

Oxidized polyethylene films for orienting polar molecules for linear dichroism spectroscopy

Kasra Razmkhah, Nikola Paul Chmel,* Matthew I. Gibson, Alison Rodger

Supplementary Information

SI.1 Effect on linear dichroism of rotating a uniaxially oriented sample in stretched film by angle χ

Let $\{x, y, z\}$ be the molecular axis system (with z the long axis which is assumed to be the orientation axis of the molecule); let $\{X, Y, Z\}$ be the laboratory fixed axis system (with Z horizontal, Y vertical); and let $\{X', Y', Z'\}$ be the film axis system (*i.e.* Z' is stretch direction and Y' is in the film perpendicular to Z'). In most of our experiments, $Z' = Z$, $Y' = Y$, but if we rotate the film this is not the case. We restrict the film-rotation to being about X , the direction of propagation of the light, so $X' = X$. Now we may write the transition dipoles in the molecular axis system as

$$\boldsymbol{\mu} = (\sin \delta \sin \alpha, \cos \delta \sin \alpha, \cos \alpha)_{xyz} \quad \text{SI(1)}$$

where δ is the angle between projection of $\boldsymbol{\mu}$ onto the x - y plane and the y axis. For a uniaxial rod: δ ranges from 0 to 2π and all final equations will be averaged over δ . We require three more angles to relate the molecular and laboratory-fixed axis systems and choose to use Euler angles:

θ is the angle between z and Z

ϕ is the angle between x and a reference line defined to be perpendicular to both Z and z

ψ is the angle between X and the reference line.

In the film axis system, a molecule lies so that z is oriented at an angle θ from the stretch direction. Using the Euler angles we may write (where subscripts indicate axis system)

$$\boldsymbol{\mu}_{\{X'Y'Z'\}} = \begin{pmatrix} \cos \phi \cos \psi - \sin \phi \sin \psi \cos \theta & \sin \phi \cos \psi + \cos \phi \sin \psi \cos \theta & \sin \psi \sin \theta \\ -\cos \phi \sin \psi - \sin \phi \cos \psi \cos \theta & -\sin \phi \sin \psi + \cos \phi \cos \psi \cos \theta & \cos \psi \sin \theta \\ \sin \phi \sin \theta & -\cos \phi \sin \theta & \cos \theta \end{pmatrix} \begin{pmatrix} \sin \delta \sin \alpha \\ \cos \delta \sin \alpha \\ \cos \alpha \end{pmatrix}_{\{xyz\}} \boldsymbol{\mu}$$

A film-rotation of χ about X takes $\boldsymbol{\mu}$ to:

$$\boldsymbol{\mu}_{\{XYZ\}} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \chi & -\sin \chi \\ 0 & \sin \chi & \cos \chi \end{pmatrix} \begin{pmatrix} \cos \phi \cos \psi - \sin \phi \sin \psi \cos \theta & \sin \phi \cos \psi + \cos \phi \sin \psi \cos \theta & \sin \psi \sin \theta \\ -\cos \phi \sin \psi - \sin \phi \cos \psi \cos \theta & -\sin \phi \sin \psi + \cos \phi \cos \psi \cos \theta & \cos \psi \sin \theta \\ \sin \phi \sin \theta & -\cos \phi \sin \theta & \cos \theta \end{pmatrix} \begin{pmatrix} \sin \delta \sin \alpha \\ \cos \delta \sin \alpha \\ \cos \alpha \end{pmatrix}_{\{xyz\}} \boldsymbol{\mu} \quad \text{SI(2)}$$

where χ is the angle of the anti-clockwise rotation of the film about X . Now

$$LD = A_Z - A_Y = k(\mu_Z^2 - \mu_Y^2) \quad \text{SI(3)}$$

so upon squaring the components in Equation SI(2) and averaging over δ , ϕ and ψ (as appropriate for a system that behaves as a uniaxial rod) we get

$$LD = A_Z - A_Y = k\mu^2 \frac{1}{4} (3\cos^2 \theta - 1) (3\cos^2 \alpha - 1) \cos(2\chi) \quad \text{SI(4)}$$

thus for a uniaxial rod the LD scales with film-rotation angle as illustrated in Figure S11 where $\cos(2\chi)$ is overlaid on the LD of progesterone as a function of film rotation angle. Similar behaviour is shown in Figures SI2–4 for DAPI, 1-pyrenecarboxyaldehyde and anthracene.

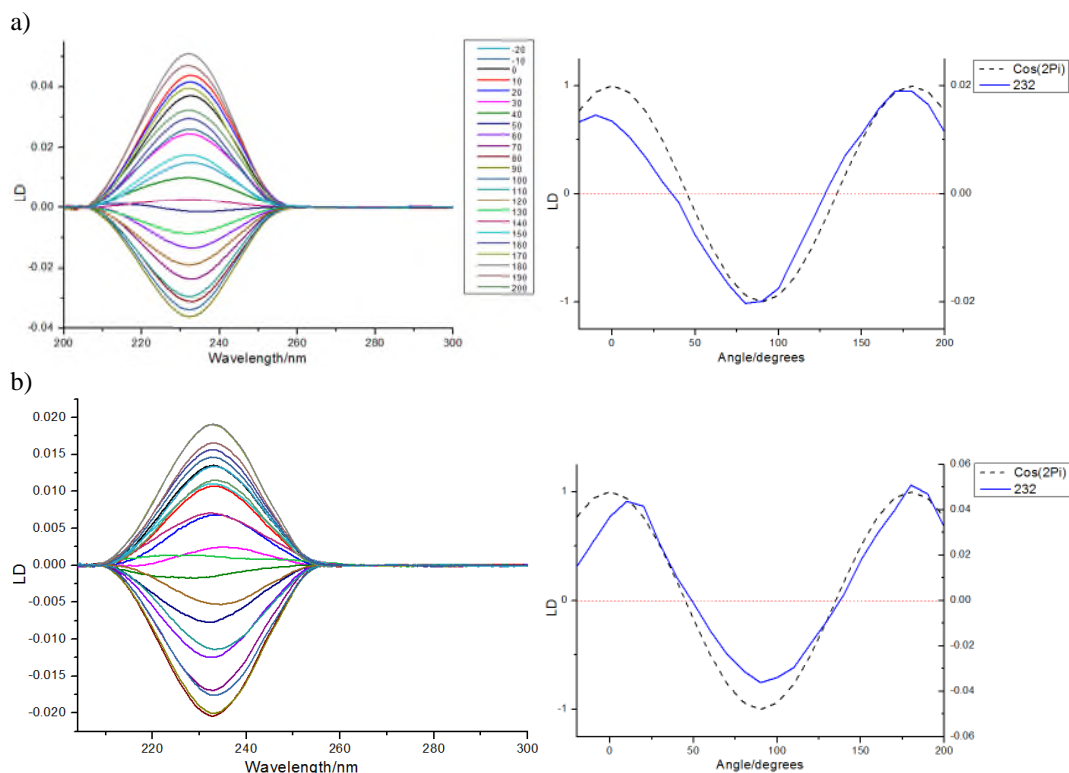


Figure S11. LD of progesterone on a) PE and b) PE^{OX} as a function of film-rotation angle. Left: wavelength scans, right: signal at 232 nm plotted as a function of rotation angle χ overlaid on a plot of $\cos(2\chi)$. Note: the film stretcher horizontal direction was not quite parallel to the PE stretch direction due to challenges of loading the film into the cylindrical holder.

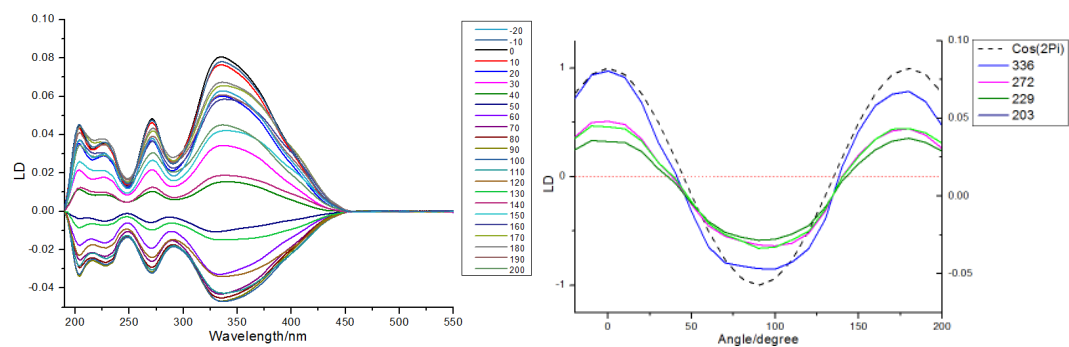


Figure S12. LD of DAPI on PE^{OX} as a function of film-rotation angle. Left: wavelength scans, right: signal at 203, 229, 272 and 336 nm as a function of rotation angle χ overlaid on a plot of $\cos(2\chi)$.

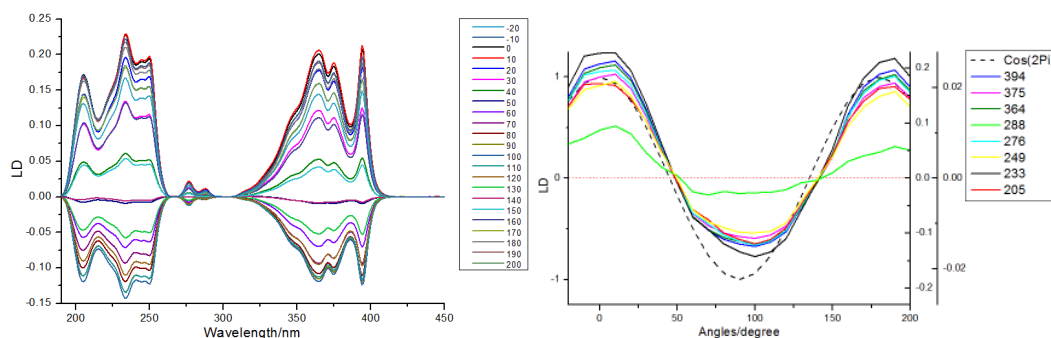
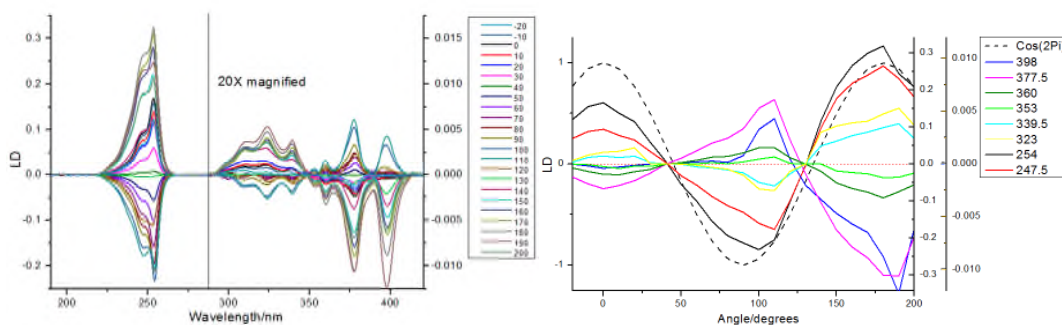


Figure SI3. LD of 1-pyrenecarboxaldehyde on PE as a function of film-rotation angle. Left: wavelength scans, right: signal at 205, 233, 249, 276, 288, 364, 375 and 395 nm as a function of rotation angle χ overlaid on a plot of $\cos(2\chi)$. Note: the film stretcher horizontal direction was not quite parallel to the PE stretch direction due to challenges of loading the film into the cylindrical holder.

a)



b)

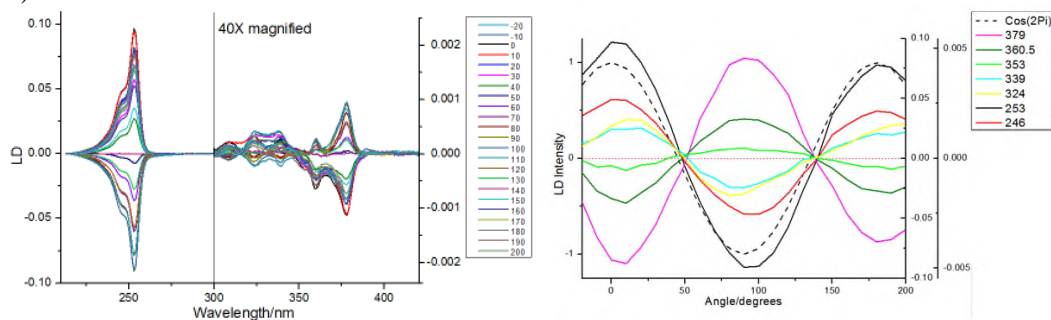


Figure SI4. LD of anthracene on a) PE and b) PE^{OX} as a function of film-rotation angle. Left: wavelength scans, right: signal at 246, 253, 324, 339, 353, 360 and 379 nm plotted as a function of rotation angle χ overlaid on a plot of $\cos(2\chi)$. Note: the film stretcher horizontal direction was not quite parallel to the PE stretch direction due to challenges of loading the film into the cylindrical holder.

The next question to ask is whether this behaviour is unique to the uniaxial rod case. Consider, for example, a perfectly oriented planar molecule with in-plane transitions lying flat on the surface of the film. Equation SI(4) reduces to

$$LD = A_z - A_y = k\mu^2 \{ \cos(2\chi)\cos(2\alpha) + \sin(2\chi)\sin(2\alpha) \} \quad \text{SI(5)}$$

Attempts to find another geometry that reduces to Equation SI(4) failed, suggesting that the Equation SI(4) film-rotation dependence is indicative of at least approximately uniaxial behaviour.

SI.2 Effect of stretch factor on LD intensity

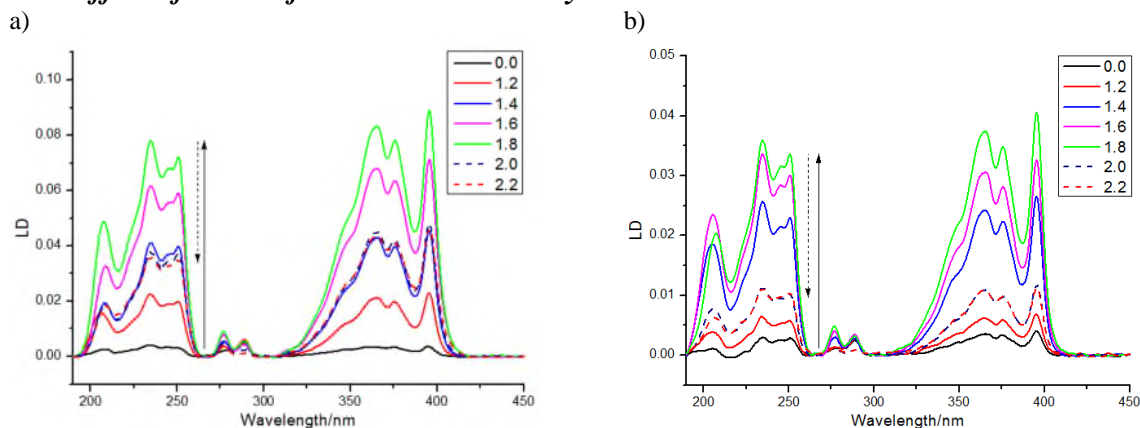


Figure SI5. LD spectra of 1-pyrenecarboxaldehyde (deposited from 0.4 mg/mL in chloroform for PE and methanol for PE^{OX} and left to dry) on (a) PE, and (b) PE^{OX} prestretched by factors ranging from 1 to 2.2×.

SI.3 Exciton coupling LD of dimers (and higher order structures) in films

To a reasonable degree of approximation, exciton interactions between molecules in films can be expressed as a sum of nearest neighbour dimer contributions (though for DNA bases, convergence does require a sum over 10–20 neighbours).[33] In this section we therefore consider only dimers of identical monomers. The degenerate coupled-oscillator model [14] describes the situation where two (or more) degenerate transition moments μ_A^{01} on chromophore **A** and μ_C^{01} on chromophore **C**, both of which go from ground state $|0\rangle$ to excited state $|1\rangle$, couple (Figure SI2). In the absence of coupling, their transition energies are the same but their orientation is not. To write the wave functions of the interacting **A/C** system we first consider an **A/C** system where **A** and **C** do not interact. The Hamiltonian, \hat{H} , of the non-interacting system is simply the sum

$$\tilde{H} = \hat{H}_A + \hat{H}_C \quad \text{SI(6)}$$

where \hat{H}_A is the Hamiltonian of isolated **A**, and similarly \hat{H}_C . The total energy of a state $|ac\rangle$ is the energy of $|a\rangle$ in **A** plus that of $|c\rangle$ in **C**. So, for example, $|01\rangle$ means **A** is in its ground state and **C** is in state $|1\rangle$ with energy $0 + \varepsilon = \varepsilon$ (taking the zero point of energy to be when both **A** and **C** are in their ground states).

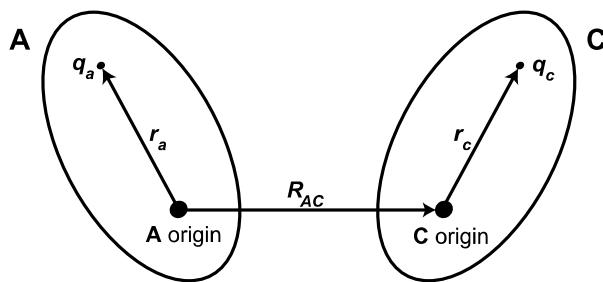


Figure SI6. Geometry of **A** and **C** chromophores.

When the electrostatic interaction, V , is ‘switched on’ between **A** and **C** then the Hamiltonian of the interacting system may be written

$$\tilde{H} = \hat{H}_A + \hat{H}_C + \tilde{V} \quad \text{SI(7)}$$

where \tilde{V} denotes the quantum mechanical operator derived from the Coulombic interaction between **A** and **C**

$$V = \sum_{a,c} \frac{q_a q_c}{|\mathbf{R}_{AC} + \mathbf{r}_c - \mathbf{r}_a|} \quad \text{SI(8)}$$

If **A** and **C** are not too close together, then \tilde{V} may be expanded using a double Taylor series expansion to give terms dependent on monopoles, dipoles, quadrupoles *etc.* of **A** and **C**. For uncharged **A** and **C**, the first term in the expansion is the dipole-dipole term:

$$\tilde{V} = \frac{\hat{\mu}_A \cdot \hat{\mu}_C - 3\hat{R}_{AC} \cdot \hat{\mu}_A \hat{\mu}_C \cdot \hat{R}_{AC}}{R_{AC}^3} \quad \text{SI(9)}$$

where R_{AC} is the vector from the **A** origin to the **C** origin (the triangular hat denotes unit vector in that direction). The **A/C** wavefunctions have the form (using the rounded bra-ket notation for unperturbed wave functions of chromophores and the pointed bra-ket notation for the wave functions of the interacting system)

$$\begin{aligned} |a\rangle|c\rangle &= |ac\rangle \\ &= |ac\rangle + \text{other terms} \end{aligned} \quad \text{SI(10)}$$

The identity of the ‘other terms’ depends on whether or not **A** and **C** are identical. If **A** and **C** are identical then their transitions are degenerate (have the same energy) and by symmetry (or degenerate perturbation theory) two states that result from the mixing of $|10\rangle$ (**A** in $|1\rangle$ and **C** in the ground state) and $|01\rangle$ are (ignoring higher order terms and other states)

$$|10_{\pm}\rangle = \frac{1}{\sqrt{2}} \{ |10\rangle \pm |01\rangle \} \quad \text{SI(11)}$$

We use real normalized wave functions and assume that permanent moments are much smaller than transition moments, then the dominant terms in the energies of these two states are

$$\begin{aligned} \varepsilon^{\pm} &= \langle 10_{\pm} | \hat{H}_A + \hat{H}_C + \tilde{V} | 10_{\pm} \rangle \\ &= \frac{1}{2} \{ \langle 10 | \pm \langle 01 | \} \hat{H}_A + \hat{H}_C + \tilde{V} \{ |10\rangle \pm |01\rangle \} \\ &= \frac{1}{2} \{ (1 | \hat{H}_A | 1) + (0 | \hat{H}_C | 0) \pm (10 | \tilde{V} | 01) + (0 | \hat{H}_A | 0) + (1 | \hat{H}_C | 1) \pm (01 | \tilde{V} | 10) \} \end{aligned} \quad \text{SI(12)}$$

So

$$\begin{aligned} \varepsilon^{\pm} &= \varepsilon^0 + \varepsilon^1 \pm \frac{1}{2} (V^{01,10} + V^{10,01}) \\ &= \varepsilon \pm V^{11} \end{aligned} \quad \text{SI(13)}$$

where,

$$\begin{aligned} V^{ba,dc} &= (ac | \tilde{V} | bd) \\ &= \frac{\mu_A^{ba} \cdot \mu_C^{dc} - 3\hat{R}_{AC} \cdot \mu_A^{ba} \mu_C^{dc} \cdot \hat{R}_{AC}}{R_{AC}^3} \end{aligned} \quad \text{SI(14)}$$

V^{11} is much smaller than ε so the two new perturbed states are close in energy.

The electric dipole transition moments for the transitions from the two excited states of equation SI(11) to the ground state $|00\rangle$ are:

$$\begin{aligned} \langle 00 | \hat{\mu} | 10_{\pm} \rangle &= \frac{1}{\sqrt{2}} \{ \langle 00 | \hat{\mu}_A + \hat{\mu}_C [|10\rangle \pm |01\rangle] \} \\ &= \frac{1}{\sqrt{2}} \{ \mu_A^{10} \pm \mu_C^{10} \} \end{aligned} \quad \text{SI(15)}$$

where the upper sign of the \pm above refers to the upper signs in all the equations.

To determine the exciton LD there are two geometry aspects to consider

- (i) the geometry within the dimer, and
- (ii) the geometry of the dimer with respect to the film.

We first consider the geometry within the dimer. This determines the energy splitting and the absorbance intensities of the two exciton bands. In the case of anthracene, all monomer π - π^* transitions are either polarized along the long axis (*e.g.* 254 nm) or the short axis (*e.g.* 379 nm). Let us work in an axis system $\{x', y', z'\}_A$ where the origin is

the centre of anthracene **A** and where z' is its long axis, y' is perpendicular to z' in the molecular plane and x' completes a right-handed axis system. Anthracene **C**, with axis system $\{x'', y'', z''\}_C$ can be oriented in an infinite number of different ways, but we shall explicitly consider ones suggested by symmetry and by the anthracene crystal structure.[32] We need the values of the angles between **A** and **C** axes to compute V . If $V=0$ then the transitions occur at the monomer energies. If $V>0$ then the in-phase combination (+ in equation SI(15)) occurs at higher energy than the monomer and the out-of-phase combination occurs at lower energy. The converse holds for $V<0$.

Whether the in-phase or out-of-phase coupling of $\mu_A^{10} = \mu_A$ and $\mu_C^{10} = \mu_C$ is higher or lower in energy is summarised in Table SI1 for some geometries. To determine the LD of these transitions we need to evaluate

$$LD = A_z - A_y \quad \text{SI(16)}$$

which requires us to relate Z and Y to the molecular axes. For simplicity we assume perfect orientation and note that high symmetry arrangements tend to be either high energy or low energy.[34] We therefore consider the case where Z is midway between z' and z'' , or perpendicular to this, or where **A** is oriented on the film with its z' along the stretch direction (*i.e.* representing the type of dimer that might be formed by depositing a monomer first) or perpendicular to it. Some of the simpler options are covered in Table SI2. Parallel dimers with twist angle $\gamma=0$ is appropriate for the parallel pair in the anthracene crystal structure, for J-aggregates, and for two anthracenes vertically stacked. It is likely that the J-aggregate has $Z=z'$, with the other axes being either uniaxial (so an average of what is given below) or one of the other two assignments. Parallel dimers with $2\gamma=90^\circ$ is appropriate for the cross of Figure 11. In this case we speculate that $Z=x'$, $Y=z'+z''$ is appropriate since it is probably an extended stack to adopt this geometry. $2\gamma=30^\circ$ or 60° are other likely structures.

To determine the exciton LD spectrum one combines appropriate sets of results in Tables SI1 and SI2.

Table S11. Position of anthracenes **A** and **C** in possible dimer structures in terms of angles between polarisation axes and the polarization axes and the line between the molecular centres. Long denotes long axis of an anthracene monomer (*i.e.* 254 nm transition), short denotes short axis of monomer (*i.e.* 379 nm transition). The reduced LD, LD^f, values are relative and assuming perfect orientation. If $V > 0$ for a given geometry then the lower energy component is the out-of-phase one. If $V < 0$ then the lower energy component is the in-phase one in the table below.

Anthracene C position	Angle between/degrees				$V \times R_{AC}^3 / \mu^2$ polarization axis	
	$\hat{\mu}_C^{long}$ and $\hat{\mu}_A^{long}$	$\hat{\mu}_C^{short}$ and $\hat{\mu}_A^{short}$	\hat{R}_{AC} and $\hat{\mu}_C^{long} / \hat{\mu}_A^{long}$	\hat{R}_{AC} and $\hat{\mu}_C^{short} / \hat{\mu}_A^{short}$	long	short
Stacked //, centers aligned: parallel z axes	0	0	90/90	90/90	1	1
Stacked //, centers aligned: perpendicular z axes	90	90	90/90	90/90	0	0
Stacked //, centers aligned: 30° z axes	30	30	90/90	90/90	0.87	0.87
Stacked //, centers aligned: 60° z axes	60	60	90/90	90/90	0.5	0.5
Stacked //, centers aligned: z axes at angle 2γ	2γ	2γ	90/90	90/90	$\cos\gamma$	$\cos\gamma$
J-aggregate (head to tail in-plane)	0	0	0/0	90/90	-2	1
Crystal parallel pair	0	0	82.8/82.8	26.6/26.6	0.95	-1.39
Crystal skewed pair	14.4	54.2	70.6/61.5	75.4/39.1	0.49	0.0
Stacked //, centers displaced: z axes at angle 2γ with $\hat{R}_{AC} = (\sqrt{1-b^2-c^2}, b, c)$	2γ	2γ			$\cos 2\gamma - 3c[(\cos 2\gamma)c + (\sin 2\gamma)b]$	$\cos 2\gamma - 3b[(\cos 2\gamma)b + (\sin 2\gamma)c]$

Table S12. In-phase and out-of-phase LD magnitudes for some anthracene dimer geometries. $Z=z'+z''$ denotes the dimer lies so that the stretch direction of the film is midway between the z' and z'' axes of **A** and **C** etc. For uniaxial orientation average the entries in the neighbouring columns.

Geometry	Transition dipoles in A coordinates				
x' and x'' parallel. 2γ twist angle between anthracene long axes.	$\mu_A^{long} = (0, 0, 1)_{x'y'z'}$ $\mu_C^{long} = (0, \sin(2\gamma), \cos(2\gamma))_{x'y'z'}$ $\mu_A^{short} = (0, 1, 0)_{x'y'z'}$ $\mu_C^{short} = (0, \cos(2\gamma), -\sin(2\gamma))_{x'y'z'}$	$Z = z', Y = y'$		$Z = z', Y = x'$	
		Long	Short	Long	Short
		In-phase $\frac{1}{2}((1 + \cos 2\gamma)^2 - \sin^2 2\gamma)$	In-phase $\frac{1}{2}(\sin^2 2\gamma - (1 + \cos 2\gamma)^2)$	In-phase $\frac{1}{2}(1 + \cos 2\gamma)^2$	In-phase $\frac{1}{2}\sin^2 2\gamma$
		Out-of-phase $\frac{1}{2}((1 - \cos 2\gamma)^2 - \sin^2 2\gamma)$	Out-of-phase $\frac{1}{2}(\sin^2 2\gamma - (1 - \cos 2\gamma)^2)$	Out-of-phase $\frac{1}{2}(1 - \cos 2\gamma)^2$	Out-of-phase $\frac{1}{2}\sin^2 2\gamma$
		$Z = x', Y = z'$		$Z = x', Y = y'$	
		Long	Short	Long	Short
		In-phase $-\frac{1}{2}((1 + \cos 2\gamma)^2)$	In-phase $-\frac{1}{2}\sin^2 2\gamma$	In-phase $-\frac{1}{2}\sin^2 2\gamma$	In-phase $-\frac{1}{2}((1 + \cos 2\gamma)^2)$
		Out-of-phase $-\frac{1}{2}((1 - \cos 2\gamma)^2)$	Out-of-phase $-\frac{1}{2}\sin^2 2\gamma$	Out-of-phase $-\frac{1}{2}\sin^2 2\gamma$	Out-of-phase $-\frac{1}{2}((1 - \cos 2\gamma)^2)$
		$Z = y', Y = z'$		$Z = y', Y = x'$	
		Long	Short	Long	Short
		In-phase $\frac{1}{2}(\sin^2 2\gamma - (1 + \cos 2\gamma)^2)$	In-phase $\frac{1}{2}((1 + \cos 2\gamma)^2 - \sin^2 2\gamma)$	In-phase $\frac{1}{2}\sin^2 2\gamma$	In-phase $\frac{1}{2}((1 + \cos 2\gamma)^2)$
		Out-of-phase $\frac{1}{2}(\sin^2 2\gamma - (1 - \cos 2\gamma)^2)$	Out-of-phase $\frac{1}{2}((1 - \cos 2\gamma)^2 - \sin^2 2\gamma)$	Out-of-phase $\frac{1}{2}\sin^2 2\gamma$	Out-of-phase $\frac{1}{2}((1 - \cos 2\gamma)^2)$
$Z = z'+z'', Y = z'-z''$		$Z = z'+z'', Y = x'$			
Long	Short	Long	Short		
In-phase	In-phase	In-phase	In-phase		

		$\cos^2 \gamma$ Out-of-phase $-\sin^2 \gamma$	$-\cos^2 \gamma$ Out-of-phase $\sin^2 \gamma$	$\cos^2 \gamma$ Out-of-phase 0	0 Out-of-phase $\sin^2 \gamma$
		$Z = z' - z'', Y = z' + z''$		$Z = z' - z'', Y = x'$	
		Long	Short	Long	Short
		In-phase $-\cos^2 \gamma$ Out-of-phase $\sin^2 \gamma$	In-phase $\cos^2 \gamma$ Out-of-phase $\sin^2 \gamma$	In-phase 0 Out-of-phase $\sin^2 \gamma$	In-phase $\cos^2 \gamma$ Out-of-phase 0
Crystal structure skewed pair	$\mu_A^{long} = (0, 0, 1)_{x', y', z'}$ $\mu_C^{long} = (-\cos 83.9, -\cos 77.0, \cos 14.4)_{x', y', z'}$ $\mu_A^{short} = (0, 1, 0)_{x', y', z'}$ $\mu_C^{short} = (-\cos 38.8, -\cos 54.2, \cos 77.0)_{x', y', z'}$	$Z = z', Y = y'$		$Z = z', Y = x'$	
		Long	Short	Long	Short
		In-phase $\frac{1}{2}((1 + \cos 14.4)^2 - \cos^2 77.0)$ Out-of-phase $\frac{1}{2}((1 - \cos 14.4)^2 - \cos^2 77.0) \sim 0$	In-phase $\frac{1}{2}(\cos^2 77.0 - (1 + \cos 54.2)^2)$ Out-of-phase $\frac{1}{2}(\cos^2 77.0 - (1 - \cos 54.2)^2) \sim 0$	In-phase $\frac{1}{2}((1 + \cos 14.4)^2 - \cos^2 83.9)$ Out-of-phase $\frac{1}{2}((1 - \cos 14.4)^2 - \cos^2 83.9) \sim 0$	In-phase $\frac{1}{2}(\cos^2 77.0 - (1 + \cos 38.8)^2)$ Out-of-phase $\frac{1}{2}(\cos^2 77.0 - (1 - \cos 38.8)^2) \sim 0$

SI.4 NMR of PE film

^1H NMR, ^{13}C NMR, COSY, HMQC and HMBC solution spectra were collected for samples of PE films in 1,2-tetrachloroethane- d_2 at 373K using a Bruker Spectrospin DRX-500. The spectra were internally referenced using the residual protio solvent resonances relative to tetramethylsilane ($\delta = 0$ ppm).

Two distinctly different $-\text{CH}_3$ groups were identified in the ^1H NMR (δ 0.91, t; δ 0.96, m) and the ^{13}C NMR (δ 10.76; δ 13.78 ppm respectively). Two CH groups have also been identified (^1H NMR $\delta \sim 1.34$ ppm; ^{13}C NMR δ 37.47 and 39.01 ppm). The presence of clear crosspeaks in the HMBC spectrum between CH carbon at 39.01 ppm and CH_3 protons at 0.91 ppm shows presence of pendant CH_3 groups attached to the polymer chain. Further crosspeaks connect the CH carbon at 39.01 ppm to CH_2 protons from the main polymer chain (Fig. SI7).



Figure SI7. NMR peak assignment for a sample of film used for LD measurements. Green stars mark the observed crosspeaks in the HMBC spectrum. (left) Polyethylene chain, (right) polypropylene chain.

The relative content of polypropylene in the film estimated from the ^1H NMR spectrum is approximately 1.5% (w/w).