Structural and Photophysical Templating of Conjugated Polyelectrolytes with Single-Stranded DNA

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ABSTRACT: A promising approach to influence and control the photophysical properties of conjugated polymers is directing their molecular conformation by templating. We explore here the templating effect of single-stranded DNA oligomers (ssDNAs) on cationic polythiophenes with the goal to uncover the intermolecular interactions that direct the polymer backbone conformation. We have comprehensively characterized the optical behavior and structure of the polythiophenes in conformationally distinct complexes depending on the sequence of nucleic bases and addressed the effect on the ultrafast excited-state relaxation. This, in combination with molecular dynamics simulations, allowed us to detail atomistic-level understanding of the structure–property correlations. We find that electrostatic and other noncovalent interactions direct the assembly with the polymer, and we identify that optimal templating is achieved with (ideally 10–20) consecutive cytosine bases through numerous π-stacking interactions with the thiophene rings and side groups of the polymer, leading to a rigid assembly with ssDNA, with highly ordered chains and unique optical signatures. Our insights are an important step forward in an effective approach to structural templating and optoelectronic control of conjugated polymers and organic materials in general.

INTRODUCTION

Control over the conformation of functional molecules in order to tailor their optoelectronic properties has tremendous potential for technological applications, especially for organic π-conjugated polymers that have gained extensive interest over the past few decades. In particular, the strong correlation of the photophysical properties of conjugated polythiophenes to their backbone conformation has been under intensive investigation. Achieving a highly ordered and extended backbone conformation is of considerable relevance, since intrachain coupling is in this case dominant, and important delocalization as well as coherent long-range migration of excitons and charges can be realized. Such directional energy and charge transport along the chain can be exploited in electrical components, e.g., nanowires for molecular devices, cathodes in next generation batteries, capacitors, nanosensors, nanophotonics, quantum information technologies, or artificial light-harvesting systems. Optically, such extended conformations in polythiophenes are characterized by a red-shifted absorption, by mirror image symmetry in the absorption and emission spectra that also show an increased ratio of the first to second vibronic peaks, and by an enhanced radiative decay rate. This behavior is related to the high intrachain delocalization and can be classified as J-aggregate-like.

Unfortunately, the random-coiled form of conjugated polythiophenes is typically more favored in solutions and thin films, limiting the desired extended π-conjugation along the backbone. Strategies to induce extended backbone conformations range from chemical modification of the polymer (mostly the side chains), to noncovalent approaches, such as control of the electronic coupling through processing protocols, dilution within an inactive solid polymer matrix (polyethylene or polypropylene), or supramolecular assembly with templating molecules. Templates under consideration include cyclodextrins and polysaccharides for the formation of rod-like inclusion complexes, as well as extending charged polythiophenes through electrostatic interactions. Recently, nucleic acids (NAs) have emerged as particularly advantageous in directing molecular conformation, since they can conveniently induce a broad range of higher-order architectures in chiral nanoassemblies with unique and readily controllable properties. The ability of NAs to template
supramolecular, programmed, and reproducible self-assembly through a combination of noncovalent interactions has been demonstrated upon complexation with conjugated polymers, surfactants, proteins, nanoparticles, and dyes. Complexation of conjugated polymers with NAs is facilitated by the presence of charged side groups on the backbone of conjugated polyelectrolytes (CPEs). The strong electrostatic interactions that develop between single stranded (ss) DNA and CPEs, together with more specific and directional supramolecular effects, allow precise manipulation of the CPE conformation. Moreover, intermolecular packing between polymer backbones is in this case removed, allowing access to the properties of isolated conducting polymer chains with superior ease compared to other methods.

In the present work, we focus on complexes of ssDNA with cationic poly(1H-imidazolium,1-methyl(-3-[2-[((4-methyl-3-thienyl)oxy]-ethyl]-chloride, abbreviated here as CPT (Figure 1). Cationic polythiophenes such as CPT are successful optical sensors of DNA chains in numerous biological assays, whereby the strong conformational changes induced in CPT upon complexation with ssDNA are the lead cause for exquisite sensitivity. Intriguingly, the previous biosensing work has revealed a tremendous impact of the ssDNA sequence on the optical and excited-state behavior of the polymer. The strong red-shift of the absorption band of CPT alone is likely due to local environment effects (e.g., change in polarity) caused by the interactions with ssDNA. The complexation with ssDNA induces some chirality to the polymer with a preferential right-handed helical structure. This conformation is however flexible and varies with temperature. At 55 °C, the absorption band blue-shifts (increase in chain disorder) with no evident CD signature in the visible region.

Our study provides predictive understanding in an effective approach of structurally templating the optoelectronic properties of organic molecules.

RESULTS AND DISCUSSION

Optical Response of CPT/dA20 and CPT/dC20. We start by considering two extreme cases where the homonucleotide ssDNA sequence containing 20 bases either strongly templates the CPT conformation (dC20) or does not lead to significant ordering (dA20). We correlate this to the optical properties of the complexes.

Figure 2 shows the stationary absorption and circular dichroism (CD) spectra for the two ssDNAs alone and with CPT in aqueous phosphate buffered saline (PBS) solution. The ssDNAs only absorb in the UV region, and their bands and corresponding CD signal are in agreement with the literature. When dA20 is mixed with CPT at 20 °C (Figure 2a), an unstructured broad band appears around 510 nm, which is ascribed to the π-π* transition of the polymer. This is different from the structured absorption band of CPT alone at 20 °C (also pictured in Figure 2a), where we have previously shown significant H-aggregation in relatively ordered chains. This suggests that assembly with dA20 disrupts intermolecular stacking but does not support ordering of the polymer chains. Indeed, the broadness of the band indicates an ensemble of disordered backbone conformations in the complex. This is similar to the broad band at 398 nm of CPT alone at 55 °C (Figure 2a), which we have assigned to random coiled chains at high temperature. The strong red-shift of disordered CPT/dA20 compared to disordered CPT alone is likely due to local environment effects (e.g., change in polarity) caused by the interactions with ssDNA. The complexation with dA20 induces some chirality to the polymer with a preferential right-handed helical structure.

This conformation is however flexible and varies with temperature. At 55 °C, the absorption band blue-shifts (increase in chain disorder) with no evident CD signature in the visible region. On the other hand, the CD signal due to dA20 in the UV region, indicating a right-handed helical conformation, changes only slightly upon complexation with CPT at any temperature, in agreement with the calculated CD spectrum (see Figure S6) and the UVRR results below, implying that the secondary structure of dA20 is largely unaffected by assembly with CPT, pointing to weak interactions in the complex.

The experimental findings are strongly supported by our MD simulations. Those show that the noncomplexed dA20 fragment displays almost no conformational flexibility and maintains a rigid conformation throughout the simulation, stabilized by stacking interactions between adenine bases (Figure S5a and close contact analysis below), in agreement with the literature. In the complex with CPT, two independent MD runs show limited specific interactions between the polymer and dA20 as well as an unstable structure of CPT/dA20 (Figure 2c). While CPT displays flexibility (in agreement with the broad unstructured absorption spectrum), the dA20 fragment maintains a significant degree of helicity during most of the simulation time scale (1.54 μs), albeit in the form of two helices approximately comprising the first five and methyl substitution on C5 favors syn–anti conformations of CPT, further contributing to torsional order of the polymer.

Figure 1. Molecular structure of cationic poly(1H-imidazolium,1-methyl-3-[2-[((4-methyl-3-thienyl)oxy]-ethyl]-chloride (CPT).
the last 15 adenines, respectively. We have further quantified the helical order and chirality in the MD simulations, using an average local chirality index (CI_{i,i+1}, see Computational Methods for details), similar to the one recently reported.\textsuperscript{53} The average chirality index distribution of dA20 alone is very similar to that of the same ssDNA fragment in the complex with CPT (Figure 2e), and the positive values point to a right-handed helical configuration, which, as discussed above, is maintained in CPT/dA20. The distribution of the chirality index of CPT in CPT/dA20 visits only positive values, in agreement with the CD signal in the CPT-absorbing region, thus confirming that a right-handed helicity is also induced in the polymer backbone.

In stark contrast to the absorption spectrum of CPT/dA20, the spectrum of the CPT/dC20 complex shows a red-shifted absorption, strong vibronic structure (with a spacing of 1447 cm\(^{-1}\) due to the symmetric C–C and C=C stretching of the thiophene units), and a predominant 0–0 transition at 594 nm (Figure 2b), as generally observed for extended polythiophene chains with a large degree of order.\textsuperscript{25,26} Here, the \(A_{0-0}/A_{0-1}\) ratio is 1.24 (for a complex formed at 55 °C and then cooled to 20 °C, and 1.16 if directly prepared at 20 °C, Figure S3). This is, to the best of our knowledge, the highest ratio observed so far, even higher than for P3HT in nanofibers.\textsuperscript{27} In addition, once formed, the CPT/dC20 complex is very rigid compared to CPT/dA20, as the absorption band shape remains largely unaffected by temperature variations (see Figure S3a). Moreover, an induced CD signal due to CPT in a left-handed helical conformation appears in CPT/dC20 between 450 and 670 nm (Figure 2b), suggesting the induction of different helical structures upon complexation with each of the ssDNA chains. The trend of the experimental CD signals for CPT in the two complexes (a shift from right-handed to left-handed conformations when going from CPT/dA20 to CPT/dC20) is qualitatively reproduced by the MD simulations with more left-handed conformations being sampled for CPT in CPT/dC20 compared to CPT/dA20. The distribution of the local chirality indices of CPT is broad including both positive and negative values with a large statistical error (Figure 2e). This suggests that in spite of the length of the MD simulation (1.56 \(\mu\)s), the sampling of the local chirality index of CPT in CPT/dC20 is not yet fully converged, preventing a direct quantitative comparison of the theoretically predicted absolute CPT handedness with the experimental one. Overall, the MD simulations confirm that CPT/dC20 adopts and maintains a structure that is stabilized by persistent intermolecular...
interactions (see below) between the ssDNA and the polymer (Figure 2d). All this points to strong conformational templating of CPT by dC20, leading to extended isolated chains with predominant intrachain coupling and J-aggregate-like behavior. In comparison, the absorption spectrum of CPT alone at 5 °C is also pictured in Figure 2b, where the polymer is in an ordered conformation but shows H-aggregation between CPT chains. Here, the $A_{0-0}/A_{0-1}$ ratio is only 0.93 and the 0-0 peak is suppressed due to the interchain coupling.

Given the strong interactions between CPT and dC20, the conformation of the ssDNA strand is also significantly affected in the complex. dC20 alone has a characteristic CD signal with a dominant positive band at 288 nm and a negative band at 265 nm, suggesting the presence of a moderate portion of i-motif structure (Figure S4), as expected for cytosine-rich DNA strands at pH 7.3 (i-motif formation is generally more important at slightly acidic pH, when hemiprotonation of cytosines favors the formation of hydrogen bonds between them, see SI). MD simulations show that dC20 has a high degree of flexibility and adopts several different structures, including both extended and compact configurations (Figures S5b/c) that sample right- and left-handed orientations (Figure 2e). While compact dC20 structures are observed (e.g., Figure S5b), which are mainly stabilized by a varying number of H-bonds between cytosine bases, the i-motif structure is not evidenced by MD simulations since the simulations were performed with fixed protonation states. Nevertheless, the mixture of secondary structures is theoretically demonstrated as well. This is in stark contrast to the more rigid dA20 and likely favors the assembly of dC20 with CPT. In the complex, the CD feature of dC20 is dramatically changed (Figure 2c), in agreement with the reduced ellipticity in the calculated CD spectrum (Figure S6), indicating that the secondary structure...
of the ssDNA strand is strongly modified upon complexation with CPT (see also UVRR results below). The absorption peak at 274 nm is also less intense in the complex, possibly due to hypochromism induced by a partial alignment of the transition dipole moments when the bases are stacked. This phenomenon is known for double stranded DNA, which absorbs less compared to the denatured form. The MD simulations confirm that the chirality distribution of dC20 in CPT/dC20 is fully shifted to negative values (left-handed corresponding values in the two complexes (Figure S9 in was calculated for CPT alone and compared to the intrachain order in CPT/dC20. Moreover, the relative absorption of CPT, therefore we observe only contributions associated with vibrations of the conjugated polymer (mainly the thiophene backbone). The spectra are similar to the RR spectra of CPT that we have reported before and assigned based on DFT calculations. The deconvolution of the RR spectra is shown in Figure S8, and the band assignment is summarized in Table S5. The position, intensity, and line width of the Raman bands are strongly dependent on the ssDNA participating in the complex. In the case of CPT/dA20, the bands appear essentially at the same position as in the case of the polymer alone, while a 3–4 cm⁻¹ downshift is observed in the case of CPT/dC20. Moreover, the relative intensities of the C–C (~1400 cm⁻¹) and C=O (1487 cm⁻¹) stretches in CPT/dC20 are distinctly different than in the other complexes or the polymer alone, with the C–C intensity dominating. Taken in conjunction with the downshifts in the bands, this signifies an increase in the electronic conjugation of the CPT backbone caused by a greater inter-ring planarity, demonstrating a more extended conformation for CPT in the CPT/dC20 complex. The intensity of the C–C band increases further with excitation at 320 nm, due to resonance with even more planar and lower energy chain segments. In addition, the spectrum of CPT/dA20 exhibits broader line widths, showing inhomogeneity and torsional disorder of the CPT conformation. In contrast, the narrow peaks observed in the CPT/dC20 spectrum reflect the rigidity and homogeneity of the CPT conformation in the complex. With the help of MD simulations, the distribution of the S–C–C–S dihedral angles (between adjacent thiophene rings) was calculated for CPT alone and compared to the corresponding values in the two complexes (Figure S9 in SI). Overall, the occurrence of a dihedral angle corresponding to a planar conformation (around 0°, ~180° or +180°) follows the trend CPT/dC20 > CPT/dA20 > CPT alone, which agrees with the increased degree of planarity for CPT/dC20 witnessed by RR spectroscopy with visible excitation.

**Backbone Planarity of CPT in the Complexes with dA20 and dC20.** A more in-depth experimental investigation of the backbone planarity of CPT upon complexation with the different ssDNA chains was achieved by using resonance Raman (RR) spectroscopy. This confirms the high degree of intrachain order in CPT/dC20.

Figure 3a presents the fingerprint region of the RR spectra of CPT complexes with visible excitation (for the extended range spectra, see Figure S7), which were normalized with respect to the intensity of the band at ~1487 cm⁻¹. At the used wavelengths (473 and 532 nm), we are on resonance with the π–π* absorption of CPT, therefore we observe only contributions associated with vibrations of the conjugated polymer (mainly the thiophene backbone). The spectra are similar to the RR spectra of CPT that we have reported before and assigned based on DFT calculations. The deconvolution of the RR spectra is shown in Figure S8, and the band assignment is summarized in Table S5. The position, intensity, and line width of the Raman bands are strongly dependent on the ssDNA participating in the complex. In the case of CPT/dA20, the bands appear essentially at the same position as in the case of the polymer alone, while a 3–4 cm⁻¹ downshift is observed in the case of CPT/dC20. Moreover, the relative intensities of the C–C (~1400 cm⁻¹) and C=O (1487 cm⁻¹) stretches in CPT/dC20 are distinctly different than in the other complexes or the polymer alone, with the C–C intensity dominating. Taken in conjunction with the downshifts in the bands, this signifies an increase in the electronic conjugation of the CPT backbone caused by a greater inter-ring planarity, demonstrating a more extended conformation for CPT in the CPT/dC20 complex. The intensity of the C–C band increases further with excitation at 320 nm, due to resonance with even more planar and lower energy chain segments. In addition, the spectrum of CPT/dA20 exhibits broader line widths, showing inhomogeneity and torsional disorder of the CPT conformation. In contrast, the narrow peaks observed in the CPT/dC20 spectrum reflect the rigidity and homogeneity of the CPT conformation in the complex. With the help of MD simulations, the distribution of the S–C–C–S dihedral angles (between adjacent thiophene rings) was calculated for CPT alone and compared to the corresponding values in the two complexes (Figure S9 in SI). Overall, the occurrence of a dihedral angle corresponding to a planar conformation (around 0°, ~180° or +180°) follows the trend CPT/dC20 > CPT/dA20 > CPT alone, which agrees with the increased degree of planarity for CPT/dC20 witnessed by RR spectroscopy with visible excitation.

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torsional angle between the cytosine and the deoxyribose, induced by specific interactions between dC20 and CPT that are absent in CPT/dA20. Indeed, according to our MD analysis, the distribution of dihedral angles between the base and the sugar for dC20 alone and assembled with CPT shifts by 20° (Figure 3d), while no such difference is seen for the sugar-base dihedral angle of dA20 (Figure 3c). Moreover, the MD close contact analysis shows that strong π-stacking develops between the cytosines of dC20 and the thiophenes and imidazoles of CPT (Figure S15.1 and S15.2). These π-stacking interactions are responsible for the modification in the deoxyribose ring puckering and/or twist of the glycosidic bond. They are also the main reason for the important differences observed between the CPT/dC20 and CPT/dA20 complexes. Characteristically, five cytosines stack against a thiophene ring in CPT/dC20 during more than 50% of the total simulation time, and two more cytosines for more than 40% of the time (Figure S15.1). In contrast, only three adenines stack against a thiophene for more than 40% of the total MD time in CPT/dA20. As depicted in Figure 4, the close contact analysis also shows that strong hydrogen bonding, rather than stacking, predominantly determines the conformation of dC20 in the assembly, in line with the loss of intra-DNA stacking once CPT is added (Figure S15.4). The MD simulations indicate that these intra-DNA H-bonding interactions commonly occur in conjunction with cytosine–thiophene stacking interactions, as depicted in Figure 4, contributing to the overall conformational stability of CPT/dC20 (more pictures of noncovalent interactions can be found in Figures S14 and S17). On the other hand, chalcogen bonds within CPT, between the sulfur atoms of the thiophenes and the oxygen atoms of the alkoxy side chains,40 are found to have a negligible effect (see detailed discussion in the SI, section S5.5).

Effect of dC Length on CPT/dC Complex Formation. Since the cytosines of the ssDNA strand stack with every second thiophene of CPT (Figure 4), this suggests that consecutive sequences of cytosines favor maximal π-stacking occurrence and chain extension. We thus investigate what length of dC induces the best templating of CPT, which consists of an average of 42 thiophene units (estimated using the number-averaged molecular weight, Mn).

Figure 5a shows the absorption and CD spectra of CPT complexed to dC strands of 5 to 80 bases, obtained by gradually adding the ssDNA to a solution of CPT in PBS buffer until a 1:1 ratio of thiophenes to nucleobases (monomeric equivalence) is achieved. For ssDNA oligomers with 10 units or more, the strong templating effect is always observed, yielding the characteristically structured absorption and CD spectra of CPT. Templating is typically complete at a thiophene/nucleobase ratio of 1:0.75–1 (maximal A_300/A_280 ratio, see Figure S20 for the titration results). However, the A_300/A_280 ratio decreases as the ssDNA length increases (inset of Figure 5a, Table S7). Optimal templating resulting in the most ordered and extended CPT conformation is achieved with dC10 (A_300/A_280 = 1.19). This ssDNA strand is about 4 times shorter (in terms of number of monomers) than an average CPT chain. We also note that excellent templating with dC10 already occurs at half the monomeric equivalence (Figure S20b), in line with the fact that the cytosines stack with every second thiophene of CPT. We suggest that (two to four) 10 nucleobase units are ideal to wrap around segments of CPT forming a compact structure via mainly electrostatic and π-stacking interactions as shown in Figure 2d, leading to significant local ordering and intrachain coherence. For longer ssDNA segments (especially >20 bases), the assembly over the entire length of the two chains is more challenging and might compete with increased intra-DNA interactions. Noteworthy is the similar shape of the UV-CD signature for dC80 alone and CPT/dC80 (Figure S21), showing that complex formation leads in this case to a smaller change in the ssDNA conformation, ultimately explaining the lower templating effect in this complex (A_300/A_280 = 1.06).

Finally, we find that complex formation is not complete for one monomeric equivalent of dC0, since only a slight effect on the polymer absorption and CD signal is observed, and a shoulder around 400 nm due to disordered CPT chains remains visible (Figure 5a). To achieve significant templating with dC0, an important excess of ssDNA needs to be added.
Leaving this solution for 1 day then leads to a narrow vibronic absorption structure with $A_0 \sim A_{-1} / A_{0} = 1.27$ (Figure S23). We conclude that five cytosine units can already induce significant local intrachain order in CPT, involving a sequence of about 10 thiophenes. However, complexation is in this case slow and unfavorable (requiring excess ssDNA) due to modified cooperativity (see Figure S23). Titrating concentrated CPT into a dilute dC$_5$ solution (instead of vice versa) does not lead to any templating (while the titration order is irrelevant for the longer dC$_n$ chains), highlighting the inability of the short dC$_5$ chains to disrupt CPT aggregates in the concentrated stock solution used for the titration (Figure S24).

Generalization to Other ssDNA and Polythiophene Systems. Having understood the specific interactions that induce characteristic conformations in complexes of CPT with dA$_{20}$ and dC$_{20}$, we now generalize our findings to different homonuclear and mixed ssDNA sequences, as well as to thiophene polyelectrolytes carrying different side chains. We confirm that the CPT/dC$_{20}$ combination is the most effective in templating an extended polymer conformation.

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The absorption spectra of CPT complexed to different ssDNA sequences (20-base length, 55 °C for best complex formation) are shown in Figure 5b. The homonucleotides dT$_{20}$ and dG$_{20}$ cause weak templating similar to dA$_{20}$, while dC$_{20}$ stands out from all other investigated sequences. The behavior of dT$_{20}$ agrees with previous work and with our RR measurements (Figure S7), which indicate that thymine bases do not stack strongly with thiophenes, possibly due to the extra methyl group compared to cytosine.$^{53}$ The templating strength of mixed ssDNA oligomers (Table S1) is highly variable and does not necessarily correlate with the number of cytosines in the sequence. For example, the assembly of CPT with d[(TTCC)$_5$] (50% cytosine bases) leads to unstructured and blue-shifted absorption of CPT, possibly due to the weak stacking of the intermittent cytosine pairs with thiophenes, or due to strong intra-DNA interactions. This confirms that the excellent templating of dC$_{20}$ via extended cytosine-thiophene stacking relies on consecutive cytosine sequences, not just pairs interspersed between other bases. Nevertheless, for biologically more relevant sequences containing the four natural DNA bases in random order (T$_{406}$ and T$_{406}$RC, with 30% and 10% cytosines, respectively)$^{52}$ an intermediate templating effect can be achieved, with an optical response between those of CPT/dA$_{20}$ and CPT/dC$_{20}$ (Figure S5b). For CPT/T$_{406}$, the (+/−)CD signal at 520 nm indicates an induced right-handed helicity of CPT that is quite stable with temperature (Figure S26). Together with the visible RR result in Figure 3a, we thus find that the polymer adopts a more ordered conformation in the relatively rigid complex with
T406 but does not reach the level of CPT/dC20. From the CD response of T406 in the UV range and the UVRR spectra (Figures S10 and S25), we also conclude that the ssDNA structure in the complex is not strongly modified compared to T406 alone. Interestingly, d[(AT(TAT)3] and d[AT(AAT)3], that contain adenines separated by thymines (but no cytosines), result in a more structured absorption spectrum than T406 when complexed with CPT. We suggest that the adenines π-stack in this case with CPT, since our MD simulations evidence some adenine–thiophene stacking in CPT/dA20 (Figure S15.1), which competes with strong interactions between the adenine bases. Disruption of the adenine–adenine stacking by the thymine bases in d[(AT=(TAT)]3 and d[AT(AAT)]3 can therefore explain the better complexation with CPT. However, having guanine bases between adenine pairs (d[(GGAAG)]3) does not lead to the same effect, showing the intricate interplay of ssDNA-CPT and intra-DNA interactions that leads to efficient conformational templating in the complexes.

With the aim to examine whether the interactions responsible for templating in the CPT/dC20 system can extend to other thiophene polyelectrolytes, we chose two other polymers that were previously studied in DNA complexes (Figure S27). P3HT-Im and P3HT-PMMe3 have different cationic side groups (phosphonium and imidazole, Figure Sd), which are attached to the Cβ position of the thiophene backbone via a six-carbon chain (without the oxygen atom present in CPT). Moreover, the methyl group from the Cβ position is missing. Even though the counterion in these polymers is bromide, its concentration is 4 orders of magnitude lower than the chloride concentration in the PBS buffer, and therefore was not considered to affect the conformation of the polymer. The RR spectra of these two polymers resemble the well-known P3HT Raman spectrum, but differ from the one of CPT, where the C=C stretching mode is split due to alkoy substitution at the Cβ position. According to the literature, a more prominent peak around 1378 cm⁻¹ (C=C stretching mode), a red-shift of the C=C symmetric stretching band toward ~1450 cm⁻¹, a reduction of the full-width-half-maximum (fwhm) of this C=C mode and a less prominent peak at ~1520 cm⁻¹ (antisymmetric stretching mode of C=C) are all indications for a more planar P3HT backbone. These characteristic changes are most pronounced for both complexes of P3HT-PMMe3 and P3HT-Im with dC20, while dA20 has the opposite effect on the conformation of each polymer (broad RR bands, less intense C=C peak, C=C mode shifted to higher wavenumbers, Figures 5d and S28). However, even though the effect of the ssDNA sequence on the conformation of the polymer is similar across a variety of cationic polyelectrolytes, with dC20 having the largest tendency to enhance backbone torsional order, its templating ability is significantly reduced with P3HT-Im and P3HT-PMMe3 (see absorption spectra, Figures 5c and S27). Their weak templating must result either from the longer alkyl group in the cationic side chain and/or the absence of the Cβ methyl substituent, since our MD simulations show that chalcogen interactions (involving the alkoy oxygen) have no decisive effect on the CPT conformation (section S5.5). Indeed, the methyl substituent in CPT restricts the possibility of cisoid (syn-syn) conformations between neighboring thiophenes, which were found quite preponderant for the interactions of P3HT-PMMe3 with ssDNA or dsDNA. Such cisoid conformations contribute to steric repulsion between the side chains inducing overall more torsional backbone disorder. Moreover, the longer alkyl chains occupy a larger volume than in CPT, possibly limiting the essential polymer–DNA π-stacking in the complexes. A systematic study of CPT side chains is under way to explore in detail the structural characteristics of the side chains necessary to form well-ordered polymer chains.

**Excited State Relaxation of CPT/ssDNA Complexes.** In the previous sections, we have addressed the ground state conformation of polymer/ssDNA complexes. However, it is imperative to understand the impact of templating on the
excited state behavior, especially for the extended CPT conformation in the complex with dC20, to assess the suitability for technological applications involving e.g. extended intra-chain exciton delocalization or directional long-range exciton migration. Here, we combine resonance Raman intensity analysis (RRIA) and transient absorption (TA) spectroscopy. RRIA offers a glimpse of the excited state structural evolution in the Franck−Condon region, as the band intensities are associated with specific geometrical changes upon excitation, while TA provides crucial insights on the lifetime and nature of the excited state.

Interestingly, even though the ssDNA sequences induce different CPT conformations, the nature and lifetime of the excited state are roughly similar in the different complexes. Figure 6 shows a selection of TA spectra for the CPT/dA20 and CPT/dC20 complexes at different time delays following excitation at 400 nm (CPT/T406 in Figure S29, 580 nm excitation in Figure S30, and global analysis in Figures S31 and S32). For all complexes, a positive broad band centered at ∼1050 nm is ascribed to the excited state absorption (ESA) of the S1 singlet exciton, while the ESA of more localized excitons in random-coiled CPT chains is narrower and centered around 950 nm. Moreover, the TA features decay in all complexes with lifetimes of a few picoseconds (2.5−4 ps) and a few tens of picoseconds (22−28 ps, Tables S8−S9), with the dynamics of the ESA and GSB bands mirroring each other, meaning that we are probing the same exciton population (Figures 6b and S31 and S32). The fast exciton quenching (vs a lifetime of hundreds of picoseconds in CPT alone) could be due to additional nonradiative deactivation paths offered by the specific interactions with the ssDNA and energy dissipation to the environment, or to charge transfer followed by ultrafast recombination (since no TA signatures of polarons are seen). Finally, no long-lived species are formed in the complexes contrary to CPT alone in solution, where long-lived polarons are generated at low temperature and intersystem crossing populates the triplet state at high temperature. Along with the fast exciton quenching, this is additional proof that the assembly of CPT with the different ssDNA sequences is always achieved and leads to isolated CPT chains, as polaron formation is usually observed in polythiophenes with interchain interactions. The absence of triplet generation provides additional support for the higher torsional order of CPT in all complexes, as intersystem crossing is aided by torsional disorder.

With the knowledge that only one excited state species is present (intrachain delocalized excitons), we can use RRIA to evaluate the early time structural evolution of CPT in the various complexes. RRIA requires first the quantification of
resonance Raman cross sections ($\sigma_{R}$ section S9.1.1). The absolute $\sigma_{R}$’s for all the RB bands of CPT were calculated for excitation at 473 nm for CPT/T406 and CPT/dA20 and at 532 nm for CPT/dC20 (Table S10), which is always $\sim$1900 cm$^{-1}$ to the blue side of the $\lambda_{\text{max}}$ of the absorption spectrum. These cross sections along with the absorption cross section for each complex were then simultaneously modeled (see sections S9.1.2–3). The fits to the absorption spectra are shown in Figure 2, while Figures S33–S35 show the RR excitation profiles (REP’s) for CPT in all the complexes, i.e., the calculated $\sigma_{R}$ as a function of excitation energy. The fitting parameters are reported in Table S11. We find that the $C_{60}$–$C_{60}$ stretch exemplifies the highest displacement ($\Delta$) in CPT/dC20 compared to other modes, i.e., the largest change in bond length upon excitation, while the $C_{60}$–$C_{60}$ symmetric stretch (also reflecting the transition toward a quinoidal state) becomes increasingly important as we move from CPT/dC20 to CPT/dA20 with $\Delta$ about 3 times as large in the latter complex (Figure 7a). The total reorganization energy, $\lambda$, calculated from mode-specific reorganization energies ($\lambda_{\text{tot}} = \sum \lambda_{i} = \sum \omega_{i} \Delta_{i}$), also demonstrates a 3 times larger structural evolution on going from the ground to the excited state in the case of dA20 ($\lambda$ = 1119 cm$^{-1}$ for dC20, 1627 cm$^{-1}$ for T406, and 3024 cm$^{-1}$ for dA20, see Figure 7a). In addition, we see doubling of the inhomogeneous broadening from 450 cm$^{-1}$ (56 meV) in CPT/dC20 to 900 cm$^{-1}$ (112 meV) in CPT/dA20, indicating the larger number of energetic sites available due to conformational disorder. This illustrates an overall larger conformational rearrangement in response to the change of electron density in the excited state for the more flexible complexes, where our RR measurements and the MD simulations show that the polymer is less tightly bound to the ssDNA and the CPT conformation is less planar in the ground state with more torsional disorder.

Structural changes in the excited state are also reflected by the temporal evolution of the spectral shapes from TA spectroscopy. In particular, the clear vibronic structure of the TA spectra of CPT/dC20 in the GSB/SE region allows isolation of the time-dependent SE spectra after subtracting the leading to a total Stokes shift of 74 meV), and an increase of $\sigma_{\text{absolute}}$ maintaining delocalization of the excited state and possibly to limited (mainly electronic) relaxation within <200 fs, that can be reproduced with identical parameters. This points early emission spectrum is a mirror image of the absorption structural evolution on going from the ground to the excited complex were then simultaneously modeled (see sections S9.1.2–3). The total reorganization energy, $\lambda$, was calculated from mode-specific reorganization energies ($\lambda_{\text{tot}} = \sum \lambda_{i} = \sum \omega_{i} \Delta_{i}$), also demonstrating a 3 times larger structural evolution on going from the ground to the excited state in the case of dA20 ($\lambda$ = 1119 cm$^{-1}$ for dC20, 1627 cm$^{-1}$ for T406, and 3024 cm$^{-1}$ for dA20, see Figure 7a). In addition, we see doubling of the inhomogeneous broadening from 450 cm$^{-1}$ (56 meV) in CPT/dC20 to 900 cm$^{-1}$ (112 meV) in CPT/dA20, indicating the larger number of energetic sites available due to conformational disorder. This illustrates an overall larger conformational rearrangement in response to the change of electron density in the excited state for the more flexible complexes, where our RR measurements and the MD simulations show that the polymer is less tightly bound to the ssDNA and the CPT conformation is less planar in the ground state with more torsional disorder.

CONCLUSIONS

We have investigated here the templating effect of ssDNA oligomers with different sequences on cationic polythiophenes. The conformational and photophysical behavior of the polymer/ssDNA complexes was studied using a powerful combination of spectroscopic techniques supported by MD simulations, leading to significant expansion of knowledge and understanding of the systems. We find that in all complexes, strong electrostatic interactions develop between the two components, leading to reduced polymer aggregation so that the properties of isolated chains can be accessed. However, large variations in the templating effect between different polymer/ssDNA combinations show the importance of additional noncovalent interactions. We identify CPT/dC as the complex displaying the most pronounced templating effect, highlighted by the most extensive intrachain coupling and optical response of the polymer. The first key to this effective templating is the extensive succession of cytosines in dC (ideally 10–20 bases), which favors $\pi$-stacking with the thiophene/imidazole rings of CPT over strong intra-DNA interactions, inducing a more planar and tighter conformation of the polymer. In contrast, CPT interacts mainly electrostatically with dA20 (H-bonding and $\pi$-stacking are weak), allowing conformational flexibility of the polymer, while dA20 maintains a rigid helical structure in the complex due to strong adenine–adenine stacking. Mixed ssDNA sequences induce a variable degree of order in CPT, depending on the intricate interplay of ssDNA-CPT and intra-DNA interactions, but never approaching the one of dC20. We find that the second key to effective templating resides in the nature of the polymer side chains. Substituting CPT with another imidazole-based polythiophene (P3HT-Im) causes poor templating even with dC20 because the cationic side chains are in this case too long to induce a good conformational fit with the ssDNA, and the absence of an
additional methyl group on the thiophenes enhances torsional disorder on the backbone.

Finally, we show that supramolecular assembly with ssDNA strongly affects the excited-state properties of CPT, leading to intrachain delocalized excitons with a relatively short lifetime and the absence of any long-lived polaron or triplet states. In addition, excited-state structural relaxation is significantly reduced, with the rigid CPT/dC20 complex having a particularly small reorganization energy. This maintains intrachain exciton delocalization, favoring (possibly coherent) directional exciton migration along the chains. Linearity of the conjugated chain previously allowed isolated polydiacetylene (PDA) to function as electrical conductive nanowires due to the ability to transmit charge over long distances by coherent tunnelling,102,103 or to exhibit e

EXPERIMENTAL SECTION

Materials. CPT (Figure 1) was synthesized as previously described.3,105 It has a molecular weight (Mw) of 22 kDa (Mn = 11 kDa), with a polydispersity index (PDI) of 2.0. Each monomer unit of 2628 g/mol contains one positive charge on the ionic side-chain, compensated by a Cl− counterion. Cationic poly[(3-(6'-trimethylphosphonium)hexyl)thiophene-2,5-diy1] (P3HT-PMe3) and poly[3-(6'-imidazolium)hexyl)thiophene-2,5-diy1] (P3HT-Im; Figure 5d) were synthesized as previously described.104 P3HT-PMe3 and P3HT-Im have number-averaged molecular weight (Mn) of 17.7 kDa and 18.1 kDa (PDI = 1.27), and the molecular weight of each monomer unit is 320.01 g/mol and 326.117 g/mol, respectively. Each monomer unit is compensated by a Cl− counterion. A stock solution of each polymer (monomeric concentration of 2 × 10−3 M) was prepared in water (puri
ed through a Synergy water puri
er as a solvent

For experiments with di
c20, minor portions of 0.1 M HCl or NaOH were added, either to lower or raise pH, respectively. The pH titrations were carried out at 20 °C using H2O, NaCl, or PBS buffer as a solvent for salt-dependence studies. The reported pH values (measured with accuracy of ±0.05 pH units) are those obtained before the CD spectra were taken.

Absorption Spectroscopy. Absorption spectra were recorded with a UV/vis/NIR Lambda 900 spectrometer (PerkinElmer). A quartz cuvette with an optical path length of 10 mm was placed inside the temperature-controlled cuvette holder (Flash300/E, Quantum Northwest), and the temperature was allowed to stabilize for 5–10 min. A small magnetic stir bar was placed in the cuvette, and the stirring speed could be controlled with the cuvette holder.

Circular Dichroism Spectroscopy. CD spectra were recorded with a J-715 spectropolarimeter (Jasco). A quartz cuvette with an optical path length of 10 mm was placed inside the temperature-controlled holder of the spectropolarimeter. For the pH titration of dC20, CD spectra were recorded with a Jasco J-815 CD Spectrometer using EPR Suprasil tubes (diameter: 4 mm).

Transient Absorption Spectroscopy. TA spectra were recorded using femtosecond pulsed laser pump–probe spectroscopy. The solutions were placed in a quartz cuvette with an optical path length of 2 mm (Starna Cells Inc.) placed inside the temperature-controlled holder and held by a piece of aluminum. Pump excitation at 400 nm (200 fs resolution) was achieved by frequency doubling the fundamental 800 nm laser output (from a Ti:sapphire laser system with regenerative amplification providing 35 fs pulses at a repetition rate of 1 kHz, Astrella, Coherent). As an alternative, an excitation beam at 800 nm (<100 fs resolution) was generated with a commercial optical parametric amplifier (OPera Solo, Coherent). The pump diameter was 1.0 mm, and the pump intensity was 400 kW/nm. The beam diameter was 400 μm, and the excitation frequency doubled the fundamental 800 nm laser output (from a Ti:sapphire laser system with regenerative amplification providing 35 fs pulses at a repetition rate of 1 kHz, Astrella, Coherent). As an alternative, an excitation beam at 800 nm (<100 fs resolution) was generated with a commercial optical parametric amplifier (OPera Solo, Coherent). The pump diameter was 1.0 mm, and the pump intensity was 400 kW/nm.

Phosphate buffered saline (PBS) was pur chased from Thermo Fisher Scientific (catalogue number: 10010–031, pH 7.4, KH2PO4 1.06 mM, Na2HPO4 2.97 mM, NaCl 155 mM) and was used to dilute polymer and ssDNA stock solutions to different monomeric concentrations depending on the experiment: 7.3 × 10−3 M for stationary absorption and CD measurements, 1.5 × 10−4 M for TA and RR experiments in dA20 and T406, and 3 × 10−4 M for RR experiments in dC20. For cationic polythiophene/ssDNA experiments, solutions with monomeric equivalence were prepared, with one positive charge from cationic polythiophene for one negative charge of ssDNA in order to have a complete formation of the complex form (see titration in Figure S19).12,51 The order of addition for all the solutions was the following: PBS (solvent), cationic polythiophene, ssDNA. We note that the CPT/dC20 complex was formed and studied at 55 °C only for the stationary absorption and CD measurements. In order to avoid precipitation effects during the longer RR and TA measurements, the CPT/dC20 complex was formed and studied at 20 °C, although this decreases the A0−/A∞ ratio to 1.16 (see Figure S3b).

For experiments with different lengths of dC, aqueous solutions (0.1 mM, oligomer concentration) of homocytosine of five different lengths (5, 10, 20, 40, and 80 bases) were also purchased from Sigma-
were averaged 3000 times at each time delay, and the entire range of measured time delays (between −4 ps and 1 ns) was scanned five times, without any noticeable signs of degradation. Wavelength calibration was accomplished with a series of 10 nm bandpass filters. To avoid polarization effects, the relative polarization of the probe and pump pulses was set at the magic angle. All spectra were corrected for the chirp of the white-light probe. MATLAB and IgorPro software were used for data analysis.

**Resonance Raman Studies.** Resonance Raman (RR) spectra of cationic polythiophene/ssDNA complexes were obtained with excitation at 435.69, 473, 532, and 266 nm. The 532 and 266 nm excitation wavelengths employed in the RR experiments were provided by the second and fourth harmonics of a Q-switched Nd:YAG laser (PRO-230, 30 Hz, Spectra Physics), and the 435.69 nm was produced via Raman shifting at 532 nm in a 1 m tube containing H₂ gas. The 473 nm excitation was obtained from a CW diode laser (Ultralasers, 50 mW OEM DPSS Laser). The excitation light was focused into a spinning cell consisting of an EPR Suprasil tube (diameter: 4 mm) attached to a rheostat-controlled motor for choice of rotation speed. Use of the spinning cell prolonged the lifetime of the samples. Modest excitation energies (2.1 mW at 473 and 435.69 nm, 0.1 mW (3.3 μJ per pulse) at 532 nm, and 0.07 mW at 266 nm (≈2.5 μJ per pulse)) were employed to avoid decomposition of the sample, which was monitored by obtaining the absorption spectrum of the sample before and after exposure. The Raman scattered light was collected in a backscattering geometry and delivered to a 0.75 m focal-length Czerny–Turner spectrophotograph, equipped with a 1200-grooves/mm holographic grating for the visible wavelengths and a 2400 grooves/mm holographic grating for excitation at 266 nm. The slit width was set to 100 μm providing for 5 cm⁻¹ spectral resolution at the visible wavelengths used in this work and 7 cm⁻¹ at 266 nm. The scattered light was detected by a LN₂-cooled 2048 × 512 pixel, back-illuminated UV-enhanced CCD detector (Spec10:2KBUV/LN, Princeton Instruments). Each spectrum with excitation in the visible is accomplished with the use of cyclohexane. MATLAB and ORIGIN software were used for spectral treatment and analysis.

### COMPUTATIONAL METHODS

**MD Simulations.** For the ssDNA fragments only, the system featured the respective ssDNA 20mer (dC₀₂₀ or dA₀₂₀), approximately 5000 water molecules and 20 Na⁺ counterions for charge neutralization. The parmbsc1 force field was used for ssDNA, while water was modeled with the TIP3P108 force field with corresponding parameters for Na⁺ ions.¹⁰⁹ Both systems were first equilibrated at 300 K and 1 atm, and then the production phase was carried out for a total of 1.8 μs, with a time step of 2 fs. Bonds involving H atoms were kept fixed using the SHAKE algorithm.

For all CPT/ssDNA assemblies, two separate simulations were performed for each system with different initial distances between the ssDNA and the polymer (10 and 30 Å, respectively). The resulting periodic boxes contained approximately 30 000 and 54 000 water molecules, respectively. In addition to the solvent and the ssDNA and CPT 20mers, the system setup for both simulations also included a biologically relevant 150 mM concentration of Na⁺ and Cl⁻ ions, and 25 000 water molecules and 150 mM NaCl) was also carried out. The aforementioned parametrization for CPT, H₂O, Na⁺, and Cl⁻ was used. The simulation protocol used for the DNA and CPT/DNA systems was also employed here, amounting to 1.5 μs of total simulation time in the production phase.

**Chirality Analysis.** For two neighboring nucleobases, i and i + 1, their local chirality index, CI_{i,i+1}, is defined as

\[
CI_{i,i+1} = \frac{r_{i,i+1}(\mu \times \mu_{i,i+1})}{|r_{i,i+1}| |\mu| |\mu_{i,i+1}|}
\]

In eq 1, \(r_{i,i+1}\) is the vector connecting the centers of mass of the nucleobases i and i+1, while \(\mu\) and \(\mu_{i,i+1}\) are unit vectors that are perpendicular to their respective planes. The average local chirality index for a given frame of the trajectory is then obtained by averaging the indices over the entire length of the ssDNA.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.0c02251. Additional computational and spectral data (absorption, resonance Raman, CD, transient absorption) and resonance Raman intensity analysis. Data shown in the main figures are available at https://boris.unibe.ch/id/eprint/146048 (PDF)

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Author Contributions

L.P. and E.N. equally contributed to this work. CPT polymer was synthesized by M.L.’s group and P3HT-PMe3 and P3HT-IIm polymers were synthesized and provided by S.C.’s and M.S.’s groups. Spectroscopic data were collected by L.P., E.N. and E.A. and analyzed by L.P., E.N., S.C.H. and E.A. The experiments were conceived and supervised by N.B and S.C.H. P.D. conducted and analyzed the MD simulations which were supervised by U.R. All the authors discussed the results. N.B. and S.C.H. wrote the manuscript with input from all other authors.

Notes

The authors declare no competing financial interest.

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REFERENCES
