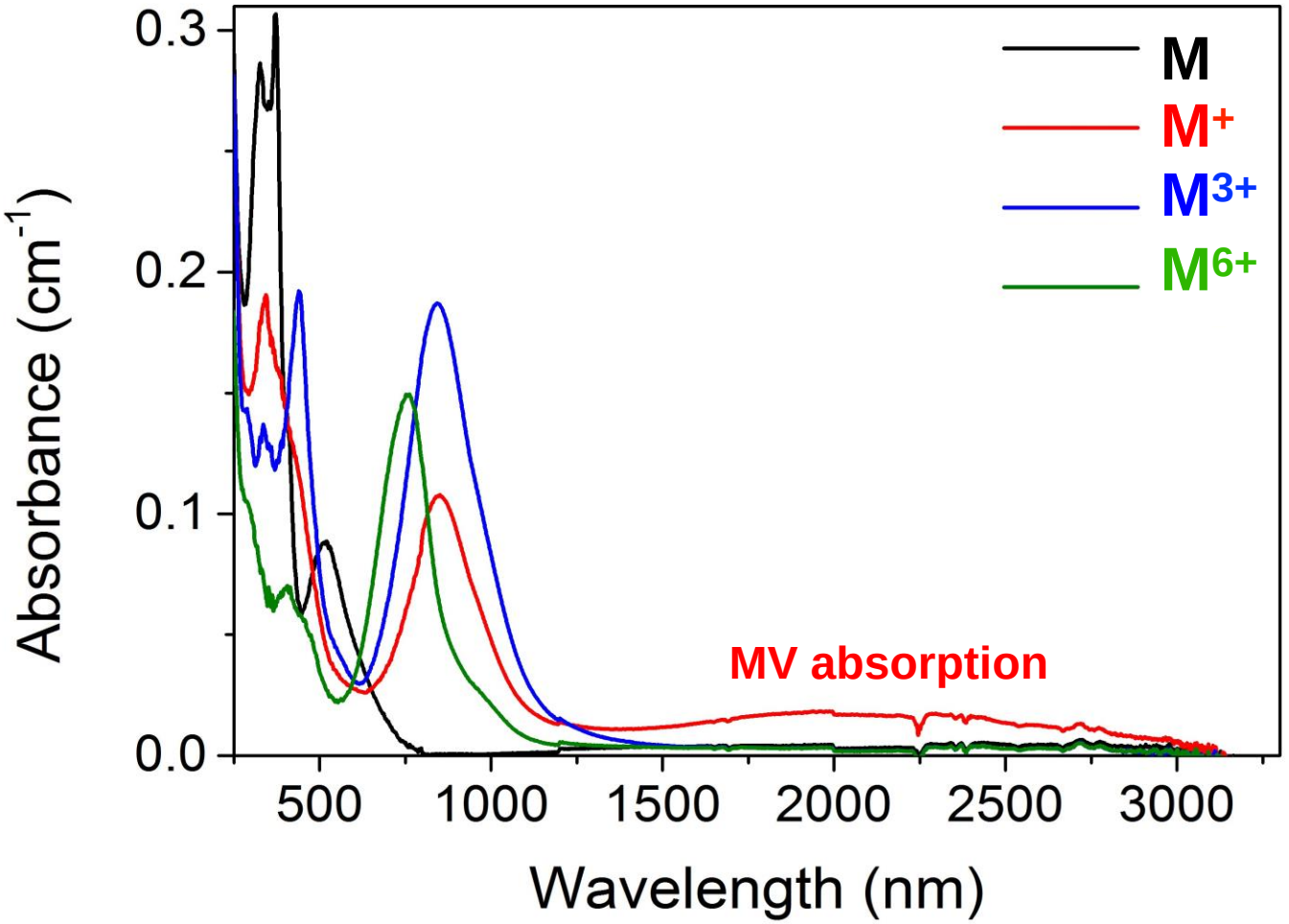
Electrochemistry

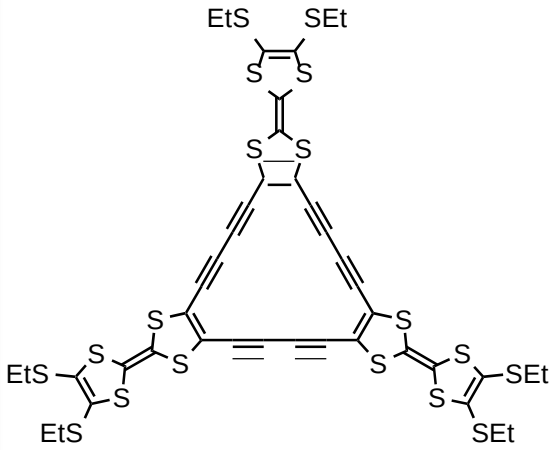




CH_2Cl_2 + 0.1 M Bu_4NPF_6

Spectroelectrochemistry

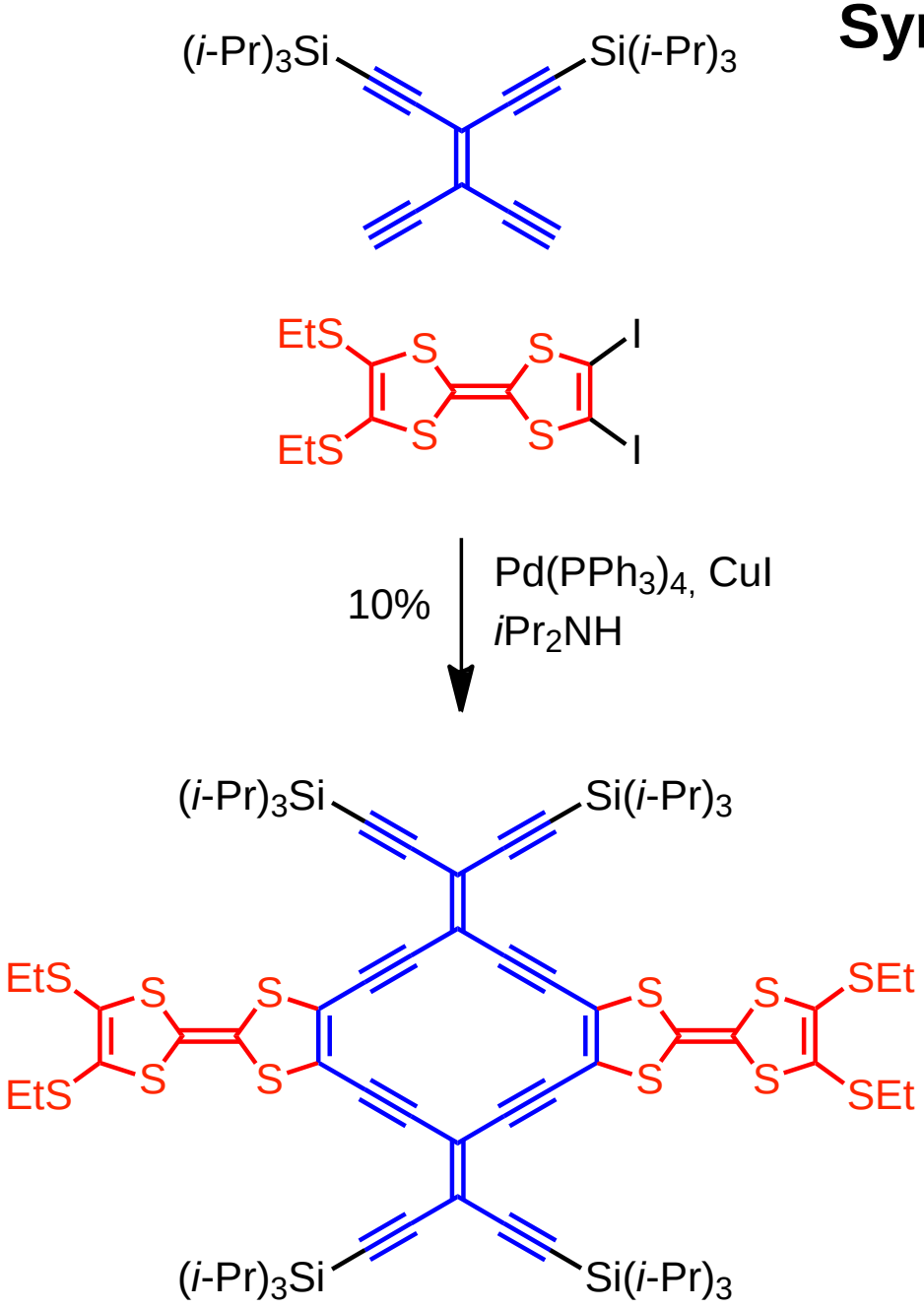


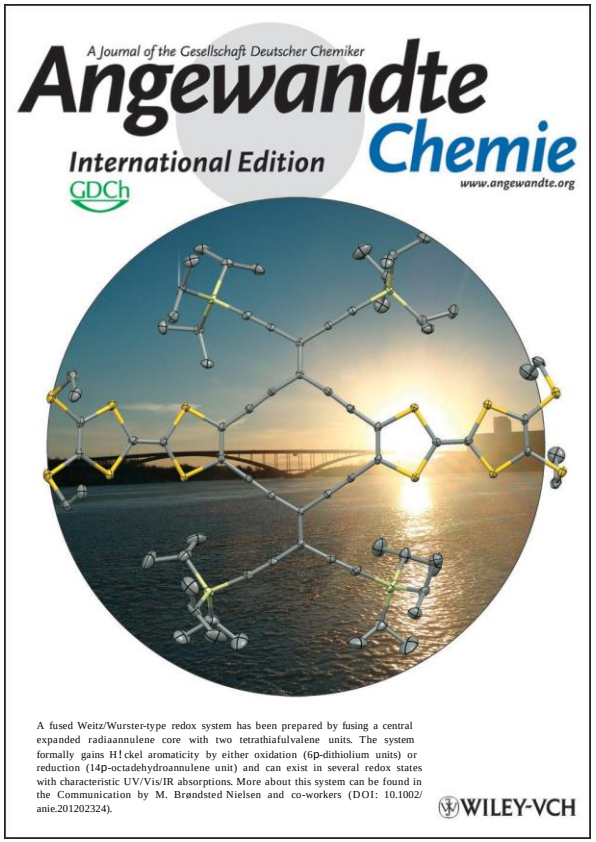


CH_2Cl_2 + 0.1 M Bu_4NPF_6

Synthesis of TTF-Radiaannulene

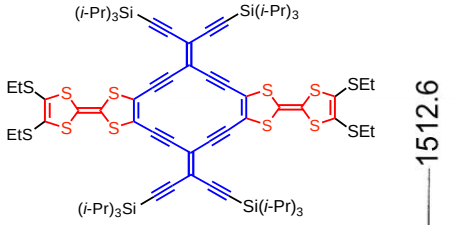
by Sonogashira Couplings

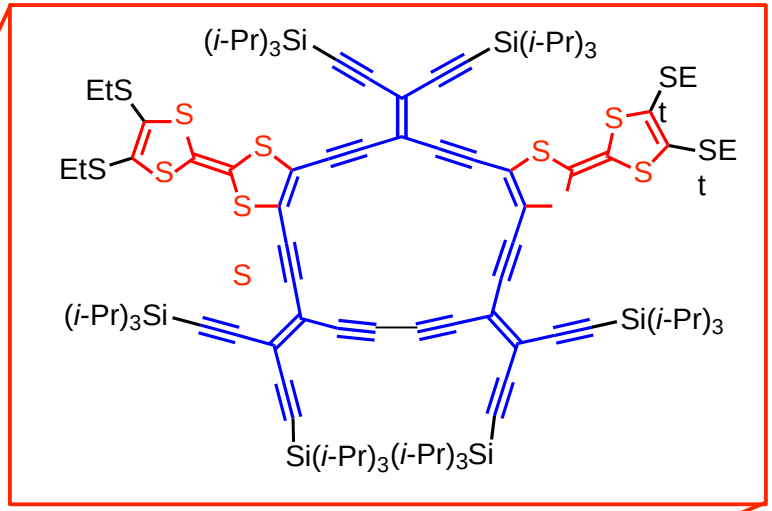


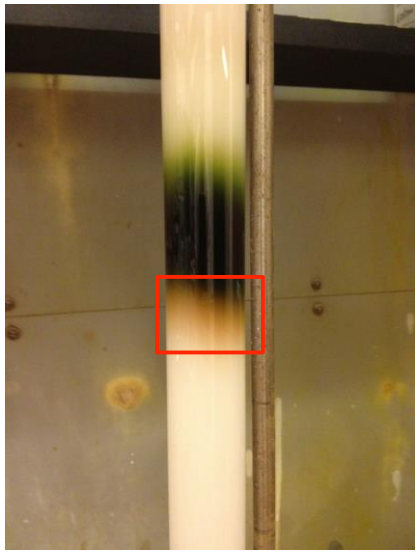


K. Lincke, A. F. Frellsen, C. R. Parker, A. D. Bond, O. Hammerich, M. B. Nielsen, *Angew. Chem*. **2012**, *51*, 6099-6102 .

MALDI MS

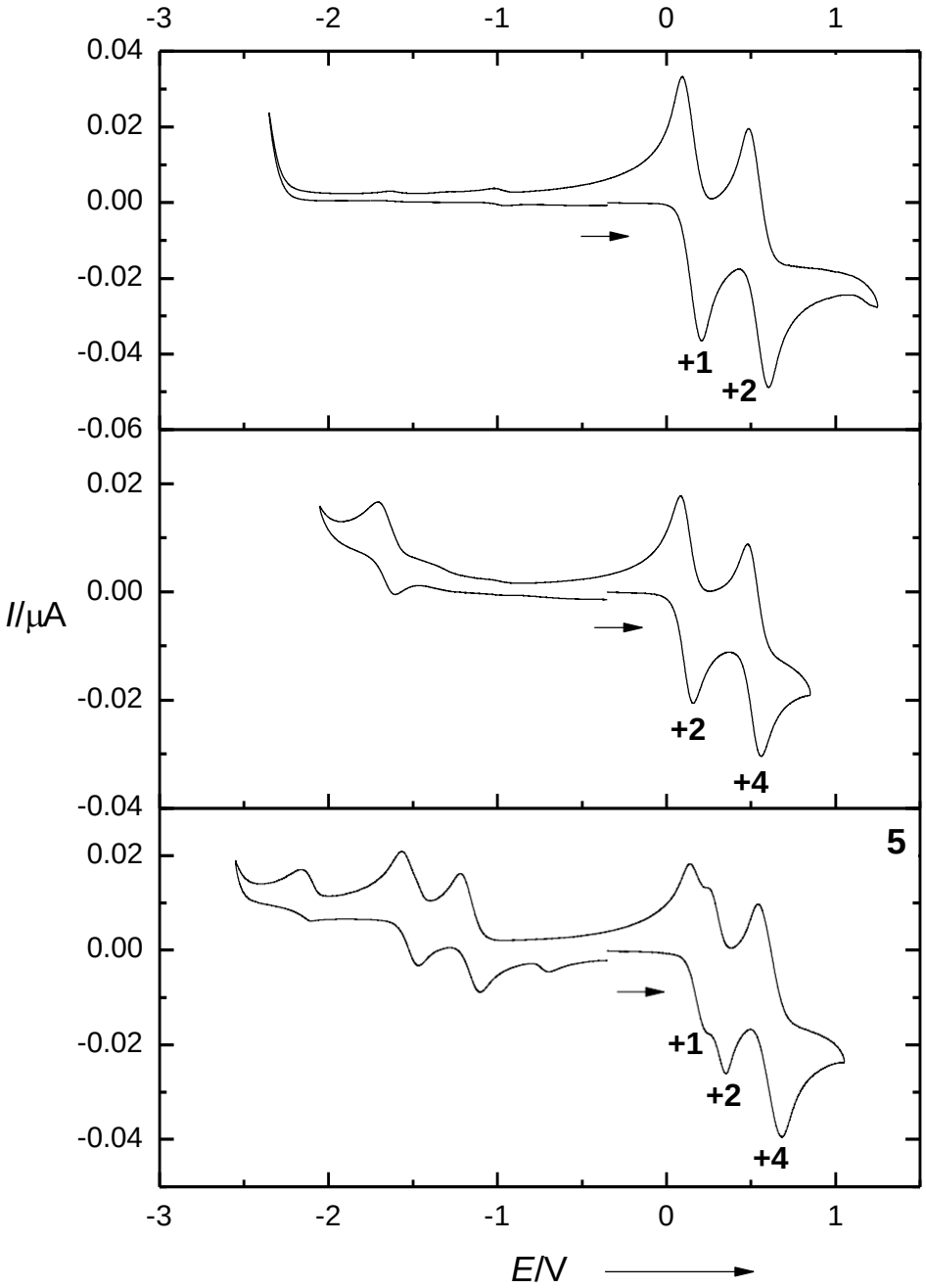


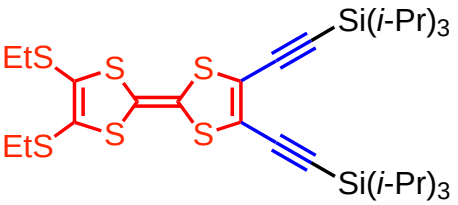


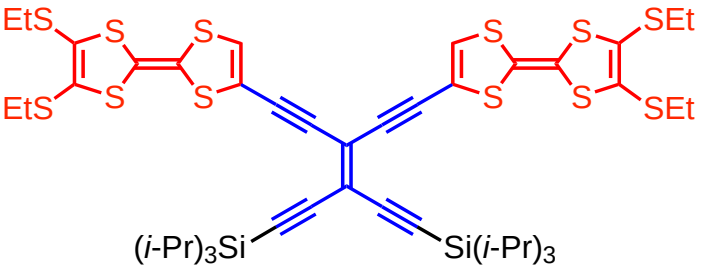


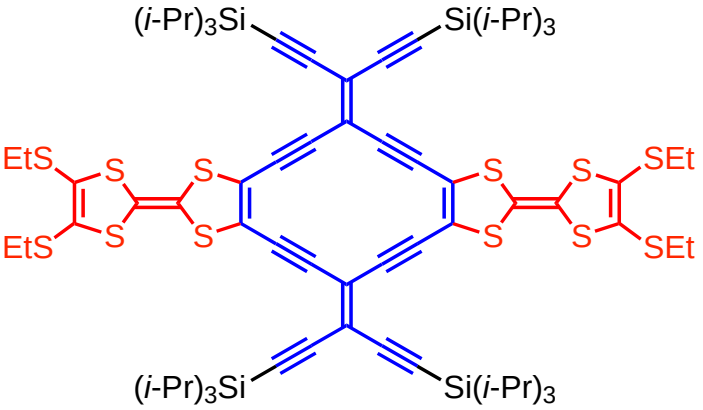
Size exclusion chromatography

Cyclic Voltammograms

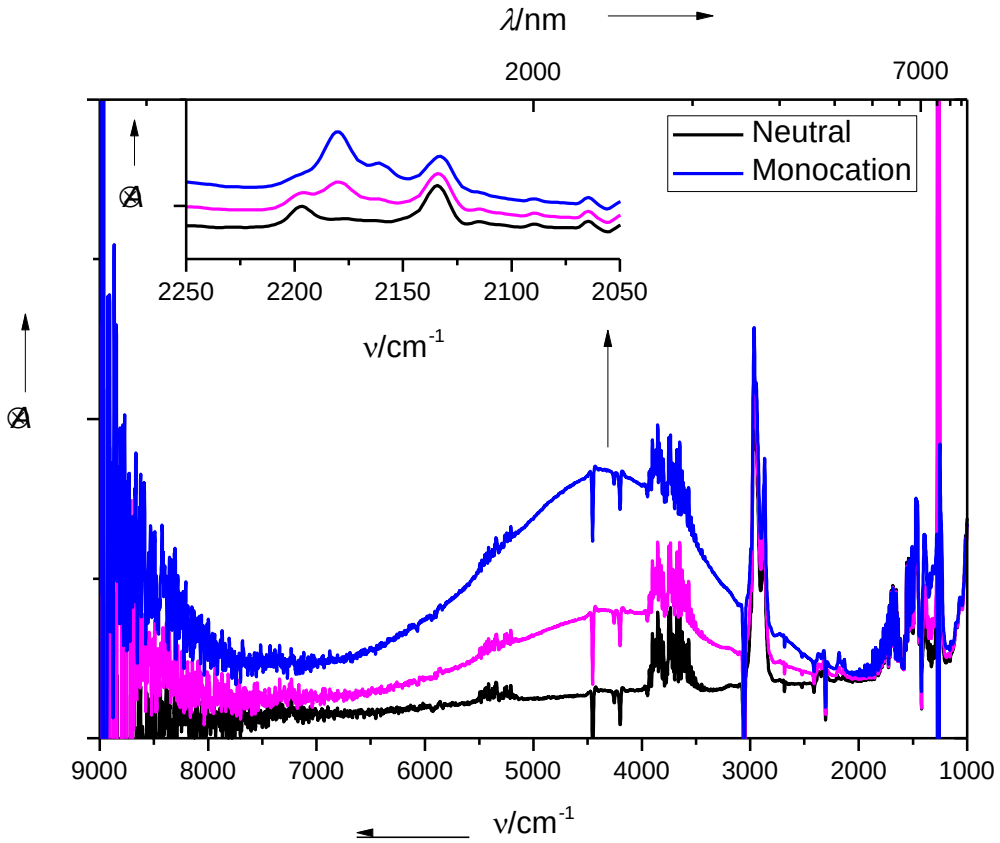


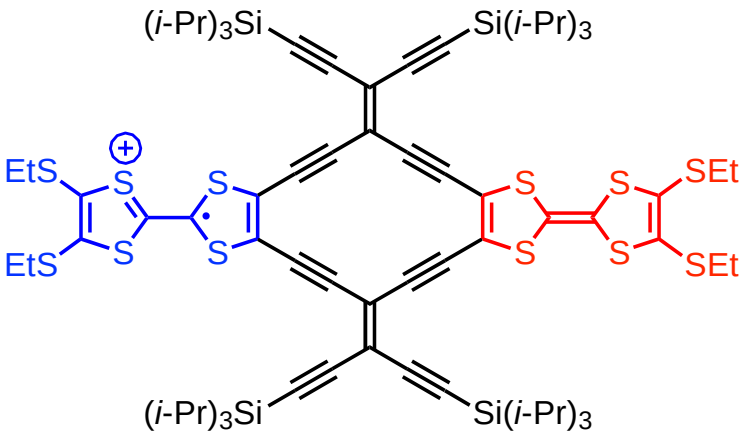






Spectroelectrochemistry





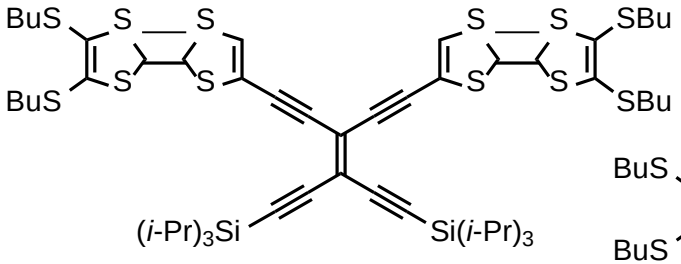
FWHM = 2131 cm^{-1}

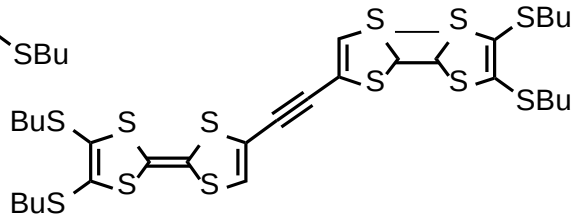
Theory – Class II:
$(2310 \times \nu_{max})^{1/2}$ = 3125 cm^{-1}

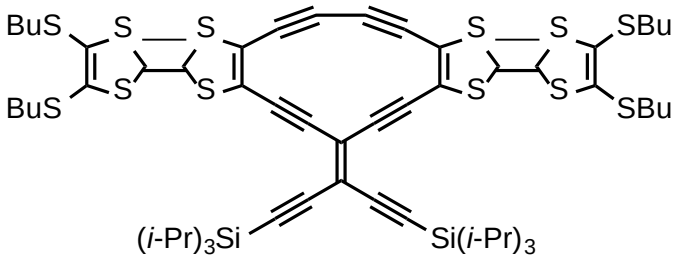
Radical cation: low-energy MV absorption

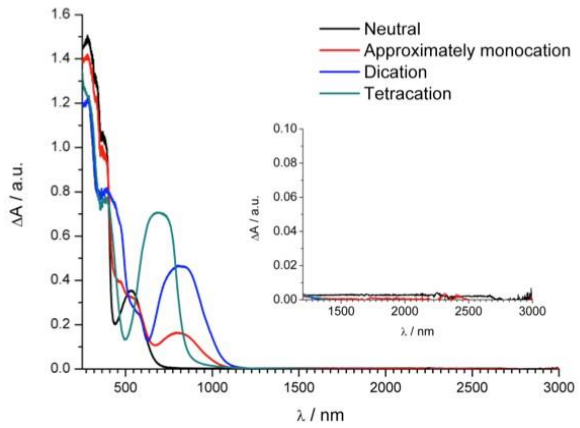
Spectroelectrochemisty of Bis-TTFs

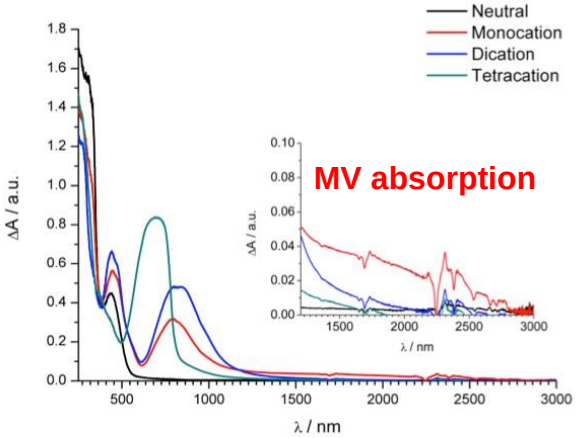
$M \rightarrow\!\!\rightarrow M^{+} \rightarrow\!\!\rightarrow M^{2+}$

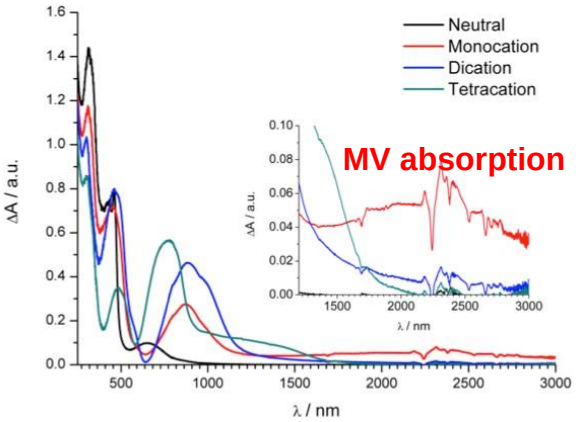






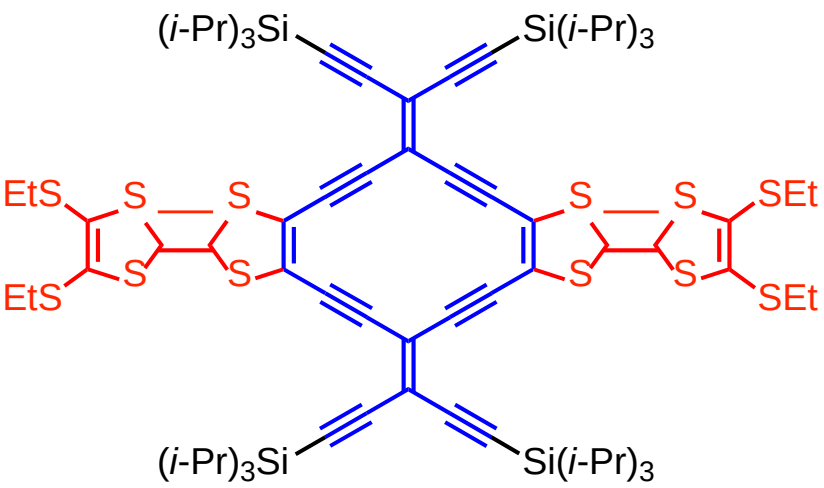






MV absorption: short distance or cyclic structure

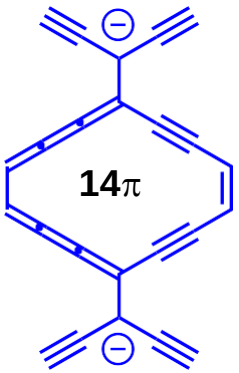
BJOC **2015**, *11*, 930-948.



Neutral core: NICS(π)$_{zz}$ = -8.4 ppm
Dianion core: NICS(π)$_{zz}$ = -33.2 ppm

➡ ***Gain in aromaticity (Wurster type)***

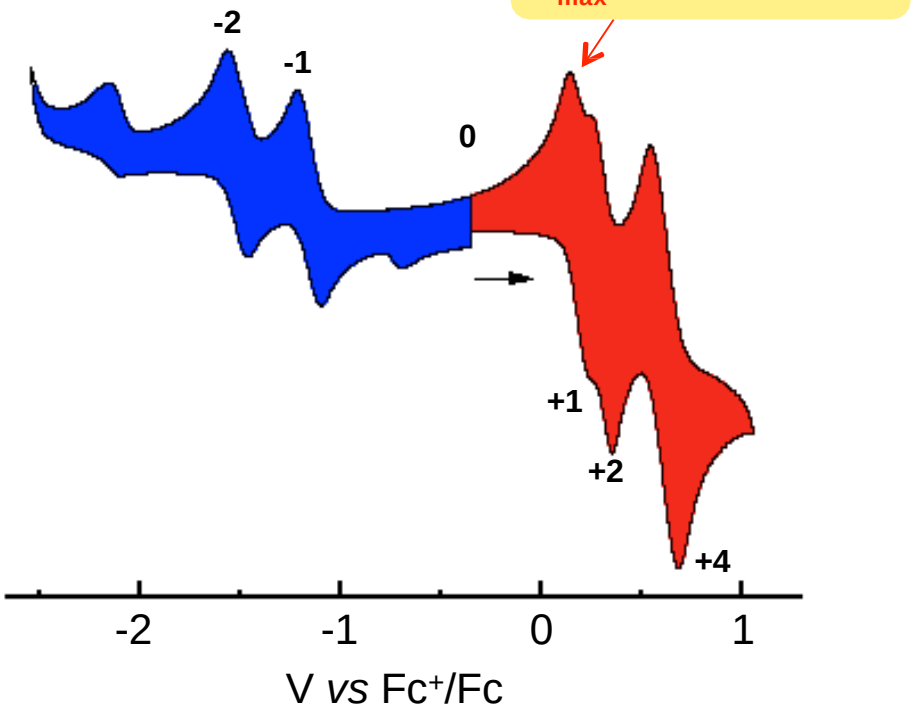
Hückel 4*n*+2



Cyclic voltammogram:

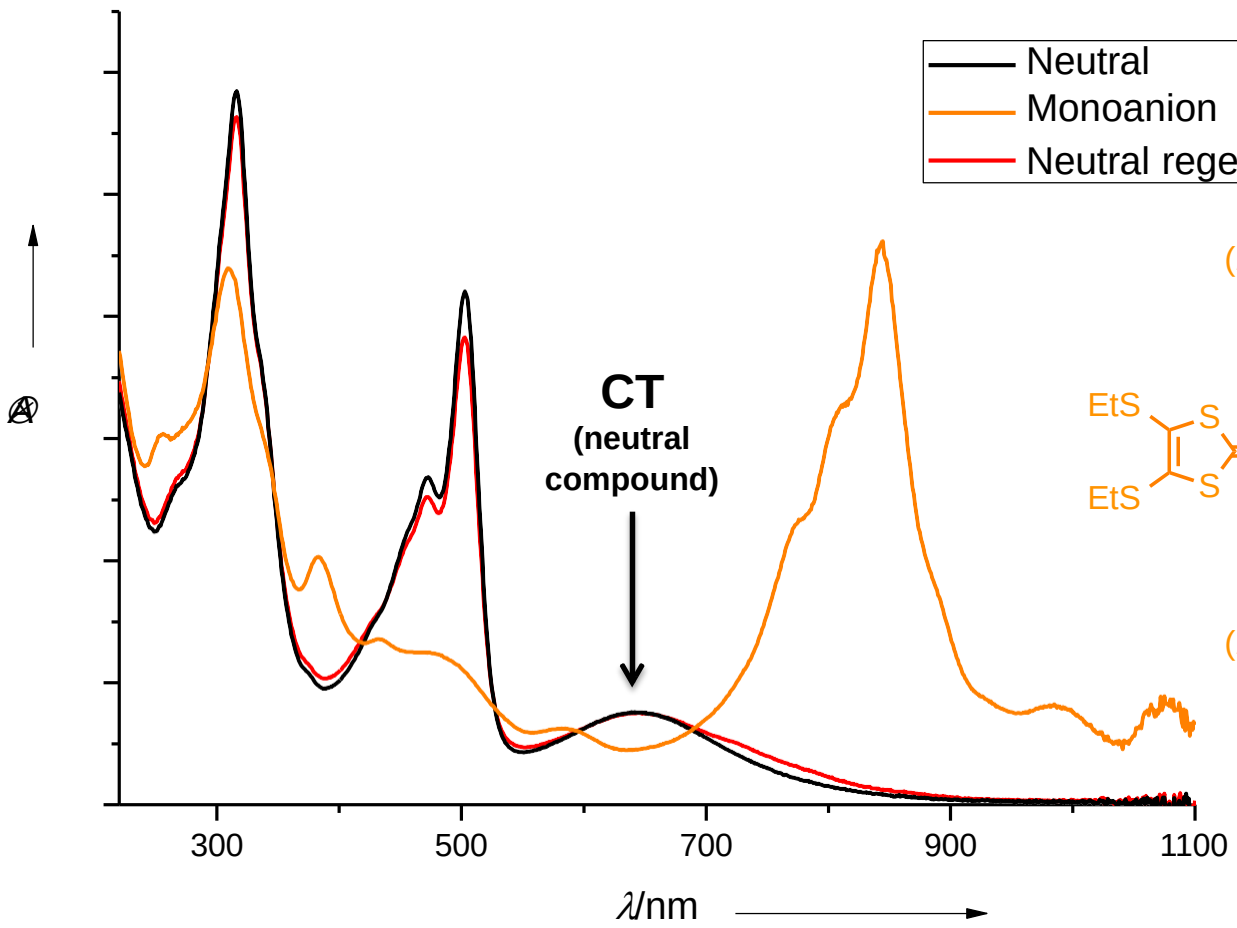
6 redox states

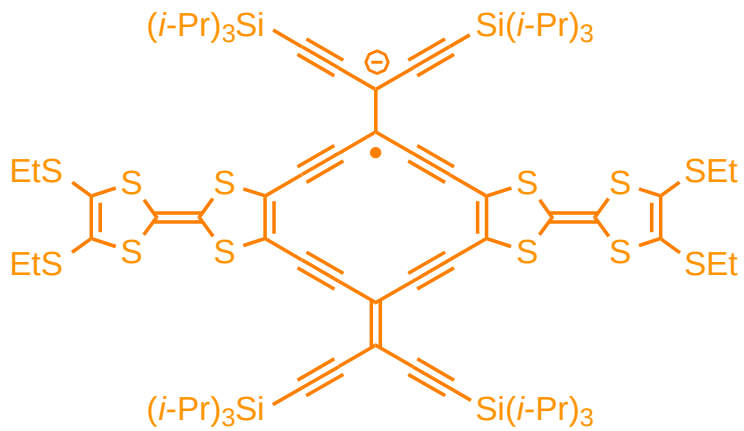
Mixed valence state: λ_{max} ca. 2250 nm



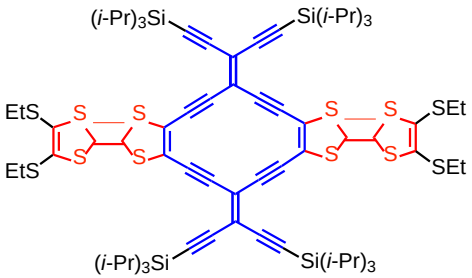
K. Lincke, A. F. Frellsen, C. R. Parker, A. D. Bond, O. Hammerich, M. B. Nielsen, *Angew. Chem*. Int. Ed. **2012**, *51*, 6099-6102 .

Spectroelectrochemistry – Generation of Monoanion

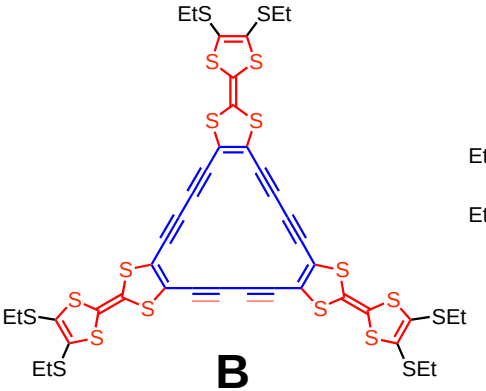




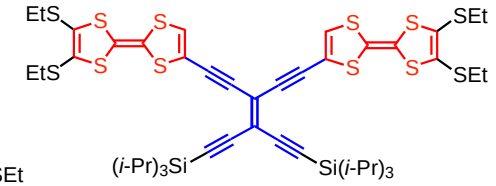
HOMO-LUMO Gap Comparison of Neutral Compounds



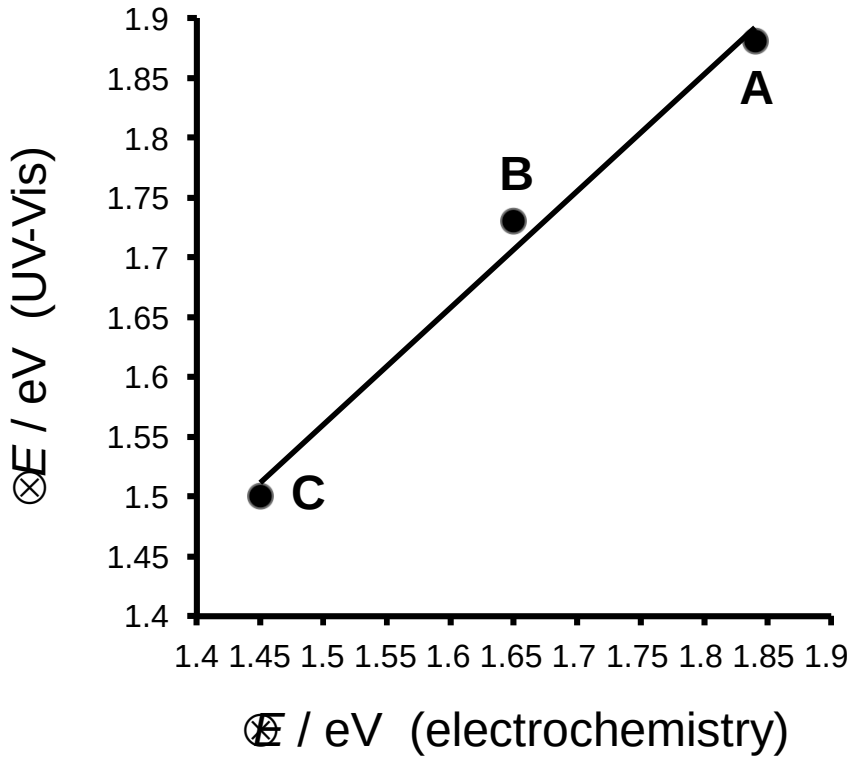
C

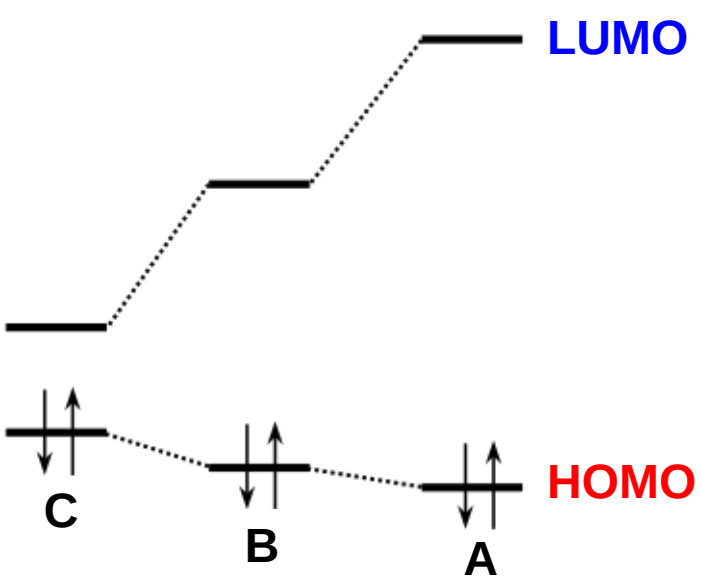


B



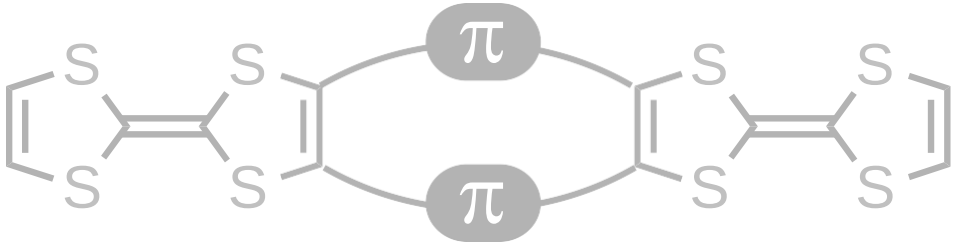
A

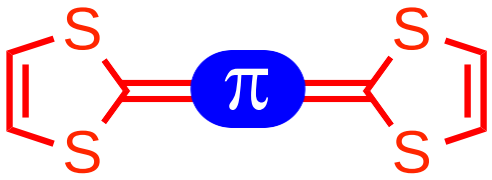




Outline

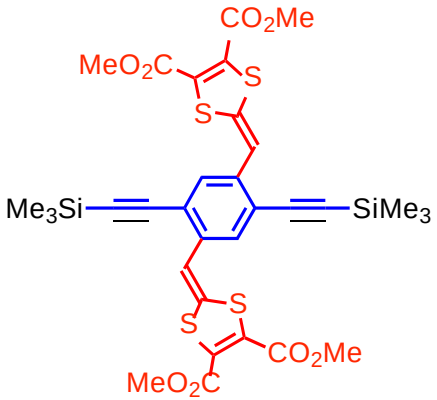


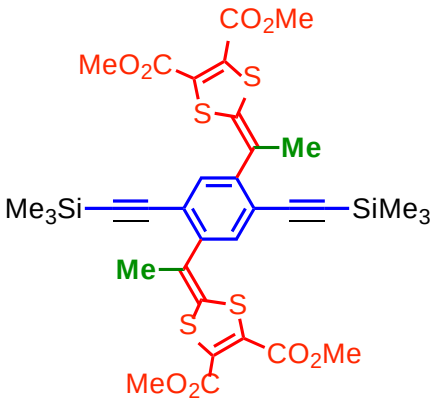




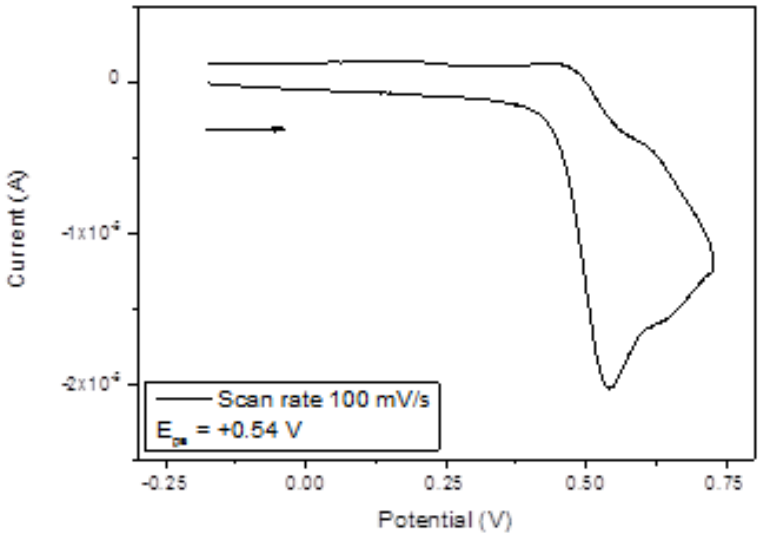
- **Redox properties?**
- **Optical properties of oxidized species?**
- **Interactions between redox centers?**

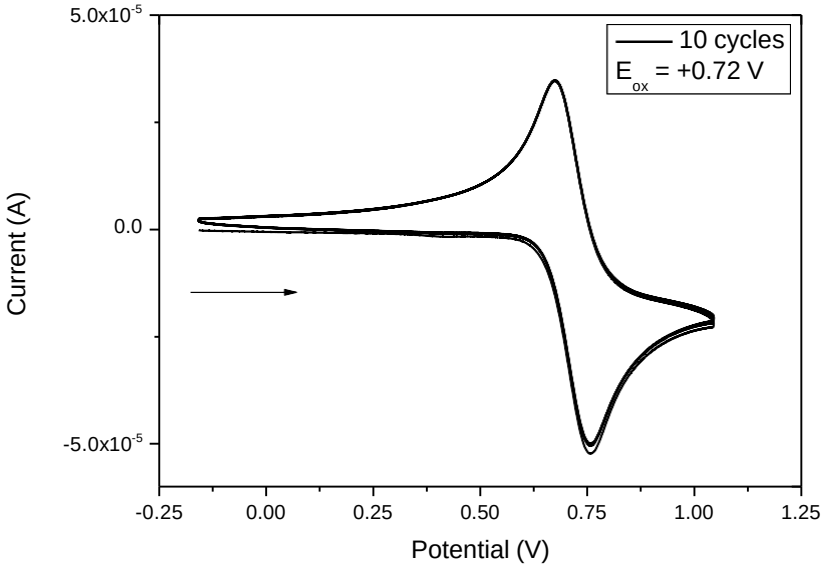
Electrochemistry – Cyclic Voltammetry





Independent redox centers (Class I)

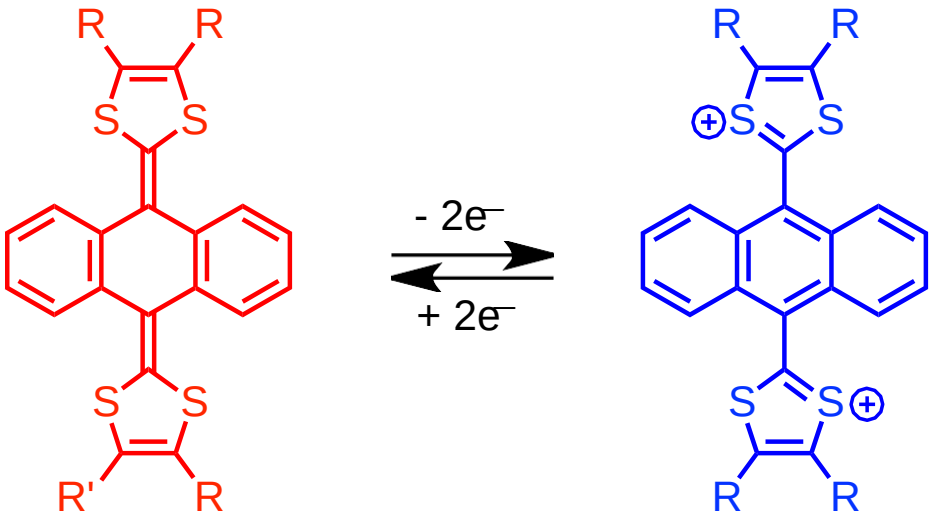




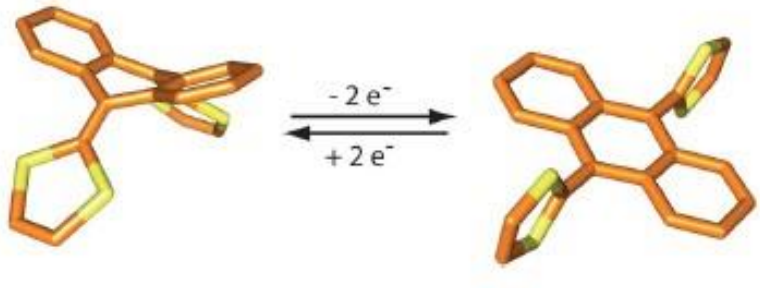
CH_2Cl_2 + 0.1 M NBu_4PF_6
Potentials *vs* Fc^+/Fc

J. Am. Chem. Soc. **2014**, *47*, 16497−16507.

Potential Inversion



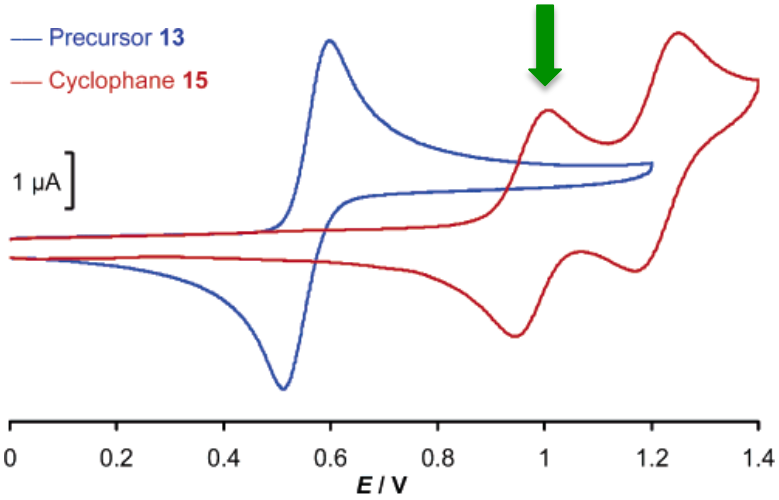
$E_2 < E_1$

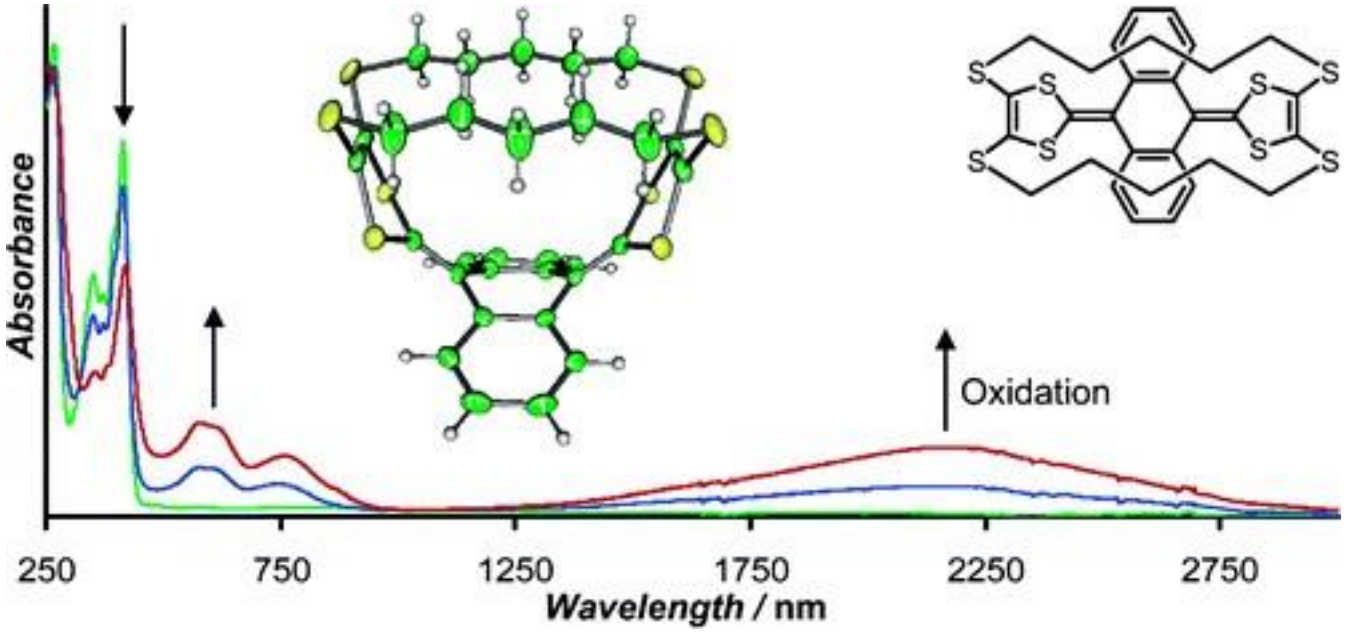


F.G. Brunetti, J.L. López, C. Atienza, N. Martín,
J. Mater. Chem. **2012**, *22*, 4188-4205.

Rigid Cyclophane

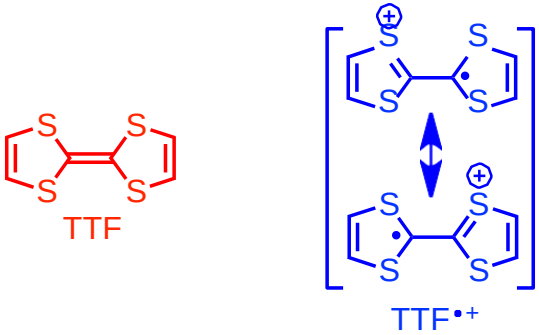
Intermediate radical cation



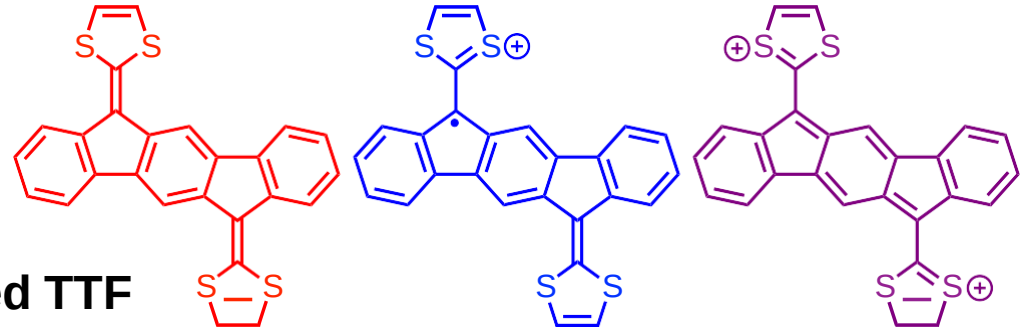


C. A. Christensen, A. S. Batsanov, M. R. Bryce, *J. Am. Chem. Soc.* **2006**, *128*, 10484-10490.

Extended TTFs





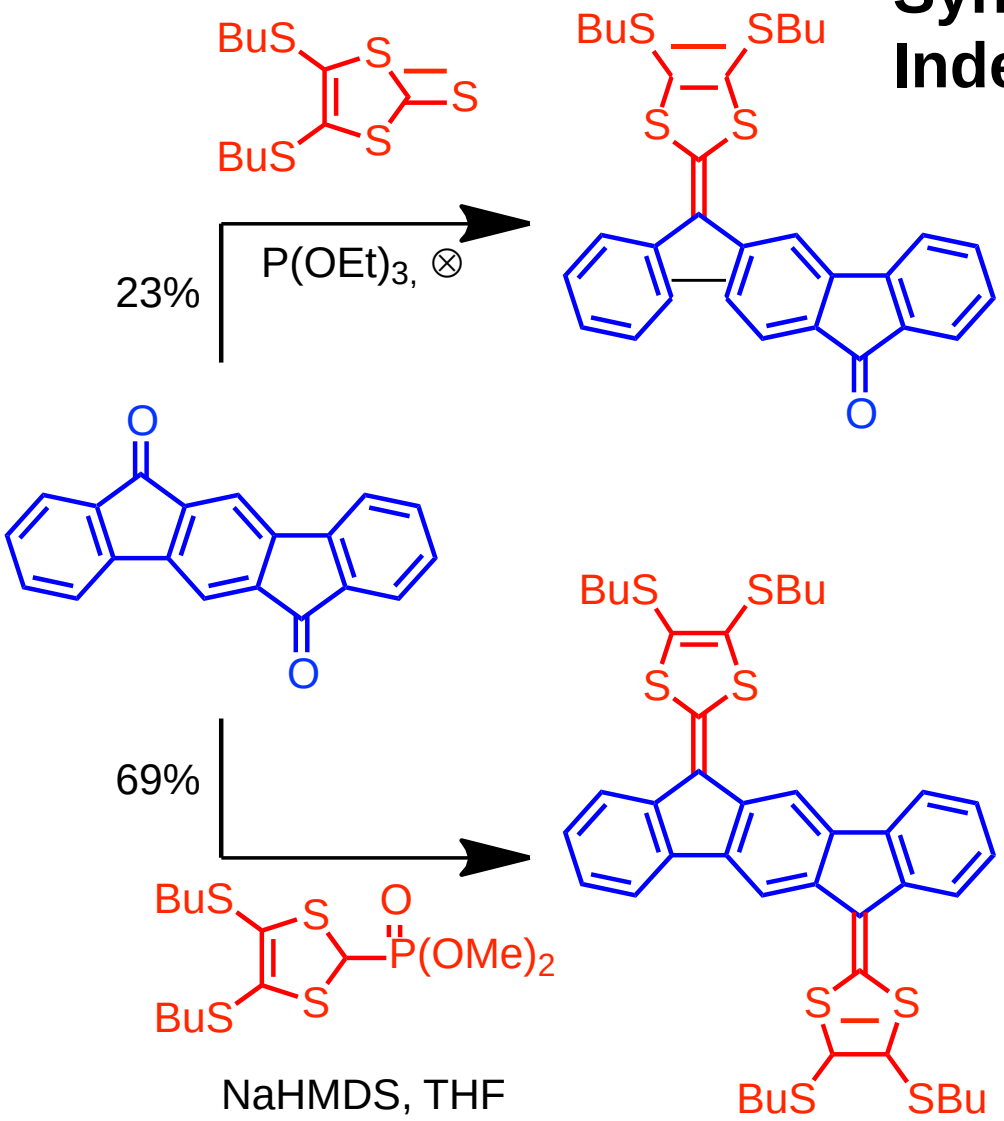


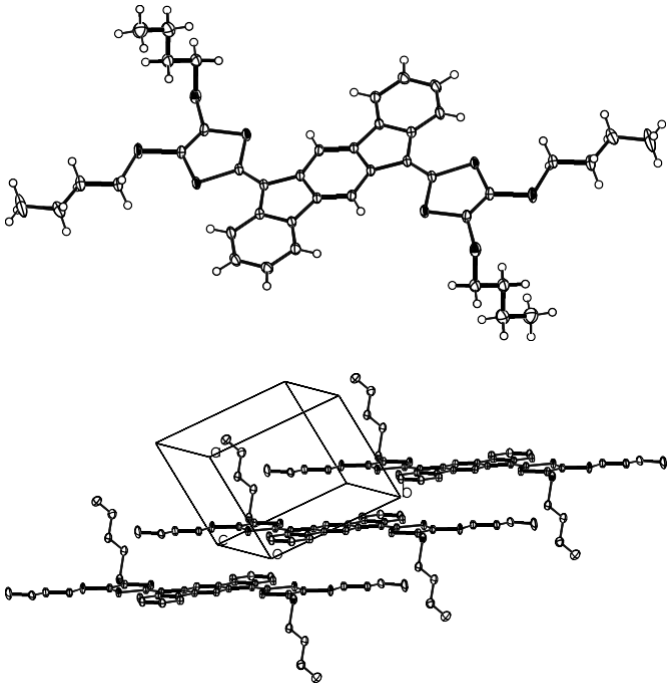
Indenofluorene-extended TTF

Intermediate?

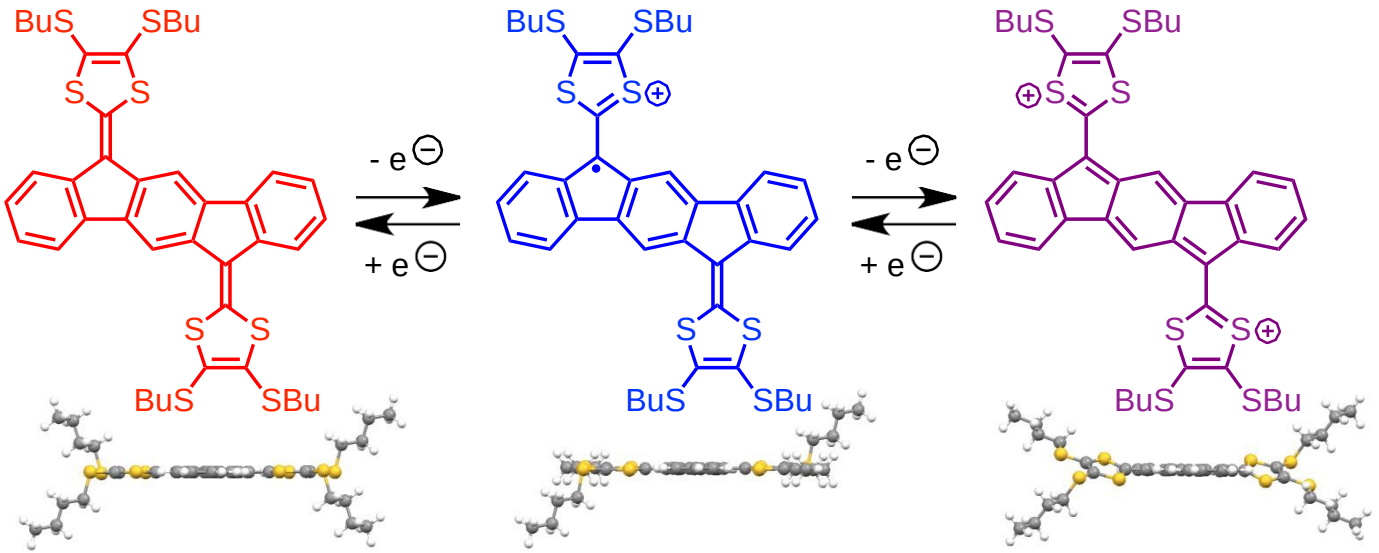
Fully delocalized?

Synthesis of Indenofluorene-Extended TTF

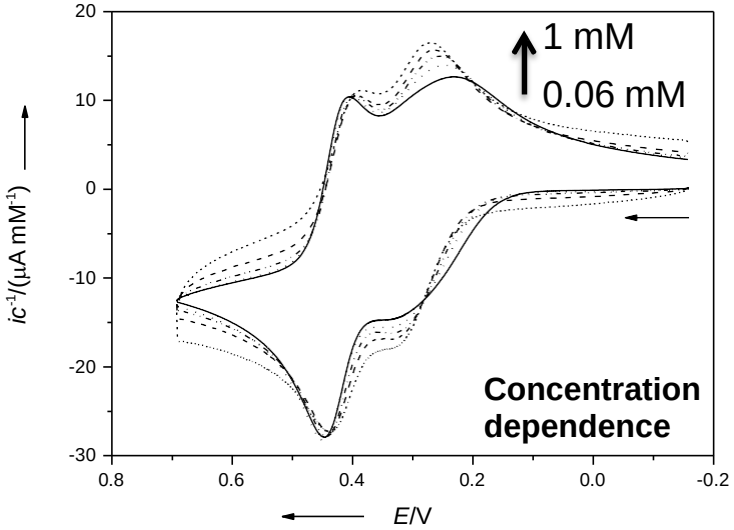


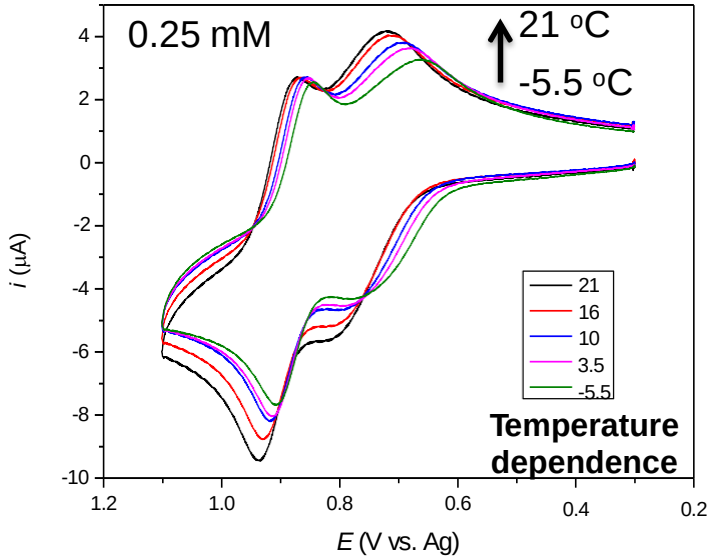


J. Mater. Chem. **2014**, *2*, 10428-10438.



Cyclic Voltammetry

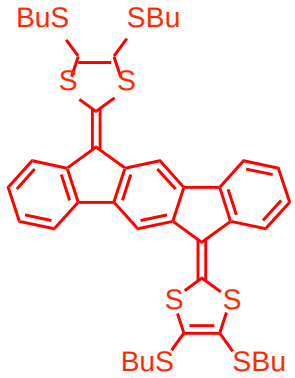




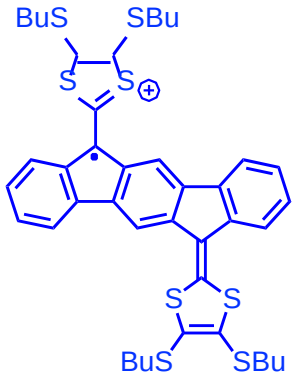
CH_2Cl_2 (0.1 M Bu_4NPF_6); Potentials *vs* Fc^+/Fc

Intermolecular interactions

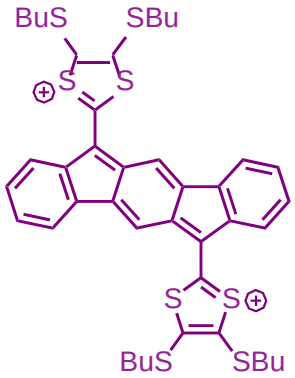
Simulation of Cyclic Voltammogram



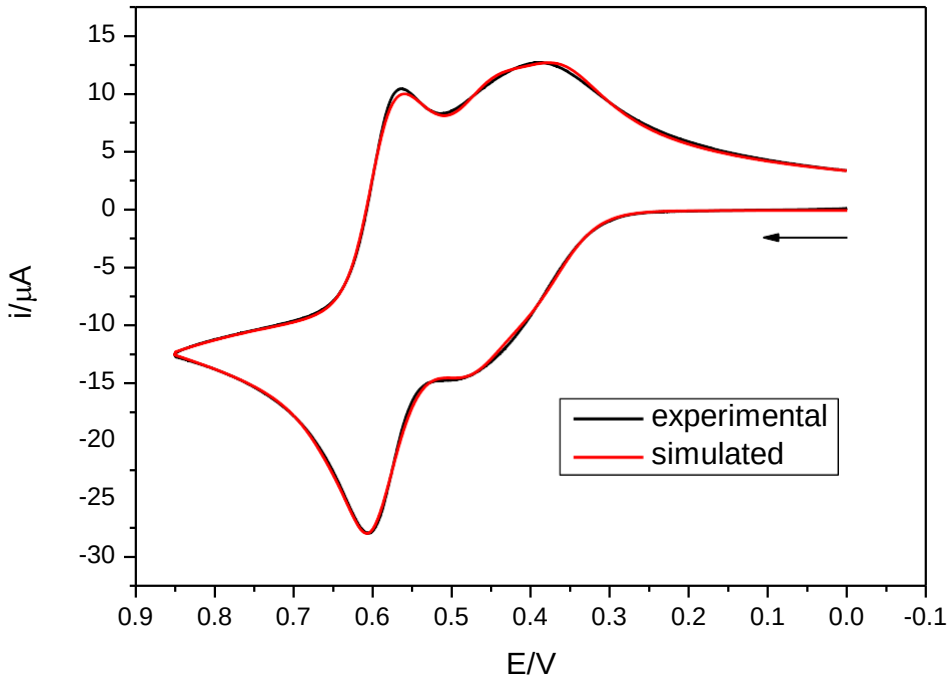
n



c^+



d^{2+}



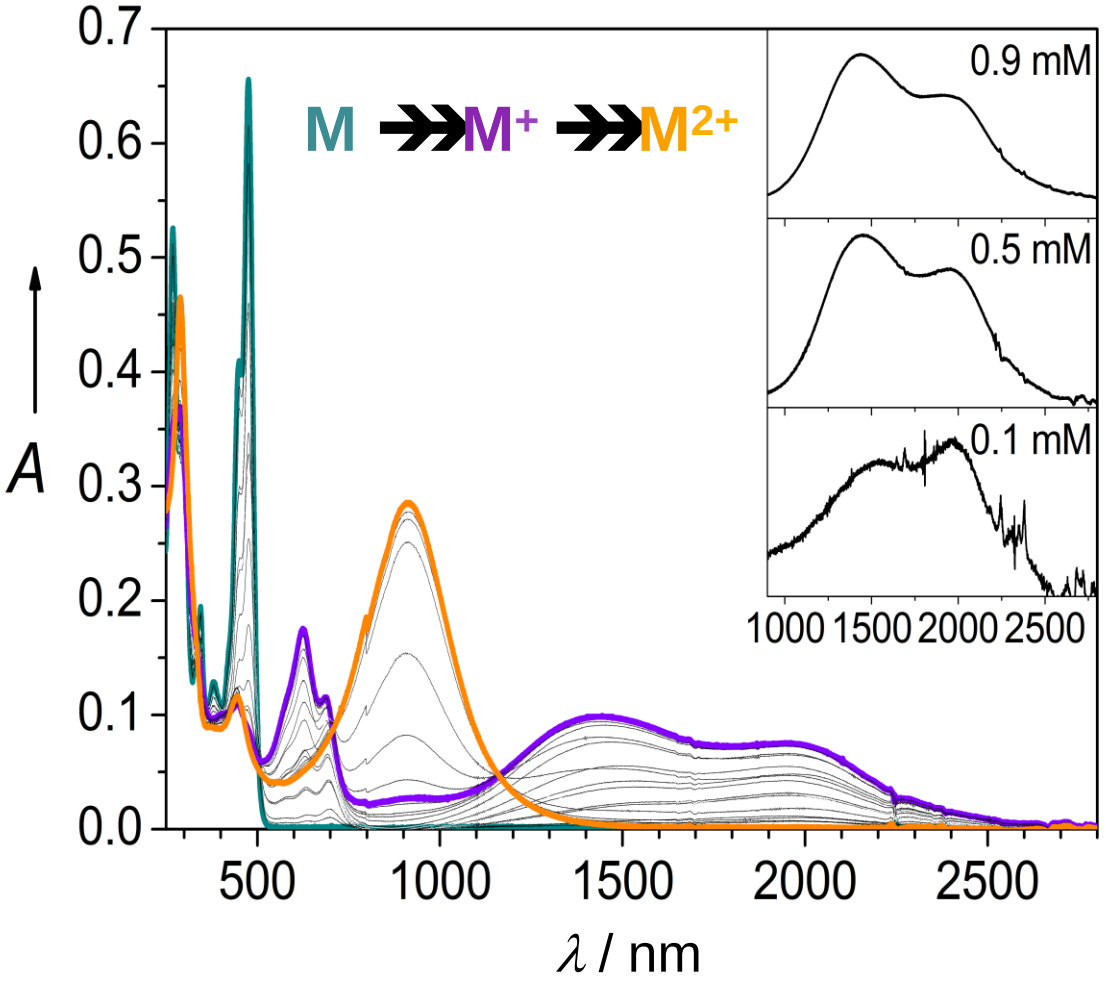
redox-1	$\mathbf{d}^{2+} + e^-$	⇌	$\mathbf{c}^{\cdot+}$
redox-2	$\mathbf{c}^{\cdot+} + e^-$	⇌	**n**
redox-3	$[\mathbf{c}\text{-}\mathbf{c}]^{2+} + e^-$	⇌	$[\mathbf{n}\text{-}\mathbf{c}]^{\cdot+}$
redox-4	$[\mathbf{n}\text{-}\mathbf{c}]^{\cdot+} + e^-$	⇌	$[\mathbf{n}\text{-}\mathbf{n}]$
Eq.-1	$\mathbf{n} + \mathbf{n}$	⇌	$[\mathbf{n}\text{-}\mathbf{n}]$
Eq.-2	$\mathbf{c}^{\cdot+} + \mathbf{n}$	⇌	$[\mathbf{n}\text{-}\mathbf{c}]^{\cdot+}$
Eq.-3	$\mathbf{c}^{\cdot+} + \mathbf{c}^{\cdot+}$	⇌	$[\mathbf{c}\text{-}\mathbf{c}]^{2+}$
Eq.-4	$\mathbf{c}^{\cdot+} + \mathbf{c}^{\cdot+}$	⇌	$\mathbf{n} + \mathbf{d}^{2+}$
Eq.-5	$[\mathbf{n}\text{-}\mathbf{c}]^{\cdot+} + \mathbf{c}^{\cdot+}$	→	$[\mathbf{c}\text{-}\mathbf{c}]^{2+} + \mathbf{n}$
Eq.-6	$[\mathbf{n}\text{-}\mathbf{c}]^{\cdot+} + \mathbf{d}^{2+}$	⇌	$[\mathbf{c}\text{-}\mathbf{c}]^{2+} + \mathbf{c}^{\cdot+}$
Eq.-7	$\mathbf{c}^{\cdot+} + [\mathbf{n}\text{-}\mathbf{n}]$	⇌	$\mathbf{n} + [\mathbf{n}\text{-}\mathbf{c}]^{\cdot+}$
Eq.-8	$\mathbf{d}^{2+} + [\mathbf{n}\text{-}\mathbf{n}]$	⇌	$\mathbf{c}^{\cdot+} + [\mathbf{n}\text{-}\mathbf{c}]^{\cdot+}$

Complexes:

neutral – neutral
neutral – cation
cation – cation

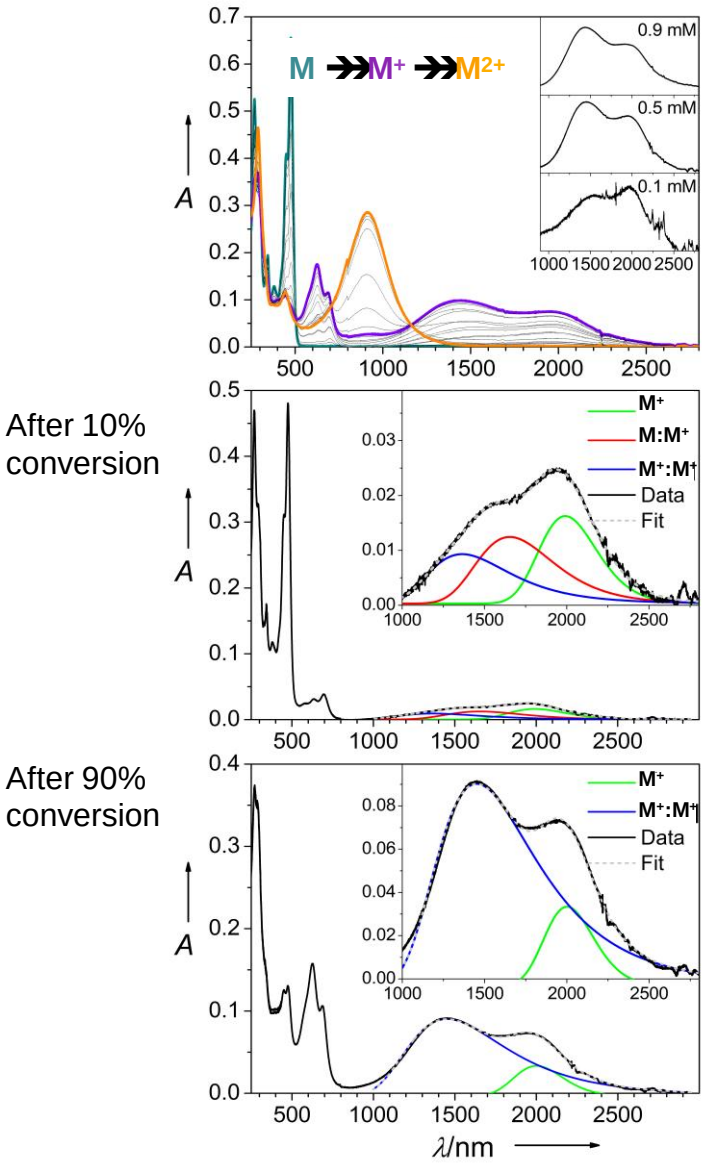
Spectroelectrochemistry

Relative intensities of low-energy absorptions are concentration dependent



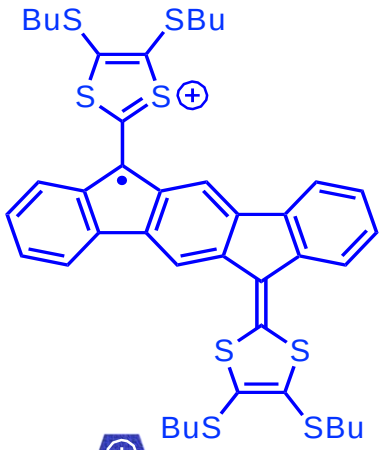
J. Mater. Chem. **2014**, *2*, 10428-10438.

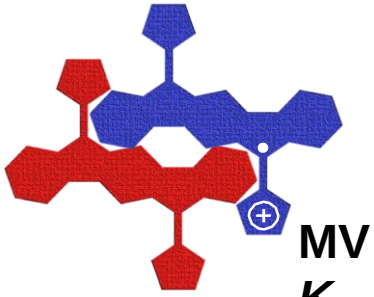
Spectroelectrochemistry



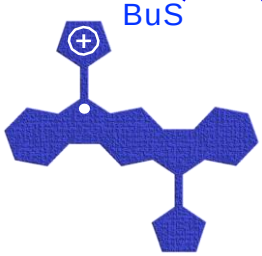
After 10% conversion

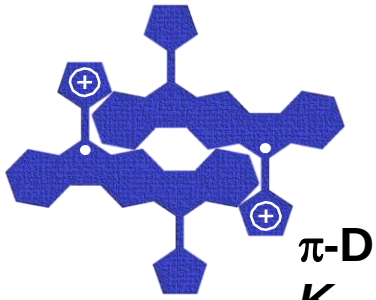
After 90% conversion





MV Dimer:
K_{as} = 7.8 x 10^4 M^{-1}





π-Dimer:
K_{as} = 1.8 x 10^4 M^{-1}

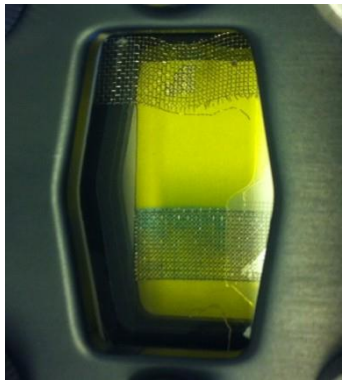
[TTF•TTF$^+$]: K_{as} = 6.0 M^{-1}

[TTF$^+$•TTF$^+$]: K_{as} = 0.6 M^{-1}

S. V. Rosokha, J. K. Kochi, *J. Am. Chem. Soc.* **2007**, *129*, 828-838

Ottle cell







Progression from yellow to blue solution upon oxidation

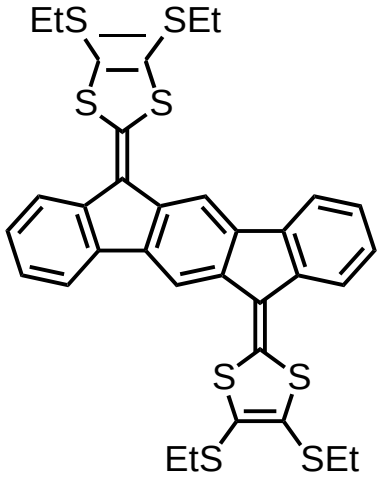
(neutral to dication)

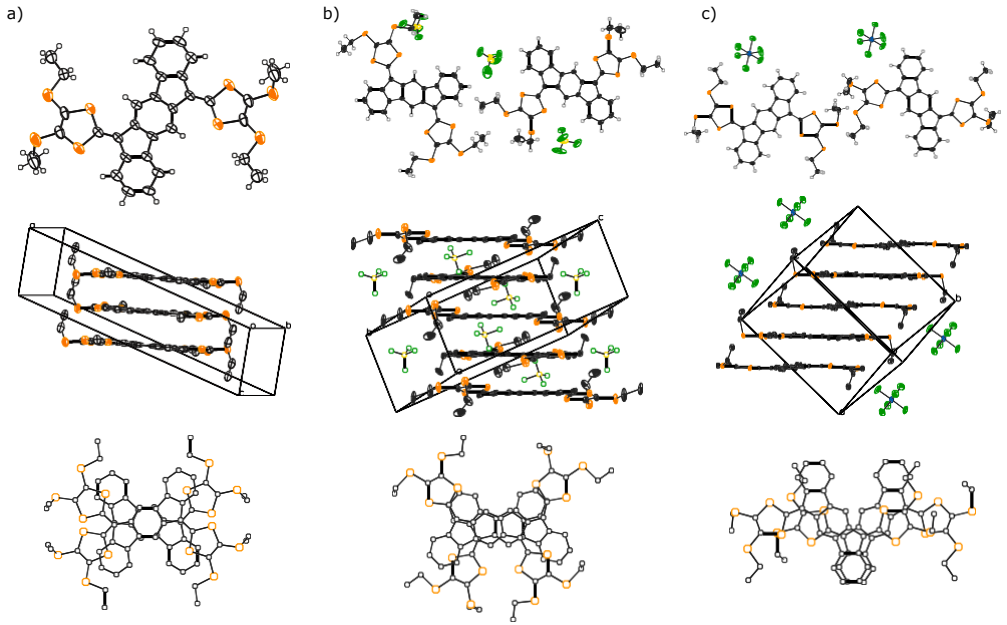
Electrocrystallization

Solvent: PhCl + counter electrolyte





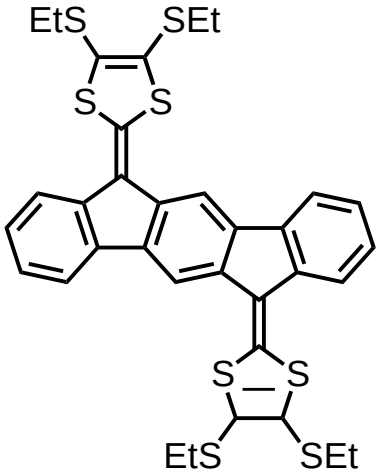




Cation•PF_6 Cation•Dication•$(BF_4)_{1.5}$ Cation•TaF_6

J. Mater. Chem. **2014**, *2*, 10428-10438.

Conductances of Salts



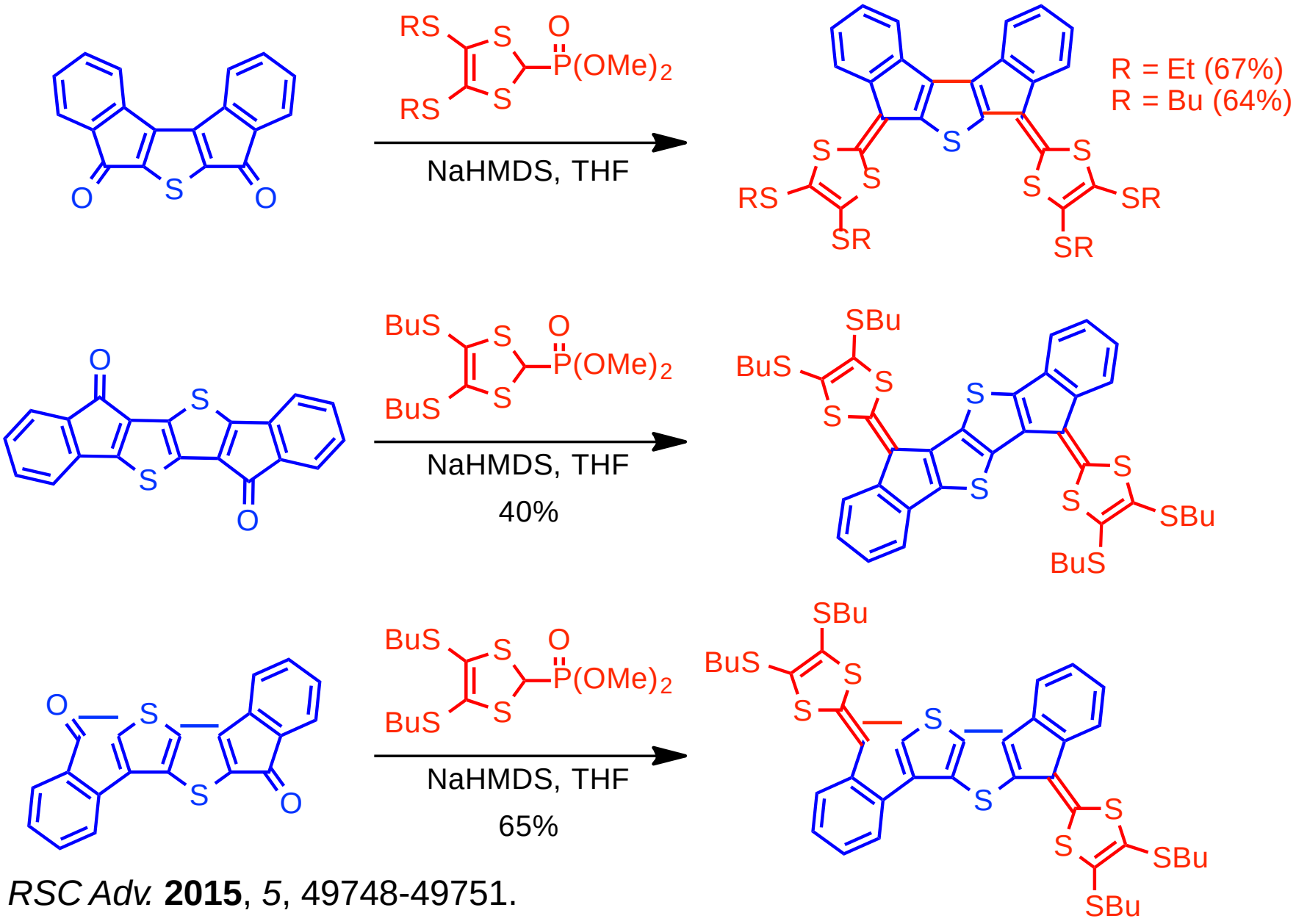
IFTTF

	298 K		77 K	
Sample	ρ [Ω m]	σ [S m^{-1}]	ρ [Ω m]	σ [S m^{-1}]
IFTTF•PF_6	0.326	3.07	2809	0.00035
IFTTF•$(BF_4)_{1.5}$	7.72	0.13	556000	0.0000018
IFTTF•TaF_6	0.188	5.32	14173	0.000071

semiconductors

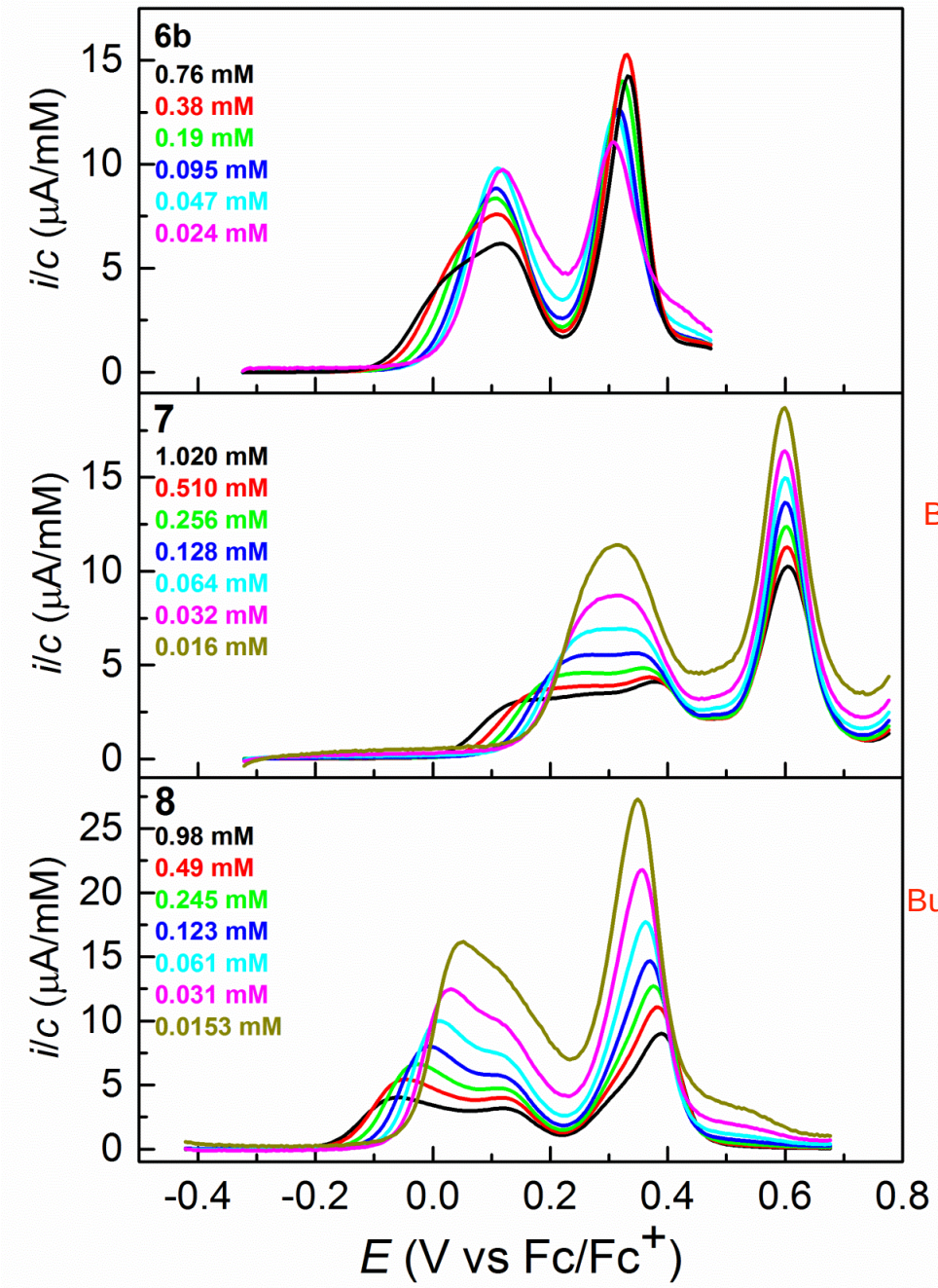
CAN WE ENHANCE THE CATION ASSOCIATIONS?

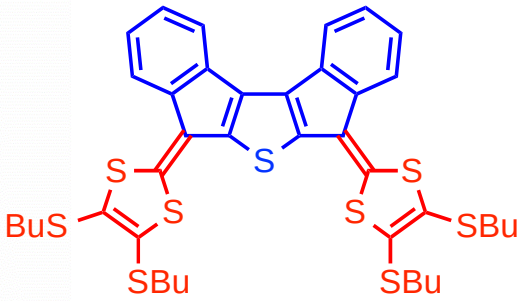
Incorporation of Fused Thiophene Units



RSC Adv. **2015**, *5*, 49748-49751.

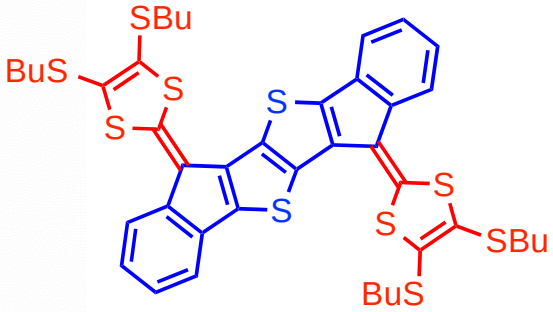
Differential Pulse Voltammograms





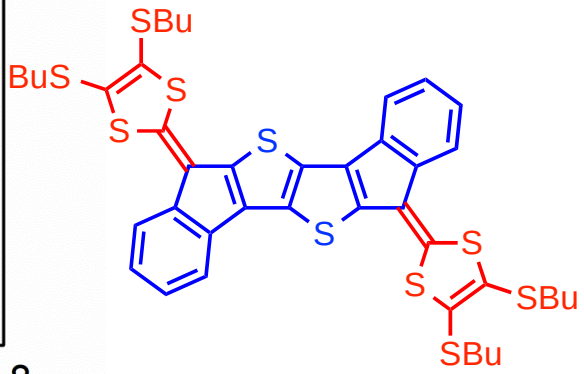
MV Dimer:
K_{as} = 1.8 x 10^4 M^{-1}

π-Dimer:
K_{as} = 2.8 x 10^3 M^{-1}



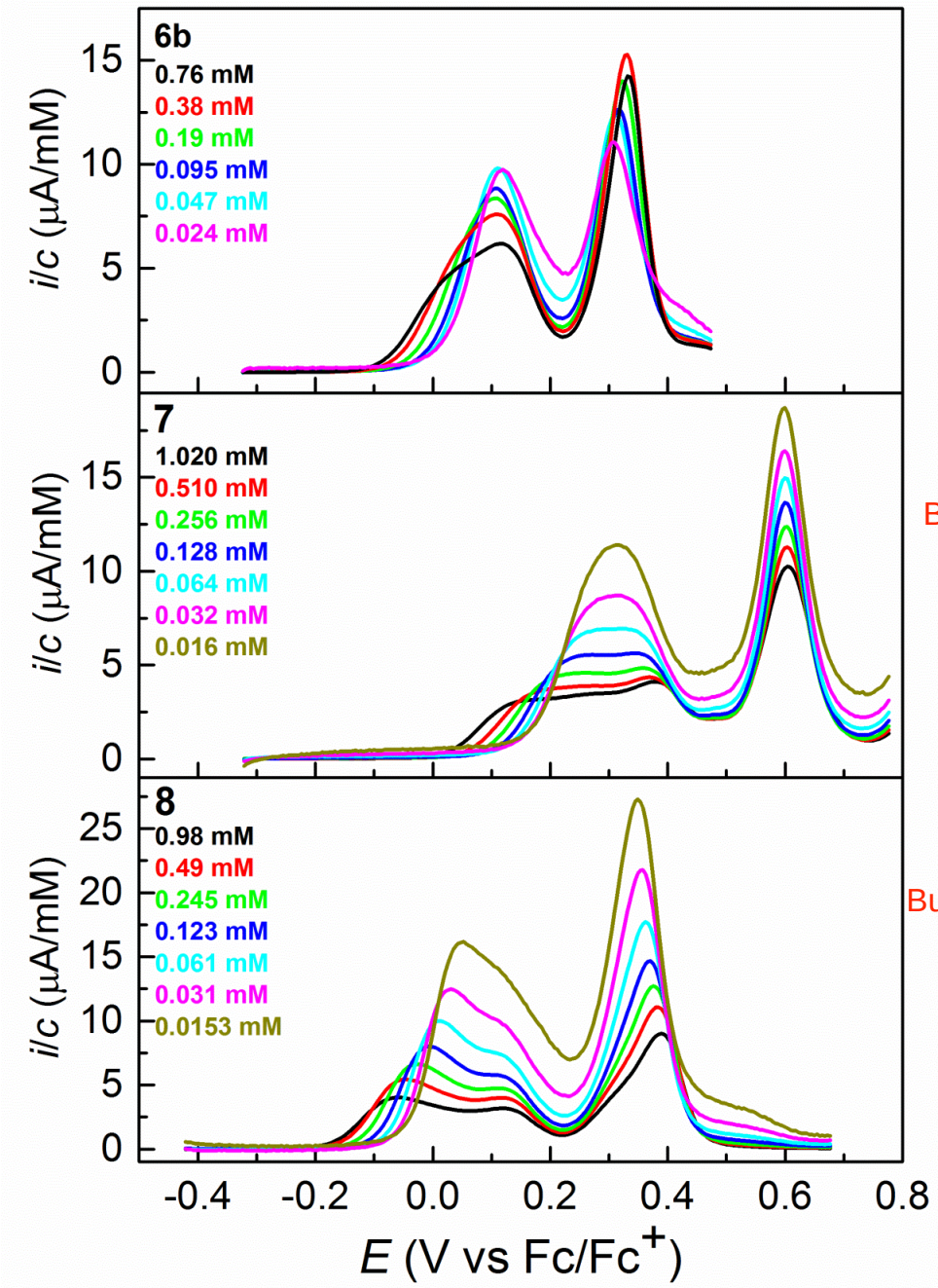
Associations increase

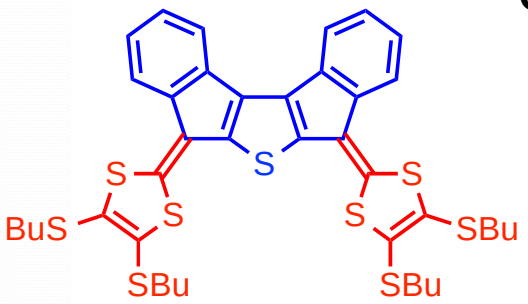
(by one order of magnitude)



RSC Adv. **2015**, *5*, 49748-49751.

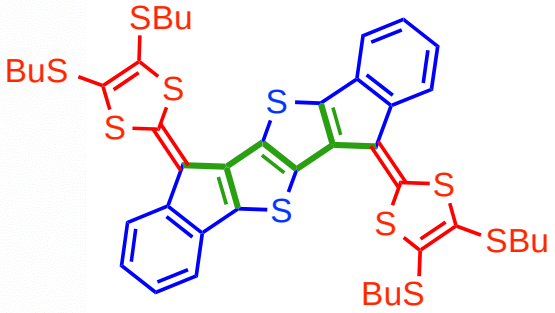
Differential Pulse Voltammograms





Oxidation Potentials

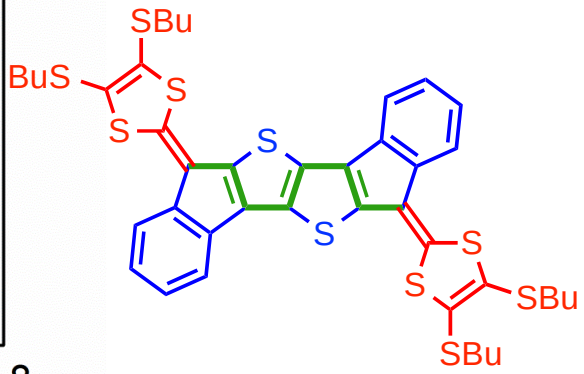
+0.14 V, +0.31 V



+0.32 V, +0.60 V

Cross-conjugation

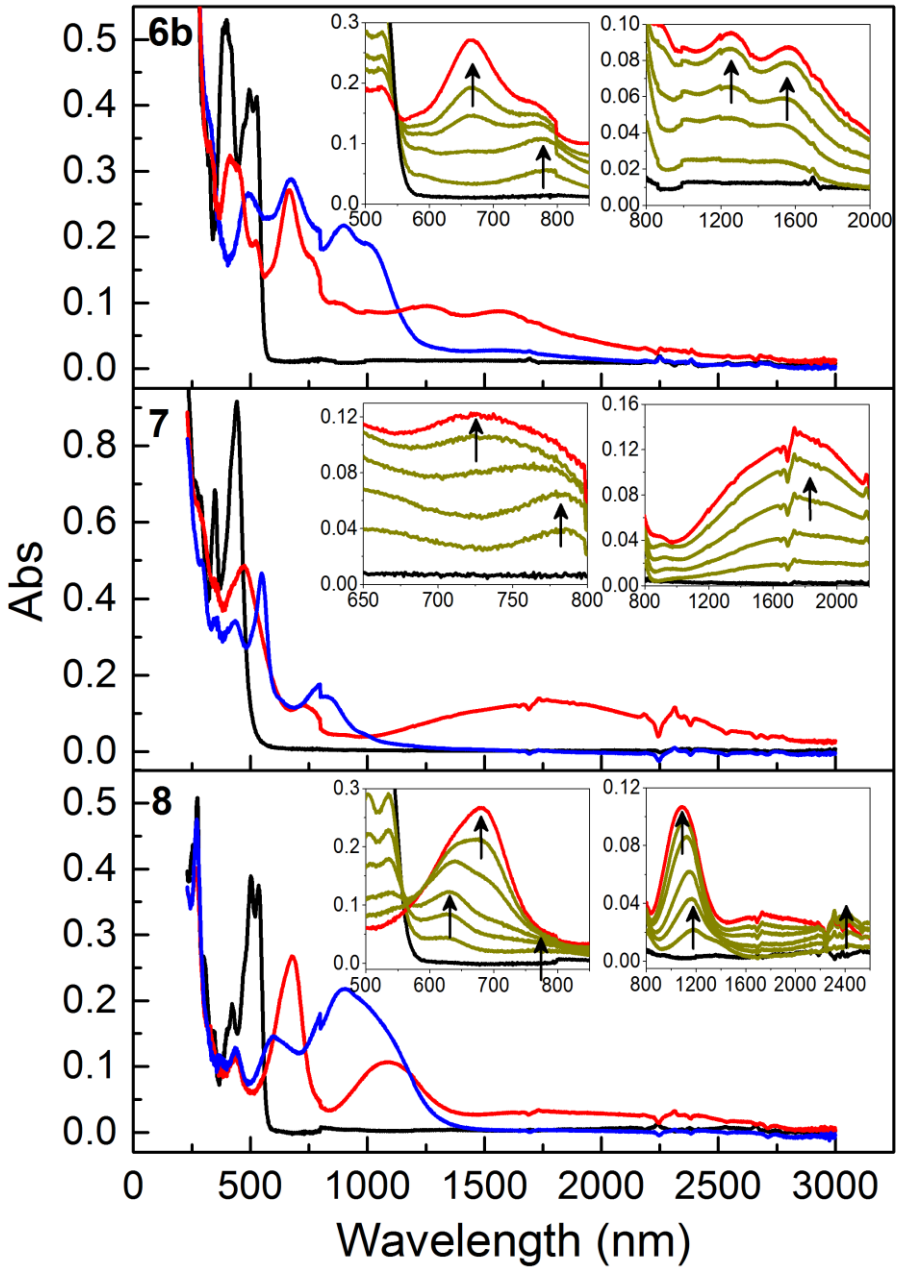
(weakest donor)

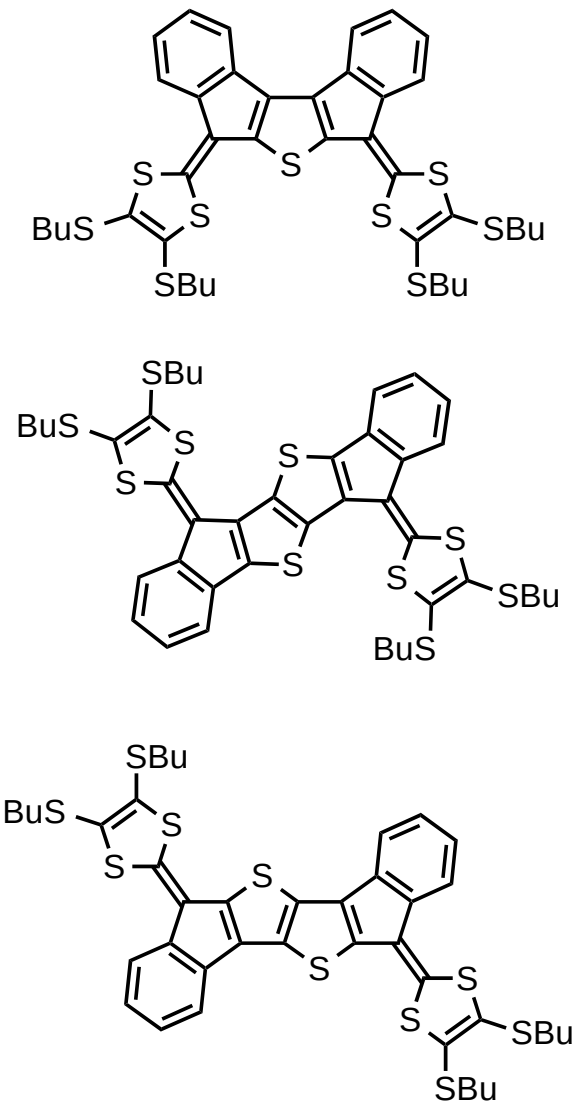


+0.09 V, +0.33 V

Linear conjugation

Spectroelectrochemistry M ➔➔M^{+} ➔➔M^{2+}





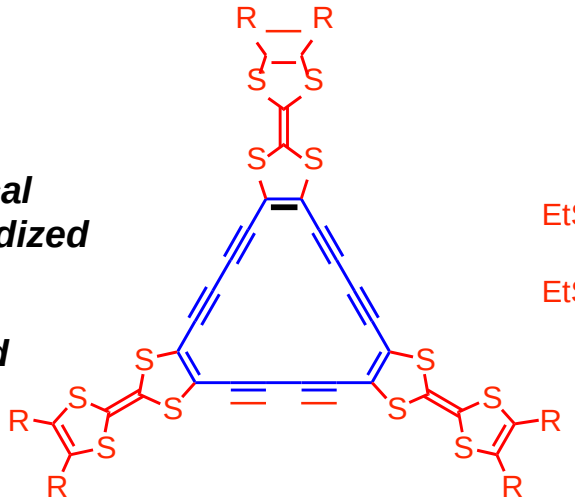
Conclusions

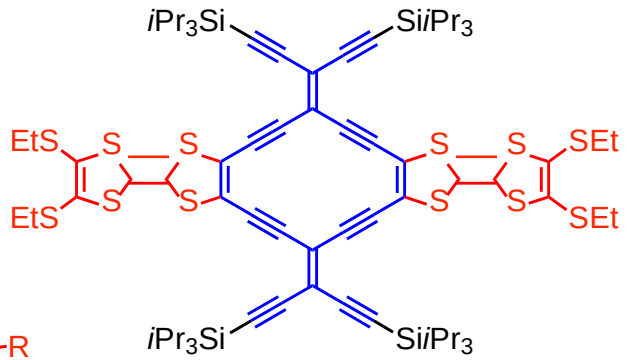
TTF-Acetylene Macrocycles

Strong charge-transfer chromophores

Multiple redox states with distinct optical properties – molecules can both be oxidized and reduced

Interactions between TTFs are enforced in the cyclic structures in comparison to acyclic ones (MV absorptions of radical cations)





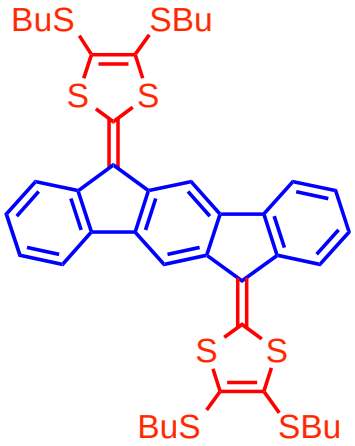
Combined Weitz and Wurster type redox system

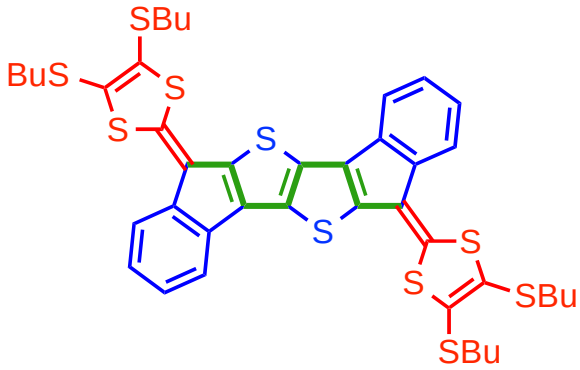
Indenofluorene-Extended TTFs

Strong associations between cations - Tectons for self-assembly

Broad UV-Vis-NIR absorptions

Thiophene units enhance donor strength significantly when redox centers are connected in linearly conjugated pathway





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