New Organic Media for Information Storage

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funding: NSF-MRSEC seed project
Project Goals

- develop a new medium and mechanism for molecular scale information storage
  - demonstrate a redox storage mechanism
  - achieve 100 Tb/in² storage density in molecular thin film medium
    (assumed molecular diameter of 2.5 nm gives $10^{14}$ molecules/in²)
Molecular Redox State as Information Storage Unit

Advantages:
• electrical control of state-change (write)
• fast state switching
• electrical control of readout
challenges:
• charge states must be chemically stable
• charge states must be spatially stable (image stability)
• need to be able to discharge on demand

\[ \Delta G^\circ = 0 \]
need \( \Delta G^* > 40 \text{kT} \approx 1 \text{eV} \)
**approach:**
build shell/core molecular architecture with radial redox gradient
--- to trap charge

**charge injection**

![Diagram of molecular architecture with radial redox gradient](image)

higher E°  
lower E°

shell/core exchange barrier  
$\Delta G^* \geq \Delta E^\circ$ (redox gradient)
trapping the charge with the redox gradient

charge the core  
stop site/site charge exchange

E

shells

ΔE°

core

trapping the charge with the redox gradient
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
Can we prepare redox-gradient dendrimers with overlap yet weak electronic coupling between shell and core?

Yes - we use meta-connections at benzene as the shell/core junction.
Some Examples

5-Site System

$\text{4AA/PD}$

9-Site System

$\text{6AA/3PD}$

more examples: *better encapsulation of core*

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

8AA/1PD 9-site array
more examples: manipulation of core group and potential

E_1^{0.9} = 0.35 V
estimated gradient = 0.32 V

E_1^{0.9} = 0.31 V
estimated gradient = 0.36 V

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more examples: .... changing the shell potential

Predicted redox gradient: ~ 0.8 V

pPD core EP ~ 0.48 V

AA shell EP ~ 1.28 V
gradient
core ~ 0.34 V
PD middle ~ 0.47 V
Ar₂N- outer ~ 0.67 V

12AA/6PD/PT
19 site array

X=OMe
C₁₄₂H₁₂₉N₁₀O₁₆, 2231g/mol
Do the shell/core dendrimers charge localize at the core as planned?

yes, as evident by:

- Oxidation Potentials
- UV-vis-nIR
- ESR of radical cations
oxidation of 4AA/PD

4AA/1PD
5-site shell/core array

\[ E_1 = 0.49 \]

\[ E_2 = E_3 = 0.87 \text{ V vs SCE} \]

\[ E_1^{\circ} = 0.46 \text{ V} \]

\[ E_2^{\circ} = 0.92 \text{ V} \]

\[ E_1^{\circ\prime} = 0.48 \text{ V} \]

\[ E_2^{\circ\prime} = 0.86 \text{ V} \]

\[ E_3^{\circ\prime} = 0.98 \text{ V} \]
UV-vis-nIR of PD radical cations

Internal charge-transfer excitation in nIR of 2AA/PD and 4AA/PD

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**ESR of 4AA/PD radical cation**

ESR for 4AA/PD⁺:

\[ a(2N) = 5.75 \text{ G} \]

\[ a(12H) = 0.214 \text{ G} \]

\[ a(8H)_{\text{meta}} = 0.384 \text{ G} \]

\[ a(8H)_{\text{ortho}} = 0.567 \text{ G} \]

\[ a(4H) = 0.774 \text{ G} \]
study bulk film electronic switching properties

- film preparation: spin coating on ITO glass
- electrolyte: 0.1 M NaClO₄ in H₂O
Charge injection in TAPD films on ITO glass

\[ \text{TAPD} \]

E(1) = 0.36 V  
E(2) = 0.81 V  
TBAP in CH\(_2\)Cl\(_2\)

Charging of film in aq. electrolyte  
0.1 M NaClO\(_4\)/H\(_2\)O

solution

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<th>I (µA)</th>
<th>E (mV) vs. SCE</th>
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<td>3</td>
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film

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<th>time (min)</th>
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- CPC at 0.55 V  
- CPC at 0.90 V
CPC of 100 nm films on ITO-glass electrode

The diagram shows the electrochemical potential ($E^\circ$) of different compounds: TAPD (0.46), 2AA/PD (0.48), and 4AA/PD (0.49). The graph plots charging at 0.55 V of 100 nm films on ITO, with the mask giving a 0.31 cm$^2$ film.
Charge migration in films

Vapor deposited 300 nm films

Film emersion in aq NaClO₄

9 hours

Shell/core pattern of redox array influences charge transport kinetics
to charge the core of the core/shell film...

charge the shell & core, then discharge shell.

need isolably stable shell-charged RG dendrimer
-- work in progress … see poster.
• Conclusions

• a variety of redox-gradient shell/core arrays have been synthesized

• cation states reside exclusively at the core of shell/core structures

• charge transport between molecules in shell/core films (under core potentials) is poor in redox-gradient shell/core arrays

• core-charged bulk films can be prepared only by shell/core “over charging” followed by shell discharging