# Probing a Conjugated Polymer's Transfer of Organization-Dependent Properties from Solutions to Films

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The functional properties exhibited by conjugated polymer films in devices, such as light-emitting diodes, field-effect transistors, sensors, and solar cells, are not only dependent on the polymer's individual properties but also on how it is organized in the film. For a solution-processed conjugated polymer, the final architecture in the solid film is dependent on the dynamic assembly from the solution state.[1,2] Variations in the film architecture may ultimately lead to remarkably different functional properties. In this report, we show that, depending on the solvent from which a conjugated polymer film is cast, opposite circular polarization in the luminescence can be obtained. This demonstrates the utility of supramolecular preorganizing polymers in solution to control the functional properties of the solid film.

One of the most extensively studied classes of $\pi$-conjugated polymers for optoelectronic applications is poly(*p*-phenylenevinylene) (PPV) because of its stability, easy processability, and good electrical and luminescent properties.[3] By incorporating chirality into such a conjugated polymer (**1**),[2] we were able to use circular dichroism (CD) and circularly polarized luminescence (CPL) spectroscopy to analyze the organizations of the polymer in its ground[4] and excited[5] states, respectively.

Figure 1a displays the degrees of circular polarization in absorption ($g_{abs}$) and luminescence ($g_{lum}$) in spin-cast films of **1**. The *g* values are defined as $g_{abs} = 2(\epsilon_L - \epsilon_R)/(\epsilon_L + \epsilon_R)$ and $g_{lum} = 2(I_L - I_R)/(I_L + I_R)$, where $\epsilon_L$ and $\epsilon_R$ are the molecular extinction coefficients for left and right circularly polarized light, and $I_L$ and $I_R$ are the luminescence intensities of left and right circularly polarized light.[4a] Figure 1b shows the corresponding normalized UV–vis absorption and fluorescence spectra, which are similar in shape despite the different processing conditions of each film.

When **1** was spin-cast from a "good" nonpolar solvent (in which the polymer easily dissolves), such as chloroform, the resulting film exhibited no significant CPL. However, annealing the film (at 45 °C for 30 min) in the presence of chloroform vapor enabled the polymer chains to self-assemble from a disordered state to a more thermodynamically favored chiral organization,[2,6] giving rise to CD and CPL signals. The annealed film's preferential emission of *right* circularly polarized light ($g_{lum} < 0$) correlates with the negative $g_{abs}$ at the red edge of the absorption spectrum, suggesting that the luminescence and absorption transitions involve polymer chains having the same type of chiral organization.[7,8]

The CD spectrum shows relatively strong bisignate (or "split") Cotton effects with a zero-crossing centered at the polymer chain's $\pi-\pi^*$ transition (around 441 nm in the UV–vis absorption spectra, Figure 1b). Such bisignate Cotton effects are expected from exciton coupling[10] between obliquely oriented neighboring transition dipole moments, suggesting that the polymer chains were aggregated in a

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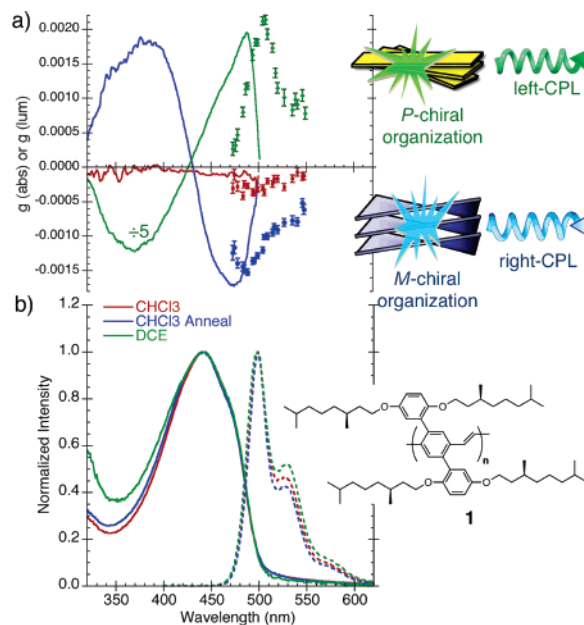‡ Eindhoven University of Technology.



**Figure 1.** (a) The *g* values of absorption (lines) and luminescence (markers), and (b) normalized absorption (solid lines) and fluorescence (dashed lines) of films spin-cast from 1,2-dichloroethane (DCE) and chloroform, before and after annealing. The $g_{abs}$ values of the DCE film were plotted at 20% of their actual values for easier comparison. Insets: schematic of the polymer backbone organizations[9] of chiral poly(*p*-phenylenevinylene), **1**, and their circularly polarized luminescence (CPL).

chiral organization.[11] The annealed film's negative CD couplet[12] signified that the polymer had a predominantly *M*-chiral organization.

In contrast, when **1** was spin-cast from a less polar solvent,[13] 1,2-dichloroethane (DCE), the resulting film emitted predominantly *left* circularly polarized light ($g_{lum} > 0$), which was opposite to the luminescence polarization of the annealed film spin-cast from chloroform. Correspondingly, the film's positive CD couplet suggested that it had a *P*-chiral organization.[14]

To investigate the origin of the films' organization-dependent CPL, we examined the corresponding self-assembled aggregate solutions. We measured the CPL of the polymer dissolved in chloroform and 1,2-dichloroethane (Figure 2a). Compared to CHCl₃, DCE is a "poorer" solvent for the polymer, allowing the polymer chains to aggregate and self-assemble in solution. In DCE, the polymer exhibited *left* CPL, consistent with the corresponding spin-cast film (Figure 1a). Thus, the luminescence polarization was transferred from the solution state into the film state by directly spin-casting the DCE aggregate solution. During the spin-coating process, the rapid evaporation of solvent kinetically trapped the polymer in the chiral organization existing in the solution. Ad-
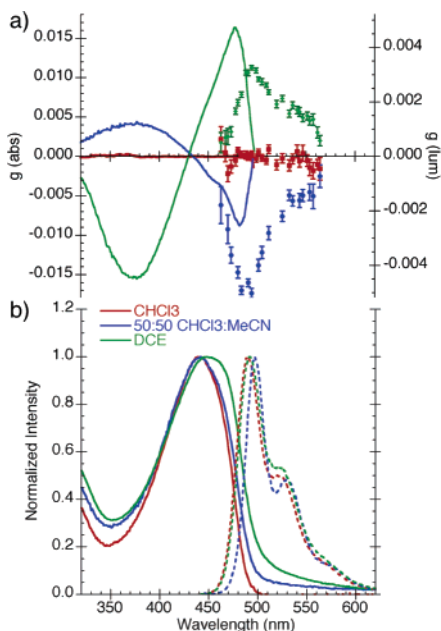
**Figure 2.** (a) The *g* values of absorption (lines) and luminescence (markers), and (b) normalized absorption (solid lines) and fluorescence (dashed lines) of solutions of **1**.

ditionally, the CD spectrum of the aggregate solution suggested a *P*-chiral organization, consistent with the film spin-cast from DCE.

In the "good" nonpolar solvent, chloroform, the polymer did not aggregate and self-assemble; therefore, the solution's fluorescence was not circularly polarized at all. Since it has been observed that the polymer aggregates in poorer solvents, a very polar solvent,[13] acetonitrile, was added to the nonpolar chloroform solution to induce self-assembly. In a polar 50:50 solvent mixture of CHCl₃ and MeCN, the polymer displayed preferential emission of *right* CPL and a negative CD couplet, both of which appear similar in shape to those exhibited by the annealed film.[15] Therefore, the chiral architecture in the annealed film is likely the same type of organization existing in the 50:50 CHCl₃:MeCN solution aggregates.

Solvent-induced inversions of CD spectra have been previously described in other π-conjugated polymer aggregate solutions.[9,16] Here, we have shown that the chiral organizations induced in *solution* can be brought to expression in the PPV *film*, ultimately affecting one of its main functional properties: light emission. This is not trivial since the luminescence from a PPV film originates predominantly from excitations that have migrated from the bulk to chain segments with longer-than-average effective conjugation lengths,[17] which may be in different environments than those of the absorbing chromophores.[8] The fact that the circular polarizations in luminescence and long-wavelength absorption were of the same sign in *both* the films and the corresponding solutions suggests that the molecular organizations observed in the solutions were also imposed on the luminophores in the polymer films.

In conclusion, the observation of fluorescence with opposite polarizations from films and solutions of the same chiral polymer exemplified the dynamic transfer of organization and functional properties from solution to the solid film. This demonstration

magnifies the importance of processing effects on a polymer film's functional properties.

**Supporting Information Available:** Details of experimental procedures, annealing experiments, CPL, CD, UV–vis absorption, fluorescence, and fluorescence quantum yield measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA063027C