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Chiroptical Properties of Glucose-Substituted Poly(p-phenylene-ethynylene)s in Solution and Aggregate State

Gennaro Pescitelli,[†] Omar Hassan Omar,[‡] Alessandra Operamolla,[§] Gianluca M. Farinola,[§] and Lorenzo Di Bari*,[†]

[†]Dipartimento di Chimica e Chimica Industriale, Università di Pisa, via Risorgimento 35, I-56126 Pisa, Italy
[‡]CNR-ICCOM Istituto di Chimica dei Composti OrganoMetallici, Via Orabona 4, I-70126 Bari, Italy
[§]Dipartimento di Chimica, Università degli Studi di Bari Aldo Moro, Via Orabona 4, I-70126 Bari, Italy

S *Supporting Information*
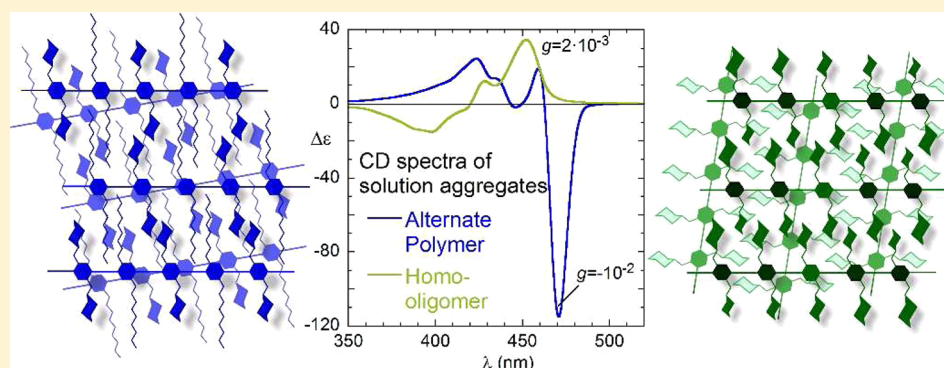
ABSTRACT: The aggregation behavior of two D-glucose-substituted phenyleneethynylenes, an alternate copolymer (**AP**) and a homooligomer (**HO**), has been investigated by means of UV–vis absorption, circular dichroism (CD) and fluorescence spectroscopy. CD reveals superior capability to detect the early stages of aggregation and to provide information about aggregate geometries. The multiband CD spectrum of the **AP** and of analogous chiral PPEs is rationalized on the basis of the exciton coupling between vibronic transitions localized on proximate portions of the chromophoric chains.

Conjugated organic polymeric and oligomeric semiconductors[1] have attracted much interest during the past decades because of their wide applications as active materials in new generation optoelectronic devices. These include low energy–consumption displays[2] and lighting sources,[3] flexible transistors,[4] organic solar cells[5] and highly specific biological and chemical sensors.[6] The fundamental properties of conjugated polymers, such as light absorption and emission, charge and exciton transport, depend not only on their molecular structure, but also on the supramolecular interactions and the nano/mesoscale organization in the solid state.[7] While good intermolecular communication, which takes place through π-stacking, is mandatory for efficient charge transport in organic polymer-based devices,[8] too strong interactions may lower the diffusion length of excitons and significantly reduce luminescence quantum yields.[9] The control of polymer interchain spacing and/or alignment is a practicable strategy to prevent unwanted interactions.[10] The introduction of stereodefinite chiral elements in conjugated polymers[11–13] has been exploited as a structural modification able to generate a regular twist or oblique angle between proximate chains, disrupting the perfect cofacial stacking.

Among the various classes of organic semiconductors, poly(p-phenyleneethynylenes) or PPEs display remarkable luminescence properties and often excellent stability characteristics in comparison to other classes of conjugated polymers.

PPEs are very interesting cases of study in the functionalization with chiral pending groups and several examples have been reported so far.[14–16] We and others have demonstrated that introduction of small enantiopure moieties (often derived from biomolecules, e.g., monosaccharides, aminoacids, nucleosides) as substituents on the conjugated skeleton of PPEs significantly affects their solid state organization and opens intriguing possibilities in enantioselective sensing applications.[17–24]

Here we describe the chiroptical properties and solid state organization of two related glucose-substituted PPEs, namely the oligomer **HO** ($n \approx 10$) and the alternate copolymer **AP** ($n \approx 40$), (Scheme 1), demonstrating the impact on solid state supramolecular organization of the substitution with D-glucose units. The two polymers were synthesized by Cassar–Heck–Sonogashira cross-coupling of bis(trimethylsilyl)arynes with diiodo arenes. The synthetic protocol furnished polymers with high structural regularity ensuring functionalization of each

Scheme 1. Structure of Glucose-Substituted PPE Polymers
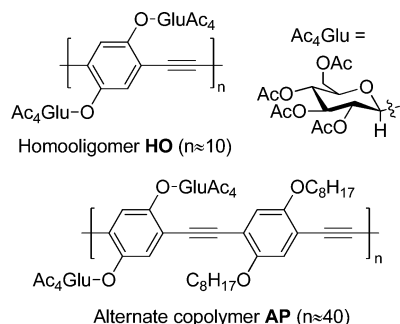
repetition unit with the pendant chiral groups and preventing the formation of butadiyne defects.[14]

Formation of aggregates was early detected by absorption and luminescence spectroscopies for the alternate copolymer **AP** in chloroform/methanol (used as solvent/non solvent) mixtures.[14] An in-depth- investigation of chiral polymers and their solid state properties may be performed by means of chiroptical techniques such as circular dichroism (CD) and circular polarization of luminescence (CPL). CD in particular senses chirality at various structural levels (constituent monomer, single polymer chain, supramolecular aggregates) with specific responses, therefore it is especially suited to monitor the presence of aggregates and to study their structure.[25]

Figure 1 reports the UV−vis absorption and CD spectra of PPEs **HO** and **AP** in chloroform. In conditions of low
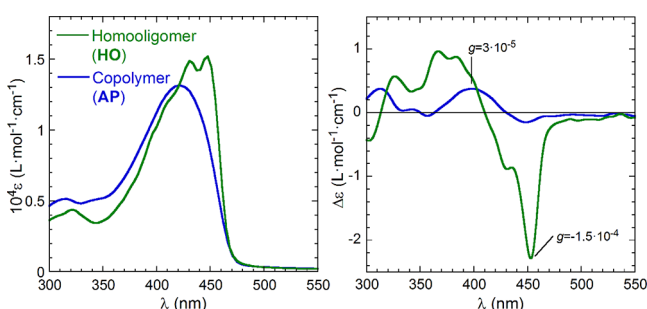

Figure 1. UV−vis absorption (left) and CD spectra (right) of PPEs **AP** (blue) and **HO** (green) in chloroform, normalized per monomer (**AP**, 1.7×10^{-4} M; **HO**, 1.0×10^{-4} M; 0.5 cm cell).

concentration in a good solvent, the polymeric chains are isolated. The two compounds show the characteristic $\pi-\pi^*$ absorption band for dialkoxy-substituted PPEs between 400 and 450 nm.[26,27] This band is more intense and structured for the oligomer (**HO**). It is likely that the small distance between the bulky glucose substituents in **HO** polymer chains has an effect similar to that observed on PPE polymers with pentiptycene groups,[28] consisting in a reduced torsional freedom. This effect causes the vibrational fine structure to emerge even for not-aggregated species.[29] We shall demonstrate that the analysis of CD spectra of **HO** and **AP** is in agreement with this interpretation. A useful parameter is the dissymmetry ratio $g=\Delta\varepsilon/\varepsilon$, evaluated for a CD maximum or minimum, which is a measure of the extent of perturbation exerted by a chiral environment on a chromophore.[30] The copolymer **AP** has a low g value (Figure 1) representative of an intrinsically achiral chromophore, weakly perturbed by a chiral

moiety. This value is similar to that expected for a single benzene ring substituted with glucose units (compound **m** in the Supporting Information). On the contrary, a more complex CD profile with a 5-fold larger g value is observed for the oligomer **HO**, witnessing a more profound perturbation, associated with a conformationally homogeneous system, possibly characterized by a twisted chromophore.

Figure 2 shows the absorption, CD and fluorescence spectra for the two PPEs in chloroform/methanol solvent mixtures
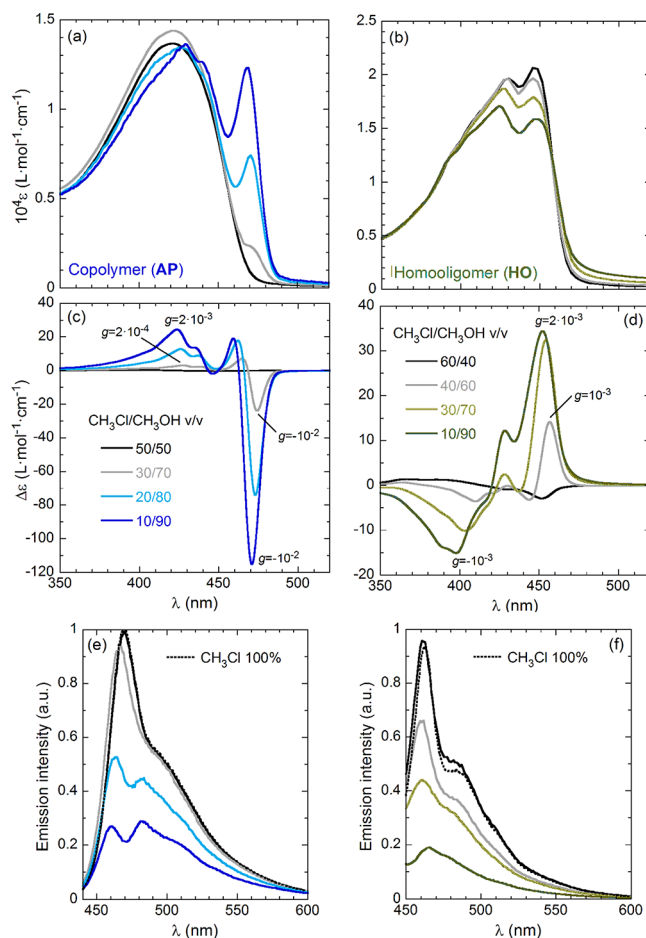

Figure 2. UV−vis absorption (top), CD (center) and fluorescence (bottom) spectra of PPEs **AP** (left) and **HO** (right) in chloroform/methanol mixtures, normalized per monomer (9×10^{-5} M; 1 cm cell).

with increasing methanol fraction (a poor solvent). These conditions are known to promote the formation of solution aggregates which mimic thin films.[31] In fact, the CD spectra of **HO** and **AP** in the presence of large amounts of methanol have similar profile to CD spectra measured on thin films (Supporting Information). This justifies the characterization of solution-state aggregates as good models for solid-state ones, based on the use of the more accessible solution techniques. The evolution of the absorption (Abs, Figure 2a) and fluorescence (Flu, Figure 2e) spectra of the copolymer **AP** follows the expected trend: a so-called aggregate Abs band emerges at 470 nm due to the planarization of the conjugated backbone forced by aggregation,[29] which also quenches the fluorescence. The spectroscopic effects of aggregation are most striking in the CD spectra, which show a series of intense bands with alternating sign (Figure 2c). The most red-shifted CD signal is observed at 470−473 nm (nearly corresponding to the

Abs planarization band) and attains a *g* value of −0.01, with a remarkable 1000-fold increase with respect to the solvated **AP** species. This large value is allied with strong interactions between distinct polymeric chains close to each other in the aggregates. It is noteworthy that the *g* value at 470 nm reaches its maximum already for the 30:70 chloroform/methanol mixture, where only a small Abs shoulder is visible. In these conditions the few aggregates formed have already a well-defined structure which is preserved upon further aggregation. To examine thermochromism of polymer **AP**,[32,33] low-temperature Abs and CD spectra were recorded in dichloromethane, a good solvent itself (Supporting Information). The Abs spectrum at 188 K shows a red-shifted planarization band, which is absent at room temperature (RT). On the contrary, the CD spectrum at 188 K, though changed and more intense with respect to RT, remains very different from the one of aggregate species shown in Figure 2c.

For the oligomer **HO**, the evolution of Abs spectra upon methanol addition is less evident than for the polymer **AP** (Figure 2b). This is due to two related factors: as discussed above, glucose groups introduce some rigidity even in the isolated polymer chains, and prevent an effective aggregation. Still, CD and Flu spectra (Figure 2d,f) demonstrate that some aggregation does occur starting from 60% methanol mixture. The *g* value at 450 nm measured for the aggregates in $CHCl_3$/ MeOH mixture is around 10^{-3}, a 10-fold increase with respect to chloroform. Thus, the comparison between CD spectra of **HO** and **AP** gives an immediate proof of the different propensity toward aggregation. Moreover, the CD spectra are largely dominated by—and reflect the geometry of—the aggregate species, while Abs and Flu spectra unavoidably show large contributions from nonaggregated ones.

Interestingly, both **HO** and **AP** remain moderately emissive upon aggregation. In particular, the copolymer **AP** retains 43% of its emission (integral ratio between Flu spectra in 100% $CHCl_3$ and 10:90 $CHCl_3/CH_3OH$, Figure 2e), which demonstrates that Glu units represent efficient substituents for reducing the quenching of aggregated PPE, as they combine the properties of bulkiness and chirality.[34]

A structural model for the aggregates of **AP** and **HO** at molecular level which explains most of the experimental observations is shown in Figure 3, inspired from Zhan and Swager.[34] The copolymer **AP** chains are essentially planar and are arranged in a cofacial and quasi-parallel fashion with a small negative twist between chains, and lateral interdigitation between alkyl groups.[35] Contrarily, the oligomer **HO** chains

Figure 3. Idealized structural models for the aggregates of copolymer **AP** (a) and oligomer **HO** (b).

are not perfectly planar and stack one on the other almost orthogonally, with a small positive deviation from 90° and lateral interactions involving Glu groups, reminiscent of the compact crystalline structures observed for peracetylated sugars.[36] The opposite sign of the twist angle between proximate chains for the two PPEs, inferred from the sign inversion of the major CD signals, is related to the two different supramolecular arrangements sketched in Figure 3, and in particular to the different packing modes involving the glucose units.

One aspect of PPE chemistry that CD spectroscopy helps clarify is the role played by inter- vs intrachain effects in determining optical and photophysical properties of aggregates.[25,31−33,37,38] It is interesting to note that while the respective effects of chromophore planarization and aggregate formation are indistinguishable in the Abs spectra, the opposite is true for CD, as demonstrated by variable-temperature experiments described above: chromophore planarization can explain the profound changes that Abs and Flu spectra undergo upon aggregation;[39] the intense CD spectra with *g* values around 10^{-2} typical of PPE aggregates call for strong interactions between polymer chains, allowing for an effective exciton-coupled CD (ECCD) mechanism. The typical signature of the exciton coupling between two equivalent chromophores is a conservative bisignate CD couplet, namely, two CD bands of similar intensity (or integral) and opposite sign, with crossover or zero-point centered around the chromophore absorption maximum.[40] Although apparently more complicated, the CD spectra of **AP** and **HO** aggregates (Figure 2c,d) are roughly conservative in the 350−500 nm region, that is, the sum integral of positive peaks is almost equal to that of negative peaks (0.75:1 for **AP** in 10:90 $CHCl_3$/ CH_3OH). To reconcile the observed CD profiles of PPEs with ECCD expectations it is necessary to take into account the vibronic progression of the former, as it has been demonstrated for polythiophenes.[41] On a quantitative ground, this requires the calculation of vibrationally resolved Abs and CD spectra. A very accurate high-level treatment is nowadays feasible, at least for small molecules, which is based on adiabatic harmonic approach and may account for both intensity borrowing (Herzberg−Teller effect) and normal modes rotation upon electronic transition (Duschinsky effect).[42] The application of such treatment to exciton-coupled systems is currently under development.[43,44] We employed a simplified method, known as the linear coupling model or vertical-gradient (VG) approximation,[45] which assumes that the ground and excited states have different equilibrium positions but share the same Hessians. Also, the Franck−Condon (FC) approximation was used and Herzberg−Teller effects were neglected. We label the method FC|VG.

As a computational model to describe the interaction between two proximate fragments of PPE chains in the aggregates of **AP** (we focus on this polymer rather than on the oligomer **HO**), we used a dimer of 1,4-bis(phenylethynyl)-benzene (**BPEB**) with the two molecules in a face-to-face arrangement at a distance of 6 Å and a twist angle τ=-15° (Figure 4). The Abs spectrum of **BPEB** shows a distinct vibrational progression at low temperatures consequent to planarization.[46] Use of **BPEB** as model kept computational times relatively short, without losing the main characteristics of the first π−π* excitation of PPE, which is localized in a reduced central portion of the chain.[47] In the closely related context of chiral π-stacked oligophenylenevinylenes, it has been demon-
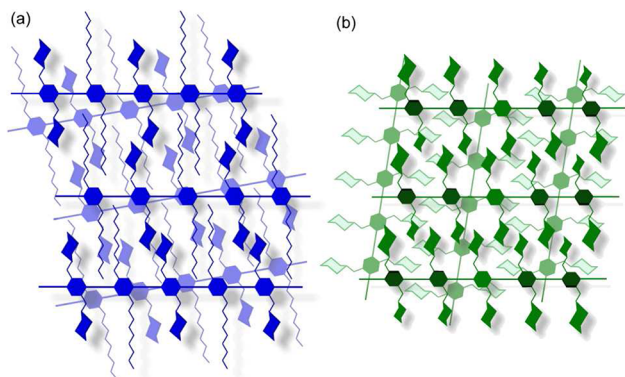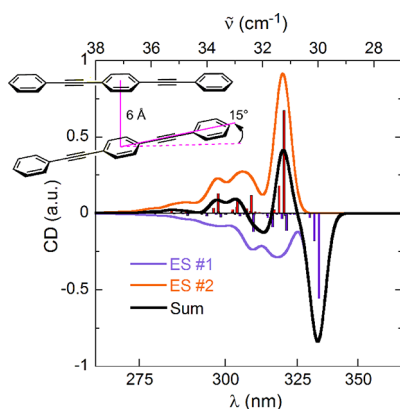
Figure 4. FC|VG-calculated CD spectrum with CAM-B3LYP/TZVP for the **BPEB** dimer shown. The spectra for the first two excited states (ES no. 1 and no. 2, in color) were obtained as sum of Gaussians (650 cm^{-1} half-height width) applied to individual vibronic components (vertical bars). The black spectrum is the total sum weighted to account for the asymmetry of experimental couplet (Figure 2c). The x-axis is linear in wavenumbers (top labels) but shown as increasing wavelengths (bottom labels) for better comparison with Figure 2. The corresponding Abs spectra are reported in the Supporting Information.

strated that vibronic excitons responsible for observed optical properties of the aggregates are confined to two or three neighbor molecules.[48] Moreover, for a twisted arrangement between PPE chains as depicted in Figure 3a, the effective local ECCD interaction occurs between the closest short fragments on two proximate chains. Additionally, we believe that each polymer chain is itself twisted to some degree, so that various chains of **AP** intertwine together forming helical bundles,[7,49] making the local interaction between closest chain portions even more important.

Vibrationally resolved spectra were calculated by means of the FC|VG method described above, employing density functional theory (DFT) and its time-dependent version (TDDFT) at CAM-B3LYP/TZVP level for ground and excited states calculations,[50] respectively (see Supporting Information for details). Despite the simplified model and crude approximations employed, the calculated CD spectrum (Figure 4) reproduces well the main features observed in the experimental CD spectra of PPE aggregates, such as **AP** (Figure 2c) and similar ones.[16,25,34,49,51] In particular, it is evident how the combination of the various exciton-coupled vibronic components, relative to the two excited states (ES nos. 1 and 2), alters profoundly the shape of the resultant spectrum with respect to a standard CD couplet. The intense negative CD band calculated at 334 nm is mainly due to the 0−0 transition leading to the first excited state. We infer that the most red-shifted and intense signal consistently found in CD spectra of PPE aggregates (e.g., at 470 nm for **AP**, see Figure 2c) has a similar vibronic origin, and needs not to be assigned to a charge-transfer or any other isolated transition.[25] The 0−0 band for the second excited state is largely canceled by the overlap with several 0−1 vibronic components of the first one, involving mainly C−C, C=C and C≡C stretching vibrations at 1170, 1680−1690 and 2360 cm^{-1}, respectively (see full assignment in the Supporting Information); hence, its intensity appears very reduced, as experimentally found too.

In conclusion, CD spectra of chiral PPE aggregates may be interpreted by considering both intrachain effects (planarization and vibrational progression) and chain interactions of the exciton-coupling type, furnishing important information about the extent and modes of aggregation.

The in-depth understanding of different structural levels involved in the aggregation of chiral substituted conjugated polymers will contribute to the design of chiral functionalities for fine control of solid state aggregation and properties of conjugated polymers.

■ ASSOCIATED CONTENT

⑤ Supporting Information
Experimental Section, NMR data for **HO** and **AP** in CDCl$_3$, CD spectra of thin films of **HO** and **AP**, Abs and CD spectra of a monomeric model of **HO**, variable-temperature Abs and CD spectra of **AP** in dichloromethane, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*Telephone (+39)0502219298. E-mail ldb@dcci.unipi.it.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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