Molecular Information Storage in Dendrimers

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Project Objective

develop a new medium and mechanism for molecule-based charge storage (information storage)

- mechanism: charge storage in molecules
- medium: molecular film of redox-gradient dendrimers
- potential molecular resolution: molecular diameters of 1-3 nm - 100 Tb/in² storage density (~10¹⁴ molecules/in²)
part of the challenge ….

**spatial stability - must inhibit charge migration**

need conducting material that will store charge

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

require \( \Delta G^* > 40 \) kT (~1 eV)
**approach:**

build redox-gradient dendrimers (RGDs) designed to capture and “trap” the charge

![Diagram showing charge injection and one-way transport with labeled energy levels and exchange barrier](image-url)

- **charge injection**
- **one-way transport**
- **higher E°**
- **lower E°**

The diagram illustrates the concept where charge injection leads to one-way transport, with energy levels (higher and lower) and a shell/core exchange barrier represented by \( \Delta G^* \geq \Delta E^\circ \) (redox gradient).

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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
1. custom dendrimer synthesis
2. dendrimer redox properties (molecular)
3. molecular film preparation/characterization
4. probe microscopy
some examples

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

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

5-Site System

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

$\text{MW} = 1382$

9-Site System

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

$\text{MW} = 2625$


**4AA/1PD**

5-site shell/core array

<table>
<thead>
<tr>
<th>Redox Potential</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>E₁</td>
<td>0.49</td>
</tr>
<tr>
<td>E₂ = E₃</td>
<td>0.87 V</td>
</tr>
</tbody>
</table>

**CH₂Cl₂ 0.1 M nBu₄NBF₄**

- E₁°' = 0.46 V
- E₂°' = 0.92 V
- E₃°' = 0.98 V

**E₁°' = 0.48 V**
- E₂°' = 0.86 V
- E₃°' = 0.98 V

**E₁°' = 0.67 V**
- E₂°' = 0.87 V
- E₃°' = 0.98 V
ESR for 4AA/PD$^+$.  
$a(2N) = 5.75$ G

tuning the redox gradient

0.22 V (5.1 kcal/mol)  
4AA/PD

0.47 V (10.8 kcal/mol)  
4CN-4AA/PD

0.72 V (16.6 kcal/mol)  
8CN-4AA/PD
some larger RGDs

1. PTe
   *p*-phenylenetetraamine
   
   \[ \text{C}_{60}\text{H}_{54}\text{N}_{4}\text{O}_{6} \]
   [MW 927]

2. 6PD / PTe
   
   \[ \text{C}_{219}\text{H}_{192}\text{N}_{16}\text{O}_{21} \]
   [MW 3384]

3. 12AA/6PD/PTe
   
   \[ \text{C}_{381}\text{H}_{336}\text{N}_{28}\text{O}_{39} \]
   \(X = \text{OMe}\)
   [MW 5931]

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Film charging and charge migration studies

-charge migrates and equilibrates efficiently.

PTe

0; PTe\(^0\)

+1; PTe\(^{+*}\) by CPC at 0.45 V

70 C, 10 min

0

0

+1

+2

Immersed in 0.1 M NaClO\(_4\)/H\(_2\)O

50 C, 10 min

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in a shell/core film

6PD/PTe

0 : 6PD/PTe⁰
+1 : 6PD/PTe⁺⁺, CPC at 0.50 V
3.7 x 10⁻⁸ mol on ITO glass

25 °C, 30 m

70 °C, 30 m

50 °C, 30 m

immersed in 0.1 M NaClO₄/H₂O

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in a 3-tier array film

12AA/6PD/PTe

- charge transport is inhibited by shells

+1 : CPC at 0.55 V
+7 : CPC at glass 0.65 V
3.7 X 10^-8 mol n ITO glass

0.1 M NaClO4/H2O

25°C, 30 m

70°C, 30 m

50 °C, 30 m

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### Film Charge Transport as Function of Molecular Structure

#### Optical Analysis of Dissolved Film

<table>
<thead>
<tr>
<th></th>
<th>PTe core only</th>
<th>6PD/PTe shell/core</th>
<th>12AA/6PD/PTe shell/shell/core</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>N</strong></td>
<td>+</td>
<td>+</td>
<td>N</td>
</tr>
<tr>
<td><strong>before incubation</strong></td>
<td>0 : 1.0</td>
<td>0 : 1.0</td>
<td>0.17 : 0.83</td>
</tr>
<tr>
<td><strong>25 °C, 10min</strong></td>
<td>0.22 : 0.55</td>
<td>0.020 : 0.80</td>
<td>0.11 : 0.70</td>
</tr>
<tr>
<td><strong>50 °C, 10min</strong></td>
<td>0.30 : 0.48</td>
<td>0.12 : 0.75</td>
<td>0.11 : 0.68</td>
</tr>
<tr>
<td><strong>70 °C, 10min</strong></td>
<td>0.34 : 0.34</td>
<td>0.23 : 0.54</td>
<td>0.13 : 0.56</td>
</tr>
</tbody>
</table>

#### % Equilibrated
- 100%
- 30%
- ~1%
I/V characteristics of thin films on Ag and Au

probe-based charging of 4nm 8CN-4AAPD film

monitored by KPM of charged film - morphology (l), potential (r)

5 V, 5 sec before voltage pulse

500nm

substrate only (control experiment)

substrate is 30 nm SiO₂/p-Si
probe charging & discharging of films

uncharged surface

charge write

6 V, 5s

-1 V, 2s

(2x2 µm scans)

charge erase

charge rewrite

6 V, 5s
charge decay of different arylamine films on native SiO₂ /p-Si

substrate = 2.5 nm SiO₂ /p-Si (100)

little structure dependence on charge decay rate on native oxide substrate
Possible charge decay mechanisms
(A) decay via tunneling toward the conducting layer.
(B) hopping transport within molecular film.
(C) contamination (neutralization) from air atmosphere.

**Observation:** charge lifetimes increase when a thicker SiO2 layer is used and a molecular structure dependence emerges.
charge decay rates on thick oxide Si

4nm arylamine films on 30nm SiO$_2$/p-Si(100)

![Graph showing surface potential decay over time for 3PD, 4AAPD, and 8CN-4AAPD films.]

- 3PD: $t_1 = 42$, $t_2 = 423$
- 4AAPD: $t_1 = 201.8$, $t_2 = 152.5$
- 8CN-4AAPD: $t_1 = 15.7$, $t_2 = 152.5$

Surface potential (mV) vs. decay time (min)
monitoring of charge diffusion in films

electrical potential maps
4 nm 8CN-4AA/PD films on 30 nm SiO₂/p-Si (100)

observation of charge diffusion in real time

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charge peak width evolution in time

4nm arylamine films on 30nm SiO$_2$/p-Si(100)
Summary

• A chemical library of redox-gradient dendrimers (RGDs) is available and derivatives can be prepared for custom applications.

• Core charging of RGDs has been demonstrated.

• RGD films have been cast, charged, and evaluated for bulk charge transport.

• Probe-charging of 100 nm domains in continuous films has been demonstrated, with charge lifetimes of tens of hrs.