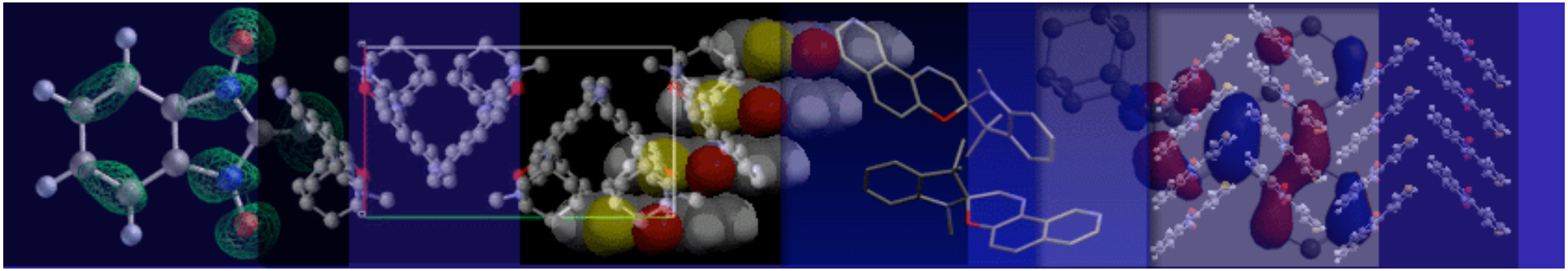


Magnetism and Charge Transport in Organic Ferromagnetic Semiconductors

Prof. Natia L. Frank

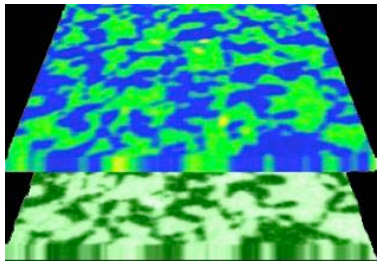
Department of Chemistry

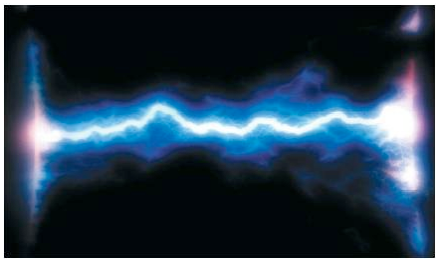
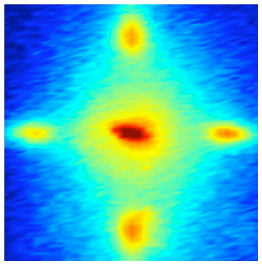
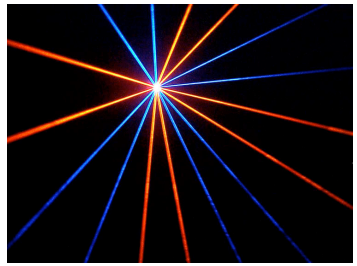
University of Victoria

Quantum Coherent Behaviour of Spins II
Pacific Institute of Theoretical Physics
Dec 4-6, 2009

University of Victoria

Multifunctional Magnetic Materials



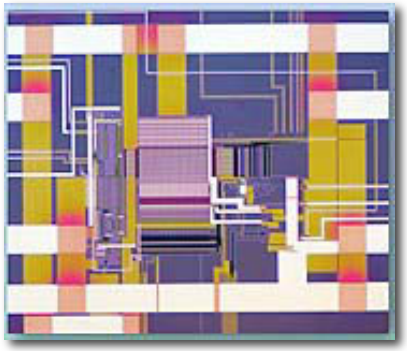




- Combining ***optical, conducting and magnetic*** functionality into one material.
- Tunable structures via organic synthesis
- Investigating the effect of ***electronic coupling*** between functionalities

- Ultra high-density data storage
- Magneto-optics
- Magneto-electronics (spintronics)
- LED display technology
- Spin-polarized transistors
- Quantum computing

New applications and configurations for electronics not yet envisioned…..

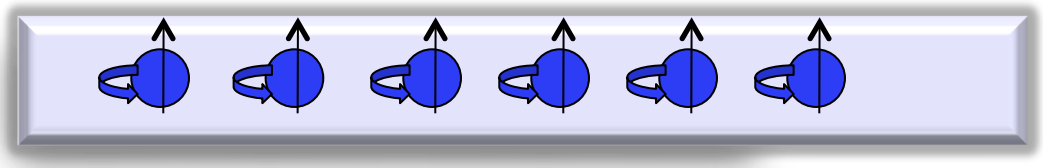
Challenges in Magnetoelectronic (Spintronic) Materials

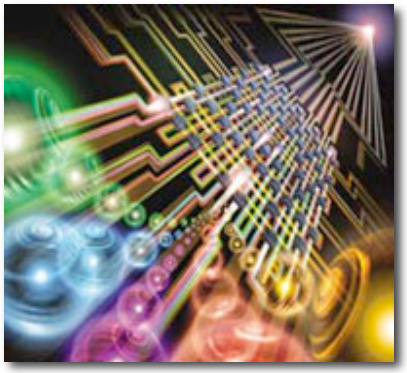


M-RAM chip (IBM) 2001

Ultra-high density data storage: Magnetoresistance
tuning resistivity with magnetic field

increasing spin polarization of conducting electrons





Nature June 2000

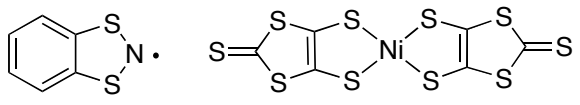
Data/Signal processing: Semiconductor spintronics
quantum computing (each spin corresponds to a bit: "qubit")
nonvolatile programmable logic (AND, OR, NAND and NOR gates)
Spin-polarized transistors (spin-FET)

Relationship between magnetic exchange and conductivity

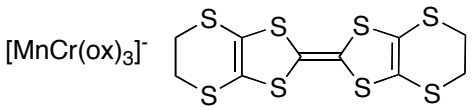
Increasing the spin relaxation time: organics

Goal: explore relationships between magnetic exchange and charge transport in organic systems

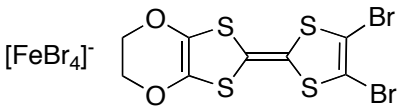
Molecule-Based Magnetoconducting Materials



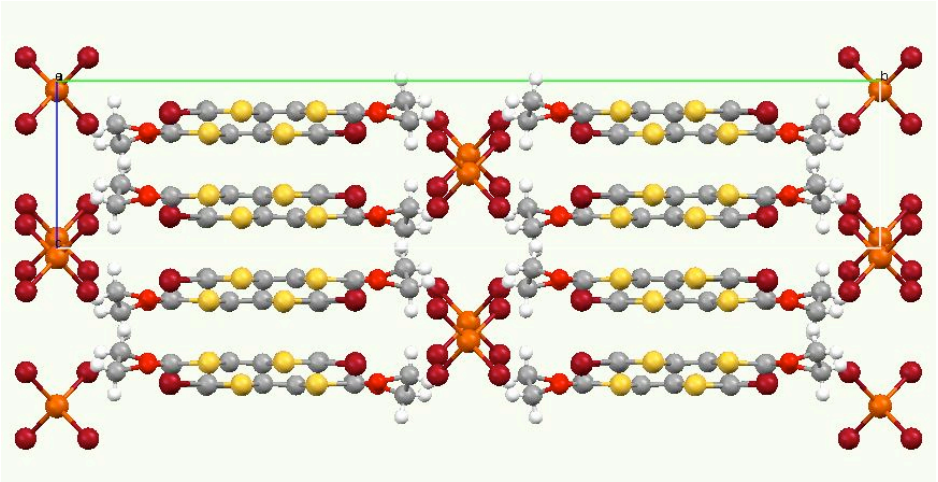
Awaga, 2008



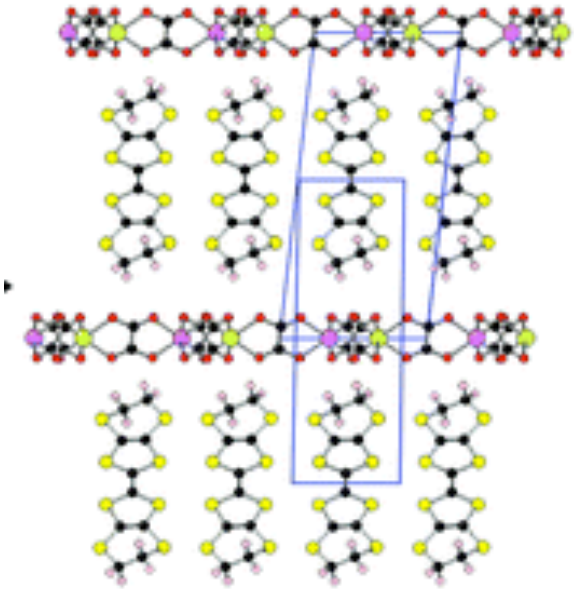
Coronado, 2000



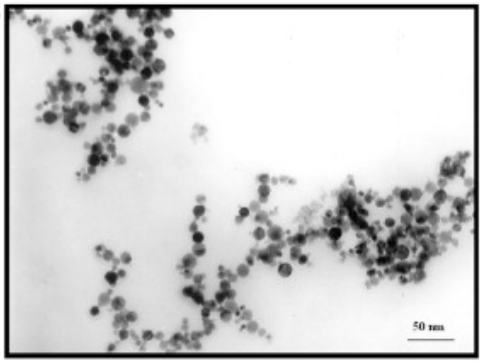
Miyazaki, 2007



Miyazaki, 2007



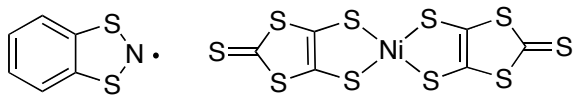
Coronado, 2000



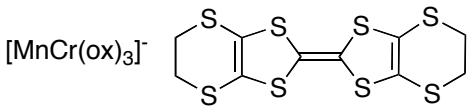
Fe3O4-PANI composites. Lee, 2008

Conducting: organic
Magnetic: metal-based

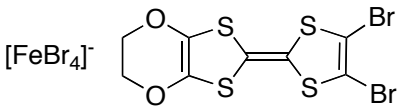
Molecule-Based Magnetoconducting Materials



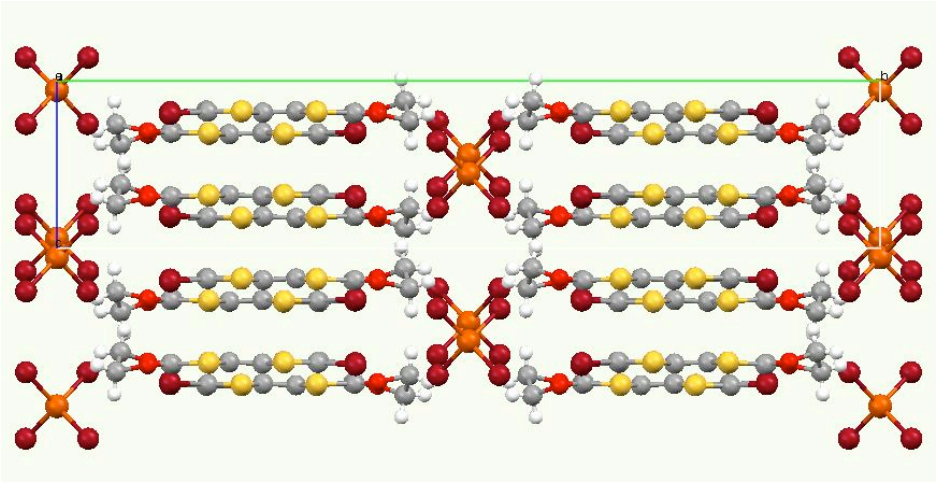
Awaga, 2008



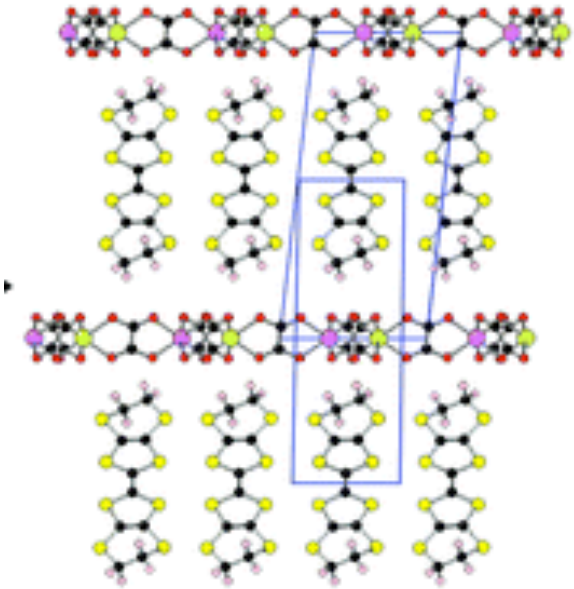
Coronado, 2000



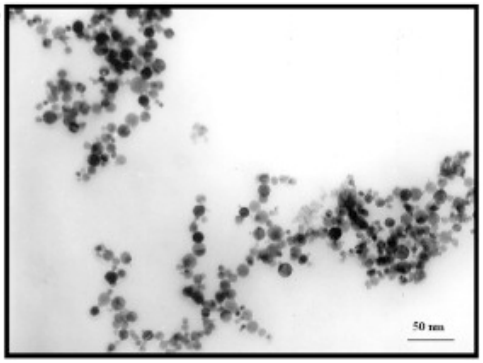
Miyazaki, 2007



Miyazaki, 2007



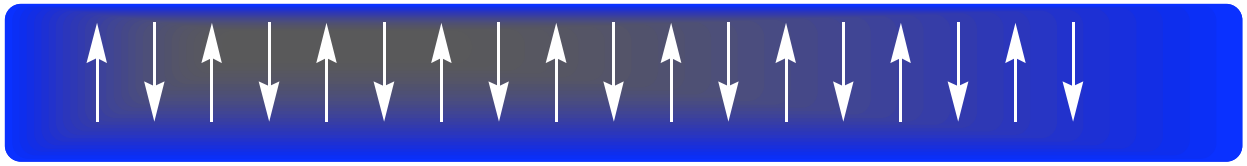
Coronado, 2000



Fe3O4-PANI composites. Lee, 2008

Conducting: organic
Magnetic: metal-based

Charge Transport



Spin Polarized-Charge Transport: FOM = % SP (100 %)

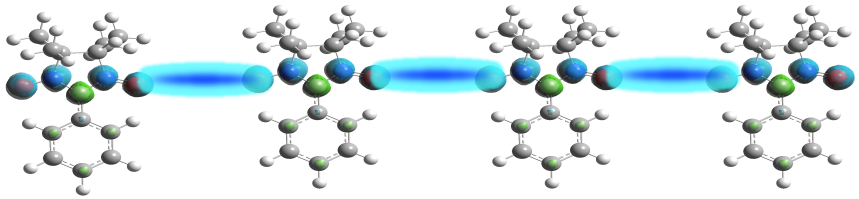
Relaxation Processes

Spin orientation of conduction electrons is a slow process (ns), compared to the rate of electron momentum decay (fs).

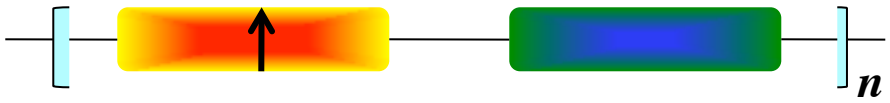
Redox-Active Open-Shell Alternating-Copolymers

Redox-Active: low band gaps: *increased conductivities*

Open-shell: Open shell (radicals) lead to intramolecular magnetic exchange and sub-band in the middle of the band gap effectively reducing the band gap



Alternating Copolymers: A-B architectures allow for synthetic ease for installation of varying bridges (B) and radicals (A).

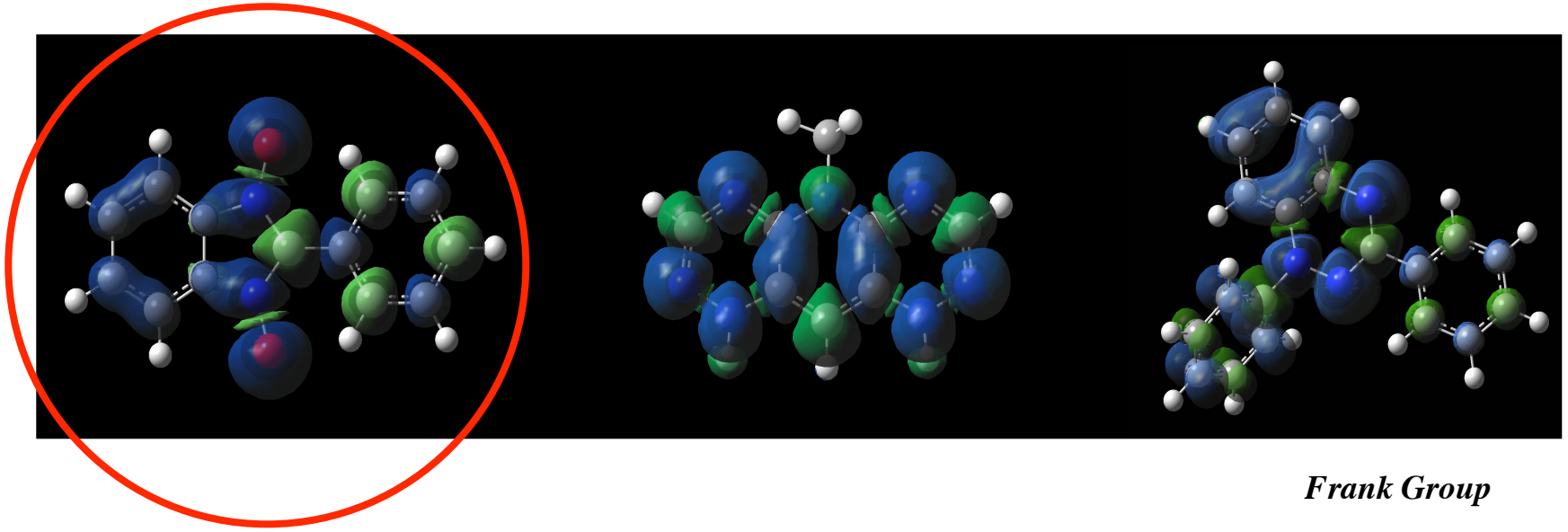


Single Component Magneto-Conducting Materials

Organic Spintronic Materials: single component systems with complementary functionality

Molecular materials with magnetic and conducting properties:
- tune magnetic exchange and charge transport
-relationship between mechanisms of exchange and transport?

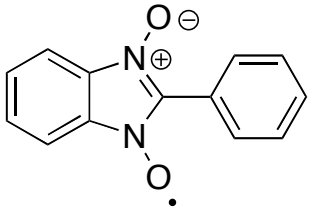
Synthetic Challenges
Processing and Detection

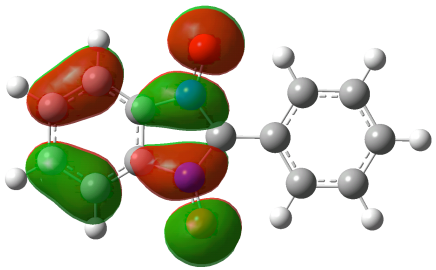


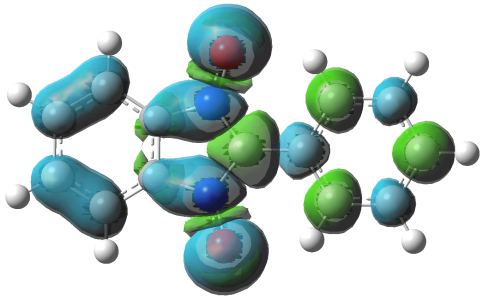
Frank Group

Spin-Delocalized Radicals: Benzonitronyhl Nitroxides (BNNs)

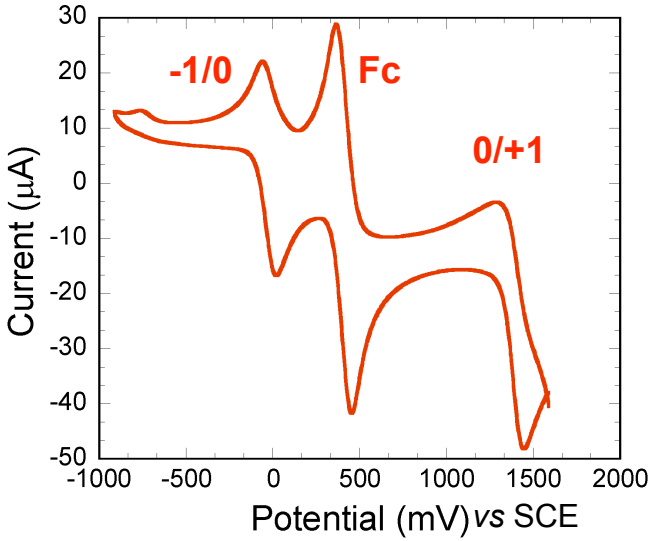
Spin-Delocalized Radicals (BNN): low redox potentials, high spin densities

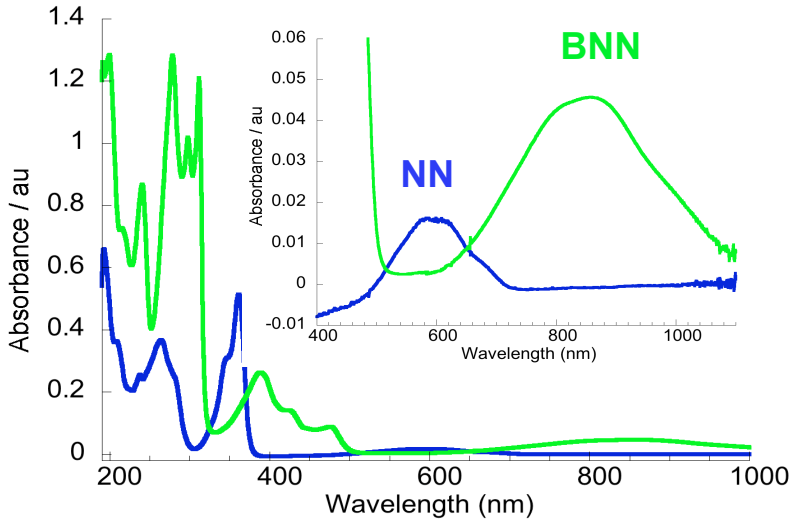






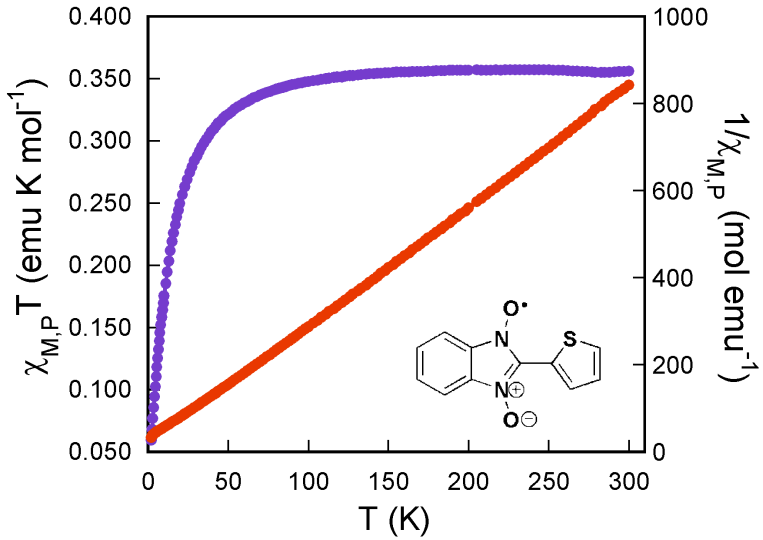
SOMO (UB3LYP/6-31G(d,p)) and spin density distribution



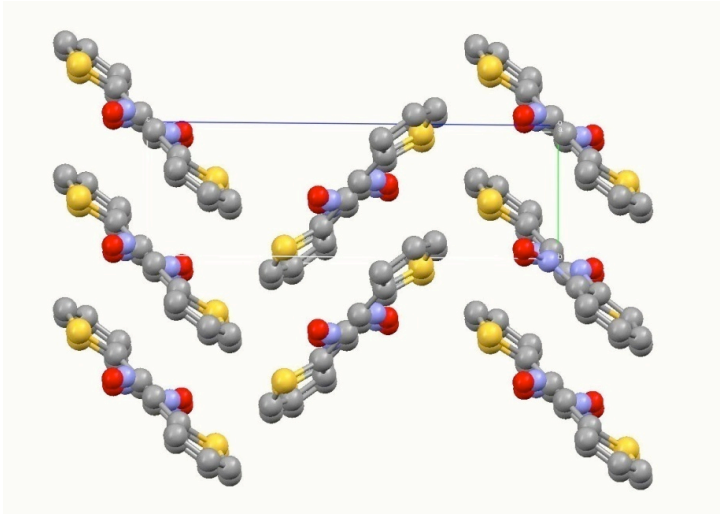


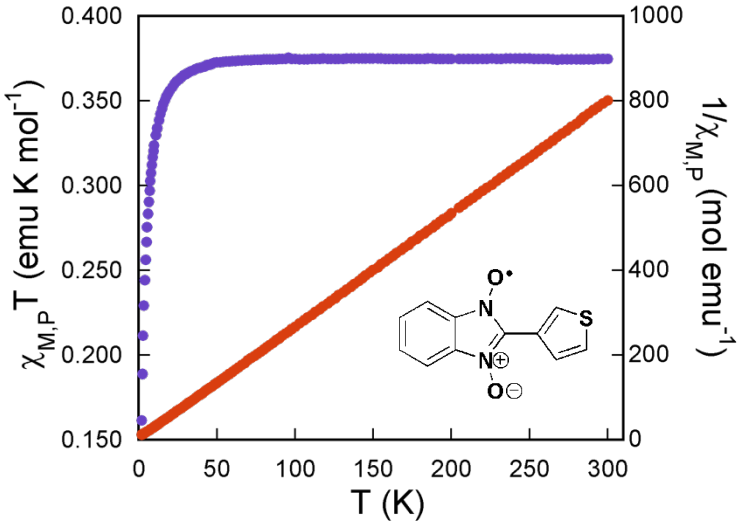
B.M. Dooley, S.E. Bowles, T. Storr, N.L. Frank* *Org. Lett.* (2007)

Magnetic Interactions are dominated by π-π chain interactions: D-A

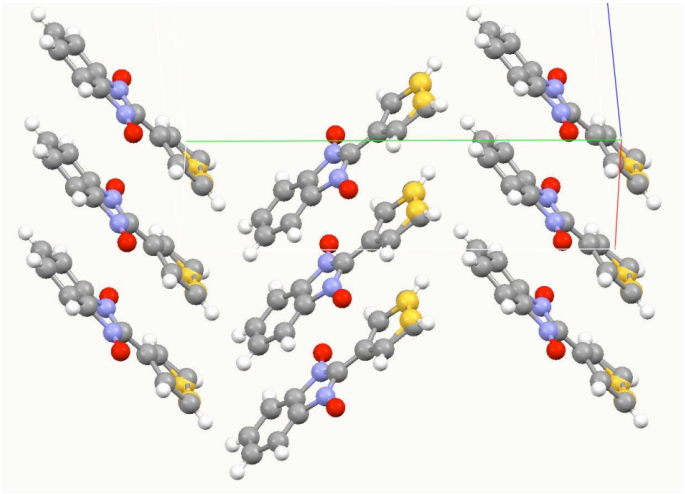


2TBNN (2-300 K), 0.1T
C = 0.364, θ= -4.6 K



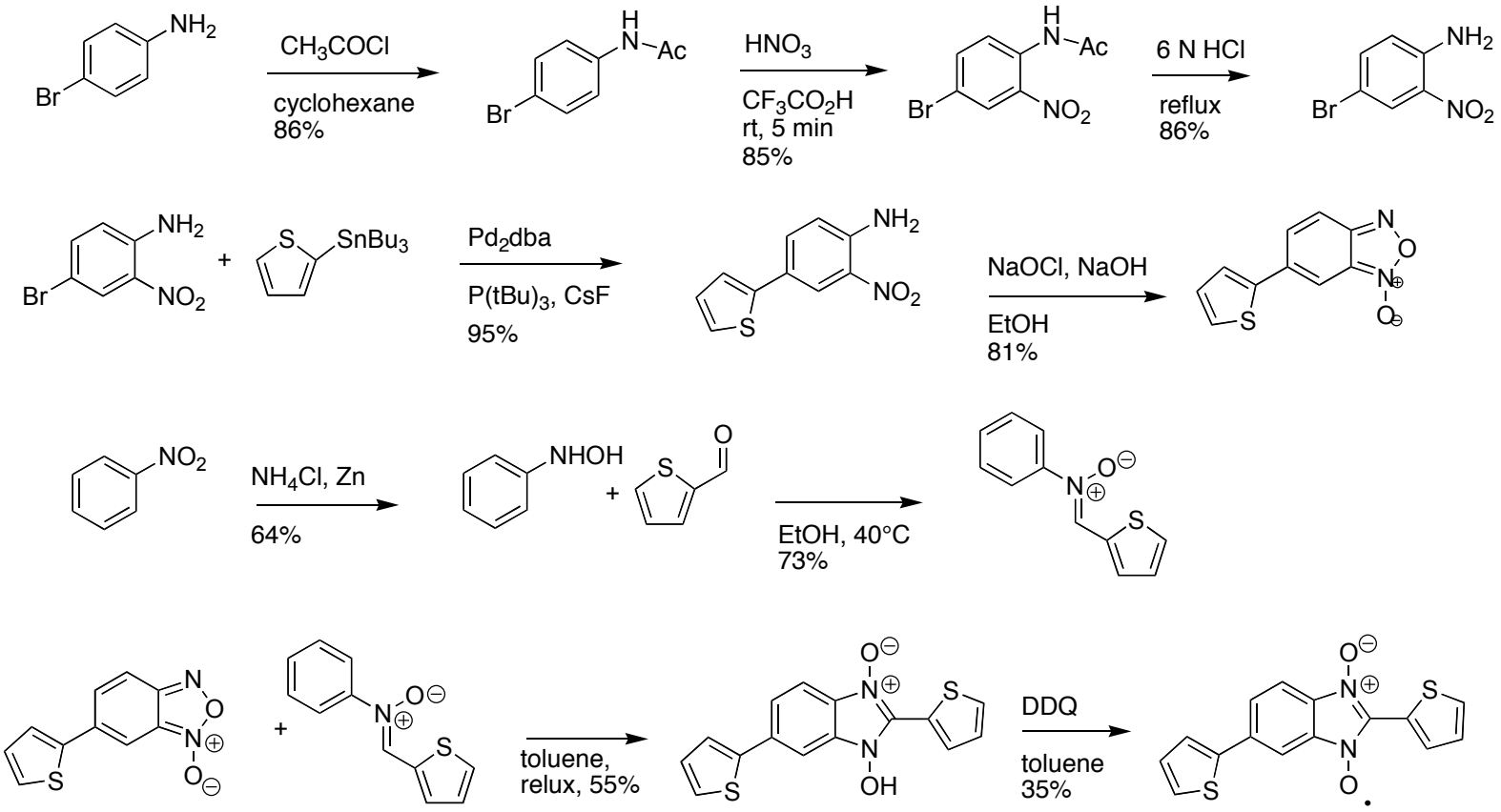


3TBNN (2-300 K), 0.1T
C = 0.377, θ= -1.0 K



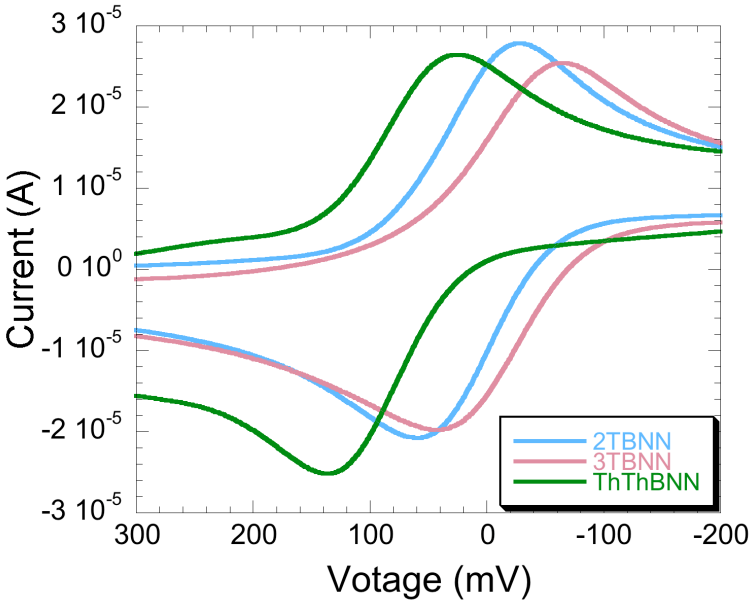
Synthesis of Extended Spin-Delocalized Radicals

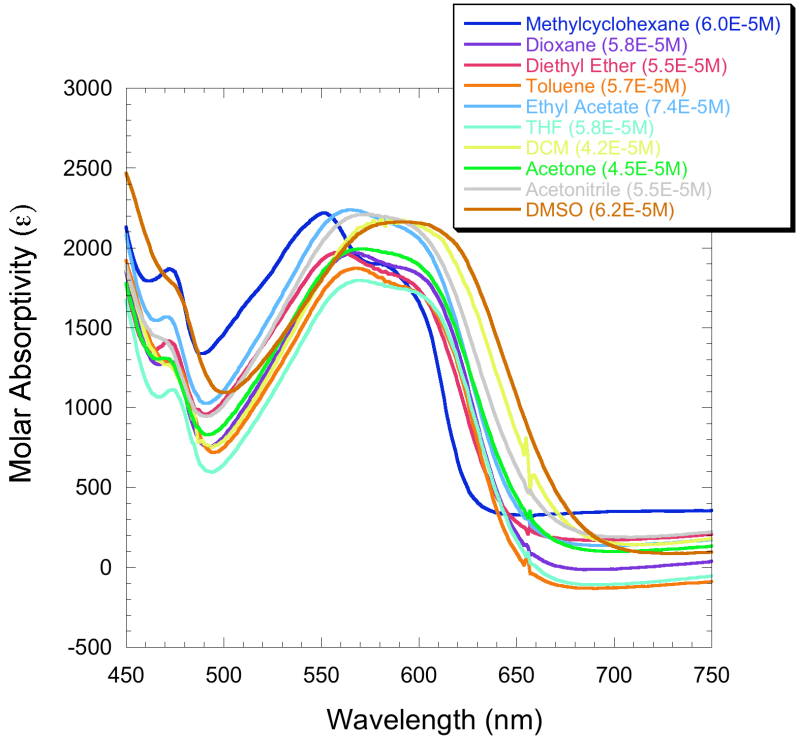
Synthetic methodology for Donor-Acceptor-Donor triads (D-A-D): Metal-Catalyzed coupling

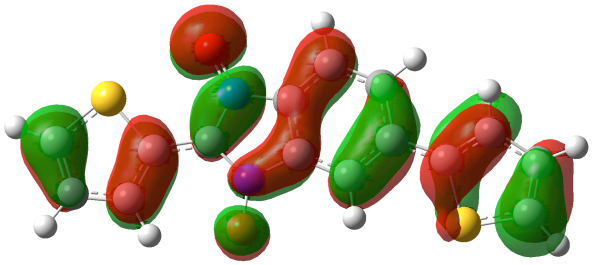


B.M. Dooley, T. Andrews, N.L. Frank*, *submitted*

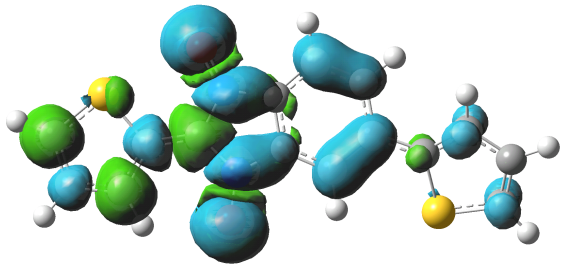
Effect of Desymmetrization in D-A-D







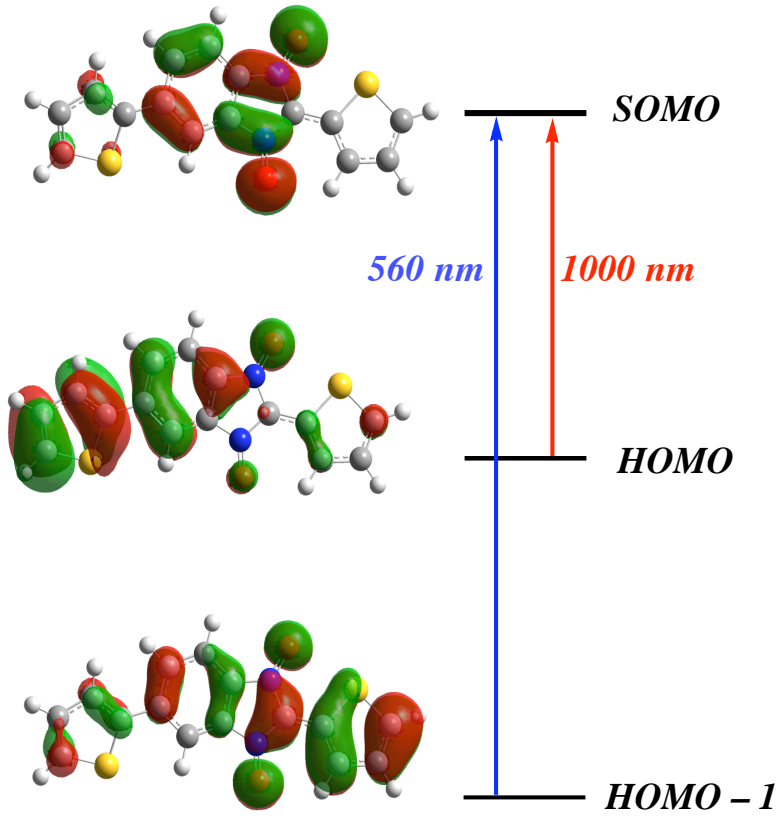
(SOMO) UB3LYP/6-311G(d,p)

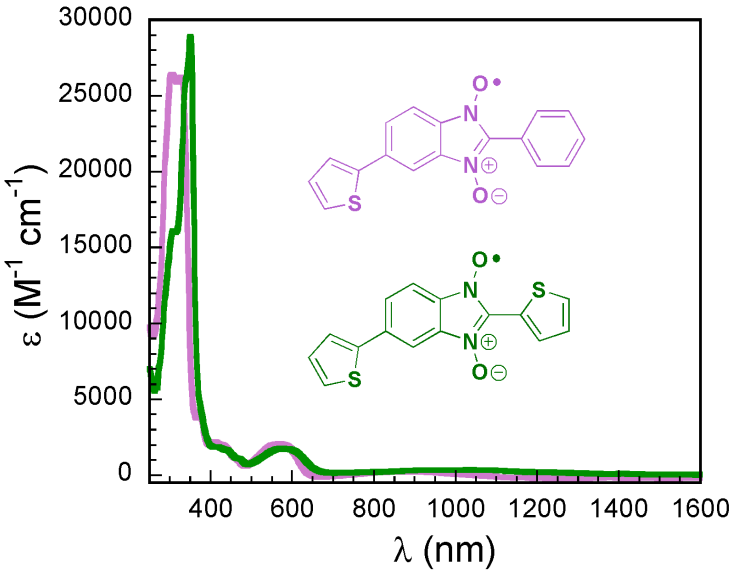


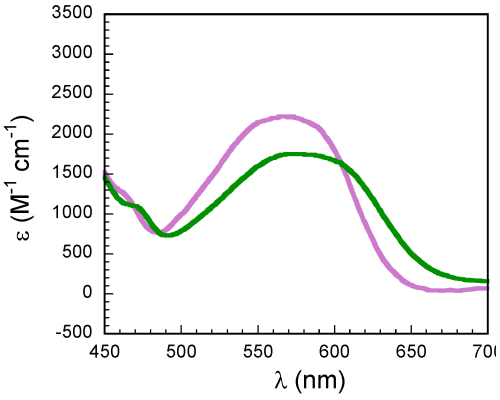
Spin Density UB3LYP/6-311G(d,p)

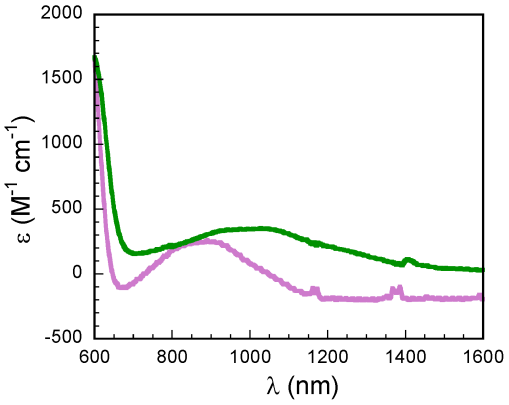
B.M. Dooley, N.L. Frank

Dual CT Absorption Bands: A-D-A triad



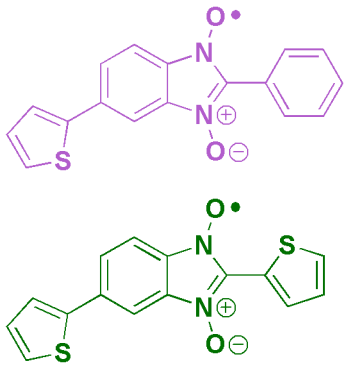


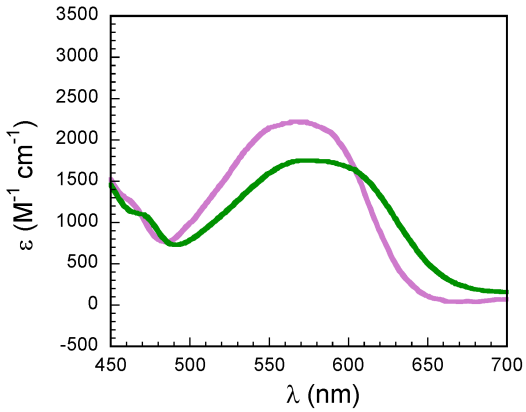


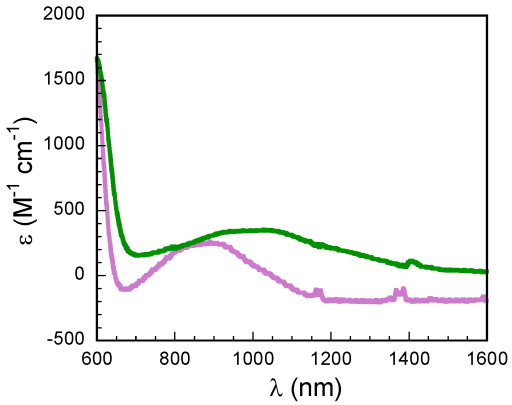


TDDFT UB3LYP/6-311G(d,p)

GMH: Electronic coupling for MV radicals ?







$$V = (0.0205)\frac{[\epsilon_{max}\Delta\tilde{\nu}_{1/2}\tilde{\nu}_{max}]^{1/2}}{r_{DA}}$$

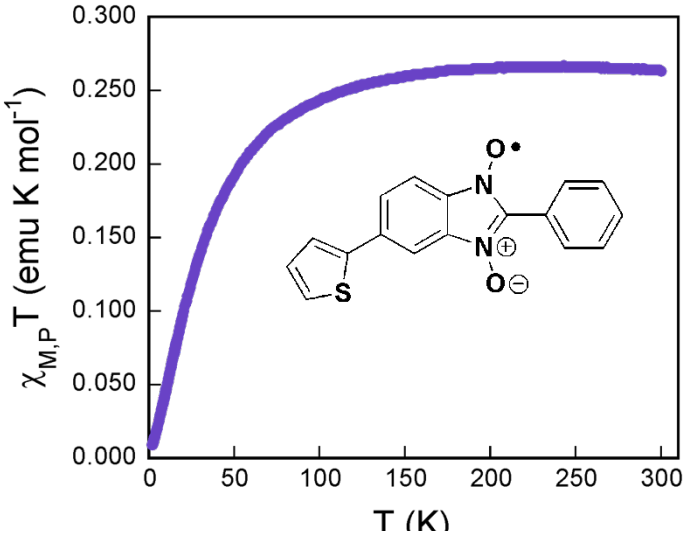
λ_{max} ~ 580 nm (17200 cm^{-1})

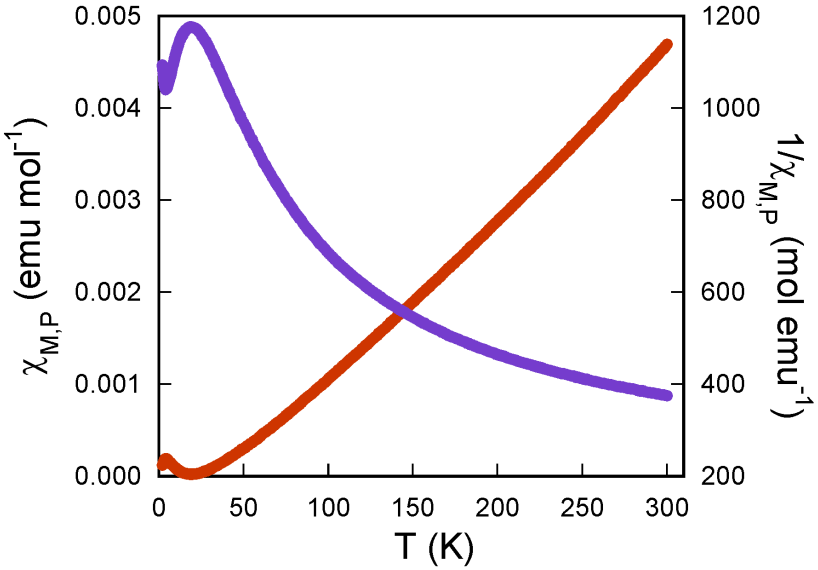
Solvent	3a *V* (cm^{-1})	3b *V* (cm^{-1})
Toluene	5500	5300
Diethyl Ether	4600	4700
Acetonitrile	4600	4700

λ_{max} ~ 1000 nm (10000 cm^{-1})

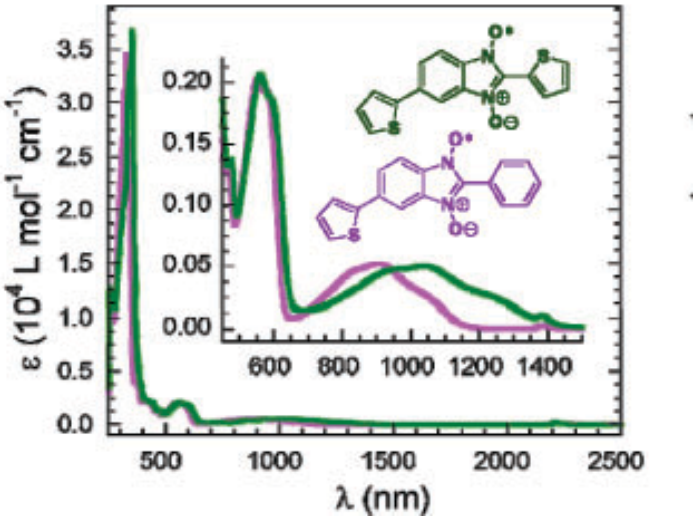
Solvent	3a *V* (cm^{-1})	3b *V* (cm^{-1})
Toluene	1600	1400
Diethyl Ether	2000	1500
Acetonitrile	1400	1600

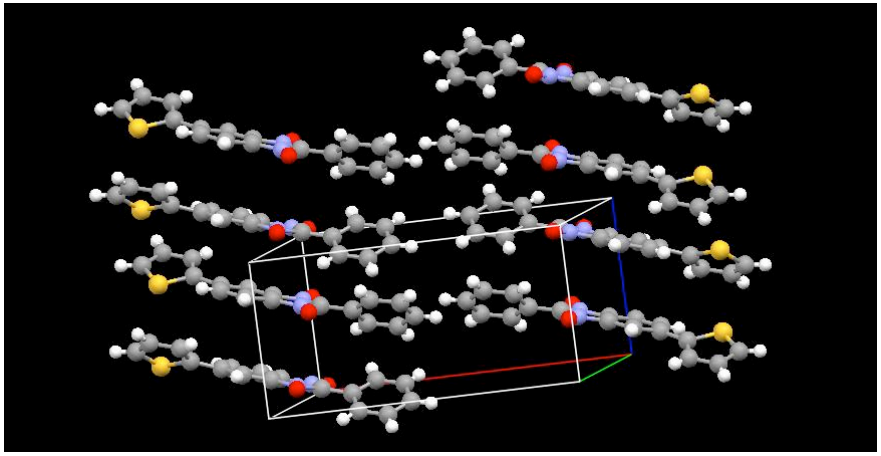
Intermolecular FM to AFM Exchange





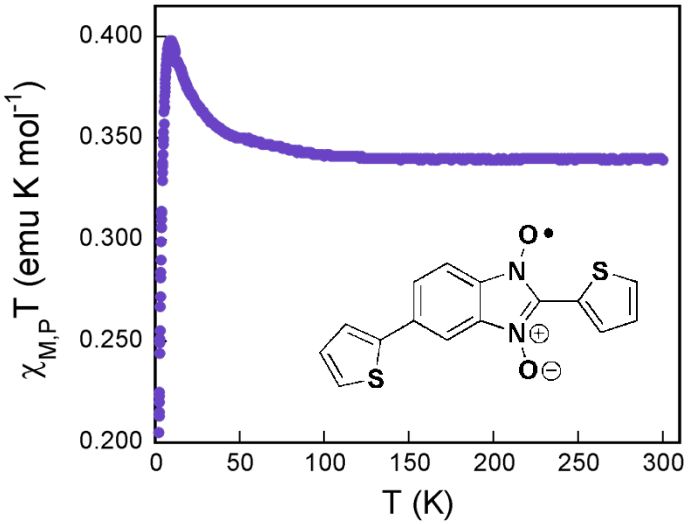
J = - 14 K, zJ' = 4, T_N = 20.0 K

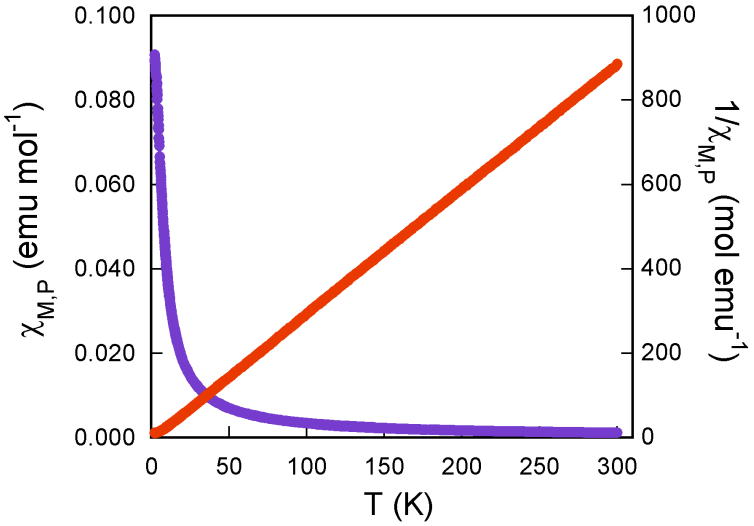




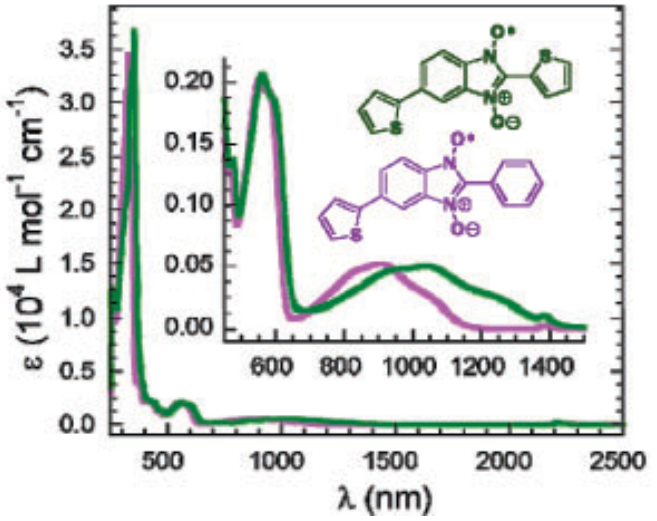
$\sigma = 10^{-7}$ S cm^{-1}

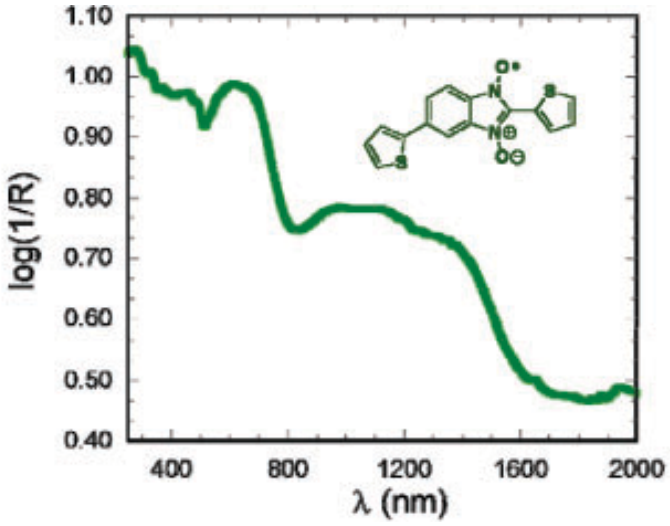
Intermolecular FM Exchange





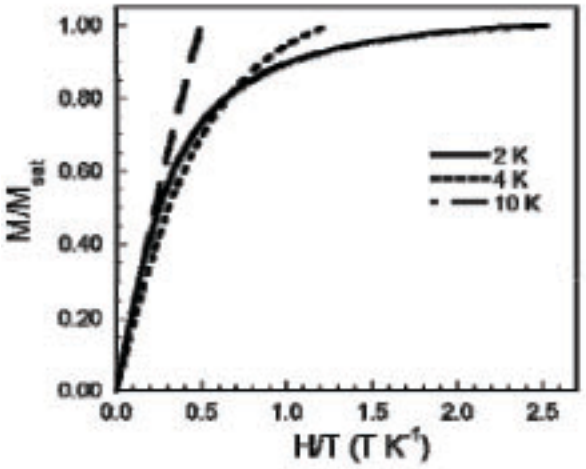
J = 9 K, zJ'= 7 K , T_m = 9.4 K

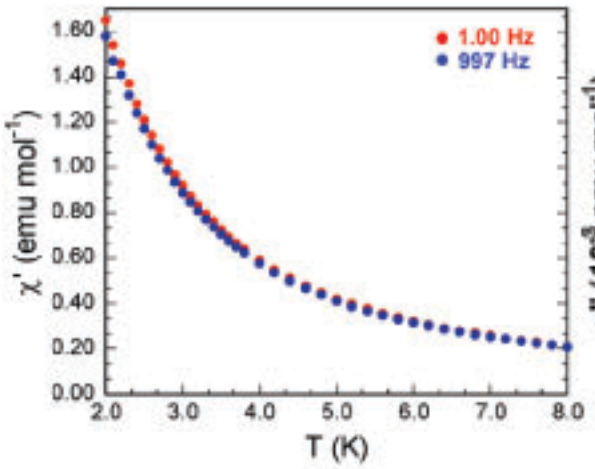


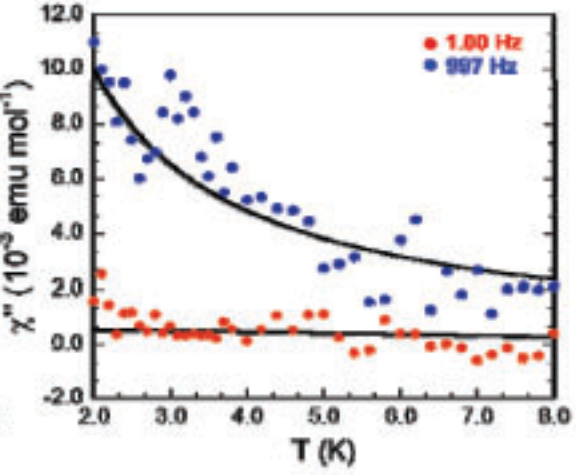


σ = 10^{-5} S cm^{-1}

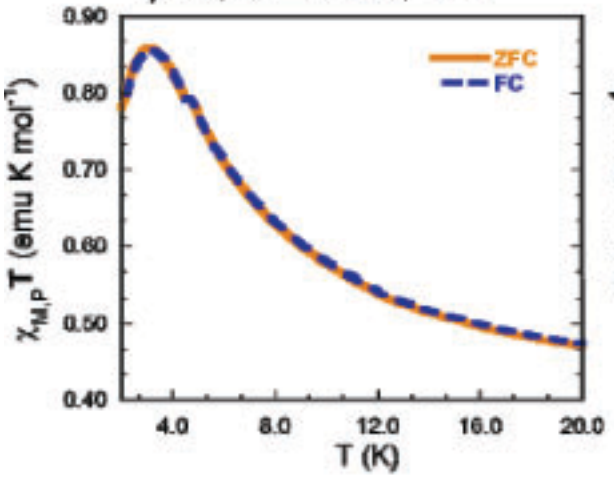
Short range ferromagnetic ordering in BTBNN



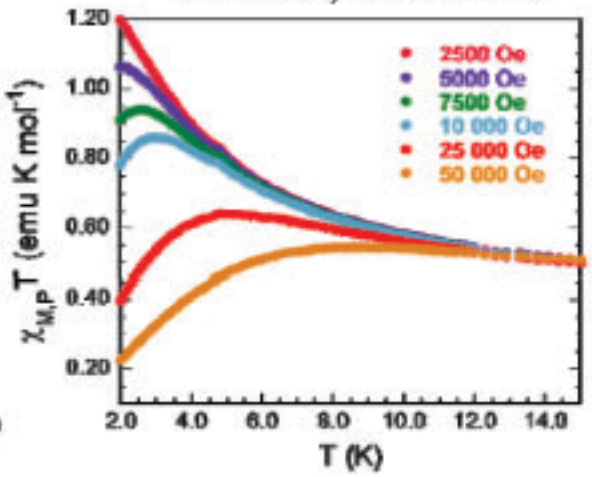




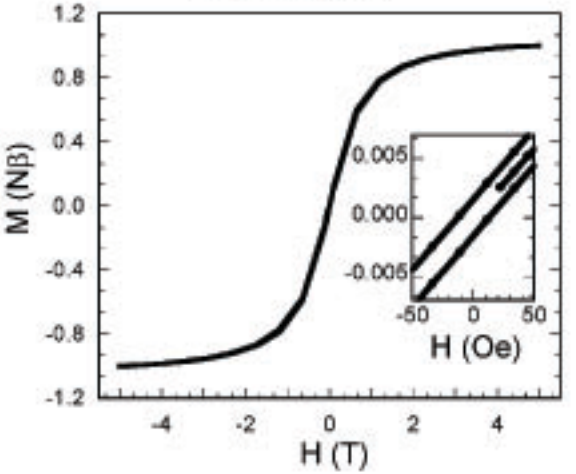
Zero field cooled-field cooled plot, 2 – 50 K, 1 T



Magnetic moment as a function of temperature and field, 2 – 40 K, 0.25 – 5 T



Hysteresis at 2 K, -5 T to 5 T

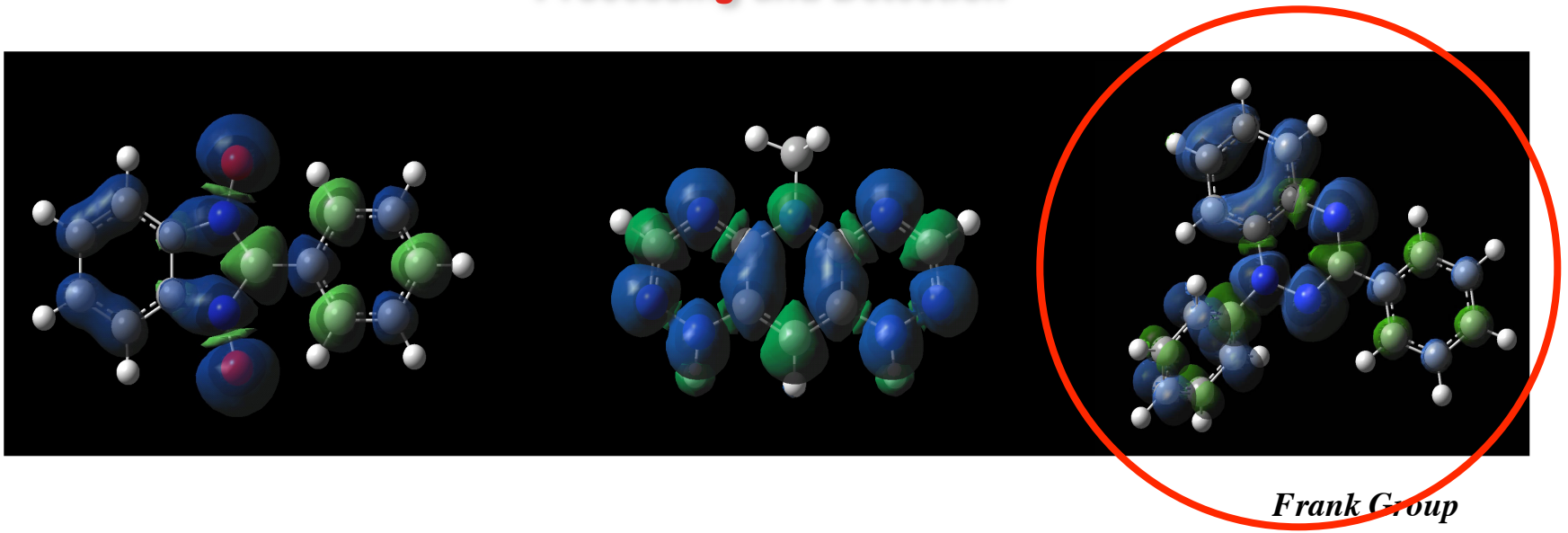


Single Component Magneto-Conducting Materials

Organic Spintronic Materials: single component systems with complementary functionality

Molecular materials with magnetic and conducting properties:
- tune magnetic exchange and charge transport
-relationship between mechanisms of exchange and transport?

Synthetic Challenges
Processing and Detection



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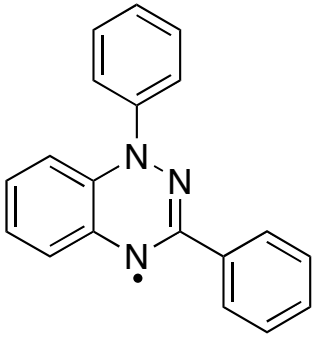
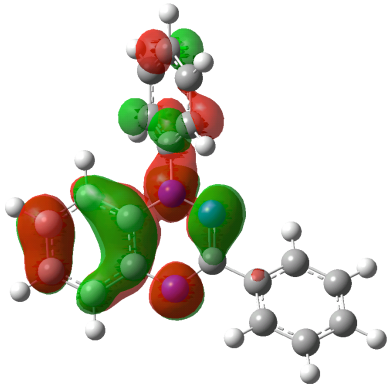
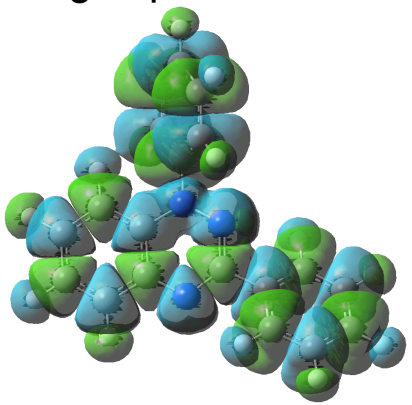
Spin-Delocalized Radicals: Benzonitronyhl Nitroxides (BNNs)

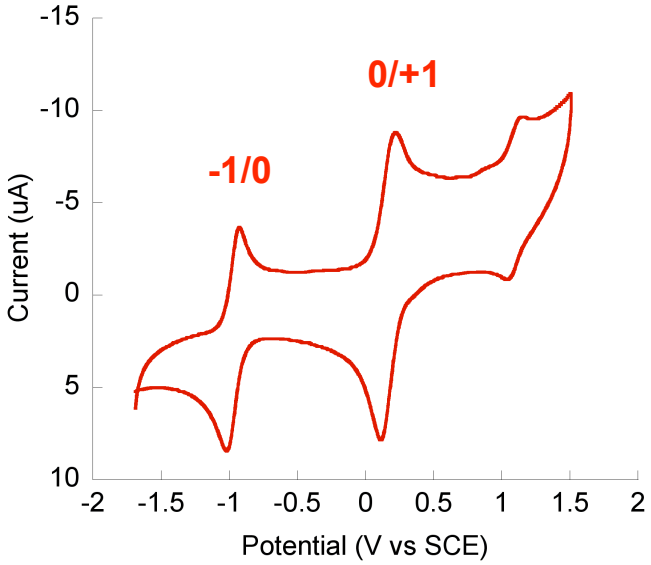
Spin-Delocalized Radicals (BNN): low oxidation potential, high spin densities

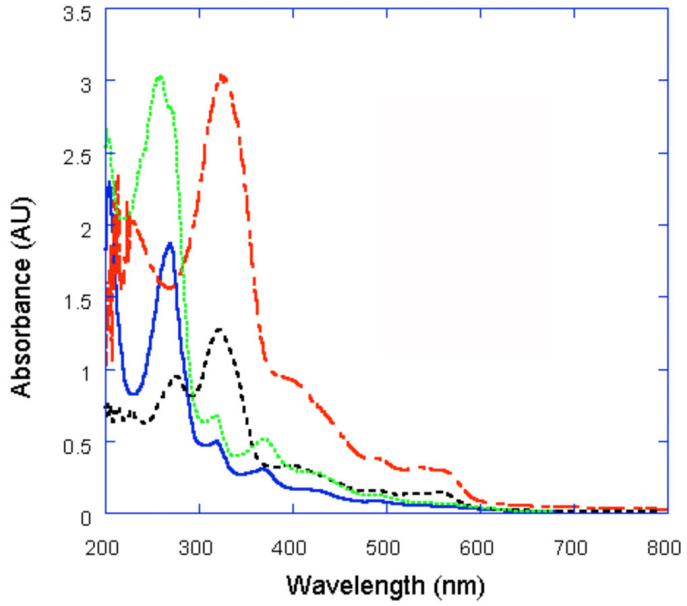






SOMO (UB3LYP/6-31G(d,p)) and spin density distribution





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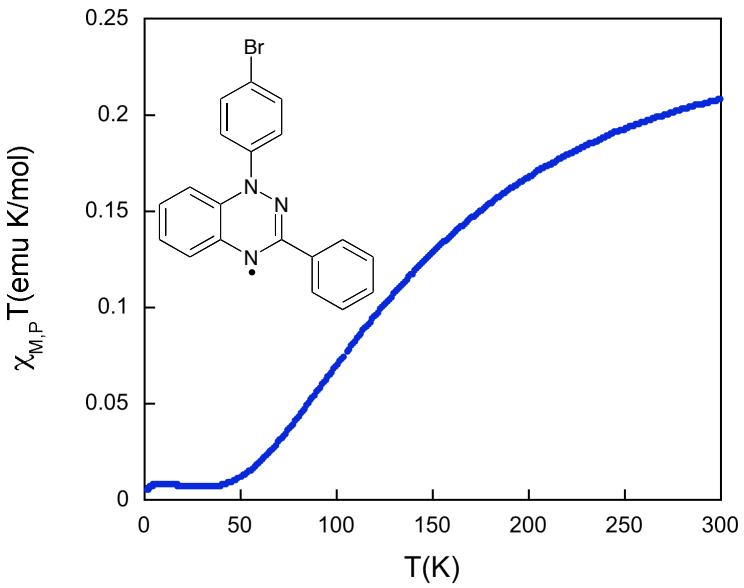
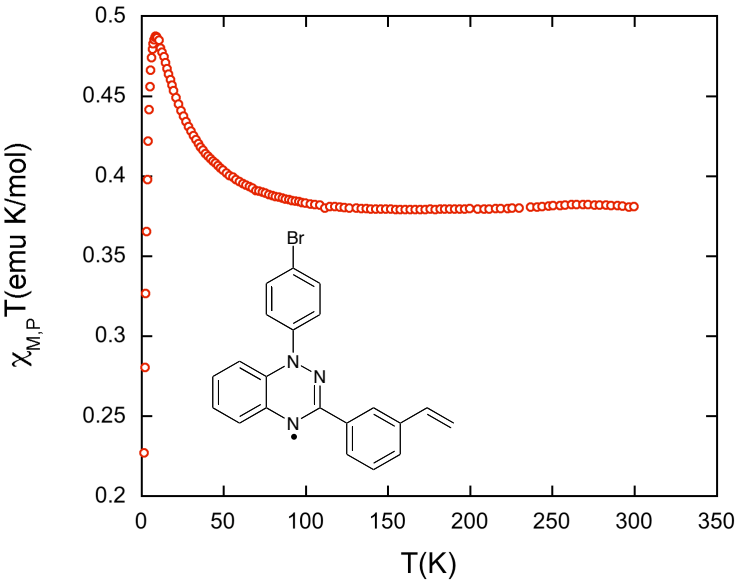
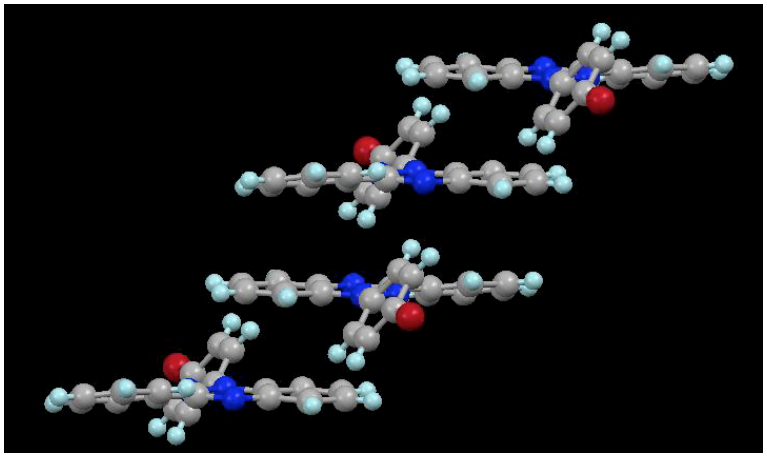
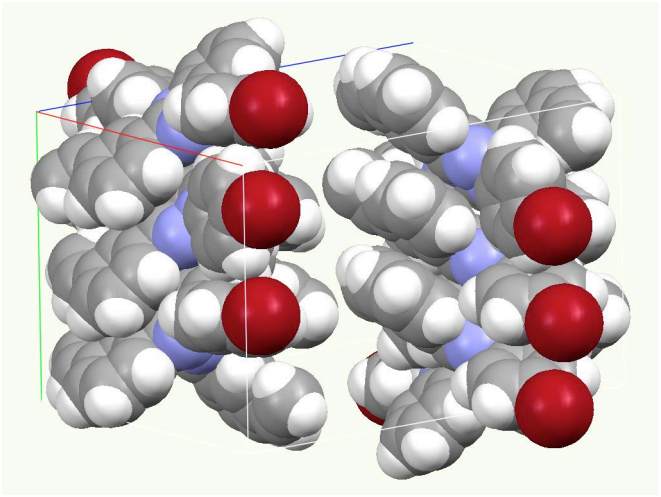
Triazinyl Radicals: Strong magnetic exchange via pi-stacking interactions

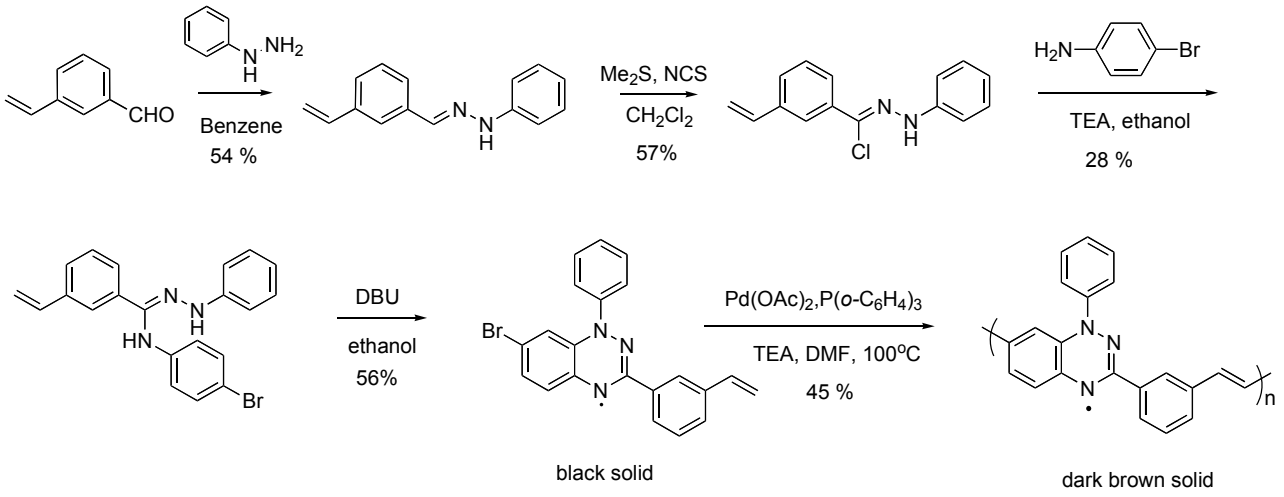








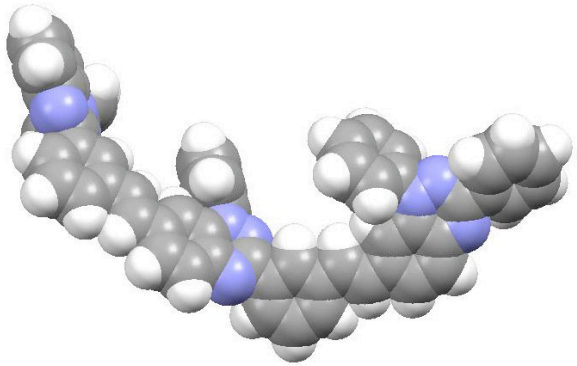
Synthesis of Extended Spin-Delocalized Polyradicals

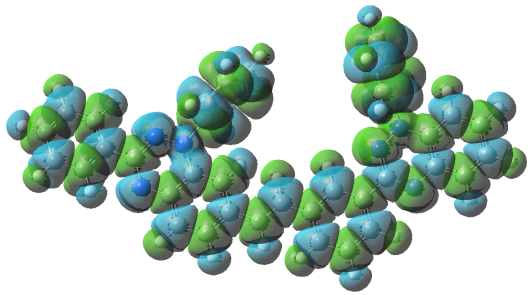


black solid

dark brown solid

GPC: (30,000-50,000 kD) PDI = 1.1-1.3
Spin content dependent on polymerization reaction conditions





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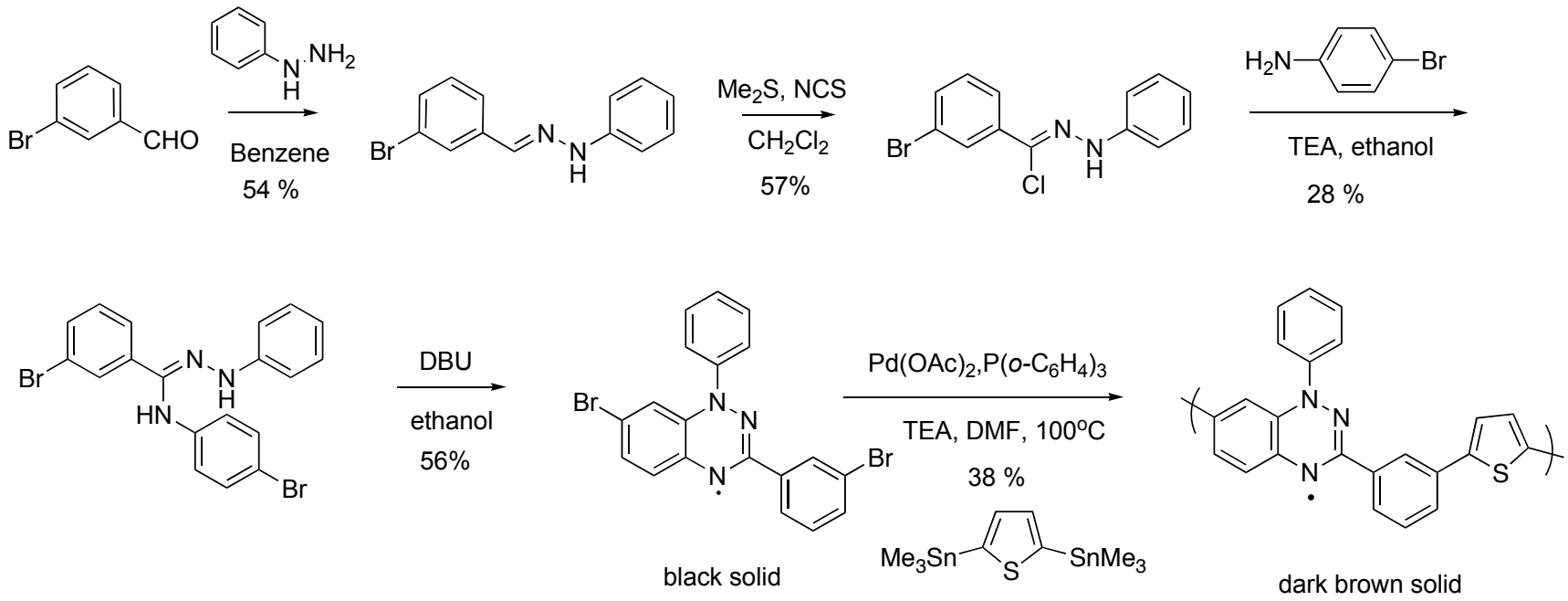
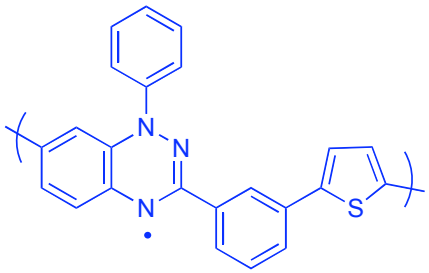
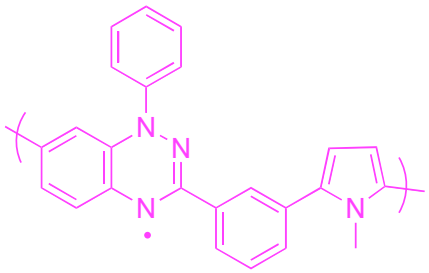
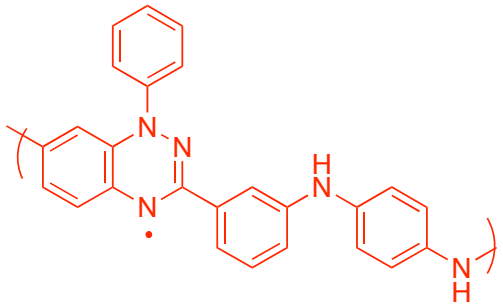
Synthesis of Extended Spin-Delocalized Polyradicals: Vary the Bridge









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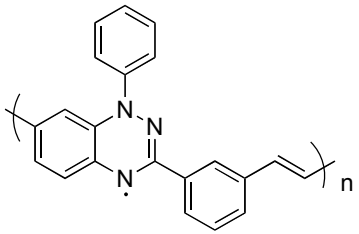
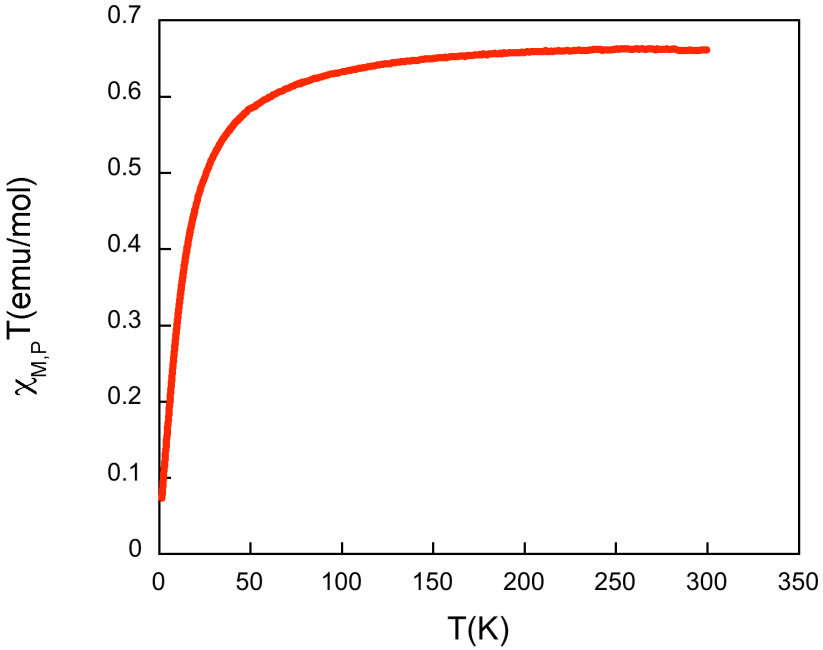
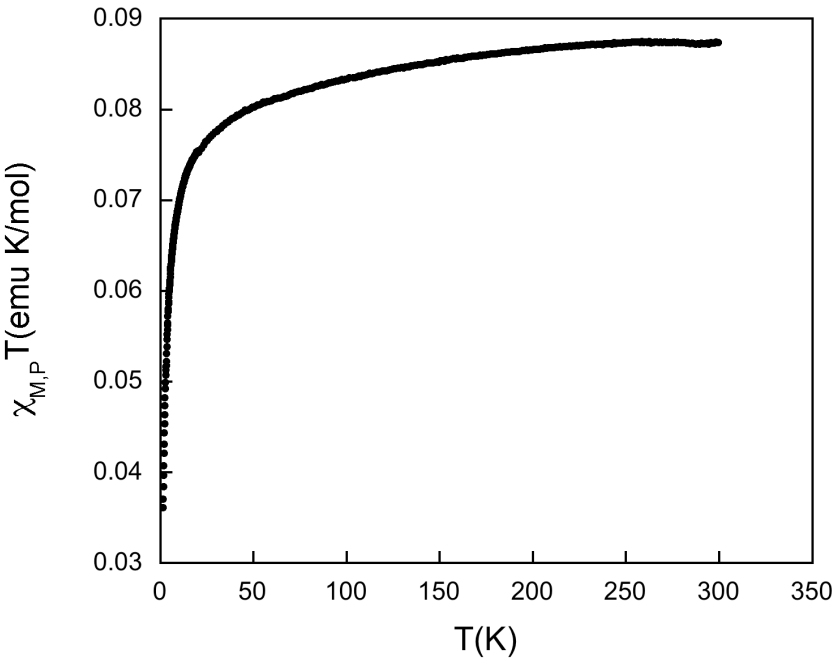
Antiferromagnetic Exchange in PPV-Trz polymer



$\sigma_{RT}=10^{-6}$ S cm^{-1}





PVC matrix

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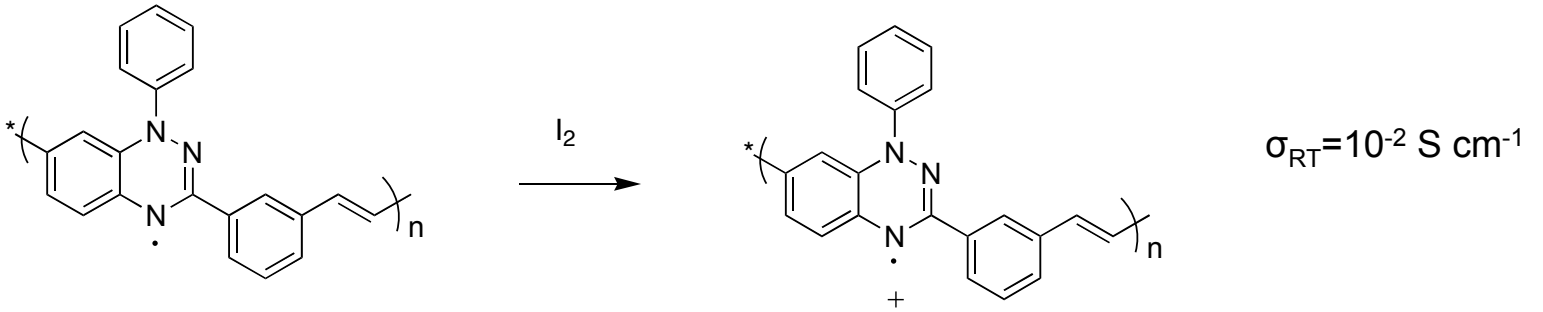
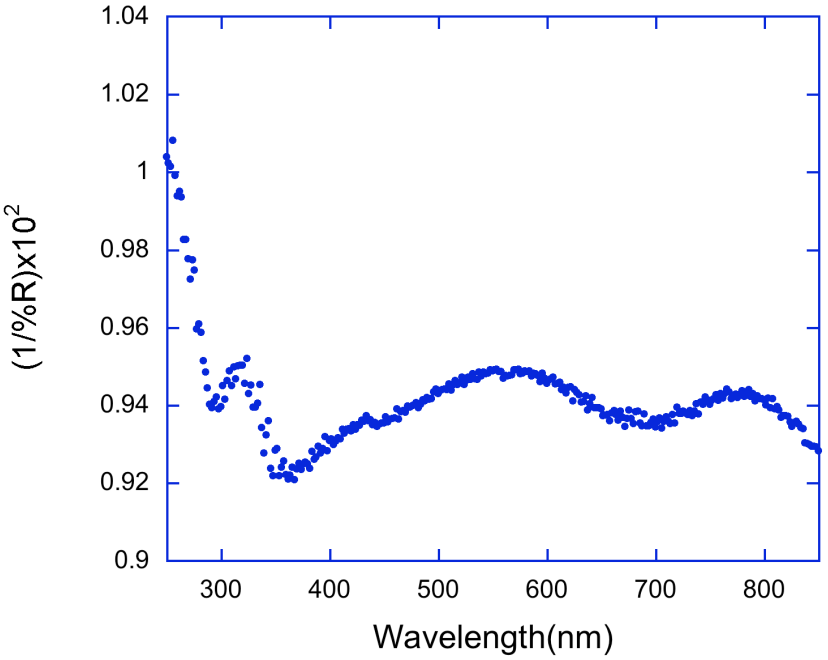
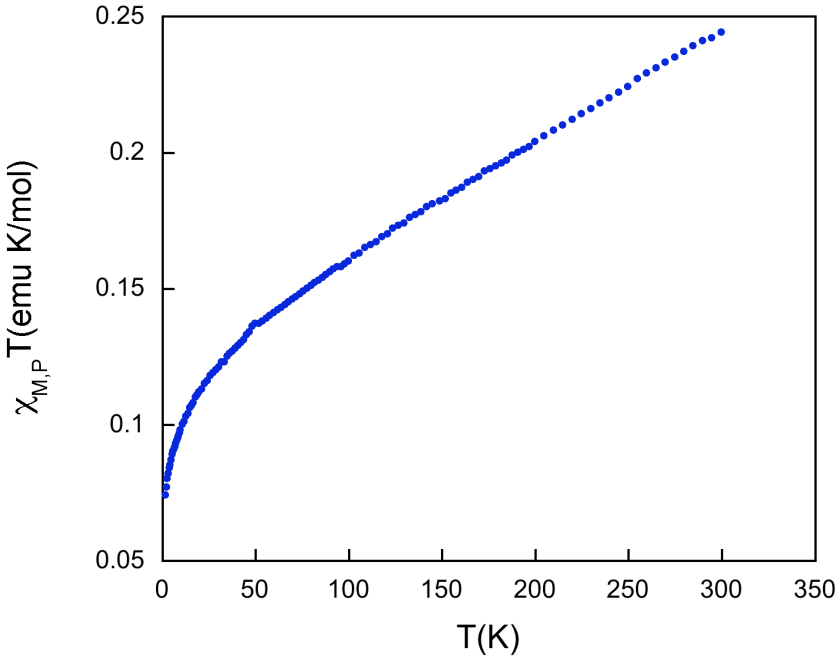
P-Doping of the PPV-Trz polymer



$\sigma_{RT}=10^{-2}$ S cm^{-1}





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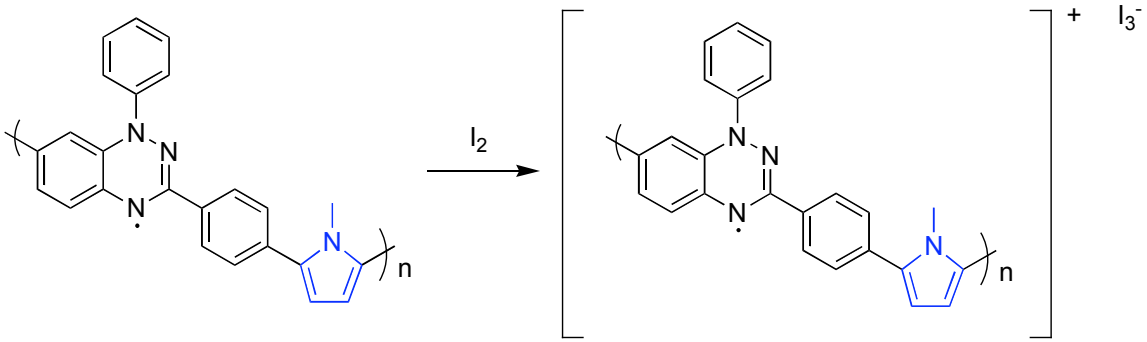
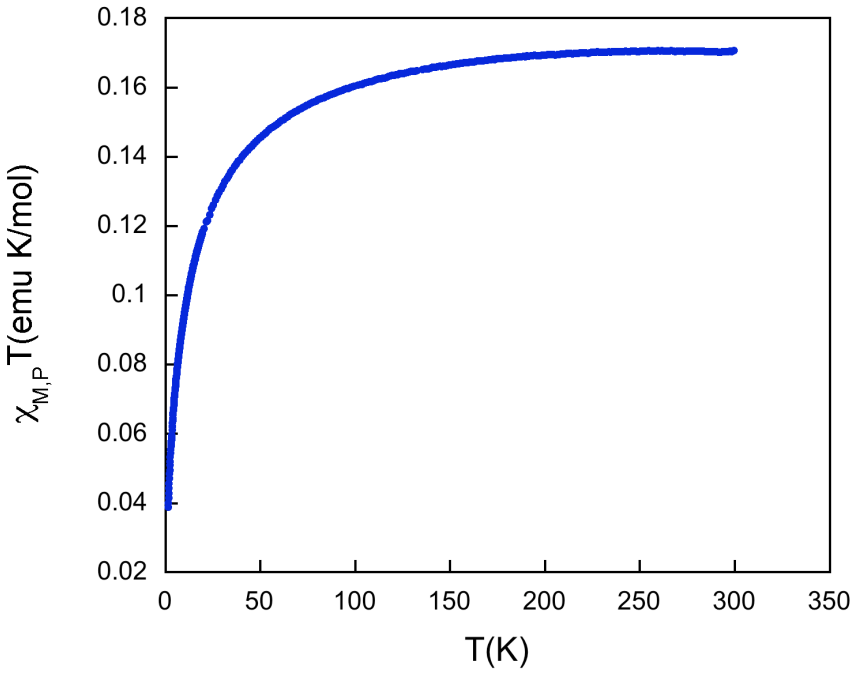
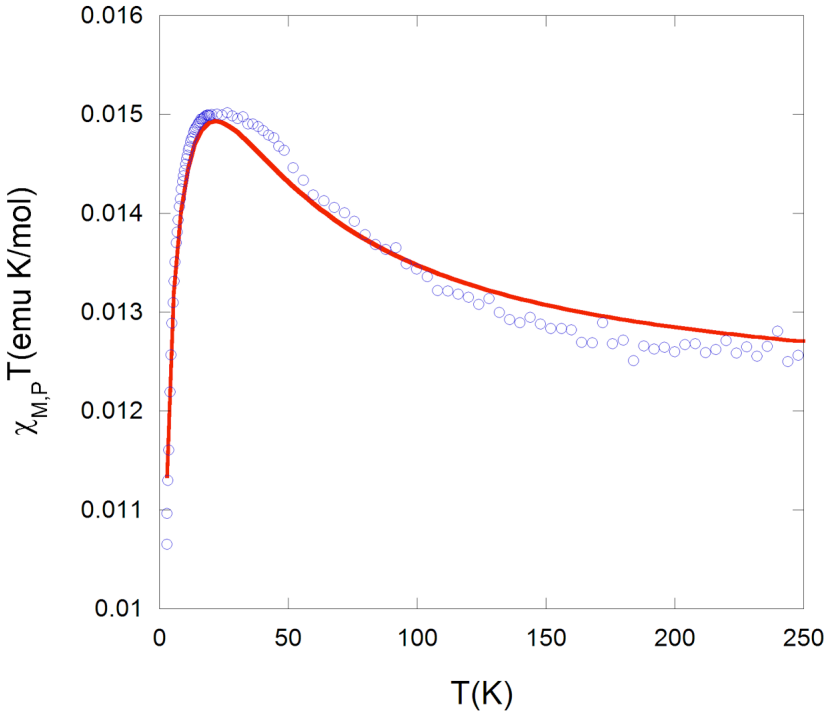
P-Doping of polyradicals with electron rich bridges

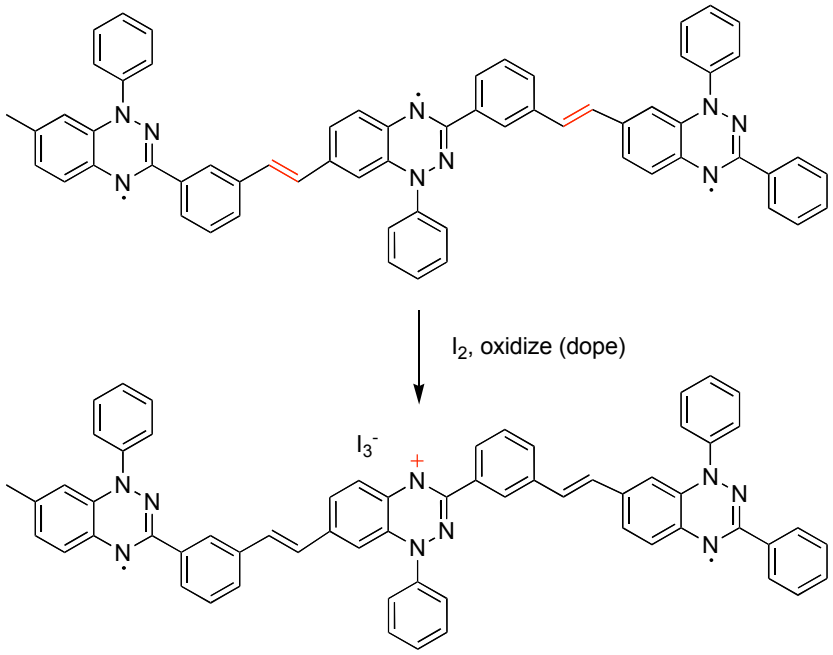






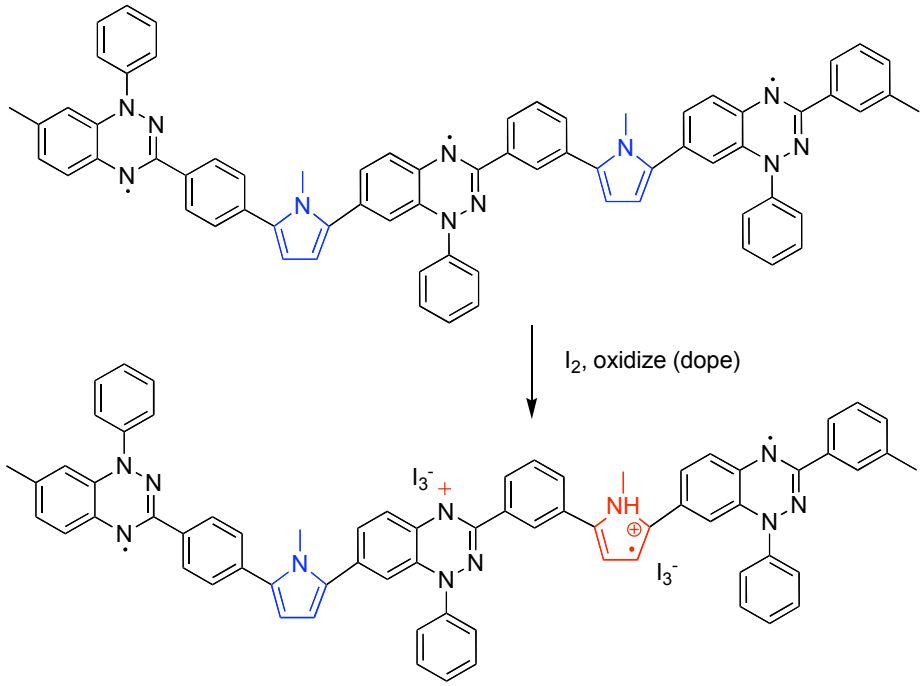
Oxidation of the PPVTrz polymer: Bridge vs radical…

Radical oxidation



AFM

Radical and bridge oxidation



FM

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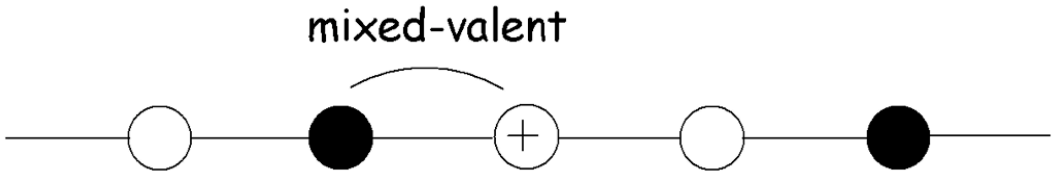
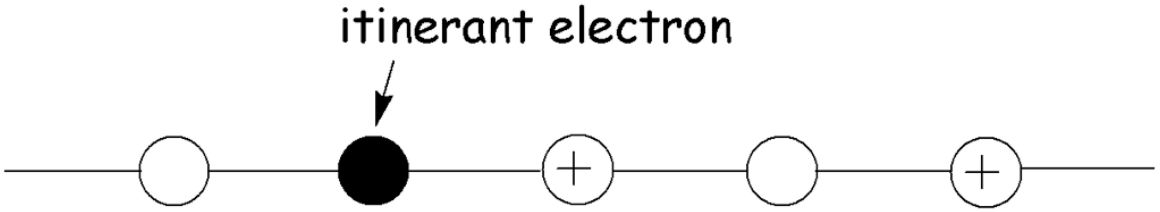
Mechanism of exchange in magnetically dilute polymers?

Lightly doped (35 % spin content)



Heavily doped (4 % spin content)



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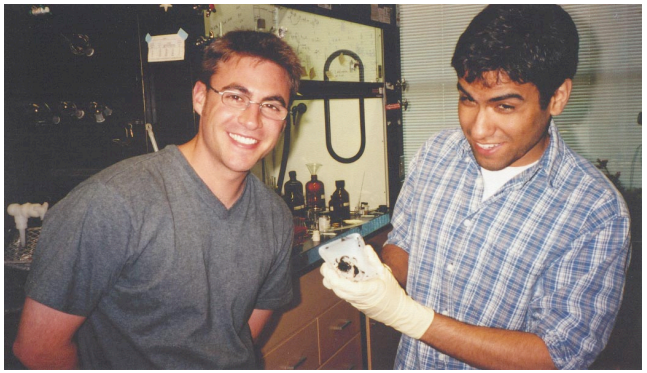
Conclusions and Future Challenges

- **Developed Synthetic Methodology for:**
  - **Benzonitronyl nitroxides (acceptors, octapolar molecules)**
  - **Benzotriazinyl radicals (donors)**
  - **Acceptor-donor dyads and triad**
  - **Open-shell conjugated polymers containing acceptors**
  - **Organic Magnetically dilute semiconductors**
- **Antiferromagnetic/Ferromagnetic interactions in solid state through pi stacking**
- **Polymer synthesis leads to high MW polymers with low polydispersity**
- **Weak antiferromagnetic interactions and Pauli magnetism**
- **Inclusion of CT interactions in BNN oligomers leads to increased exchange coupling:**
- **Change in magnetic properties upon p-doping depends on bridge structure**

Full characterization of charge transport and mobilities critical…..

ACKNOWLEDGEMENTS

Roni Kopelman and Dan Patel



Michelle Paquette with Diva Bear

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