Reduced Dimensionality in Organic Electro-Optic Materials: Theory and Defined Order

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Supporting Information

SAXS results for C1:

Thin films of C1 appeared glassy and amorphous with no visible crystalline domains. Further investigation employing small-angle X-ray scattering (SAXS), shown in Figure S-1, confirmed this result.
**Figure S-1.** Small angle X-Ray scattering results for spin coated samples of C1 on glass substrates. No sharp peaks are present that would indicate an ordered array of crystalline domains; only an “amorphous halo” is present.

**Structure of P3:**

![Structure of P3](image)

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**Figure S-2:** P3 dendrimer used for comparison. Previously reported as PSLD-33.¹

**Characterization details:**

Details regarding the Attenuated Total Reflection (ATR) for acquisition of EO coefficients and the VAPRAS instrument are presented elsewhere.²⁻⁵

A schematic of the different layers of a poled substrate is shown in Figure S-3.
Figure S-3. A schematic of different layers of an electro-optic (EO) device is shown.

Utilizing a ~90 nm thick TiO$_2$ layer causes negligible change in the applied poling field as shown in the derivation below.

\[
D = E_{\text{out}} \cdot \varepsilon_{\text{out}} = \varepsilon_{\text{EO}} \cdot E_{\text{EO}} \\
V = d_{\text{out}} E_{\text{out}} + d_{\text{EO}} E_{\text{EO}} \\
V = \left( d_{\text{out}} \left( \frac{\varepsilon_{\text{EO}}}{\varepsilon_{\text{out}}} \right) + d_{\text{EO}} \right) E_{\text{EO}} \quad \text{Approx} \left( \frac{V}{d_{\text{EO}}} \right) = E_{\text{ EO}}' \]

\[
E_{\text{ EO}}' = E_{\text{ EO}} \cdot \left[ \frac{d_{\text{out}}}{d_{\text{EO}}} \left( \frac{\varepsilon_{\text{EO}}}{\varepsilon_{\text{out}}} \right) + 1 \right]
\]

The required parameters used for these materials are shown in Table S-1.

Table S-1. Values for dielectric constants and thickness for the material systems presented.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_{\text{EO}}$</td>
<td>4 - 5.5</td>
</tr>
<tr>
<td>$\varepsilon_{\text{out}}$</td>
<td>~40$^6$</td>
</tr>
<tr>
<td>$d_{\text{EO}}$</td>
<td>~ 1.0 micron</td>
</tr>
<tr>
<td>$d_{\text{out}}$</td>
<td>~ 0.090 micron</td>
</tr>
</tbody>
</table>

Substituting the values in Table S-1 into the equation for $E_{\text{EO}}'$ above and setting $E_{\text{EO}} = 50$ V, we see that the new applied field across the EO layer is 50.6 V, a negligible change in applied field.

Simulation methods:

Our group has developed custom RBMC code in C++, compiled with ICC 11.1, and run on the “Stuart” ROCKS 5 cluster at the University of Washington. Simulations were run using the Metropolis Monte Carlo technique, using self-consistent reaction field boundary conditions and the Hamiltonian.
\[
U = \sum_i \sum_j 4 \varepsilon_i \varepsilon_j \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} + \frac{1}{\varepsilon_i r_{ij}} \left( \mathbf{\mu}_i \cdot \mathbf{\mu}_j - 3(\mathbf{\mu}_i \cdot \hat{\mathbf{r}}) (\mathbf{\mu}_j \cdot \hat{\mathbf{r}}) \right) - \frac{1}{\varepsilon_i R_c} \frac{2(\varepsilon - \varepsilon_\infty)}{(2\varepsilon + \varepsilon_\infty)} \mathbf{\mu}_i \cdot \mathbf{E}_p \quad (S1)
\]

where \( \sigma_{\text{eff}} \) is the effective Lennard-Jones contact distance, calculated for every pair of ellipsoids using the method of Perram and Wertheim,\(^8,9\) \( \varepsilon \) is the static dielectric constant, \( \varepsilon_\infty \) is the optical dielectric constant, \( r_{ij} \) is the distance between the centers of the \( i^{\text{th}} \) and \( j^{\text{th}} \) ellipsoids, \( \mathbf{\mu} \) is the dipole moment of an ellipsoid, and \( R_c \) is the cutoff radius for electrostatic interactions. Only repulsive inter-nuclear interactions were considered; the attractive component of the Lennard-Jones potential was neglected.

The dielectric constant

\[
\varepsilon = \frac{4 \pi M_z}{V_{\text{box}} E_{p,z}} + \varepsilon_\infty \quad (S2)
\]

was self-consistently calculated\(^\text{10-12}\) at the beginning of every MC cycle (every \( m \) trial moves) based on the total dipole moment \( M \) of the simulation box, with volume \( V_{\text{box}} = mN^{-1} \) (here, \( m \) denotes the number of particles and \( N \), the number density), in response to the external field \( \mathbf{E}_p \), which was defined along the \( z \)-axis. The local field \( \mathbf{E}_0 \) acting on each ellipsoid was then calculated as the field in the center of a cavity of dielectric constant \( \varepsilon_\infty \) in an infinite region of dielectric constant \( \varepsilon \), using the modified Onsager cavity field\(^\text{13,14}\)

\[
\mathbf{E}_0 = \frac{3\varepsilon}{2\varepsilon + \varepsilon_\infty} \mathbf{E}_p \quad (S3)
\]

The high-frequency dielectric constant \( \varepsilon_\infty = 2.25 \) was assumed to be the square of the refractive index of PMMA, and the polarizability of the ellipsoids themselves was neglected \( (\mathbf{\mu} = \mathbf{\mu}_{\text{gas}}) \).
Electrostatic interactions, including the external field, were switched on 1000 cycles into each simulation at the three lower densities. Simulations at $N = 5.04 \times 10^{20}$ molecules/cc used 2000 randomization cycles combined with simulated annealing during the initial portions of the simulation, and simulations at $N = 6.30 \times 10^{20}$ molecules/cc used 5000 randomization cycles and simulated annealing. Only Lennard-Jones interactions were considered during the randomization phase in order to break up the simple cubic lattice that all simulations were started from. Maximum move sizes were optimized to maximize the RMS translational and rotational displacement per move. Total energy for the simulations was recorded every cycle ($m$ steps) and simulations periodically checked to see if the energy appeared stable. A typical graph of the energy convergence is shown in Figure S-4.

![Figure S-4](image.png)

**Figure S-4.** The convergence data for a simulation run with $E_{pol} = 50 \ \text{V} / \mu\text{M}$ at $N = 2.5 \times 10^{20}$ molecules/cc is shown as an example of the typical energy convergence observed in these simulations. $U$ represents the potential energy; $\mu E$ is the interaction of the dipoles with the poling field, $\mu \mu$ represents the dipole-dipole interactions, and $LJ$ is the Lennard-Jones potential.
While runs at the lower three densities converged easily, with 40000 cycles sufficient to obtain convergence and a reasonable averaging range, the higher density simulations required longer runs and use of simulated annealing\textsuperscript{12} to obtain convergence. Runs at $N = 5.04 \times 10^{20}$ molecules/cc were run for 80000 total cycles, averaging over the last 20000, and runs at $N = 6.30 \times 10^{20}$ molecules/cc were run for 300000 cycles, averaging over the last 50000. Convergence was frustrated by the slow formation of the lower-energy centrosymmetrically ordered phase; shorter runs showed higher energies and lower $\langle P_z \rangle$ values.

**DFT Confirmation of $\beta_{HRS}(-2\omega,\omega,\omega)$:**

DFT calculations were run for the core chromophore of C1 and F2. The structures for both C1 (see Figure S-5) and F2 (see Figure S-6) were optimized in chloroform and computed with Gaussian09\textsuperscript{15} using the B3LYP level of theory with the 6-31G* basis set. The solvent reaction field was calculated with the PCM method using default parameters for the solvent. The wavelength for frequency dependent properties was set to 1906nm, the frequency used for HRS experimental measurements. All values are given in the Taylor Series convention.

The calculated value for $\beta_{HRS}(-2\omega,\omega,\omega)$ of C1 compared quite well to the experimentally ascertained value (Figure S-5).

<table>
<thead>
<tr>
<th>$\beta_{zzz}(-\omega,0,\omega)$</th>
<th>Calculated [units = ($\times 10^{-30}$ esu)]</th>
<th>Experimental [units = ($\times 10^{-30}$ esu)]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2830</td>
<td>3000 $\pm$ 300</td>
</tr>
</tbody>
</table>
**Figure S-5.** Structure of the optimized chromophore core (left). Comparison of DFT and experimental HRS hyperpolarizabilities (right). These values were corrected to 1310 nm, the frequency of the ATR measurements of EO activity.

The structure of F2 as used in hyperpolarizability calculations is shown in Figure S-6. The TDBMS protecting groups were omitted.

![Chemical structure](image)

**Figure S-6.** Optimized structure of F2 for hyperpolarizability calculations.

Hyperpolarizabilities for F2 were calculated at two wavelengths, 1906 nm (corresponding to HRS experiments) and 1310 nm (corresponding to ATR experiments). The values are given in Table S-2.

**Table S-2.** Hyperpolarizabilities [units = (× 10^{-30} esu)] for the optimized structure of F2.

<table>
<thead>
<tr>
<th>Freq. dep. $\beta$</th>
<th>1310 nm</th>
<th>1906 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta_{\text{HRS}}(0;0,0)$</td>
<td>1080</td>
<td>1080</td>
</tr>
<tr>
<td>$\beta_{zzz}(0;0,0)$</td>
<td>2438</td>
<td>2438</td>
</tr>
<tr>
<td>$\beta_{\text{HRS}}(-\omega;0,\omega)$</td>
<td>1563</td>
<td>1068</td>
</tr>
<tr>
<td>$\beta_{zzz}(-\omega;0,\omega)$</td>
<td>3540</td>
<td>2409</td>
</tr>
<tr>
<td>$\beta_{\text{HRS}}(-2\omega,\omega,\omega)$</td>
<td>7518</td>
<td>2027</td>
</tr>
</tbody>
</table>
The calculated value of $\beta_{zzz}(-\omega;0,\omega) = 3540$ at 1310nm is nearly identical to the experimentally measured value of $\beta_{zzz}(-\omega;0,\omega) = 3500$.

**Calculation of** $\langle \cos^3 \theta \rangle$:

The equation used to calculate $\langle \cos^3 \theta \rangle$ from experimental parameters with proper conversion to SI units:

$$\langle \cos^3 \theta \rangle / E_p = \left( r_{33} / E_p \right) \frac{2 \cdot 4\pi}{3 \cdot 10^5} \cdot (N \cdot 10^{20}) \cdot 10^{12} \cdot (\beta_{zzz}(-\omega;0,\omega) \cdot 10^{-30}) \frac{g(\omega)}{n_{\omega}^4} \text{ pm/V} \quad (S4)$$

**Further derivations of Reduced Dimensionality Theory:**

For the three-dimensional case, in the specific case of $n=1$, the first acentric order parameter is:

$$\langle \cos^1 \theta \rangle_{3D} = L_1(f) = \frac{e^f + e^{-f}}{e^f - e^{-f}} - \frac{1}{f} = \coth(f) - \frac{1}{f} \quad [S5]$$

For the two dimensional case, dipolar rotation is limited to a single plane containing the z-axis, the direction of the poling axis. The integral can be reduced to

$$\langle \cos^n \theta \rangle_{2D} = \frac{\int_{\theta=0}^{2\pi} \cos^n \theta e^{i \cos \theta} d\theta}{\int_{\theta=0}^{2\pi} e^{i \cos \theta} d\theta} \quad [S6]$$

The integral above may be written in terms of Bessel functions, $J_n(z)$. In the specific case of $n=1$, the result is

$$\langle \cos^1 \theta \rangle_{2D} = \frac{i \cdot J_1(-i \cdot f)}{J_0(-i \cdot f)} \quad [S7]$$
In the one-dimensional case, the dipole vectors can point only in the direction parallel or antiparallel to the field, so the probability distribution is the sum of two Dirac delta functions at \( \cos \theta = \pm 1 \), giving

\[
\langle \cos^n \theta \rangle_{1D} = \begin{cases} 
(1)^n e^{+f} + (-1)^n e^{-f} 
\end{cases} = \begin{cases} 
\tanh(f) & \text{odd } n \\
1 & \text{even } n 
\end{cases} \quad \text{[S8]}
\]

At low values of \( f \) the order parameters for \( n = 1 \) are linear in \( f \) for all dimensionalities, with the slopes being 1/1, 1/2, and 1/3 for the three different dimensions. In the limit of low \( f \):

\[
\langle \cos^1 \theta \rangle_{1D} = \frac{1}{2} f \quad \langle \cos^1 \theta \rangle_{2D} = \frac{1}{2} f \quad \langle \cos^1 \theta \rangle_{3D} = \frac{1}{3} f
\]

\[
\lim_{f \to 0} \langle \cos^1 \theta \rangle_{M-D} = \frac{1}{M} f
\]

For the 2D case, we can quantify the order parameter \( \langle \cos^3 \theta \rangle_{2D} \) in terms of Bessel functions using the identity:

\[
\cos^3 \theta = \frac{1}{4} (3 \cos \theta + 3 \cos 3 \theta)
\]

\[
\langle \cos^3 \theta \rangle_{2D} = \frac{1}{4} \int_{0}^{2\pi} (3 \cos \theta + 3 \cos 3 \theta)e^{i \cos \theta} d\theta = \frac{1}{4} \int_{0}^{2\pi} (3 \cos \theta + 3 \cos 3 \theta)e^{i \cos \theta} d\theta
\]

\[
= \frac{1}{4} \frac{-J_3(-if) + 3J_1(-if)}{J_0(-if)} = \frac{1}{4} \frac{-iJ_3(-if)}{J_0(-if)} + \frac{3}{4} \langle \cos^1 \theta \rangle_{2D}
\]

In the low \( f \) limit the third-power order parameter is proportional to the first-power order parameter. The ratio depends on the dimensionality:
\[ \langle \cos^3 \theta \rangle_{1D} = \frac{2}{3} \langle \cos \theta \rangle_{1D} \quad \langle \cos^3 \theta \rangle_{2D} = \frac{3}{4} \langle \cos \theta \rangle_{2D} \quad \langle \cos^3 \theta \rangle_{3D} = \frac{5}{3} \langle \cos \theta \rangle_{3D} \]

\[ \lim_{f \to 0} \langle \cos^3 \theta \rangle_{M-D} = \frac{3}{2+M} \langle \cos \theta \rangle_{M-D} \quad \lim_{f \to \infty} \langle \cos^3 \theta \rangle_{M-D} = \langle \cos \theta \rangle_{M-D} \]

or

\[ \lim_{f \to 0} \langle \cos^3 \theta \rangle_{M-D} = \frac{3}{2+M} \quad \lim_{f \to \infty} \langle \cos^3 \theta \rangle_{M-D} = 1 \]

For the 2D case, we want \( \langle \cos^2 \theta \rangle_{2D} \). To get this order parameter in terms of Bessel functions we use the identity:

\[ \cos^2 \theta = \frac{1}{2} (\cos 2\theta + 1) \]

\[ P_2 = \frac{3 \cos^2 \theta - 1}{2} = \frac{3 \cos 2\theta + 1}{4} \]

Then the second moment is related to the appropriate Bessel Functions:

\[ \langle P_2 \rangle_{2D} = \int_{\theta=0}^{2\pi} \left\{ \frac{3 \cos 2\theta + 1}{4} \right\} e^{f \cos \theta} d\theta = \frac{1}{4} \left\{ 1 - \frac{3J_2(-if)}{J_0(-if)} \right\} \]

For the one-dimensional case the identity holds for all values of \( f \). For the two- and three-dimensional cases, the ratio increases and goes to 1 for all dimensionalities as \( f \) goes to infinity. (All order parameters also go to one as \( f \) goes to infinity.)

One can use the generators of the order parameters to relate order parameters directly to one another. For example:

\[ y_n = \langle \cos^n \theta \rangle = \frac{G''_n}{G} \quad \text{where} \quad G''_n = \frac{d^nG}{df^n} \]

\[ y = \langle \cos \theta \rangle = \frac{G'}{G} \quad \text{and} \quad y_3 = \langle \cos^3 \theta \rangle = \frac{G''}{G} \]
We can now relate the third and first moment order parameters using the generating function:

\[
\frac{d}{df} \left( \frac{G''}{G} \right) = \left( \frac{G'}{G} \right) - \left( \frac{G'^{n}}{G^{2}} \right) G'
\]

\[
\frac{G'^{n+1}}{G} = \frac{d}{df} \left( \frac{G''}{G} \right) + \left( \frac{G'^{n}}{G^{2}} \right) G' = \frac{d}{df} \left( \frac{G''}{G} \right) + \left( \frac{G'^{n}}{G} \right) \left( \frac{G'}{G} \right)
\]

\[
y_{n+1} = \frac{dy_{n}}{df} + y_{n} \cdot y = \left( \frac{d}{df} + y \right) \cdot y_{n}
\]

We just apply this generator of the order parameters twice to get

\[
y_{2} = \left( \frac{d}{df} + y \right) \cdot y = y^{2} + y'
\]

\[
y_{3} = \left( \frac{d}{df} + y \right) \cdot y_{2} = \left( \frac{d}{df} + y \right) (y^{2} + y') = y^{3} + 3yy' + y''
\]

This is a general method to relate the first and third order parameters for all dimensionality problems. For example, for the one-dimensional case

\[
y_{2} = \tanh^{2} f + \frac{d \tanh f}{df} = 1
\]

\[
y_{3} = y
\]

For the three-dimensional case one finds

\[
y' = 1 - y^{2} - \frac{2y}{f}
\]

\[
y_{2} = 1 - \frac{2y}{f}
\]

\[
\langle P_{2} \rangle = \frac{3y_{2} - 1}{2} = 1 - \frac{3y}{2}
\]

Then
\[ y_3 = \left( \frac{d}{df} + y \right) \cdot y_2 = \left( \frac{d}{df} + y \right) \cdot \left( 1 - \frac{2y}{f} \right) = \left( \frac{2y - 2y'}{f^2} \right) + y \left( 1 - \frac{2y}{f} \right) \]
\[ = \frac{2}{f} \left( y \left( 1 - y^2 - \frac{2y}{f} \right) \right) + y \left( 1 - \frac{2y}{f} \right) = \frac{2}{f} \left( y^2 + \frac{3y}{f} - 1 \right) + y \left( 1 - \frac{2y}{f} \right) \]
\[ = \frac{2}{f} \left( \frac{3y}{f} - 1 \right) + y \]

From here one can directly obtain the ratio:
\[
\frac{y_3}{y} = 1 + \frac{6}{f^2} - \frac{2}{fy} = 1 + \frac{6}{f^2} - \frac{2 \tanh(f)}{f - \tanh(f)}
\]

which limits to 0.6 as \( f \to 0 \) and 1 as \( f \to \infty \).

As an example, we can show that the ratio limits to 0.6 by writing:

\[
\tanh(f) = f (1 - \zeta) \quad \zeta = 1 - \frac{\tanh(f)}{f} \approx \frac{1}{3} f^2 - \frac{2}{15} f^4
\]
\[
\frac{y_3}{y} = 1 + \frac{6}{f^2} - \frac{2 f (1 - \zeta)}{f - f (1 - \zeta)} = 1 + \frac{6}{f^2} - 2 \frac{(1 - \zeta)}{\zeta} = 3 + 2 - \frac{2}{\zeta} = 3 + 2 \left( \frac{1}{f^2} - \frac{1}{\zeta} \right)
\]
\[
\frac{y_3}{y} = 3 + 2 \left( \frac{\zeta - \frac{1}{3} f^2}{\frac{1}{3} f^2 \zeta} \right) = 3 + 2 \left( \frac{-\frac{2}{15} f^4}{\frac{1}{3} f^2 \cdot \frac{1}{3} f^2} \right) = 3 - 2 \cdot \frac{6}{5} = \frac{3}{5}
\]

As \( f \to \infty \), \( \zeta \to 1 \) so

\[
\frac{y_3}{y} = 3 + 2 \left( \frac{\zeta - \frac{1}{3} f^2}{\frac{1}{3} f^2 \zeta} \right) \to 3 + 2 \left( \frac{-\frac{1}{3} f^2}{\frac{1}{3} f^2} \right) = 3 - 2 = 1
\]

From this, we get both limits from the same form for \( \tanh(f) \).

For the 3D case in the low \( f \) limit, \( y \) goes as:
\[ \tanh(f) = f(1 - \zeta) \quad \zeta = 1 - \frac{\tanh(f)}{f} \approx \frac{1}{2} f^2 \left(1 - \frac{2}{5} f^2\right) \]

\[ y = \frac{1}{\tanh(f)} - \frac{1}{f} = \frac{1}{f(1 - \zeta)} - \frac{1}{f} = \frac{1}{f} \left(1 - \zeta\right) \]

\[ y \approx \frac{1}{3} f \left(1 - \frac{2}{5} f^2\right) (1 + \zeta) = \frac{1}{3} f \left(1 - \frac{2}{5} f^2 + \zeta\right) = \frac{1}{3} f \left(1 - \frac{1}{15} f^2\right) \]

From the relation of \( y \) and \( \langle P_2 \rangle \) above, we get the leading term for \( \langle P_2 \rangle \)

\[ \langle P_2 \rangle = 1 - \frac{3y}{f} \approx 1 - (1 - \frac{1}{15} f^2) = \frac{1}{15} f^2 \]

In the low \( f \) limit we can relate \( y \), \( y_3 \), and \( \langle P_2 \rangle \)

\[ y = \frac{1}{3} f \quad \langle P_2 \rangle = \frac{1}{15} f^2 \quad y_3 = \frac{1}{5} f \]

\[ y_3 = \frac{1}{5} \sqrt{15 \langle P_2 \rangle} = \frac{\sqrt{3}}{5} \langle P_2 \rangle \]

This low \( f \) limit is extremely good, even to much larger \( f \) values than one should have any right to use. An empirical functional form that works very well for any value of \( f \) is:

\[ y_3 \approx \sqrt{\frac{3}{5} \langle P_2 \rangle + \frac{2}{9} \langle P_2 \rangle^3} \approx \sqrt{\left(\frac{3}{5} \langle P_2 \rangle\right)^3} + \left(\frac{3}{5} \langle P_2 \rangle\right)^3 \]

With less than a 0.8% error (which occurs around \( f=12 \)) over the entire range of \( f \). For \( \langle P_2 \rangle \) less than \( \frac{1}{2} \), the extra term gives less than a 5% enhancement to \( y_3 \), so for most practical cases, the low \( f \) limit estimate is quite good.

References:


