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Giant Chiroptical Properties in Thin Films of a Chiral Indaceno[1,2-*b*:5,6-*b'*]Dithiophene-Based Organic Dye

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ABSTRACT

We report a new chiral indaceno[1,2-*b*:5,6-*b'*]dithiophene *bis*-thiophenylpropynone (**IDT-TPO**) dye exhibiting very noticeable chiroptical properties in thin films. While freshly prepared samples are ECD-silent, aging triggers a giant dichroic response, with ellipticity values reaching approximately 18,000 mdeg, among the highest reported to date for thin films of chiral organic dyes as neat materials. This amplification is accompanied by an unusual flattening of the main UV-Vis absorption band, and the combination of these effects produces very large g_{abs} values (exceeding 0.1). A thorough investigation, combining microscopy and spatially resolved chiroptical techniques with time-dependent density functional theory (TD-DFT) calculations, reveals that the intense chiroptical activity arises primarily from the consistent formation of right-handed three-dimensional (3D) helical architectures. Notably, the degree of circular polarization exhibits a non-monotonic dependence on film thickness: the maximum ECD intensity was found for a thinner film, rather than for the thickest one. This behavior is particularly promising for optoelectronic applications requiring efficient chiroptical responses in relatively thin active layers.

1 | Introduction

The systematic control of molecular and supramolecular chirality in synthetic organic materials, including π -conjugated systems, has started only in the last few decades [1, 2], but it has already allowed for the development of new cutting-edge technological applications, made possible by the unique properties of chiral organic materials [3–5].

Besides inherently chiral systems [6–8], the possibility of decorating an achiral π -conjugated chromophore with countless enantiopure chiral groups [9], which endow the materials with the desired technological features, leads to an unlimited variety of candidate components of active layers in organic devices [10–12]. The aggregation processes which take place during thin

film preparation further widen the chemical and structural space spanned by self-organized systems [13–15]. Researchers have only begun to explore this emerging field, in which applications such as circularly polarized (CP) OLEDs [16–19] and CP organic photodetectors [20–24], as well as spin polarization arising from chirality-induced spin selectivity (CISS) and its wide-ranging implications [25–30], are rapidly advancing toward technological maturity. There is currently a growing consensus that chiroptical and CISS properties are somehow interconnected [31, 32], although it should be emphasized that there is no single quantitative metric for “chiroptical activity,” which is intrinsically a spectral, that is, energy-dependent, property. However debatable, this notion would provide a unitary vision, suggesting that systems with strong electronic circular dichroism (ECD) signals may earn a chance to

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display significant spin polarization, which motivates further their interest.

In this regard, it is important to recall that the chiroptical signals of chiral organic materials in thin films can be either reciprocal or non-reciprocal [33, 34]. The former situation, which is the most common, is associated with a supramolecular organization showing a tilted stacking between adjacent π -conjugated chromophoric units under clockwise or counterclockwise orientation, favored by the presence of enantiopure appendages, which can be called three-dimensional (3D) chirality. It is responsible for *intrinsic* (or *true*) ECD signals, which genuinely stem from non-collinear magnetic and electric transition dipoles, following Rosenfeld's equation, and manifests itself with spectra that are identical on the two faces of the film. We typically refer to it as CDiso. On the contrary, purely *non-reciprocal* (or *apparent*) ECD signals are opposite for the two faces of the film and stem from the coupling of skewed (i.e., non-parallel and non-orthogonal) linear dichroism (LD) and linear birefringence (LB), which have an opposite sense of twist depending on the face from which they are viewed. For this reason, we generally refer to this second situation as the LDLB effect [35–38]. Following Tempelaar's theory [39], it can be associated with parallel and perfectly aligned molecular stacks of π -conjugated chromophoric units having two strong, non-degenerate and skewed electronic transition dipoles. Under this configuration, each of these aggregates exhibits skewed LB and LD lying along the stacking plane. Thus, the viewpoint of the observer (or the light direction) determines which of the two mirror image faces is chosen, defining a case of two-dimensional (2D) chirality [40].

However, even for chromophores that meet the electronic requirements of Tempelaar's model [39], it is not possible to predict a priori the presence of 2D or 3D chirality: depending on whether the molecules of a stack are perfectly aligned or adopt a constant tilt, non-reciprocal or intrinsic ECD signals can be obtained. At the same time, in the case of 2D chiral structures, it is not possible to predict which of the two faces adheres predominantly onto the substrate. The final outcome may depend on a variety of parameters, including the deposition technique adopted for the preparation of the film (e.g., drop casting, spin coating, and Langmuir techniques) and post-deposition treatments (solvent annealing, thermal annealing, or simple aging). The physicochemical properties of the substrate on which the film is deposited may also contribute, particularly through interfacial effects on molecular orientation and local anisotropies, although their influence is generally less pronounced than that of processing conditions. A further complication is that multiple aggregation pathways may also coexist in the same chiral system [41], resulting in thin films where both types of chirality coexist in different ratio, with ECD spectra exhibiting all possible intermediate situations between pure CDiso and pure LDLB [42–44].

It is worth pointing out that, in addition to CDiso and LDLB, other spurious contributions may be present in the ECD spectrum of thin films, associated with the interaction of their macroscopic linear anisotropies with the non-ideal characteristics of instrumental optics. However, by averaging the ECD spectrum of the same sample at different azimuth angles θ around the optical axis, it is theoretically possible to delete them. In all the

samples discussed below, we have observed perfectly conserved ECD spectra upon rotation at four different azimuth angles ($\theta = 0^\circ, 90^\circ, 180^\circ$, and 270°), thus excluding the occurrence of these artifactual signals.

Among π -conjugated building blocks, 4,9-dihydro-*s*-indaceno[1,2-*b*:5,6-*b'*]dithiophene (IDT) has emerged as a promising candidate for donor materials [45–52]. Its fused pentacyclic structure ensures coplanarity and extended π -conjugation [53–55]. The structural rigidity and the wide π -electron delocalization of IDT promote strong intermolecular interactions, enabling its organization into ordered structures. At the same time, IDT can be easily alkylated on the bridging carbon atoms (thanks to their CH acidity). Pd-catalyzed coupling reactions on the thiophene rings can extend π -conjugation and modulate the photophysical properties of the molecule. These degrees of freedom both concur to determine structure and optical properties of thin films. However, quite surprisingly, the chiroptical properties of chiral IDT-based materials are still almost entirely unexplored. To the best of our knowledge, only very recently the chiroptical investigation of a chiral IDT-carbo[6]helicene alternating copolymer [56] and a C_2 -chiral bifacial IDT-benzothiadiazole alternating copolymer [57] was reported, while we could not find any report on chiral IDT as a small organic molecule.

In this work, we developed a chiral indaceno[1,2-*b*:5,6-*b'*]dithiophene *bis*-thiophenylpropynone (**IDT-TPO**), decorated on the two bridging carbon atoms of the central IDT core with enantiopure (*S*)-3,7-dimethyl-1-octyl chains deriving from natural (–)- β -citronellol and elongated through an ethynyl bridge with a thienyl ketone on both sides of the IDT to provide the **IDT-TPO** shown in Figure 1. Thin films of **IDT-TPO** were prepared by drop casting and spin coating, and their chiroptical properties were investigated both in absorption (ECD) and in emission (circularly polarized luminescence, CPL).

Upon sample aging at room temperature, we observed the rapid growth of ECD signals, which reached the giant values of $\vartheta \approx 18,000$ mdeg and $g_{\text{abs}} \approx 0.3$ in 24 h. The rationalization of such unconventional properties was accomplished with the support of computational, microscopy, and spatially resolved chiroptical techniques (Figure 1).

2 | Results and Discussion

2.1 | Synthesis of Chiral IDT-TPO Dye and Characterization in Solution

Chiral **IDT-TPO** dye was easily synthesized with a five-step procedure, starting from commercially available IDT **1** (Scheme 1). In the first step, the IDT scaffold was alkylated at the two bridging carbon atoms with enantiopure alkyl chains, affording tetra-alkylated IDT **3** in good yield (56%). The two lateral thiophene rings were brominated at the α -position with *N*-bromosuccinimide to give **4** in 83% yield. Sonogashira coupling of **4** with trimethylsilylacetylene (**5**) afforded in excellent yield (92%) compound **6**, which was then desilylated under basic conditions to give bis-alkyne **7** (72% yield). Finally, **7** was subjected to a further Sonogashira reaction with thiophene-2-carbonyl chloride

The diagram illustrates three methods of thin film deposition:

- drop casting (DC):** A syringe deposits a drop of solution onto a substrate placed in a container. Arrows indicate the spreading of the drop.
- spin coating (SC):** A syringe deposits a drop of solution onto a rotating substrate. Arrows indicate the rotation and spreading of the film.
- ageing:** A substrate with a deposited film is shown under a clock, indicating the process of drying or curing over time.

The figure illustrates four optical measurement techniques using a schematic representation of a sample (orange oval) and a detector (blue rectangle) connected by a green line representing the light path.

- UV-Vis Absorption:** A light source (blue circle) emits light through a sample, which is then detected. The resulting absorption spectrum (Abs) is shown as a grey area plot with a peak around 400 nm.
- Fluorescence:** A light source emits light through a sample, which is then detected. The resulting fluorescence spectrum (Fluo) is shown as a grey area plot with a peak around 450 nm.
- Electronic Circular Dichroism (ECD):** A light source emits light through a sample, which is then detected. The resulting ECD spectrum is shown as a blue line plot with a peak around 400 nm.
- Circularly Polarized Luminescence (CPL):** A light source emits light through a sample, which is then detected. The resulting CPL spectrum is shown as a red line plot with a peak around 450 nm.

The diagram illustrates the experimental workflow for studying the time-dependent density functional theory (TDDFT) of the photochemical reaction in the reaction center (RC) of the photosynthetic reaction center (RC). The workflow is divided into four main stages:

- Time-dependent density functional theory functional theory:** Represented by a computer monitor and keyboard, indicating the theoretical calculations.
- Microscopy:** A microscope is used to observe the sample. Four panels of microscopy images are shown, labeled OM, POM, SEM, and AFM.
- SR-MMPi:** Synchrotron Radiation Microscopy (SR-MMPi) is used to study the reaction. A series of images are shown, labeled Abs, CD, LDLB, LD, LD', CB, LB, LB', and DI. The diamond logo indicates the use of synchrotron radiation.
- CPM:** Coherent Pumping Method (CPM) is used to study the reaction. Three panels of microscopy images are shown, labeled ECD, Abs, and g_{abs} .

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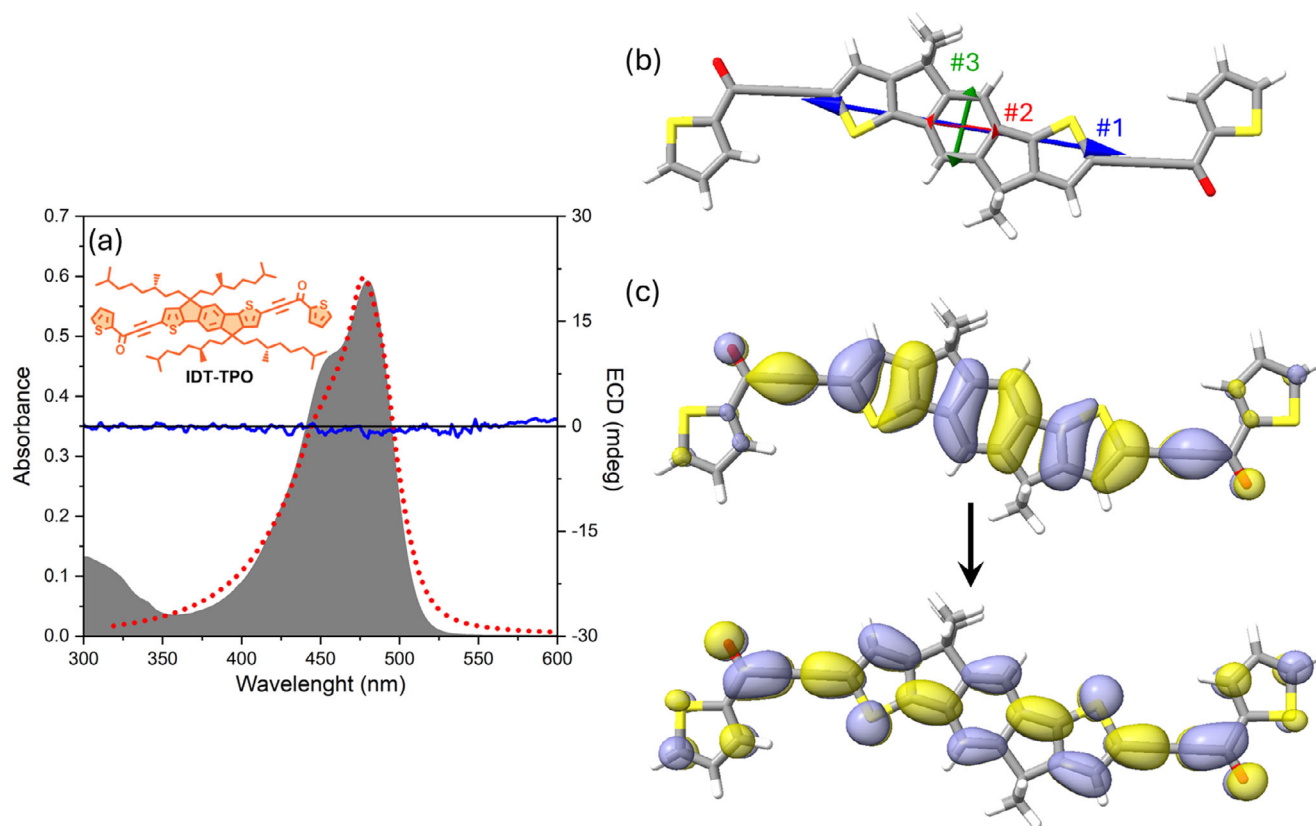


FIGURE 2 | Photophysical investigation of **IDT-TPO** in solution and calculation results. (a) UV-Vis absorption (gray profile) and ECD (blue line) spectra of **IDT-TPO** in CH_2Cl_2 (1.0×10^{-4} M) compared with the calculated vibronic spectrum for the first band (red dotted line); see text and Computational Section in [Supporting Information](#) for details. (b) Orientation of the electric transition dipole moments for the first three $\pi \rightarrow \pi^*$ transitions calculated for the truncated model of **IDT-TPO** at TDA-B3LYP/def2-TZVP//B3LYP-D3BJ/def2-SVP level, lowest energy conformer. (c) Natural transition orbitals (NTO) for the first $\pi \rightarrow \pi^*$ transition, same level of calculation (isovalue = 0.02).

(8) to afford **IDT-TPO** in 70% yield after column chromatography purification.

The preliminary photophysical characterization in CH_2Cl_2 solution (Figure 2) revealed the most prominent band between 400 and 500 nm ($\lambda_{\text{max}} = 479$ nm and a shoulder at 455 nm), attributable to the major $\pi \rightarrow \pi^*$ transition of the IDT chromophoric unit. A further smaller, more structured band is observed between 275 and 350 nm. The corresponding ECD spectrum was negligible (g_{abs} always $< 10^{-4}$), as expected on considering that the perturbation exerted by the enantiopure alkyl chains on the intrinsically achiral chromophore is very small. Accordingly, time-dependent density functional theory (TD-DFT) calculations were run on a truncated analog of **IDT-TPO**, with the alkyl chains replaced by methyl groups, to rationalize the absorption spectrum. Geometry optimizations, run at B3LYP-D3BJ/def2-SVP level in vacuo, highlighted the existence of several low-energy conformers due to rotamerism around the thiophene-C(=O), thiophene-C($\equiv$ C), and (C $\equiv$)C-C(=O) bonds (see Table S1). Excited-state calculations, run with TD-DFT at B3LYP/def-TZVP level, employing the Tamm–Dancoff approximation (TDA), predicted a single intense $\pi \rightarrow \pi^*$ transition above 450 nm, extended over the whole chromophore and oriented along its long axis (Figure 2b,c). Several other weaker transitions occurred below 350 nm, responsible for the structured absorption envelope in this region (Figure S1). For the following discussion, it is worth observing that the

second bright $\pi \rightarrow \pi^*$ transition is separated by ≈ 1 eV from the major one and almost perfectly aligned with this latter, while the third transition is separated by ≈ 1.15 eV from the major one and almost perpendicular to it (Figure 2b). The calculated electronic absorption spectra were very similar for all low-energy conformers, with differences within 7 nm between the transition wavelengths of the major band (0.04 eV in energy). The shoulder appearing on the short-wavelength side of the main absorption band is of vibronic origin; in fact, it could be reproduced by vibronic calculations (Figure 2a, red dotted trace), employing the Adiabatic Hessian After a Step (AHAS) approach implemented in the Excited State Dynamics (ESD) module [58, 59] of the Orca package [60, 61].

2.2 | Characterization of Chiral IDT-TPO Dye in Drop-Casted Thin Films

At this point, we moved on to analyze the behavior of chiral **IDT-TPO** in drop-casted thin films, obtained by depositing dropwise onto a glass substrate ~ 150 μL of a 2.0 mM solution of the dye in CH_2Cl_2 (hereafter referred to as **DC-1**). While the freshly prepared film displayed no ECD signal, after simply leaving it in the air for 24 h, a very strong chiroptical signal could be detected, as shown in Figure 3. The ECD spectrum (Figure 3a) revealed an asymmetric positive couplet between 350 and 550 nm, roughly

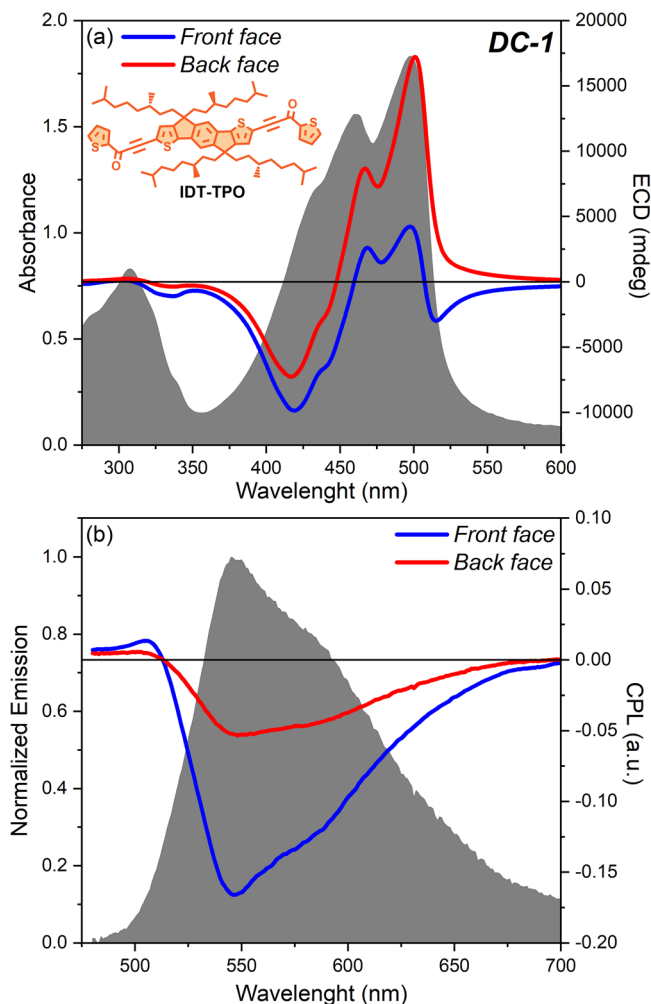


FIGURE 3 | Optical and chiroptical investigation of sample **DC-1** (drop casting, 150 μ L of a 2.0 mM solution of **IDT-TPO** in CH_2Cl_2) after 24 h of aging. (a) UV-Vis absorption (gray profile) and ECD spectra recorded for the front face (blue line) and the back face (red line). (b) Photoluminescence (gray profile) and CPL spectra recorded for the front face (blue line) and the back face (red line); excitation wavelength 365 nm.

corresponding to the main UV-Vis absorption band, with ellipticity values up to 18,000 mdeg ($\Delta A = 0.55$ absorbance units), one of the highest ever reported in the literature for thin films of chiral small organic molecule assemblies. To the best of our knowledge, similar ellipticity values have sometimes been achieved only by resorting to blends of achiral π -conjugated polymers with some enantiopure dopants and thermally annealed [62, 63], or to chiral plasmonic multicomponent systems, although this latter falls in a widely different context [64, 65]. The spectral profiles for the two faces of the drop-casted **IDT-TPO** films showed non-negligible differences: dissymmetry factors g_{abs} at 417 nm were -0.33 for the front and -0.25 for the back, while at 500 nm they were $+0.07$ for the front and $+0.29$ for the back (see also Figure S2b). In addition to the prominent positive couplet, a further small negative band at 520 nm was observed for the front face, but it was absent in the back face. Thus, the spectrum is dominated by intrinsic ECD signals, although some non-reciprocal contribution (LDLB) can be seen in the low-energy region, between 450 and 550 nm. This was even more evident when isolating the two contributions by taking the semi-sum and the semi-difference of the ECD spectra

measured for the two faces [34] (Figure S2a). Consistently with the ECD spectra, we observe very strong CPL, with significant non-reciprocal character (Figure 3b). We found a broad negative band between 500 and 675 nm, with maximum luminescence dissymmetry factor g_{lum} at 547 nm attaining the rare value of -0.34 for the front and -0.11 for the back (see also Figure S3). Intriguingly, the negative sign of the CPL band appears consistent with the lowest-energy band of the corresponding ECD spectrum only for the front face, where a small negative band is observed at 520 nm.

The remarkable chiroptical properties of **DC-1** were achieved without any post-deposition treatment other than standing in air for 1 day. This is a significant difference compared to all our previous chiral organic dyes, where the evolution toward strong dichroic signals was often made possible only by solvent or thermal annealing. To better emphasize such peculiar behavior of **IDT-TPO**, we also tried to study the evolution of the optical and chiroptical properties of **DC-1** as a function of solvent and thermal annealing. Surprisingly, keeping as-cast **DC-1** sample in a closed chamber saturated with CH_2Cl_2 vapors for 1 h did not reveal any appreciable variation: thin film remained in a disordered, ECD-silent state. A different evolution was observed when another as-cast **DC-1** sample was left in an oven at 100°C for 1 h: here, the appearance of dichroic signals was found (see Figure S4), but with a significantly lower intensity (ellipticity up to only 1500 mdeg) compared to those obtained by simple aging.

Interested in gaining more insight into this spontaneous process of aging, we studied its time evolution, especially in the first few hours after thin film deposition, through a combined spectroscopic and morphological investigation, as depicted in Figure 4. The ECD signal recorded for the back face of **DC-1** at 417 and 488 nm exhibited a nearly linear increase over time, reaching already after 210 min values of about -5200 mdeg and 8800 mdeg, respectively (Figure 4a). Both values correspond to more than 50% of the maximum intensity observed at the stationary point (after 24 h, see Figure 3a). At the same time, maximum absorbance showed a modest decrease in intensity (from 2.13 to 1.82, with a decrease of 15% in 210 min of aging) and a concomitant red shift, possibly associated with aggregation effects (Figure 4b). For completeness, full ECD and UV-Vis absorption spectra at different aging times (up to 210 min) are depicted in Figure S5 of Supporting Information. A first attempt to monitor the aging process of **DC-1** via optical microscopy (OM) under unpolarized white light was unsuccessful, since all images revealed no distinct texture. Therefore, OM measurements were repeated upon introducing a linear polarizer and a quarter-wave plate between the light source and the sample, in order to generate left-handed CP white light: in this case, images recorded at selected times (45, 70, 90, and 150 min, Figure 4c–f) revealed the growth of globular structures, which in time merged into larger clusters while new small ones became apparent.

To gain further insight into the origin of the strong chiroptical signals in aged **DC-1**, the sample aged 24 h was also subjected to spatially resolved chiroptical methods [66]. First, ECD images were acquired using the circularly polarized microscopy (CPM) technique [67], by processing two pictures of the same area backlit with right- and left-handed CP light at selected wavelengths (Figure 5). The four ECD 2D-maps shown in Figure 5 retrace

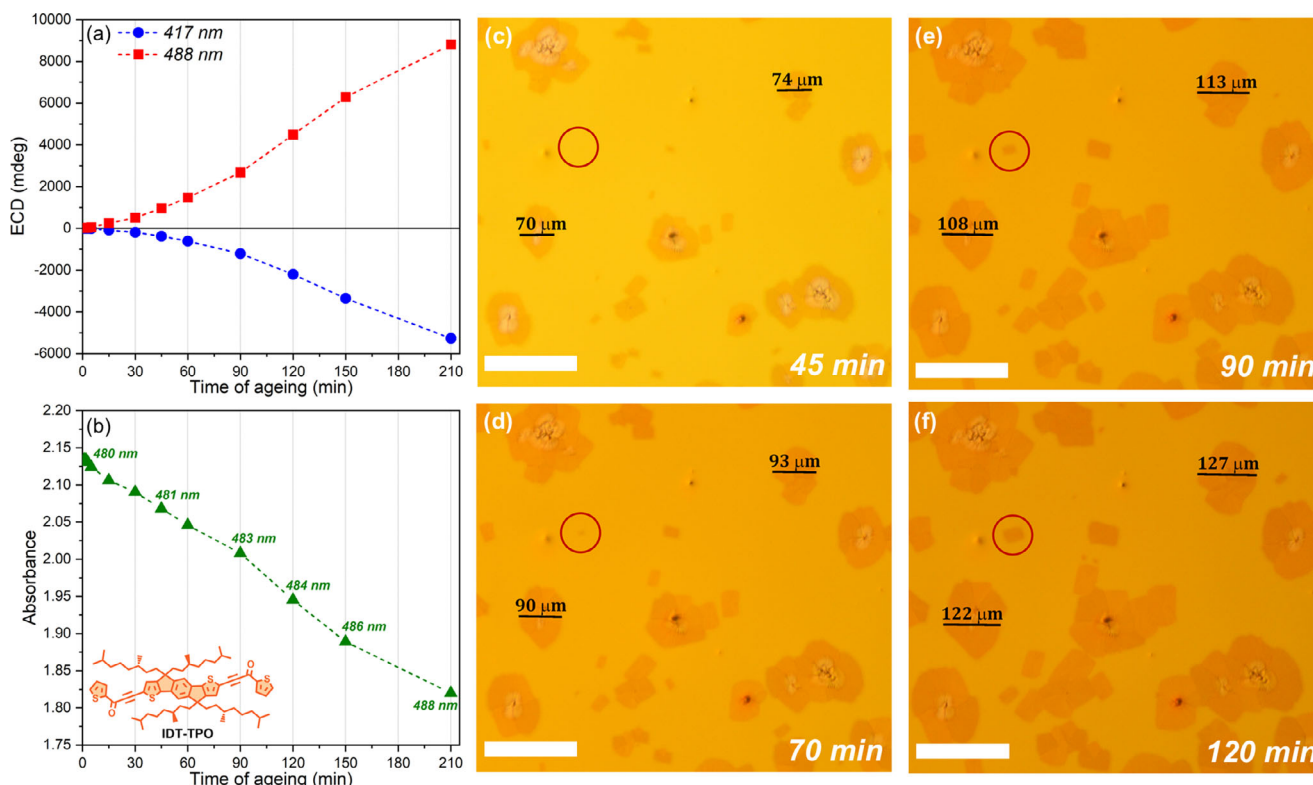


FIGURE 4 | Impact of aging on the (chiro)optical and morphological features of sample **DC-1** (drop casting, 150 μ L of a 2.0 mM solution of **IDT-TPO** in CH_2Cl_2). (a) ECD signal at 417 nm (blue points) and 488 nm (red points) recorded for the back face at different aging times (up to 210 min). (b) Maximum absorbance recorded at different aging times (up to 210 min); the wavelength of each measurement is indicated under each point. Data extracted from full spectra (see Figure S5). (c–f) OM images under left-handed CP white light at selected aging times: 45 min (panel c); 70 min (panel d); 90 min (panel e); and 150 min (panel f). The black circle highlights the appearance (at 70 min) and growth of a new glomerular feature that was not apparent at 45 min. For panels c–f: white scale bar = 200 μ m.

the same pattern of the absorbance 2D-maps (Figures S6a–S9a), indicating an ECD signal modulation with film thickness. This can be better appreciated by plotting, for the 2D-maps acquired at 434 nm, the local ECD signal of each spot as a function of the corresponding absorption: despite the remarkable dispersion of the points, a linear fit weighted by their density distribution revealed good correlations (Figure S10). However, beyond these differences, the ECD 2D-maps are consistent with the emergent ECD spectrum measured on a large sample area: at 500 nm, the positive dichroic signals in the colored regions are all more intense on the back than on the front face (Figure 5a,b), whereas at 434 nm, the opposite behavior occurs (Figure 5c,d). Also, we can observe that the ECD maps are consistently positive at 500 nm and negative at 434 nm.

Synchrotron radiation Mueller matrix polarimetry imaging (SR-MMPi) analysis of the same sample, carried out at the Diamond Light Source B23 beamline [68] (see Figure S11), allowed us to extract the 2D-maps of all the linear and circular contributions to the bulk ECD signal at 417 nm (Figure 6), although at lower spatial resolution. The 2D-map of CDiso (Figure 6b) showed a pattern rather similar to the one previously observed for the crude ECD map obtained via CPM, with spheroidal regions associated to weak (white areas) or more intense (blue areas) ECD signals. However, the same regions were also visible under unpolarized light in the corresponding absorbance 2D-map (Figure 6a), thus confirming that their occurrence was due to difference in optical

density. The sample also exhibited quite strong linear anisotropies (Figure 6d,e,g,h), but their coupling into LDLB term resulted in very small dichroic signals, with a clear predominance of spots with zero or weakly negative signals compared to those with weakly positive signals (Figure 6c).

Despite enormous differences in instrumentation and spatial resolution, CPM and SR-MMPi techniques led to a convergent conclusion: even locally, the intrinsic CDiso clearly dominates over the non-reciprocal LDLB. Moreover, the exceptionally large chiroptical signals observed in the macroscopic ECD spectrum seem to arise from homochiral 3D chiral structures homogeneously distributed across the film, apart from unavoidable variations in film thickness and, consequently, in optical density due to the drop-casting process. The reason for the relatively weak LDLB term lies in the electronic structure of **IDT-TPO** dye. As noticed above, the major electronic transition (S_0 – S_1) is well separated from the following ones, and the angle between electric transition dipole moments of various transitions is far from the ideal 45° necessary for optimal LD/LB coupling [39]. The shape of CDiso term is rationalized by assuming a stacking of dyes within a right-handed helical supramolecular structure, allowing for efficient exciton vibronic coupling [69, 70]. Still, short-range exciton coupling between purely electric transition dipoles provides an upper limit $< 10^{-2}$ for dissymmetry g_{abs} values (Figure 7a). Other reasons must then be invoked to justify the chiroptical response which is more than one order of magnitude

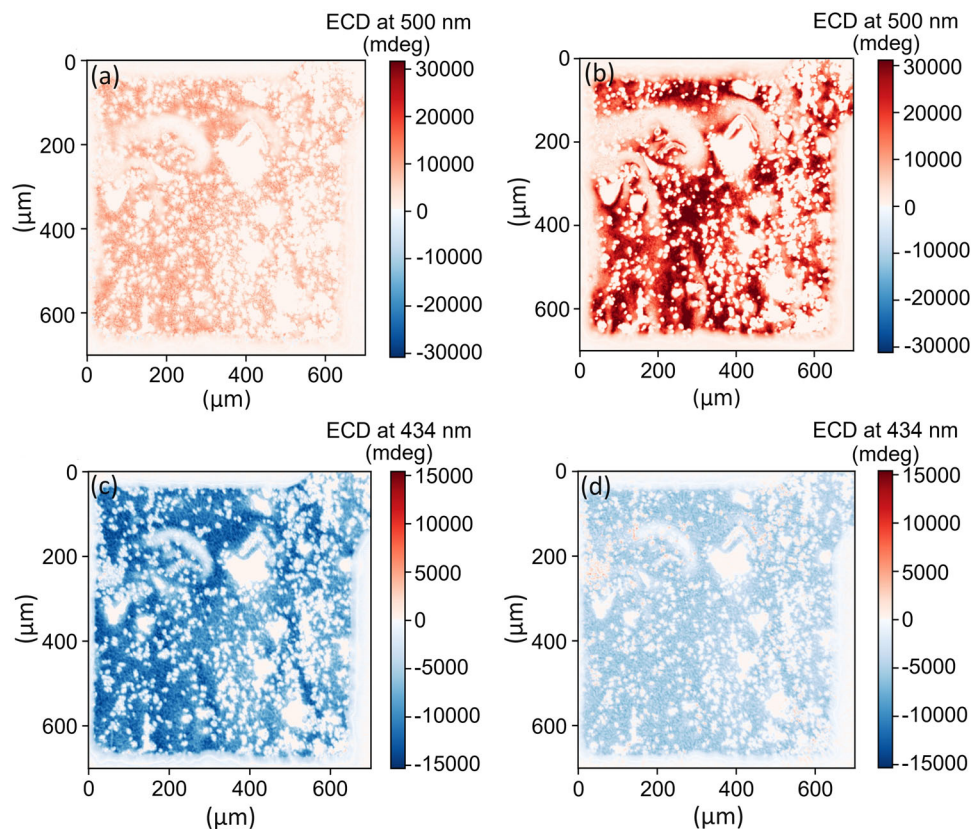


FIGURE 5 | ECD 2D-maps of sample **DC-1** (drop casting, 150 μL of a 2.0 mM solution of **IDT-TPO** in CH_2Cl_2) after 24 h of aging, acquired through the CPM technique. (a) ECD intensity at 500 nm for the front face and (b) for the back face versus x - y coordinate. (c) ECD intensity at 434 nm for the front face and (d) for the back face versus x - y coordinate.

larger. We can rule out the contribution of electric–magnetic couplings [71, 72], because the intrinsic magnetic transition moment for the S_0 - S_1 transition is small (below 10^{-20} cgs) and arranged perpendicularly to the molecular plane, yielding a negligible intermolecular coupling with electric moments in the supramolecular stack we hypothesized (Figure 7b). Rather, we invoke the role of large, ordered 3D aggregates capable of constructive long-range couplings (Figure 7c), as those occurring for instance in cylinder blue phases [62].

A possible alternative explanation is that the giant ECD values reflect a macroscopic artifact from the superposition of randomly oriented LD/LB domains along z direction, rather than being a manifestation of 3D chirality. Such a mechanism would require stacking several optically anisotropic layers perpendicular to the surface, each with a different orientation of its optical axes. The fact that the SR-MMPi depolarization index (DI, Figure 6i) stays close to 1 across the whole scanned area cannot entirely rule out the existence of a layered structure along z ; this is a well-known intrinsic limitation in the polarimetric analysis of anisotropic thin films, for which no straightforward solution is available. However, this possibility can be excluded based on a geometric argument. Since the diameter of the globular structures observed for **DC-1** in the OM images of Figure 4 is on the order of 100 μm , whereas the film thickness is typically below 1 μm , the large dimensions of the domains relative to the film thickness make significant z -axis layering unlikely.

2.3 | Characterization of Chiral IDT-TPO Dye in Spin-Coated Thin Films

After the investigation on a drop-casted film, we moved on to the standard technique for preparing homogeneous thin films on the lab-scale: spin coating. Six different samples were obtained by depositing, under optimized conditions (see Supporting Information for details) 100 μL of **IDT-TPO** solutions in CH_2Cl_2 at increasing concentrations: 5.0 mM (**SC-1**), 10 mM (**SC-2**), 15 mM (**SC-3**), 20 mM (**SC-4**), 25 mM (**SC-5**), and 30 mM (**SC-6**). A progressive increase in thickness from **SC-1** to **SC-6** was qualitatively inferred from the increasing maximum absorbance of the as-cast samples.

Since all as-cast samples were ECD-silent, we first monitored their evolution upon aging (Figures S12a–S17a). A progressive increase in the dichroic signals was systematically observed, although the time required to reach the stationary point increased with film thickness: from 45 min for **SC-1** to 120 min for **SC-6**. This is a much shorter time than was required for **DC-1** sample. For the six spin-coated films, marked flattening of the most prominent absorption band was observed during aging, becoming more pronounced with increasing thickness (Figures S12b–S17b). Absorption flattening is a well-known phenomenon [73], occurring in thin films when absorbing particles are not uniformly distributed across the total surface of the substrate illuminated by the instrumental optical beam [74]. The phenomenon has

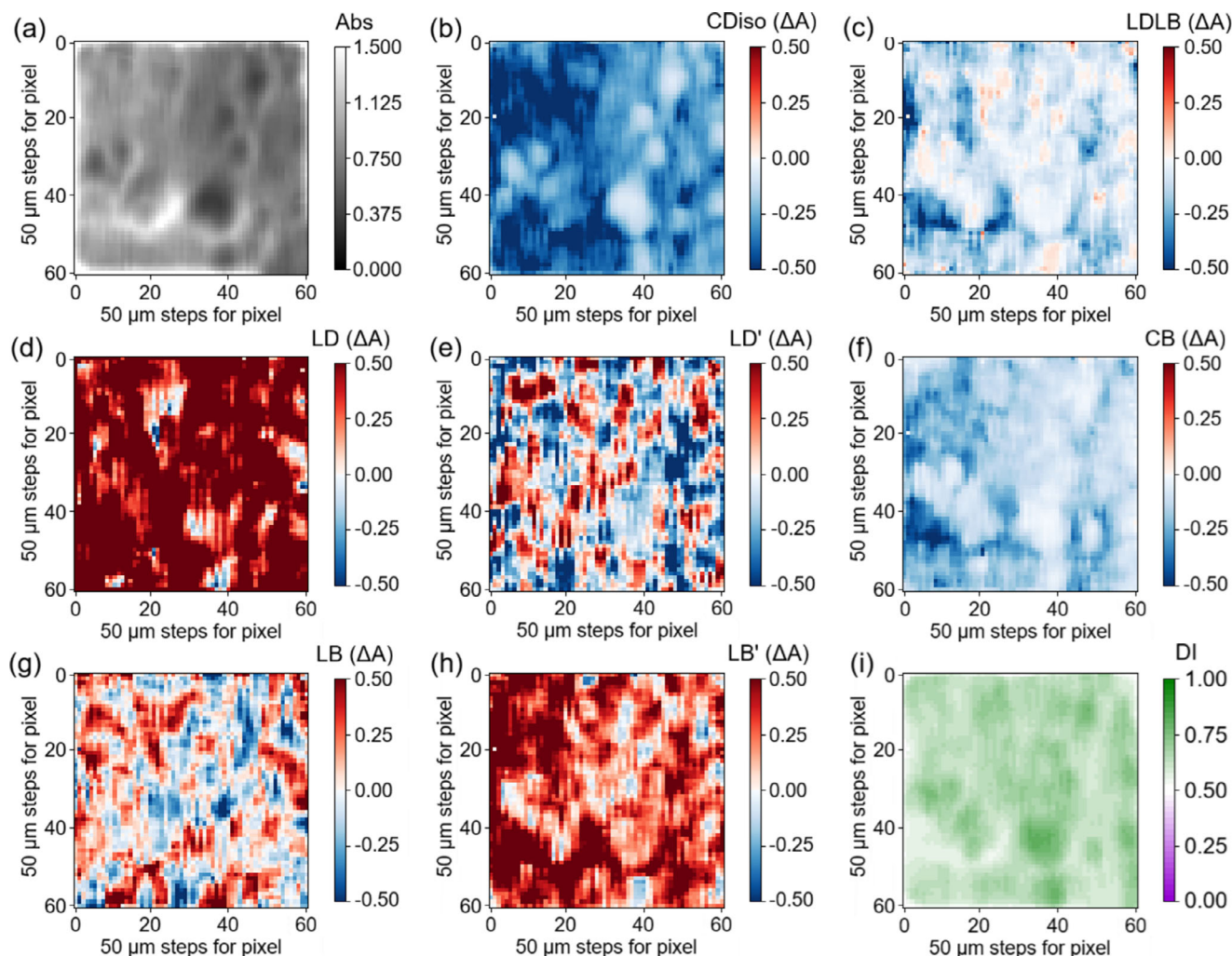


FIGURE 6 | SR-MMPi investigation of sample **DC-1** (drop casting, 150 μL of a 2.0 mM solution of **IDT-TPO** in CH_2Cl_2) after 24 h of aging, scanning for the front face of the sample a 60×60 grid array area at 50 μm steps with a beam-light diameter of 50 μm . Calculated 2D-maps of the contributions to the bulk ECD signal at 417 nm versus x - y coordinate: (a) absorbance (Abs); (b) intrinsic circular dichroism (CDiso); (c) LDLB term; (d) linear dichroism (LD); (e) 45° linear dichroism (LD'); (f) circular birefringence (CB); (g) linear birefringence (LB); (h) 45° linear birefringence (LB'); and (i) depolarization index (DI). These calculated 2D-maps were extracted from the corresponding measured maps of Mueller matrix elements M_{ij} (see Figure S11) through the analytic inversion method.

been well documented for different classes of inhomogeneous samples [75, 76], although it is not commonly encountered for spin-coated thin films. The maximum absorbance at the steady state decreased by approximately 40% for **SC-1** and up to roughly fivefold for **SC-6**, compared to the corresponding as-cast samples. It is reasonable to hypothesize that the gradual aggregation of **IDT-TPO** molecules during the aging process may lead to the generation of some spots of thin film with higher optical density and others with lower optical density, which manifests macroscopically as an absorption flattening. However, this behavior is concomitant with the enhancement of the chiroptical response, which is instead due to a gradual structural evolution of thin films from a disordered state to the final chiral aggregates of π -conjugated chromophores. Therefore, optical density inhomogeneity responsible for the absorption flattening is a consequence of the evolution of the system into chiral structures. Both these phenomena contribute to generating exceptionally strong g_{abs} factors, exceeding 10^{-1} for all thicknesses at the end of aging time (Figures S18b–S23b). It must be recalled, however, that absorption

flattening is also accompanied by distortion of ECD signals [75, 76].

The most striking features of spin-coated samples emerged from their chiroptical characterization at the stationary state, as shown in Figure 8. Starting from the thinnest sample (**SC-1**), ECD spectrum displayed for both faces an asymmetric positive couplet between 350 and 550 nm, corresponding to the main UV-Vis absorption band (Figure 8a). The shape of this purely intrinsic dichroic signal closely recalls the one previously observed for **DC-1** (Figure 3a), suggesting a similar solid-state organization composed of right-handed 3D chiral structures. A comparable ECD profile was also found for **SC-2** and **SC-3** (Figure 8b,c), although a slight mismatch between front and back face indicates the uprise of a sizable non-reciprocal contribution. From **SC-4** onward, ECD profile progressively changed with increasing thickness, leading in **SC-5** and **SC-6** to the appearance of new bands and very different spectral shapes for the two faces (Figure 8d–f). It is also worth emphasizing that **SC-5**, despite

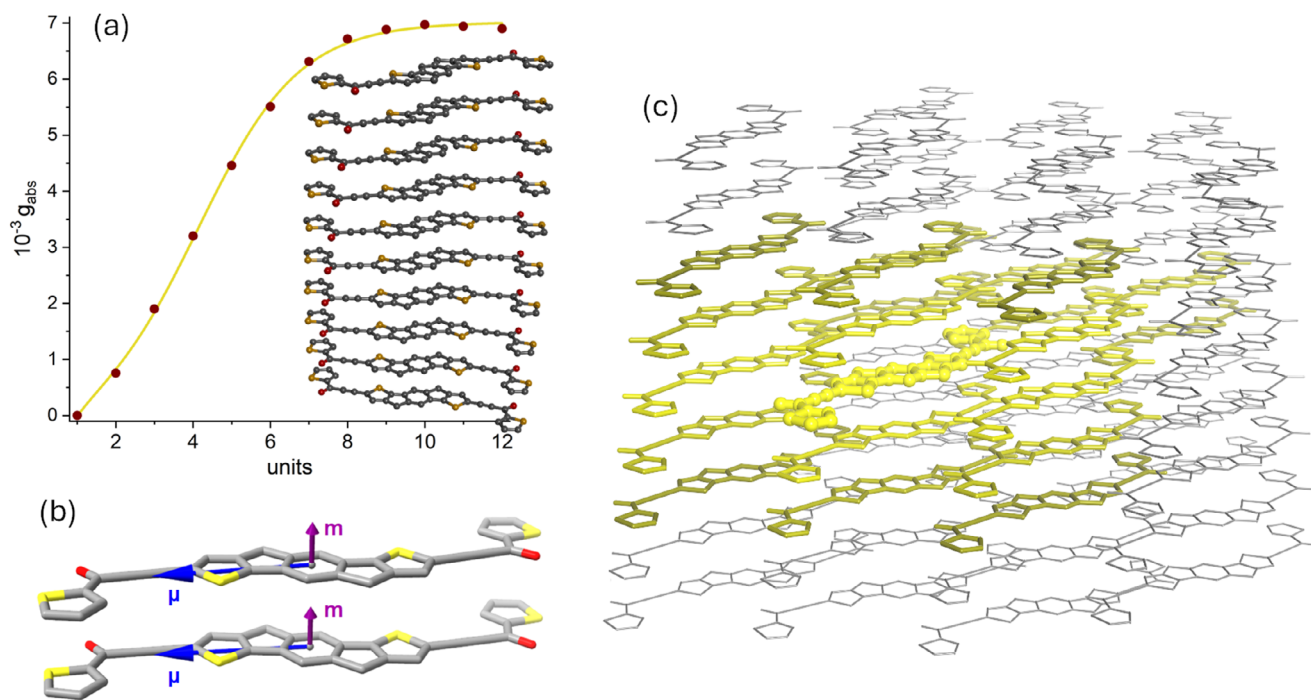


FIGURE 7 | Pictorial representation of three possible mechanisms for generating large exciton ECD values in the aggregated phases of **IDT-TPO**. (a) In 1D helical stacks of dyes, the couplet intensity soon reaches a plateau. See Computational Section in Supporting Information for details on how the plot was generated. (b) The intermolecular coupling between electric (blue) and magnetic (magenta) transition moments is weak for parallel-stacked dyes. (c) Large 3D aggregates with exciton interactions spanning dozens of dyes.

presenting an optical density very similar to **DC-1** (both have roughly the same maximum absorbance as as-cast samples), after the aging process shows very different optical and chiroptical properties (see Figure 8e vs. Figure 3a). This further confirms the crucial role played by the deposition technique in the evolution toward the most stable solid-state configuration. Upon isolating intrinsic CDiso and non-reciprocal LDLB terms in each spectrum of spin-coated samples (Figures S18a–S23a), we found that the CDiso profile remained essentially unchanged regardless of thickness. In contrast, the LDLB contribution increased steadily with thickness, as expected due to its quadratic dependence on the path length [39], exerting an increasingly dominant effect on the overall emergent ECD spectrum ($\rho = \int \text{LDLB} / \int \text{CDiso}$ grew from 0.53 in **SC-1** to 2.68 in **SC-6**, Figure 8g). Meanwhile, given the variable contribution of CDiso and LDLB depending on the film thickness, the emergent maximum dissymmetry factor $g_{\text{abs}}^{\text{MAX}}$ follows an apparently erratic trend (Figure 8h).

A more detailed study was performed on sample **SC-2**, which exhibited the strongest chiroptical response in the entire series. As we did for **DC-1** above, we compared the impact of aging with that of other post-deposition treatments: solvent annealing (CH_2Cl_2 vapors for 1 h) and thermal annealing (100°C for 1 h). In both cases, a different situation from simple aging was observed: a more pronounced flattening of the main band in the UV-Vis absorption spectrum and, more importantly, a diverse spectral profile in the ECD spectrum, characterized by dichroic signals with a greater non-reciprocal contribution but significantly weaker intensity (see Figures S24 and S25). This suggests that the **SC-2** sample can follow multiple aggregation pathways, with high temperatures playing a crucial role in

directing the evolution of **IDT-TPO** molecules toward a solid-state arrangement different from that achieved through simple aging. A further test was then carried out, leaving **SC-2** for 24 h in a closed box cooled to 0°C : this time, the resulting UV-Vis absorption and ECD spectra (Figure S26) were similar to those measured during the aging process before reaching a steady state. It follows that low temperatures do not alter the aggregation pathway of the system, but simply slow down the evolution toward the stationary state. It is also worth noting that, within the aforementioned temperature range, **IDT-TPO** does not exhibit any phase transition or glass transition that could potentially influence the aggregation modes in sample **SC-2**, as confirmed by differential scanning calorimetry (DSC) measurements (Figure S27). Finally, no significant variations in the ECD spectrum were observed when the aging of **SC-2** was performed either inside a desiccator or under an argon atmosphere (Figures S28 and S29), thereby excluding any significant role of moisture or oxygen in the aging process.

Returning to the conditions responsible for the strongest chiroptical response (that is, aging at room temperature for 50 min), **SC-2** was further examined through microscopy and spatially resolved chiroptical investigation (Figure 9). Similarly to **DC-1**, OM image of **SC-2** recorded under unpolarized white light revealed no distinct texture (Figure 9a). However, by repeating the same measurement under linearly polarized white light, a faint contrast appeared, with darker and lighter spots of a few tens of microns randomly distributed across the surface (Figure 9b). The contrast became much more pronounced under crossed linear polarizers, where the same pattern appeared as linearly birefringent structures standing out on a dark background (Figure 9c). The field-emission scanning electron microscopy

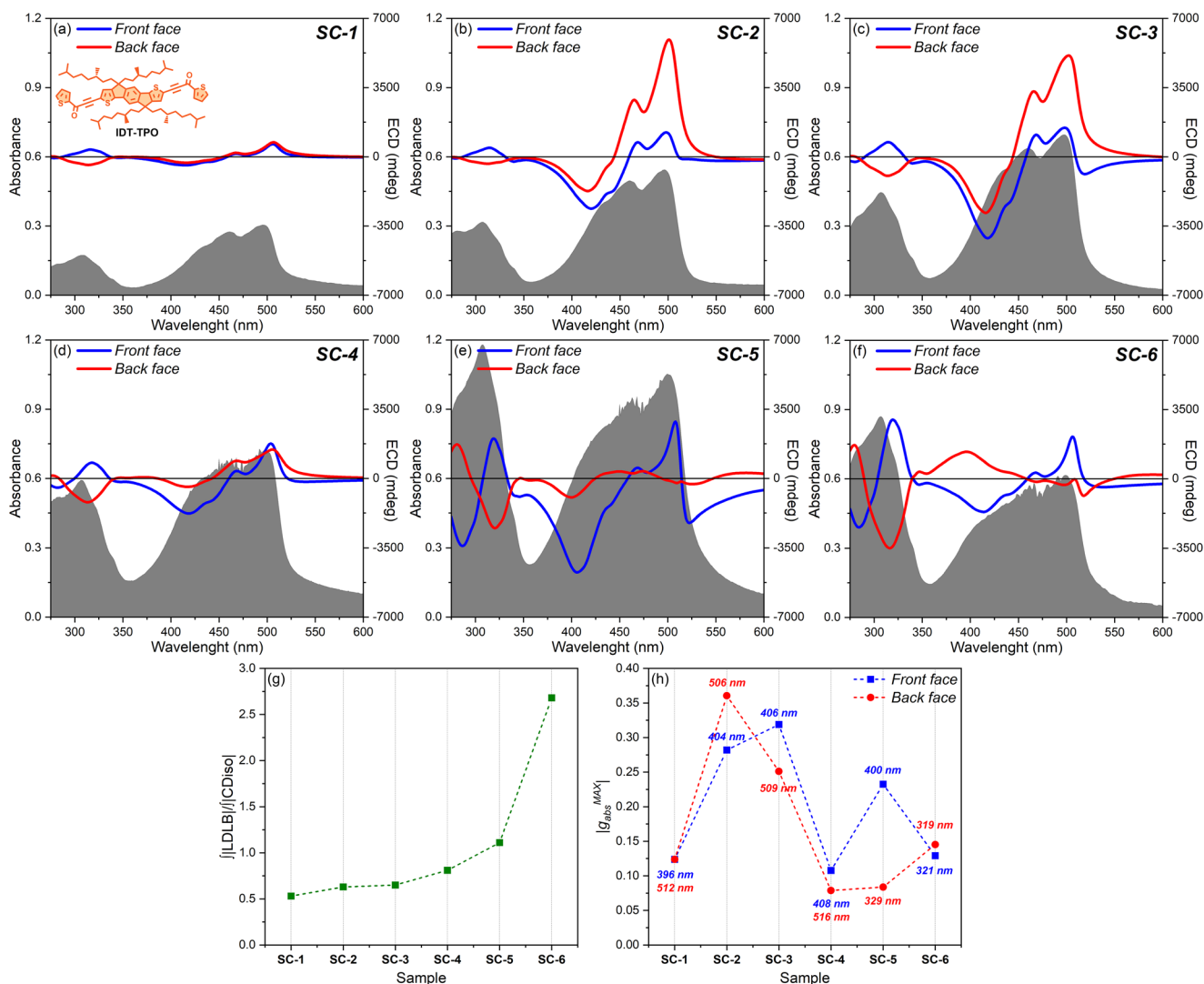


FIGURE 8 | Optical and chiroptical investigation of spin-coated thin films of **IDT-TPO** with different thickness, obtained by depositing 100 μL of **IDT-TPO** solutions in CH_2Cl_2 at increasing concentrations, at the end of aging time. UV-Vis absorption (gray profile) and ECD spectra recorded for the front face (blue line) and the back face (red line) of samples: (a) **SC-1** (5.0 mM solution, 45 min of aging); (b) **SC-2** (10 mM solution, 50 min of aging); (c) **SC-3** (15 mM solution, 60 min of aging); (d) **SC-4** (20 mM solution, 90 min of aging); (e) **SC-5** (25 mM solution, 105 min of aging); (f) **SC-6** (30 mM solution, 120 min of aging). In all cases, the aging time corresponds to reaching a stationary state. (g) Calculated $\rho = |LDLB|/|CDiso|$ ratio of each sample. (h) Maximum dissymmetry factor $|g_{abs}^{MAX}|$, recorded for the front face (blue points) and back face (red points) of each sample; wavelengths of the measurements are indicated in the graph.

(FE-SEM) image (Figure 9d) revealed a relatively homogeneous and continuous surface over large areas, without evident cracks or aggregates, consistent with the observations from polarized optical microscopy (POM). At higher magnification (Figure 9d, inset), the sample appeared densely packed, although sub-micrometric pinhole-like defects could be observed locally, suggesting the presence of limited solvent evaporation-induced porosity. Atomic force microscopy (AFM) highlighted the presence of an anisotropic surface morphology, characterized by elongated fibrillar and lamellar-like domains radially distributed over the scanned area (Figure 9e). These structures generated a pronounced height contrast, indicative of local variations in molecular organization and packing within the sample. Furthermore, AFM profilometry along a section perpendicular to a steel scalpel scratch (Figure 9f) indicated a thickness of approximately 400 nm for sample **SC-2**.

The spatially resolved (chiro)optical investigation, carried out using the CPM technique, mapped a different area than that used for the OM images, yet revealed a very similar texture. In particular, the UV-Vis absorption 2D-map at 500 nm (Figure 9g) showed that the darker and lighter spots described above correspond to regions with slightly different optical densities (absorbance ranging from about 0.69 to 0.74). In contrast, the variations were much more pronounced in terms of local dichroic signals. The corresponding ECD 2D-map, acquired for the back face at the same wavelength (Figure 9h), displayed spots with very strong positive signals (up to $\vartheta \approx 15,000$ mdeg, red areas) coinciding with regions of higher optical density, alternated with areas showing no signal or weak negative ones (white/blue areas), corresponding to regions with lower optical density. This behavior is also reflected in the corresponding dissymmetry factor 2D-map (Figure 9i), where local g_{abs} values up to +0.8 were recorded.

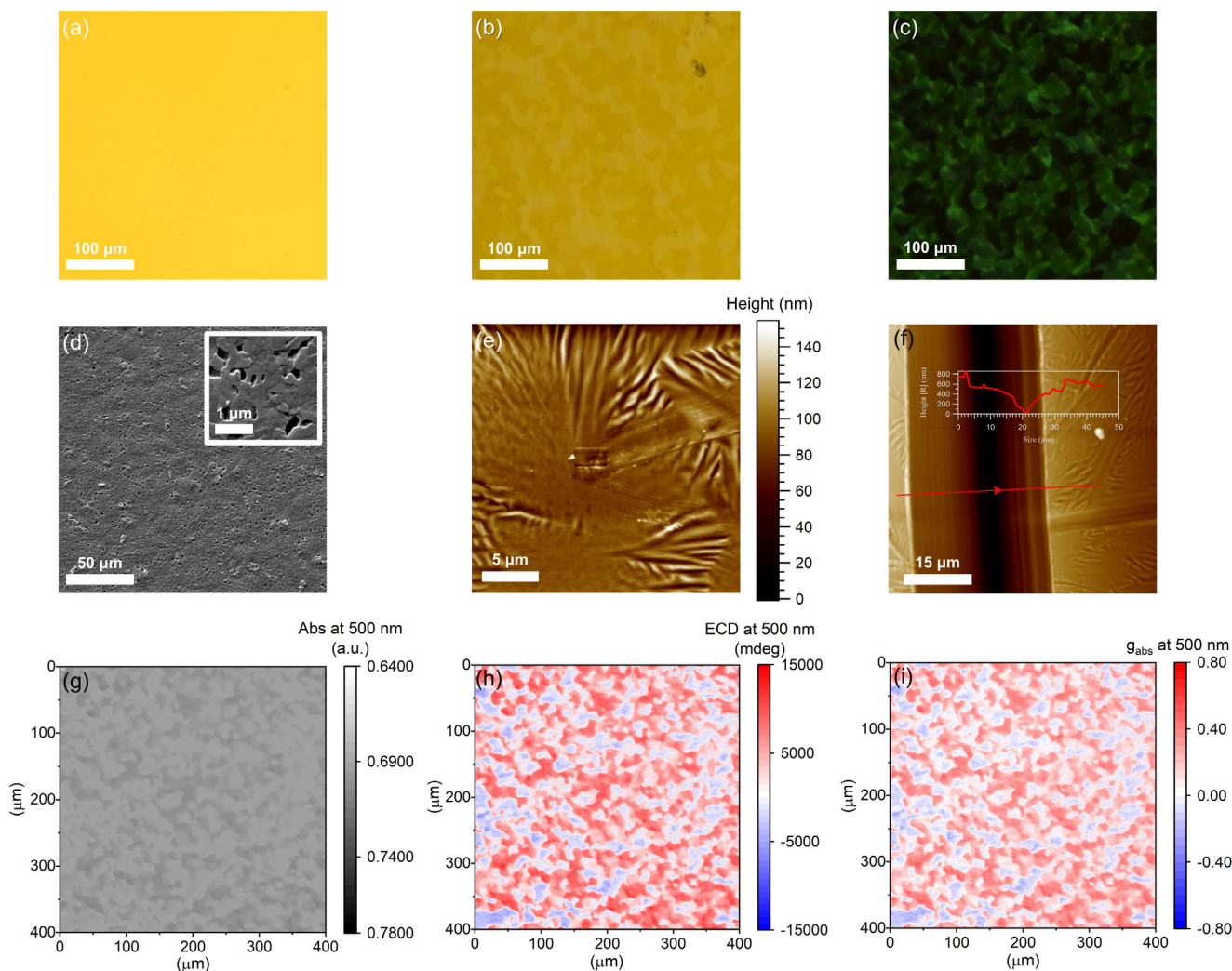


FIGURE 9 | Microscopy and spatially resolved (chiro)optical investigation of sample **SC-2** (spin coating, 100 μL of a 10 mM solution of **IDT-TPO** in CH_2Cl_2) after 50 min of aging. OM images acquired under: (a) unpolarized white light; (b) linearly polarized white light; and (c) crossed linearly polarized filters. (d) FE-SEM image acquired using the secondary electron detection mode (zoom-in of the same area in the top-right inset). (e) AFM image and (f) AFM profilometry of a section perpendicular to a steel scalpel scratch, used for the evaluation of thickness (~ 400 nm). 2D-maps, acquired through CPM technique, of: (g) absorbance intensity at 500 nm versus x - y coordinate; (h) ECD intensity at 500 nm for the back face versus x - y coordinate; and (i) g_{abs} value at 500 nm for the back face versus x - y coordinate.

CPM analysis of **SC-2** would suggest that the intense positive ECD signal at 500 nm observed at the macroscopic level predominantly originates from 3D chiral structures, responsible for the strong intrinsic CDIs. The majority of these supramolecular structures, occurring in the strongly positive regions of the 2D-map with higher optical density, involve a right-handed helicity, whereas a smaller population of left-handed structures is responsible for the weaker negative spots with lower optical density. These results would indicate a correlation between ECD signals and absorbance significantly different from that found for **DC-1**, suggesting a dependence of the sense of helicity of 3D chirality as a function of the optical density of the material. These 3D chiral architectures emerge from a background that contributes only a minor non-reciprocal LDLB, presumably associated with the white/weak colored areas of the map. This finding further confirms the peculiar behavior of **IDT-TPO**, capable of generating strong *reciprocal* ECD signals, with respect to other chiral dyes recently investigated by our group, such

as 1,4-phenylene-bis(thiophenylpropynone) (**PTPO**) [37] or bis-anthracenylthiophenyl-1,4-diketo-3,6-dithienylpyrrolo[3,4-*c*]pyrrole (**BAT-DPP**) [38], which manifest strong *non-reciprocal* ECD signals allied to LDLB term. Apart from obvious differences in the solid-state organization, the behavior of **IDT-TPO** appears to be associated with its conjugated skeleton, which is endowed with electronic transitions with electric dipole transition moments either aligned or almost orthogonal to its long axis, thus poorly suited for large LDLB.

3 | Conclusions

In conclusion, we have investigated a new chiral **IDT-TPO** dye, exhibiting remarkably strong chiroptical properties in thin films. Although all as-cast samples were initially ECD-silent, an increase in dichroic signals was consistently observed upon simple aging, without any post-deposition treatment, reaching

the exceptionally high ellipticity value of 18,000 mdeg at 500 nm ($\Delta A = 0.55$, $g_{\text{abs}} = 0.29$) in the drop-casted sample **DC-1**. These signals, dominated by the intrinsic contribution ($\rho = |\text{LDLB}|/|\text{CDiso}| < 1$), mostly originate from 3D chiral structures of the same right-handed helicity, homogeneously distributed within local domains of a few tens of microns. The enhancement in the dichroic response was accompanied by a flattening of the main UV-Vis absorption band, leading to very high g_{abs} values, consistently exceeding 10^{-1} . In the spin-coated series, there is a thickness-dependent coexistence of CDiso and LDLB, leading to circular polarization which does not scale directly with film thickness: it increases up to a maximum (found for sample **SC-2**) and then decreases. The possibility of achieving such strong chiroptical signals without relying on excessively thick films is particularly appealing for optoelectronic applications, where device performance typically deteriorates with increasing thickness.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are openly available in the repository Zenodo at [10.5281/zenodo.21157771](https://doi.org/10.5281/zenodo.21157771).

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.

Supporting File: agt270402-sup-0001-SuppMat.pdf.