Modulation of the Fermi|SOMO Energies in $^{HS}3d^5$ Fe^{III} Complexes for Current Rectification

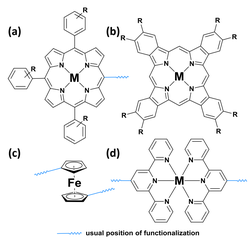
Cláudio Verani

Department of Chemistry, Wayne State University, Detroit, MI 48202

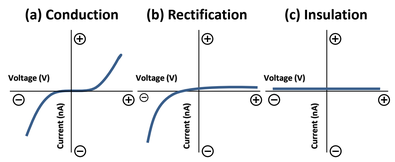
Introduction and Methodology:

❶ Molecular electronics and metal complexes

• Main coordination complexes used in molecular electronics: porphyrins, phthalocyanins, ferrocenes, and terpyridines. Urgent need to expand the vocabulary



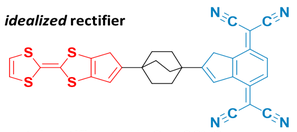
Distinct profiles of I/V curves:



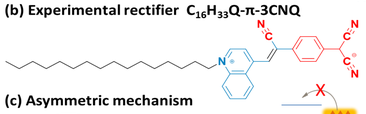
❷ Molecular rectification

• Rectification is the diode-like property of modulating an asymmetric flow of electric current, or, transferring electrons in a unidirectional way. In macroscopic electrical circuitry, rectifiers such as vacuum tubes and solid-state diodes control the mobility of current, thus enabling electrons to flow in one direction from a given point A to a point B, while preventing reversibility from point B to point A.

(a) [D-σ-A] *idealized* rectifier

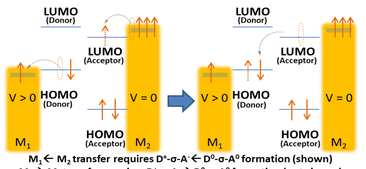


(b) Experimental rectifier $C_{16}H_{33}Q$-π-3CNQ



(c) Asymmetric mechanism

(d) Unimolecular mechanism

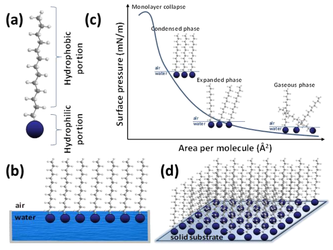


$M_1 \leftarrow M_2$ transfer requires D^+-σ-$A^-\leftarrow D^0$-σ-A^0 formation (shown)
$M_1 \rightarrow M_2$ transfer requires D^+-σ-$A^-\rightarrow D^0$-σ-A^0 formation (not shown)

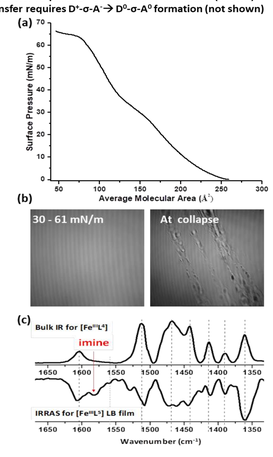
Ratner & Aviram, *Chem. Phys. Lett.*, 1974, **29**, 277 • Metzger, Ashwell, et al. *J. Am. Chem. Soc.*, 1997, **119**, 10455 • Metzger, *Chem. Rev.* 2015, **115**, 5056 • Metzger, *Nanoscale*, 2018, **10**, 10316 • Metzger, *Acc. Chem. Res.*, 1999, **32**, 950 • Metzger, *Chem. Rev.*, 2003, **103**, 3803

❸ Methodology

• Monolayers and multilayers have been used with remarkable success in the preparation of molecular rectifiers. These films are often obtained via isothermal compression of surfactants or surface-acting agents.



(a) Surface pressure vs. average area per molecule; (b) Pockels-Langmuir film at the air/water interface before substrate deposition; (c) Langmuir-Blodgett film at the air/solid interface



(a) LB Isothermal compression; (b) BAM microscopy with collapse; (c) IR of [$Fe^{III}L^4$] and IRRAS of [$Fe^{III}L^5$] LB film

Pockels, *Nature*, 1892, **46**, 418; 1893, **48**, 152 • Langmuir, *J. Am. Chem. Soc.* 1917, **39**, 1848 • Blodgett *J. Am. Chem. Soc.*, 1934, **56**, 495 • Ries, *Nature*, 1979, **281**, 287 • Möhwald et al. *Rev. Mod. Phys.*, 1999, **71**, 779 • Katz, Bao & Gilat, *Acc. Chem. Res.*, 2001, **34**, 359 • Shakya, Hindo, Verani et al., *Inorg. Chem.*, 2007, **46**, 9808 • Driscoll, Verani et al., *Chem. Eur. J.*, 2008, **14**, 9665 • Verani, Shanmugam et al. *Dalton Trans.*, 2013, **42**, 15296


Driscoll

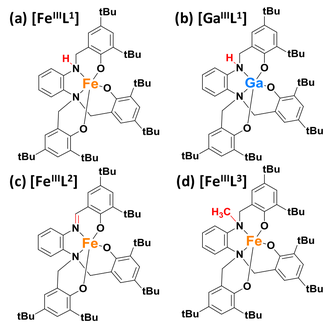

Hindo


Shanmugam

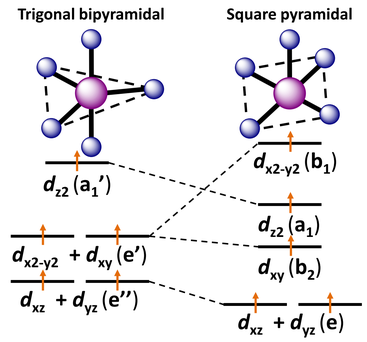
Current Rectification:

❹ Archetypes for five-coordinate Fe^{III} surfactants

$^{HS}Fe^{III}$ and Ga^{III} archetypes and geometries:



Idealized five-coordinate ligand fields



• Imbert, Hratchian, Lanznaster, Heeg, Hryhorczuk, McGarvey, Schlegel & Verani, *Inorg. Chem.*, 2005, **44**, 7414 • Lanznaster, Hratchian, Heeg, Hryhorczuk, McGarvey, Schlegel & Verani, *Inorg. Chem.*, 2006, **45**, 955 • Shakya, Allard, Johann, Heeg, Rentschler, Shearer, McGarvey & Verani, *Inorg. Chem.*, 2011, **50**, 8356 • Allard, Sonk, Heeg, McGarvey, Schlegel & Verani, *Angew. Chem. Int. Ed.*, 2012, **51**, 3178


Shakya

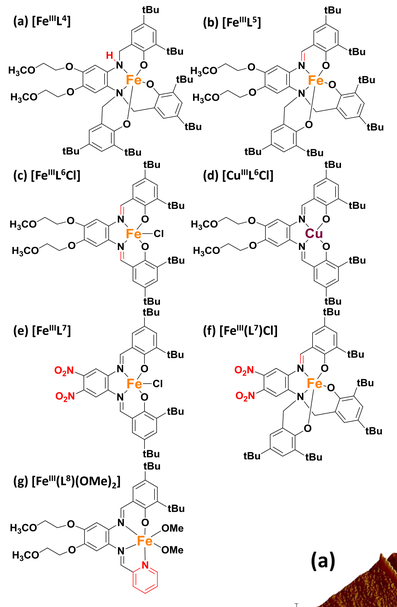

Imbert


Dr. Lanznaster

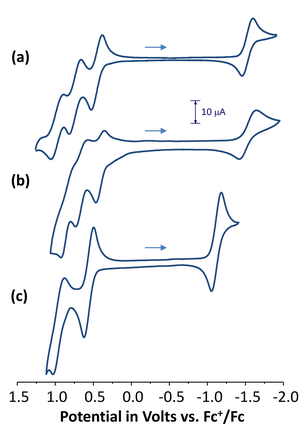

Allard

❺ Rectification with five-coordinate Fe^{III} surfactants

Currently studied $^{HS}Fe^{III}$ rectifiers and Cu^{II} insulator:

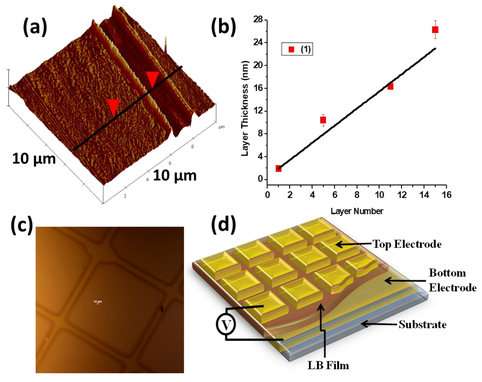


Redox responses:



(a) [$Fe^{III}L^1$], (b) [$Fe^{III}L^4$], and (c) [$Fe^{III}L^6Cl$].

Examples of surface morphology and assembly fabrication:



(a) AFM of an LB film for [$Fe^{III}L^5$] on quartz used in height measurements to determine monolayer thickness,(b) thickness (nm) *vs.* number of layers plot from mono to 15 layers; (c) an optical micrograph of the **Au|LB|Au** assembly; (d) schematic view of the assembly layout.

• Wickramasinghe, Perera, Li, Mao, Zhou & Verani, *Angew. Chem. Int. Ed.*, 2013, **125**, 13588 • Wickramasinghe, Mazumder, Gonawala, Perera, Baydoun, Thapa, Li, Xie, Mao, Zhou, Schlegel & Verani, *Angew. Chem. Int. Ed.*, 2014, **53**, 14462 • Wickramasinghe, Mazumder, Kpogo, Staples, Schlegel & Verani, *Chem. Eur. J.*, 2016, **22**, 10786 • Johnson, Wickramasinghe, Verani & Metzger *J. Phys. Chem. C*, 2016, **120**, 10578 • Johnson, Horton, Gonawala, Verani & Metzger, *Dalton Trans.*, 2018, **47**, 6344 • Brand, Juhaniewicz-Debinska, Wickramasinghe & Verani, *Dalton Trans.*, 2018, accepted.


Wickramasinghe

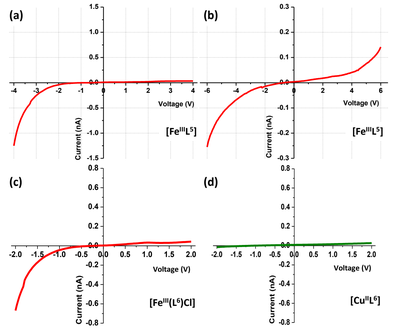

Gonawala


Dr. Mazumder

Electrode/orbital arguments:

❻ Observed rectification ratios

Selected I/V curves:



(a) rectification and (b) symmetrical response upon repeated cycles for [$Fe^{III}L^5$], (c) rectification for [$Fe^{III}(L^6)Cl$], and (d) insulation for [$Cu^{II}L^6$]

• Species [$Fe^{III}L^5$] showed *RR* values from 4.5 to 12 at ±2 V and from 3 to 37 at ±4 V.

• Species [$Fe^{III}(L^6)Cl$] showed *RR* ranging from 4 to 29 at ±2 V and from 2 to 31 at ±4 V.

• Species [$Fe^{III}(L^6)Cl$] was also probed using EGaIn/Ga_2O_3|LB|Au assemblies and yielded *RR* values of 3 and 12 at ±0.7 V and between 50 and 200 at ±1.0 V, with conversion to a sigmoidal curve after a few full scans.

• Species [$Fe^{III}(L^8)(OMe)_2$] was probed on EGaIn/Ga_2O_3|LB|Au assemblies and showed *RR* of 300 between ±1 V.

❼ Fermi/SOMO/HOMO arguments

[$Fe^{III}(L^6)(Cl)$] & [$Cu^{II}(L^6)$] in Au|LB|Au

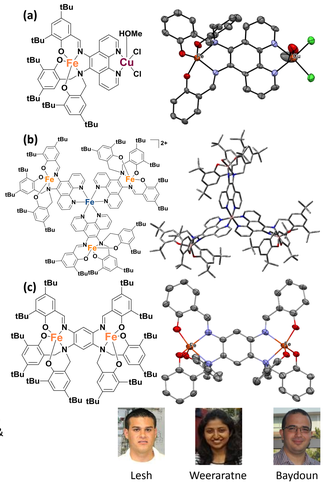
[$Fe^{III}(L^8)(OMe)_2$] in EGaIn|LB|Au

❽ Multimetallic systems for rectification enhancement

• A possible consequence of ET through the SOMOs is that the incoming electron originated at the Au electrode will likely be spin polarized.

• While this possibility will require further evaluation, it may also explain the modest rectification ratios (*RR*) observed for these systems.

• Aiming to address this issue, we are considering multimetallic species in which the presence of more than one $^{HS}Fe^{III}$ center may "amplify" the number of electrons being transferred by molecule.



• Lanznaster, Heeg, Yee, McGarvey & Verani, *Inorg. Chem.* 2007, **46**, 72 • Lesh, Shanmugam, Allard, Lanznaster, Heeg, Rodgers, Shearer & Verani, *Inorg. Chem.* 2010, **49**, 7226 • Weeraratne, Baydoun & Verani, *Dalton Trans.*, 2018, *submitted*.

Lesh

Weeraratne

Baydoun

Funding:

nano@wayne

ACS PRF

NSF CHE-0718470 CHE-1012413 CHE-1500201

Wayne State University Chemistry