Molecular Information Storage in Dendrimers

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**Project Objective**

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/in² storage density (assumed molecular diameter of 2.5 nm gives $10^{14}$ molecules/in²)
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).
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
components of the research effort

1. custom dendrimer synthesis
2. dendrimer redox properties (solution, film)
3. metal/film/metal I/V analysis
4. film probe microscopy
E_{(core)} = 0.48 V vs SCE
E_{(shell)} = 0.68 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


oxidation of 4AA/PD

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

$E_1 = 0.49$

$E_2 = E_3 = 0.87 \text{ V vs SCE}$

$E_1^{\circ'} = 0.46 \text{ V}$

$E_2^{\circ'} = 0.92 \text{ V}$

$E_1^{\circ'} = 0.48 \text{ V}$

$E_2^{\circ'} = 0.86 \text{ V}$

$E_3^{\circ'} = 0.98 \text{ V}$

$E_1^{\circ'} = 0.67 \text{ V}$

$E_2^{\circ'} = 0.87 \text{ V}$

$E_3^{\circ'} = 0.98 \text{ V}$

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ESR of 4AA/PD radical cation ; core-charging

ESR for 4AA/PD+
\( a(2N) = 5.75 \text{ G} \)

\[
\begin{align*}
\text{MeO} & \quad \text{OMe} \\
\text{MeO} & \quad \text{OMe}
\end{align*}
\]


\[
\begin{align*}
a(2N) &= 5.75 \text{ G} \\
a(12H) &= 0.214 \text{ G} \\
a(8H)_{\text{meta}} &= 0.384 \text{ G} \\
a(8H)_{\text{ortho}} &= 0.567 \text{ G} \\
a(4H) &= 0.774 \text{ G}
\end{align*}
\]
increasing shell oxidation potential

4CN-4AA/1PD

\[ E^{\circ} (1) = 0.65 \text{ V} \]
\[ E^{\circ} (2) = 1.02 \text{ V} \]
\[ E^{\circ} (3,4) = 1.34 \text{ V} \]

gradient \sim 0.47 \text{ eV}
3-tier RG dendrimer

gradient
core ~ 0.34 V
PD middle ~ 0.47 V
Ar$_2$N- outer ~ 0.67 V

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

12AA/6PD/PTe
19 site array

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charge migration in a core-only film

-charge migrates and equilibrates efficiently.

PTe

0; PTe⁰
+1: PTe⁺⁺ by CPC at 0.45 V

room temp

immersed in 0.1 M NaClO₄/H₂O

70 C, 10 min

50 C, 10 min

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in a shell/core film

6PD/PTe

0 : 6PD/PTe\(^0\)
+1 : 6PD/PTe\(^{+1}\), CPC at 0.50 V
3.7 x 10\(^{-8}\) mol on ITO glass

25 °C, 30 m

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

70 °C, 30 m

50 °C, 30 m

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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

25°C, 30 m
immersed in 0.1 M NaClO_4/H_2O

50 °C, 30 m
### optical analysis of dissolved film

<table>
<thead>
<tr>
<th>Temperature</th>
<th>PT e core only</th>
<th>6PD/PT e shell/core</th>
<th>12AA/6PD/PT e shell/shell/core</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before incubation</td>
<td>N</td>
<td>+</td>
<td>N</td>
</tr>
<tr>
<td>25 °C, 10min</td>
<td>0.22 : 0.55</td>
<td>0.020 : 0.80</td>
<td>0.11 : 0.70</td>
</tr>
<tr>
<td>50 °C, 10min</td>
<td>0.30 : 0.48</td>
<td>0.12 : 0.75</td>
<td>0.11 : 0.68</td>
</tr>
<tr>
<td>70 °C, 10min</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%
M / film / M devices - I/V analysis
Representative I/V curves in 50 nm films

$E^\circ$ (V vs SCE)

<table>
<thead>
<tr>
<th>Material</th>
<th>$E^\circ$ (V vs SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3PD</td>
<td>0.45</td>
</tr>
<tr>
<td>TAPD</td>
<td>0.46</td>
</tr>
<tr>
<td>4AA-PD</td>
<td>0.49</td>
</tr>
<tr>
<td>3AA</td>
<td>0.67</td>
</tr>
<tr>
<td>TPD</td>
<td>0.84</td>
</tr>
</tbody>
</table>

Log current (nA) vs Voltage (V)
V(t) vs. $E^*$ for Ag/50nm film/GaIn diodes

~ 1.5 V off line!

Gradient ~0.5 V

Junction potential ~0.5 V
cAFM of 5nm TAPD on Au using a Au tip

Spot #1

Spot #2

Contact mode AFM image

TAPD

#2 (bare Au)

#1 (TAPD)
Recent Probe Charging Results

2 nm 4AA/PD on native Si/SiO$_2$

morbology

write pulses 12 V

new pulse -10 V

write again 12 V

5 µm scans

potential map

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Conclusions

• Redox-gradient Dendrimers (RGDs) have been synthesized.

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

• N/C intermolecular electron exchange is inhibited in the solution and film states for these arrays.

• M/film/M devices show hole transport and switching with RGD.

• Writing/Reading/Erasing of charged domains in RGD films has be demonstrated.