Supporting Information: On the factors influencing the chiroptical response of conjugated polymer thin films

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S1 Theory and Computational Details

As stated in the main text, in the visible regime, wavelengths of interacting light are much larger (hundreds of nanometres) than the typical size of a molecule (tens of Angström). Consequently, the exponential operator responsible for the spatial term of the radiation field, $\exp(i\mathbf{k} \cdot \mathbf{r})$, when expanded as a Taylor series [1]:

$$\exp(i\mathbf{k}\cdot\mathbf{r}) = 1 + i(\mathbf{k}\cdot\mathbf{r}) - \frac{1}{2}(\mathbf{k}\cdot\mathbf{r})^2 + \cdots$$
(1)

may be truncated at zeroth order corresponding to the electric dipole approximation. First-order contributions, *i.e.* the electric quadrupole and magnetic dipole terms, only become significant for electric dipole forbidden transitions or when kr > 1 [1], where $k = 2\pi/\lambda$ and r is a spatial vector. The validity of the electric dipole approximation on the molecular scale implies that the μ is typically around three orders of magnitude larger than m [1].

Planar structures of the models of F8BT and PFO polymers (see Figure 1 main text) were optimised using DFT(B3LYP) and a def2-SVP basis set [2] as implemented within the ORCA quantum chemistry package [3]. For both systems, the C_8H_{17} side chains are replaced by methyl groups to reduce computational expense of the quantum mechanical simulation. Following optimising the structures were manipulate as required to assess the twist angle between adjacent repeat units and the number of monomers (*n*). The former was performed using the Avogadro software [4]. The dimers were generated by calculate the centre of mass of each single polymer chain. The centre of mass for the second polymer was added distance, *d* and angle ϕ from the original polymer chain.

Throughout this work, all calculations of the dissymmetry were performed using time-dependent density functional theory (TDDFT) within the approximation of the CAM-B3LYP [5] exchange and correlation functional and a def2-SVP basis set [2] as implemented within the ORCA quantum chemistry package [3]. The calculations of the electric (μ) and magnetic (m) transition dipole contributions used the length representation and the origin independent approach as described in refs. [1,6].

Throughout this work, the dissymmetry was calculated for the lowest singlet excited state using Equation 1 in the main text. For the dimers, both the excitonic split states are included as the weakly coupled nature of the dimers means that the splitting between the two Davydov bands is <0.3 eV. The relative contributions of the upper (S_2) and lower (S_1) states is governed by a Boltzmann distribution according to:

$$\frac{Int(S_2 \to S_0)}{Int(S_1 \to S_0)} = \frac{f(S_2 \to S_0)}{f(S_1 \to S_0)} \cdot \exp\left(-\frac{\Delta E_{S_2 - S_1}}{k_b T}\right)$$
(2)

where *f* is the oscillator strength associated with each state and $\Delta E_{S_2-S_1}$ corresponds to the Davydov splitting.

S2 Supplementary Results: Single Polymer Chains



Figure S1: Energy of the S_1 state (in eV) for PFO (red) and F8BT (black) as a function of the number of repeat units.



Figure S2: The ratio between the electric and magnetic transition dipole moments, μ^2/m^2 for PFO (red) and F8BT (black) as a function of the number of repeat units. This corresponds to the data presented in Figure 2a in the main text.

n	PFO		F8BT	
	μ	\boldsymbol{m}	μ	m
1	1.244	0.116	3.901	0.342
2	3.840	0.187	4.773	0.685
3	5.266	0.293	5.823	1.278
4	6.292	0.419	6.656	1.435
5	7.203	0.642	7.111	1.563
6	7.768	0.818	7.694	1.664
7	7.928	1.527	8.173	1.759
8	8.165	2.563	8.421	2.292

Table S1: The electric and the magnetic transition dipole moments for PFO and F8BT as a function of the number of repeat units (*n*). Atomic units are used throughout. A fixed twist angle (θ =40°) was used throughout.

Angle	PFO		F8BT	
	μ	\boldsymbol{m}	μ	m
-70	5.326	0.470	4.036	0.327
-60	6.689	0.345	4.623	0.578
-50	6.036	0.236	5.055	0.820
-40	6.209	0.188	5.392	1.093
-30	6.413	0.123	5.765	1.360
-20	6.505	0.085	5.978	1.564
-10	6.603	0.072	6.099	1.695
0	6.783	0.064	6.142	1.740
10	6.603	0.072	6.096	1.694
20	6.505	0.085	5.974	1.563
30	6.413	0.123	5.767	1.360
40	6.209	0.188	5.391	1.093
50	6.036	0.236	5.062	0.822
60	6.689	0.345	4.623	0.579
70	5.326	0.470	4.033	0.326

Table S2: The electric and the magnetic transition dipole moments for PFO and F8BT 2-mers (n=2) as a function of the twist angle between the monomer units.



Figure S3: (a) The ratio between the electric and magnetic transition dipole moments, μ^2/m^2 for PFO (red) and F8BT (black) as a function of the twist angle between the monomer units. (b) $\cos(\tau)$, where τ is the angle between the electric and magnetic dipole moments, as a function of the twist angle between each monomer units for PFO (red) and F8BT (black). This corresponds to the data presented in Figure 2b in the main text.

S3 Supplementary Results: Dimers

Angle	PFO	F8BT
-40	0.126	0.031
-30	0.160	0.062
-20	0.194	0.101
-10	0.232	0.122
-5	0.248	0.193
-1	0.258	0.213
0	0.260	0.215
1	0.262	0.214
5	0.262	0.182
10	0.248	0.116
20	0.196	0.090
30	0.202	0.059
40	0.160	0.030

Table S3: The coupling potential between the excitonic states (*V*) in eV for PFO and F8BT as a function of the angle (ϕ) between the monomer chains.

Distance	PFO	F8BT
5.0	0.282	0.213
6.0	0.234	0.154
7.0	0.190	0.112
8.0	0.156	0.094
9.0	0.130	0.080
10.0	0.128	0.070
20.0	0.030	0.024
30.0	0.012	0.010

Table S4: The coupling potential between the excitonic states (V) in eV for PFO and F8BT as a function of the distance (d) between the monomer chains.

In Figure 3 in the main text, we show the effect of interacting polymer chains on the magnitude of the *g*-factor, and throughout this section we used a 2-mer. It is worth emphasising that this limited size may influence the dissymmetry, as it does the excited state energies shown in Figure S1. Consequently, Figure S6 shows the dimer calculation (d=6 Å, $\theta=40^{\circ}$ and $\phi=2^{\circ}$) as a function of the number of monomer units (*n*) for PFO. This demonstrates that as *n* increases, the *g*-factor decreases until reaching convergence of ~0.02 for *n* >4. It is noted that this convergence in very similar to that observed in Figure S1. The number of atoms required for a similar study of F8BT make it very challenging and as the convergence effect show in Figure S1, is weaker than PFO and so a similarly small effect is expected for the *g*-factor.

Figure S6 illustrates that delocalisation along the oligomers may be responsible for reducing the dissymmetry. This further illustrates, as mentioned in the conclusion of the main text, that to achieve quantitative agreement between experiment and theory for a real system the effect of conformational and environmental disorder needs to be considered.



Figure S4: Dissymmetry (*g*-factor) of the S₁ state as a function of the number of monomer units (*n*) for a dimer of PFO (black). d=7 Å, $\theta=40^{\circ}$ and $\phi=2^{\circ}$.



Figure S5: $\Delta \epsilon$ for the lowest exciton couplet of the PFO model as a function of the (a) distance (*d*, n=2, $\theta=40^{\circ}$ and $\phi=10^{\circ}$) and (b) angle (ϕ , d=6 Å, n=2, $\theta=40^{\circ}$) between the monomer chains. Spectra broadened using Gaussian function 0.25 eV FWHM.



Figure S6: $\Delta \epsilon$ for the lowest exciton couplet of the F8BT model as a function of the (a) distance (*d*, n=2, $\theta=40^{\circ}$ and $\phi=10^{\circ}$) and (b) angle (ϕ , d=6 Å, n=2, $\theta=40^{\circ}$) between the monomer chains. Spectra broadened using Gaussian function 0.25 eV FWHM.



Figure S7: Direction of the electric and magnetic transition dipole moments of the lowest excitonic state of a dimer of F8BT 2-mers (n=2, $\theta=40^{\circ}$, $\phi=10^{\circ}$ and d=6 Å).

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