

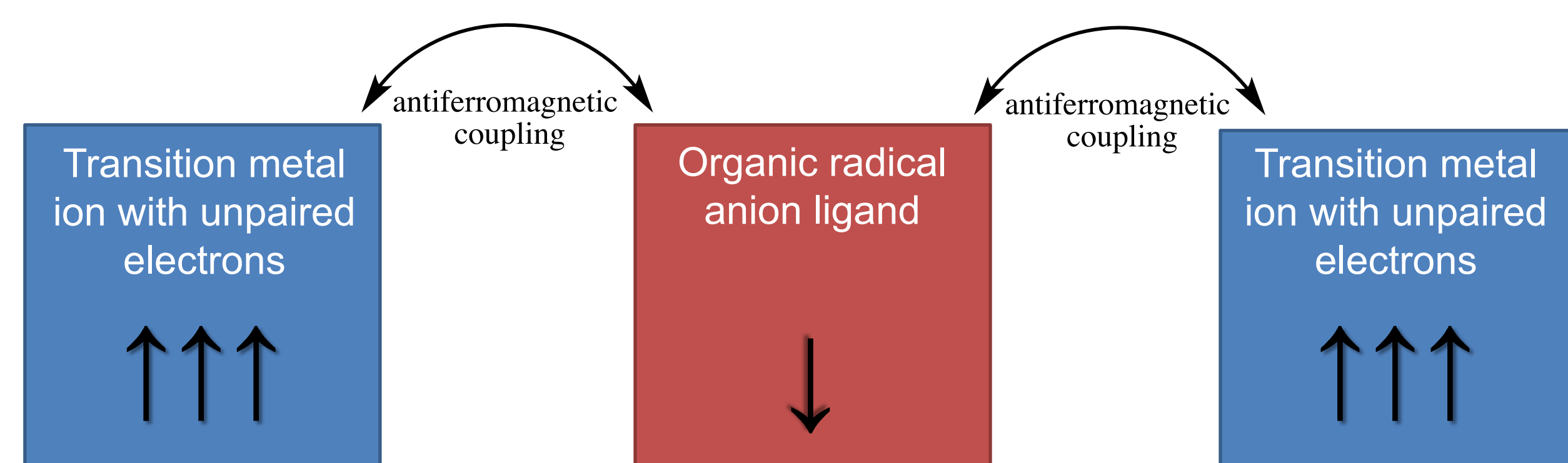


# Synthesis of Novel TCNE Analogs as Building Blocks of Molecule-Based Magnets

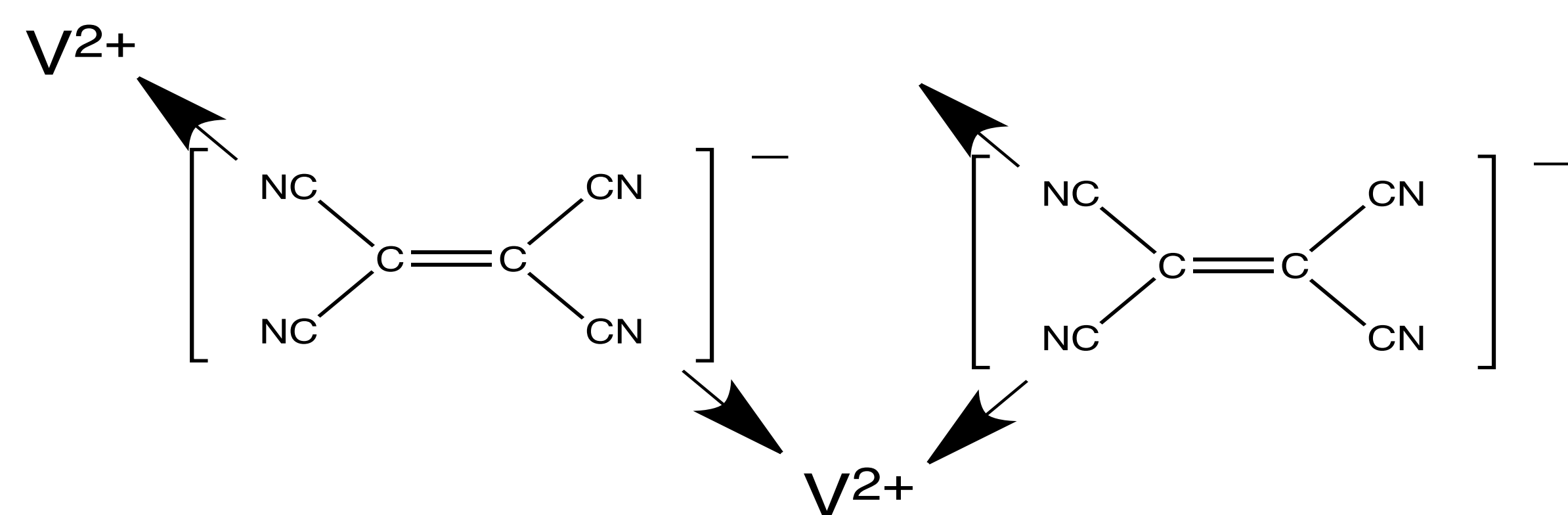
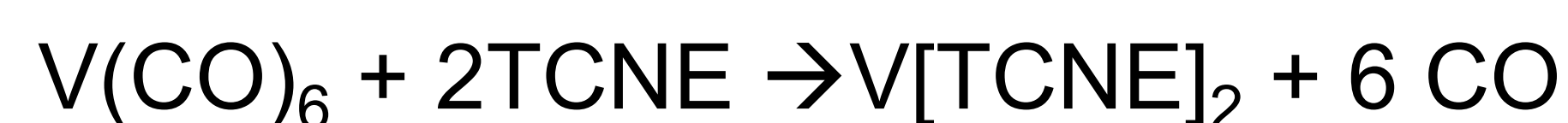
Yee Group 2019

## Molecule-based Magnets

- Magnets where a molecular orbital plays a role either by possessing unpaired electrons or mediating communication between other spins
- Building block approach taken where spin containing ions are paired with organic ligands that can be reduced by one electron
- Flexible strategy because organic chemistry can be used to modify one building block (the acceptor)

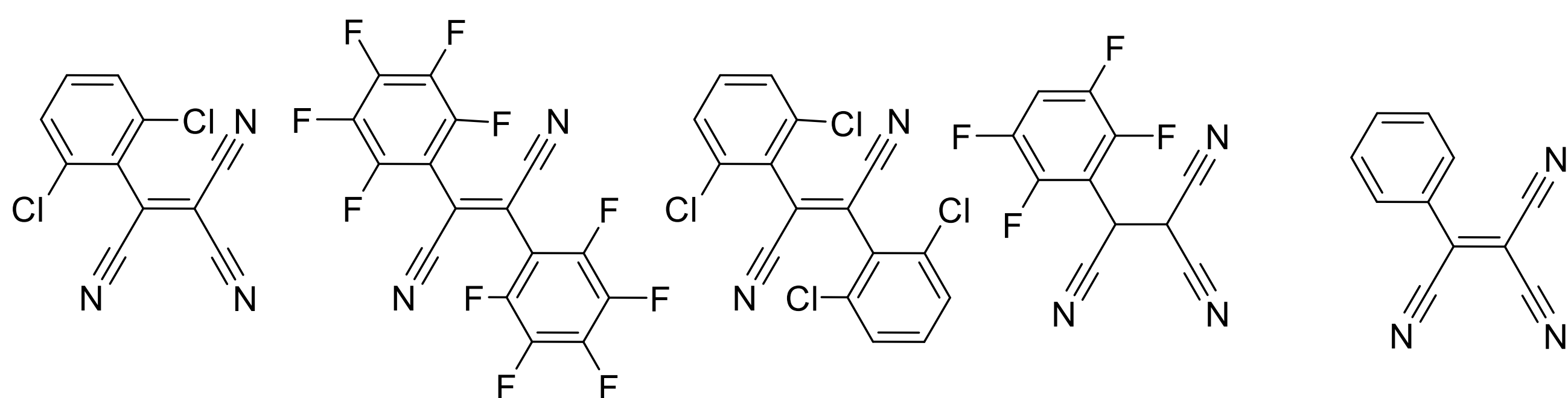


## First example: $V[TCNE]_2$



- First example of ferrimagnetism at room temperature
- Three-dimensional coordination network
- Limited structural information due to amorphous nature
- Air-sensitive
- TCNE radical anion contains an unpaired electron. It coordinates to two or more  $V^{2+}$  cations through nitrogen lone pairs.
- Each  $S = 3/2$   $V^{2+}$  has several bridging ligands coordinated to it.

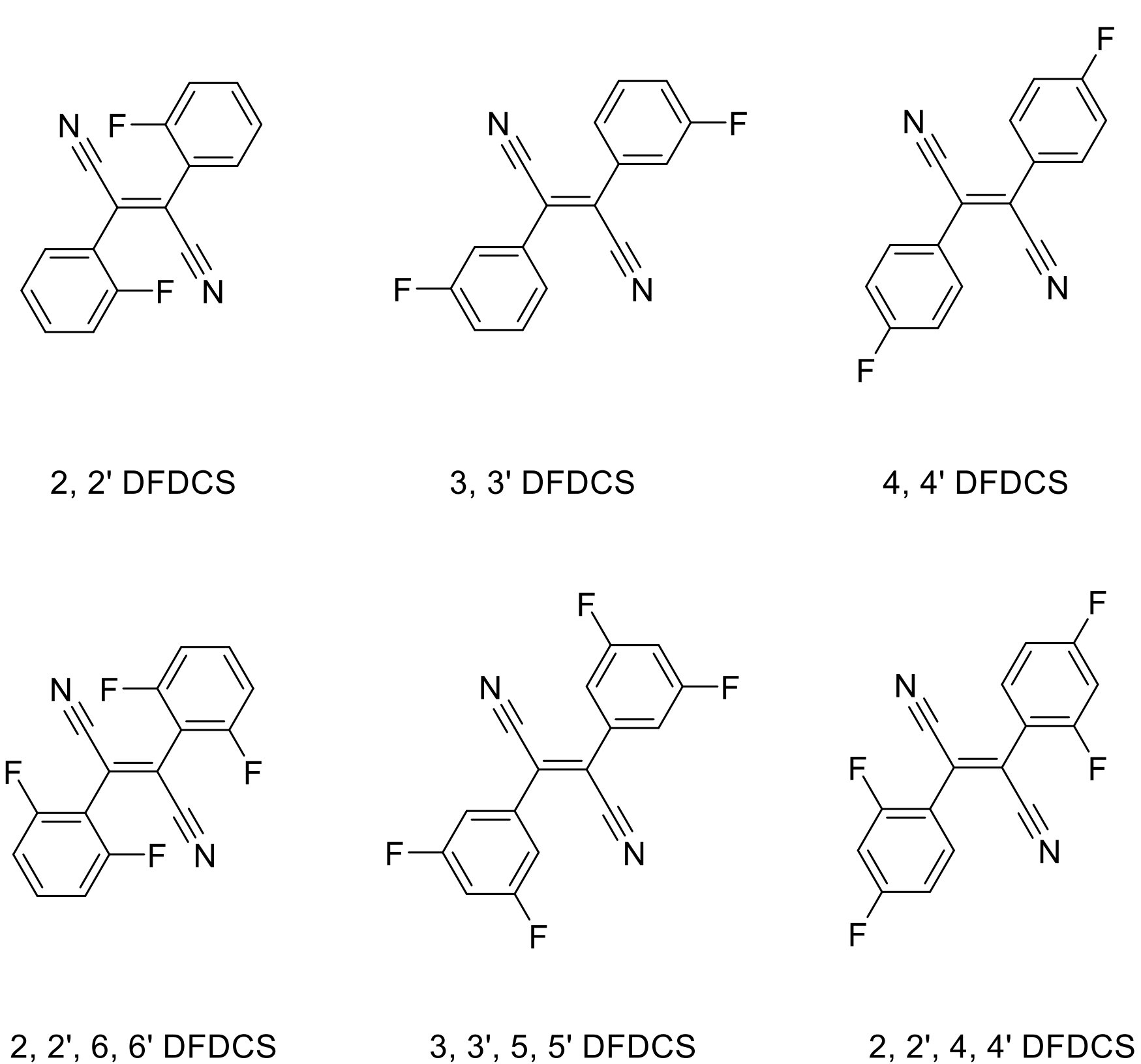
## How can TCNE be modified?



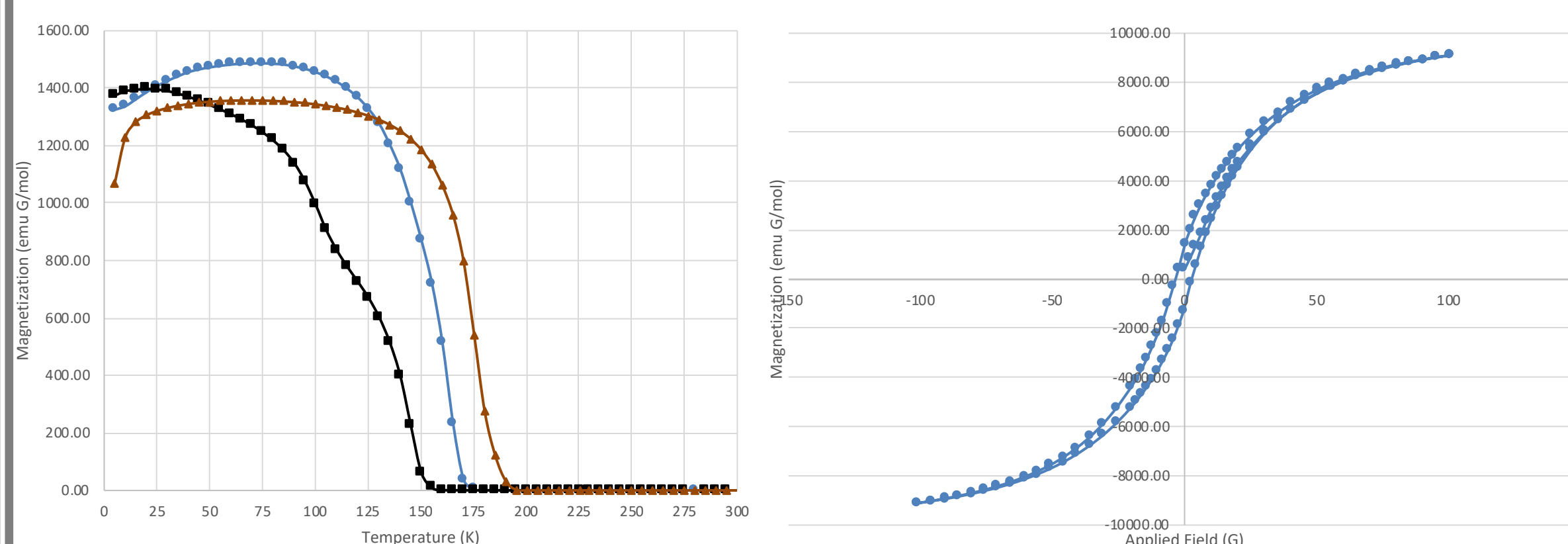
Dr. Gordon Yee  
gyee@vt.edu



## Family of Dicyanostilbenes



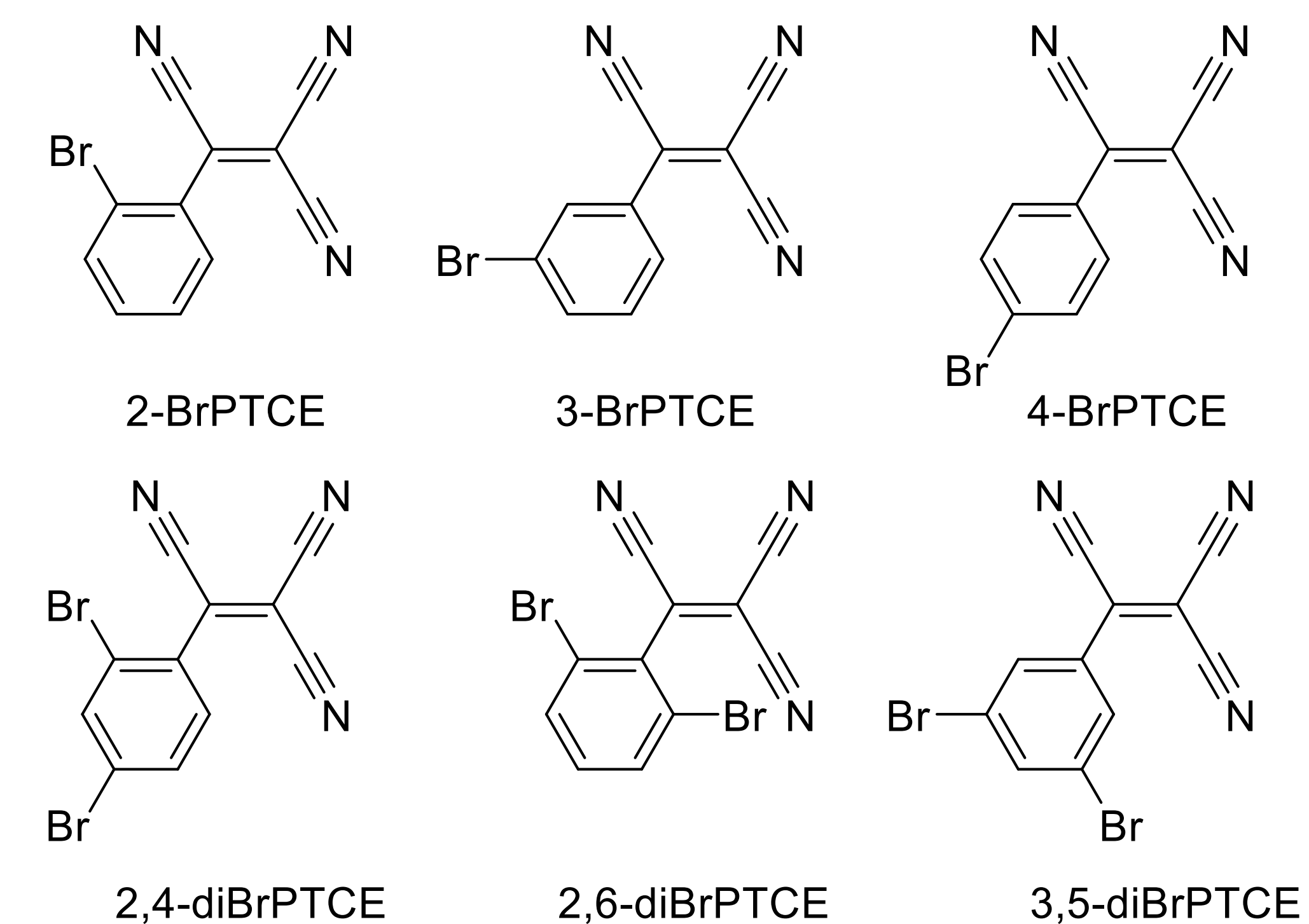
## M vs T and M vs H Curves



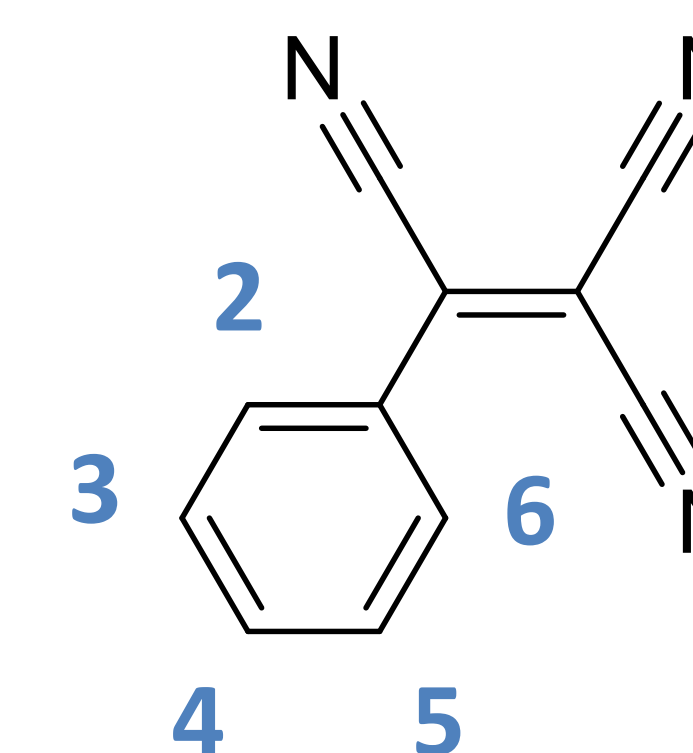
## Family of Dicyanostilbene Data

Acceptor	$T_c^a$ (K)	$E_{1/2}^b$ (V)	No. of Measurements	$M_s$ , emu G/mol
Dicyanostilbene	No Ordering	-1.44	2	N/A
2,2' DFDCS	No Ordering	Irreversible	2	N/A
3,3' DFDCS	No Ordering	Irreversible	2	N/A
4,4' DFDCS	No Ordering	Irreversible	2	N/A
2,2',6,6' DFDCS	No Ordering	-1.23	2	N/A
2,2',4,4' DFDCS	No Ordering	Irreversible	2	N/A
$V(3,3',5,5' \text{ DFDCS})_2$	170	-1.10	2	3793
$V(3,3',4,4',5,5' \text{ HFDCS})_2$	195	-1.10	2	3461
$V(2,2',3,3',5,5',6,6' \text{ OFDCS})_2$	155	-1.05	2	9105
$V(\text{DCPFS})_2^c$	205	-1.00	2	7000

## Family of $Br_n$ PTCE



## Family of $Br_n$ PTCE Data



Position	F ( $\pm 3$ K) <sup>2</sup>	Br ( $\pm 5$ K)
$V(2\text{-XPTCE})_2$	257	222
$V(3\text{-XPTCE})_2$	233	230
$V(4\text{-XPTCE})_2$	160	97
$V(2,4\text{-diXPTCE})_2$	244	N/A
$V(2,6\text{-diXPTCE})_2$	300	260
$V(3,5\text{-diXPTCE})_2$	263	N/A

## Opportunities in the Yee Group

- Synthesis
  - Organic
  - Inorganic/organometallic esp. air-sensitive synthesis
- Crystallography
- Computer modeling
- SQUID magnetometry
- Electrochemistry
- NMR

Thanks to Chris Houser, Stephen Miller, Izzi Ulate, Ryan Corkill for this work.