Molecular Information Storage in Dendrimers

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develop a new medium and mechanism for molecular scale information storage

• mechanism: charge storage in molecules

• medium: molecular film of redox-gradient dendrimers

• result: 100 Tb/in\(^2\) storage density (assumed molecular diameter of 2.5 nm gives 10\(^{14}\) molecules/in\(^2\))
one challenge ....

**Spatial stability - must inhibit charge migration**

Need conducting material that will store charge.

\[ \Delta G^\circ = 0 \]

Require \( \Delta G^* > 40 \text{kT} \) (~1 eV)
**approach:**

- build shell/core molecule with radial redox gradient to sequester and “trap” the charge
  - a redox-gradient dendrimer (RGD)
Envisioned charging/discharging of RGDs

oxidant

higher $E^o$

lower $E^o$

shell oxidation

internal CT

h$_\nu$(CT)

reductant

e$^-$
Faculty
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Organic synthesis & electrochemistry

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Thin films
- scanning probe microscopy

Jia Sun

Thin films
- electrical measurements
- morphology

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Molecular Design - Redox-Gradient Dendrimers

redox-gradient (RG) dendrimers as charge carriers

concentric shells of redox-active groups in dendrimer impart radial potential gradient

directed charge transport and charge storage properties

monodisperse, pseudo-spherical oligomer

amorphous films
example structures: RGDs

$E_{(core)} = 0.48 \text{ V vs SCE}$

$E_{(shell)} = 0.68 \text{ V}$

5-Site System

4AA/PD

15 $X = \text{OCH}_3$
MW = 1382

9-Site System

6AA/3PD

16 $X = \text{OCH}_3$
MW = 2625


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3-tier RG dendrimer

core ~ 0.34 V
PD middle ~ 0.47 V
Ar2N- outer ~ 0.67 V

X=OMe
C_{142}H_{129}N_{10}O_{16}, 2231g/mol

12AA/6PD/PTe
19 site array
what we know so far....

• Charge resides at core of RGD cations - EPR and Electrochemical studies

• Redox groups are weakly electrically coupled in the arrays - E° measurements

• Redox-gradient of dendrimers retards intermolecular charge exchange
  -- in solution (self exchange k_{ET} values are lowered by shell)
  -- in the film state (charge transport measurements) [Kim poster]

• Redox-gradient can be tuned synthetically [Duncan poster]

• Molecular films support hole transport in diode devices [Li poster]
  -- film V(turn-on) values reflect molecule E°
  -- relative mobilities can be measured

• cAFM I/V responses can be measured on nm-scale domains [Sun poster]
film substrates and redox gradients

TAPD
E_1 = 0.46 V  
E_2 = 0.92 V

4AA/PD
E_1 = 0.49V  
E_2 = 0.87V  
E_4 = 1.05V

4PD/PD
E_1 = 0.46 V  
E_2 = 0.92 V  
E_3 = 0.59 V  
E_5 = 0.79 V

core only
no gradient

redox gradient
+4.2 kcal

redox gradient
-0.7 kcal
Charge migration in films on ITO glass

- Core model
- Shell/core gradient
- Shell/core no gradient

TAPD\(^0\) 4AA\(^0/PD^0\) 4PD\(^0/PD^0\)

Immersion in aq. NaClO\(_4\) for 9 h

\[ \Delta G^\circ = -9.2 \text{ kcal} \]

Radial redox gradient in shell/core array films influences charge transport kinetics (i.e., charge storage).
redox gradients and self-exchange rates

\[ \text{M}^{+\bullet} + \text{M} \rightleftharpoons \text{M} + \text{M}^{+\bullet} \]

\( k_{\text{ET}} = 3.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1} \)

Gradient 0.18 V

\( k_{\text{ET}} = 3.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1} \)

Gradient 0.47 V

\( k_{\text{ET}} = 2.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1} \)

Gradient 0.72 V

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M / film / M devices - I/V analysis

R = 10 kΩ

Ga-In tip

Organic film

Ag

Glass
representative I/V curves in 50 nm films
turn-on V vs. $E^*$ for Ag/50nm film/GaIn diodes

Li and Duncan Posters
turn-on V vs. $E^*$ for Ag/50nm film/GaIn diodes

Li and Duncan Posters
cAFM of 5nm TAPD on Au using a Au tip

Contact mode AFM image

Sun Poster
The bright and dark dots were created by applying +12 V and –12 V to the AFM tip when it is in contact with the grounded PMMA/Si(111) films for 10 s.

Xu and Sun Posters
future studies....

• Charge transport in large gradient molecules

• Tailor surface groups for ordering (or attachment) properties
  -- liquid crystal phases
  -- covalent binding to surfaces

• Evaluate origin of electrical switching in multilayers

• cAFM and STM on RGDs and RGD composites for charge writing in nm domains
20nm 3PD on HOPG - bias dependent response

Bias -3V, set point 10pA

Bias 0.656V, set point 5pA

Bias 1.59V, set point 5pA

Bias 2.59V, set point 5pA

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Conclusions

- Redox-gradient shell/core arrays have been synthesized.

- The arrays sequester charge at the core on initial charging.

- 0/+ intermolecular electron exchange is inhibited in the solution and film states for these arrays.

- M/film/M devices support hole transport and switching with RGDs.

- RGDs on HOPG give bias dependent STM imaging. - further studies underway to evaluate molecular I/V responses