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.1–5 In particular, the strong correlation of the photophysical properties of conjugated polythiophenes to their backbone conformation has been under intensive investigation.5–10 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.11–15 Such directional energy and charge transport along the chain can be exploited in electrical components, e.g., nanowires for molecular devices,16–18 cathodes in next generation batteries,19 capacitors,20,21 nanosensors,22 nanophotonics, quantum information technologies, or artificial light-harvesting systems.16,23,24 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,25–27 and by an enhanced radiative decay rate.26,28 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.28 Strategies to induce extended backbone conformations range from chemical modification of the polymer (mostly the side chains),1,2,29 to noncovalent approaches, such as control of the electronic coupling through processing protocols,27 dilution within an inactive solid polymer matrix (polyethylene or polypropylene),10 or supermolecular assembly with templating molecules. Templates under consideration include cyclodextrins30–33 and polysaccharides34 for the formation of rod-like inclusion complexes, as well as extending charged polythiophenes through electrostatic interactions.35 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 conformational and optical response of the polymer. The complex formed of CPT and homonucleotide oligocytosine (dC) strands (Table S1) is especially noteworthy. Here, the exceptionally high ratio of the first to second vibronic peaks in the absorption spectrum points to uncommon intrachain coherence in highly ordered and extended chains. To fundamentally understand the atomic-level interactions that direct this unique and very desirable templating effect, we combine stationary absorption, circular dichroism (CD), femtosecond transient absorption (TA) and resonance Raman (RR) spectroscopy with resonance Raman intensity analysis (RRIA) and molecular dynamics (MD) simulations. We compare different ssDNA sequences, different lengths of dC strands, and various side chains on the polythiophene backbone. This establishes the structure–property correlations that link the degree of order in the backbone, the chirality of the induced conformation, and the specific interactions that develop between the cationic polythiophenes and each ssDNA strand to the optical and excited-state behavior of the complexes. We pin down key parameters leading to the strong templating effect in the CPT/dC supramolecular assembly. On the one hand, a succession of 10–20 cytosines shows the best templating ability, as this enables numerous π−π interactions between the cytosine and thiophene moieties. On the other hand, the short alkyl side chains on the polythiophene backbone facilitate further stacking interactions between the cytosines and imidazoles that stabilize the complex, while methyl substitution on C6 favors syn−anti conformations of CPT, further contributing to torsional order of the polymer. 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 CPT 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.

CPT/dA20 at 20 °C shows a (+/−) CD signature with a positive band centered at 593 nm and a negative band at around 500 nm (unlike achiral CPT alone, Figure S2), meaning that 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 (Figure S2). 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 55a 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

![Figure 1. Molecular structure of cationic poly(1H-imidazolium,1-methyl-3-[2-[(4-methyl-3-thienyl)oxy]-ethyl]-chloride) (CPT).](https://dx.doi.org/10.1021/acs.chemmater.0c02251)
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)\textsubscript{i,i+1}, see Computational Methods for details), similar to the one recently reported.\textsuperscript{53} The average chirality index distribution of dA\textsubscript{20} 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/dA\textsubscript{20}. The distribution of the chirality index of CPT in CPT/dA\textsubscript{20} 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/dA\textsubscript{20}, the spectrum of the CPT/dC\textsubscript{20} complex shows a red-shifted absorption, strong vibronic structure (with a spacing of 1447 cm\textsuperscript{-1} due to the symmetric C–C and C=\textsuperscript{S}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\textsubscript{0,0}/A\textsubscript{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/dC\textsubscript{20} complex is very rigid compared to CPT/dA\textsubscript{20}, 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/dC\textsubscript{20} 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/dA\textsubscript{20} to CPT/dC\textsubscript{20}) is qualitatively reproduced by the MD simulations with more left-handed conformations being sampled for CPT in CPT/dC\textsubscript{20} compared to CPT/dA\textsubscript{20}. 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 μs), the sampling of the local chirality index of CPT in CPT/dC\textsubscript{20} 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/dC\textsubscript{20} 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.66−68 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.55 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.27

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).54,69,70 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.\textsuperscript{71} This phenomenon is known for double stranded DNA, which absorbs less compared to the denatured form.\textsuperscript{22} The MD simulations confirm that the chirality distribution of dC\textsubscript{20} in CPT/dC\textsubscript{20} is fully shifted to negative values (left-handed orientations) of the average CI\textsubscript{140} sampling larger absolute values of the average local chirality indexes compared to dA\textsubscript{20} in CPT/dA\textsubscript{20}.

**Backbone Planarity of CPT in the Complexes with dA\textsubscript{20} and dC\textsubscript{20}** 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/dC\textsubscript{20}.

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\textsuperscript{-1}. At the used wavelengths (473 and 532 nm), we are on resonance with the \(\pi-\pi^*\) 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.\textsuperscript{55} 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/dA\textsubscript{20}, the bands appear essentially at the same position as in the case of the polymer alone, while a 3–4 cm\textsuperscript{-1} downshift is observed in the case of CPT/dC\textsubscript{20}. Moreover, the relative intensities of the C–C (~1400 cm\textsuperscript{-1}) and C=\(\equiv\)C (1487 cm\textsuperscript{-1}) stretches in CPT/dC\textsubscript{20} 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/dC\textsubscript{20} complex.\textsuperscript{55} The intensity of the C–C band increases further with excitation at 532 nm, due to resonance with even more planar and lower energy chain segments. In addition, the spectrum of CPT/dA\textsubscript{20} exhibits broader line widths, showing inhomogeneity and torsional disorder of the CPT conformation. In contrast, the narrow peaks observed in the CPT/dC\textsubscript{20} 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/dC\textsubscript{20} \(\gg\) CPT/dA\textsubscript{20} \(\varpropto\) CPT alone, which agrees with the increased degree of planarity for CPT/dC\textsubscript{20} witnessed by RR spectroscopy with visible excitation.

**Atomic-Level Details of the CPT-ssDNA Interactions** We have shown that dA\textsubscript{20} does not induce strong conformational changes in CPT, while dC\textsubscript{20} leads to a tighter structure for the CPT/dC\textsubscript{20} complex, with pronounced optical signatures of the polymer. To understand this selective response to different ssDNA bases, we have investigated the atomistic-level interactions in the complexes during the MD simulations using a close contact analysis. We evaluate (1) electrostatic interactions between the negatively charged phosphate groups of the ssDNA and the positively charged imidazole side-chains of CPT, (2) various types of \(\pi-\pi^*\) stacking (between the cytosine/adenine bases and the thiophenes or imidazoles of CPT, intra-DNA \(\pi-\pi^*\) stacking between the nucleobases, intra-CPT \(\pi-\pi^*\) stacking between the thiophene and imidazole rings), and (3) intra-DNA and CPT/DNA H-bonding (between the NH\textsubscript{1} groups of the nucleobases and the oxygen of the CPT thiophenes). This is then experimentally confirmed by RR spectroscopy in the UV (266 nm), which interrogates structural changes that occur in the various ssDNAs upon complexation with CPT.

We find that electrostatic interactions are crucial to bringing the CPT and ssDNA strands together and play a significant role in both the CPT/dA\textsubscript{20} and CPT/dC\textsubscript{20} complexes (Figures S11–S14). This agrees with the efficient assembly of CPT with both ssDNA strands, evidenced by the stationary absorption and CD spectra, as well as via the reduced excited-state lifetimes of both complexes (see below). In CPT/dA\textsubscript{20}, the pronounced intra-DNA \(\pi-\pi^*\) stacking (between neighboring adenine bases, Figure S15.3) and thiophene–imidazole interactions within CPT (Figure S15.5) prevail over the stacking between the ssDNA and CPT units (adenine-thiophene/imidazole, Figure S15.1 and S15.2), leading to conformational flexibility and broad absorption of CPT in the complex. The MD simulations also show that CPT/dA\textsubscript{20} displays limited intra-DNA H-bonding interactions between NH\textsubscript{2} groups of adenine bases and phosphate groups, and a similar number of weak CPT-DNA H-bonds (Figures S17 and S18a). Thus, electrostatic interactions are principally responsible for the overall structure of CPT/dA\textsubscript{20}. The weak adenine-CPT stacking is experimentally confirmed by the UVRR analysis. Figure 3b presents the UVRR spectra of each ssDNA alone and in the complex (extended spectral range in Figure S10). The spectra of the ssDNAs are similar to those previously reported (see Table S6 for the assignment of the main bands).\textsuperscript{73–76} Characteristic bands of ssDNA are associated with in-plane vibrational modes of the base rings and exocyclic bonds. Sugar and phosphate vibrations are not enhanced at this excitation wavelength and are therefore not identified in the UVRR spectra. As reported in the past,\textsuperscript{69} the vibrational bands in the UVRR spectra of NAs are highly sensitive to structural changes. Thus, the great similarity displayed between the Raman spectra of dA\textsubscript{20} and CPT/dA\textsubscript{20} reflects the resistance to deformation due to the intrinsic rigidity of single-stranded dA\textsubscript{20}, which is stabilized by the stacking interactions between adenine bases.\textsuperscript{64,65}

In contrast, the Raman bands at 991, 1297, 1381, and 1532 cm\textsuperscript{-1}, which correspond to vibrational modes of cytosine localized near the glycosidic bond, experience an intensity decrease when dC\textsubscript{20} assembles with CPT (Figures 3b and S10). Previous work has shown that these base vibrations are affected by the deoxyribose ring puckering and the glycosidic bond orientation defined by the torsion angle (\(\phi\)).\textsuperscript{65,77–79} The conformational sensitivity of the in-plane base vibrations derives from vibrational coupling with the adjacent C(1′)-H bend from the deoxyribose ring (see Figure S10c). Therefore, the changes observed in peak amplitude are likely associated with a transition in sugar puckering and alteration of the
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 cytosines stack with every other thiophene in the sequence, due to the long distance between bases imposed by the phosphodiester bond. The close contact analysis also shows that nucleobase–imidazole interactions in CPT/dC20 are much more abundant than in CPT/dA20 (Figure S15.2). Both π–π interactions thus play a decisive role in defining the compact structure of CPT/dC20 and are further complemented by thiophene–imidazole stacking within the CPT backbone (Figures 4 and S15.5).

Intra-DNA cytosine stacking in dC20 is not as strong as the adenine interactions in dA20 (Figures S15.3 and S15.4), rendering the cytosines available for π-stacking with the thiophenes and imidazoles from CPT. Moreover, the MD close contact analysis demonstrates a significant decrease in cytosine stacking once CPT is added (Figure S15.4). Any secondary structure that dC20 can adopt on its own is thus disrupted, and the ssDNA chain is forced into a different conformation during complex formation as attested by UVRR and the CD signature in the UV (see Figures 2c and 3b). Finally, the local structure of the CPT/dC20 complex is stabilized by H bonds within the dC20 strand, mainly between amine groups of cytosine and oxygen atoms of phosphate, which are far more abundant than weak H bonds between DNA and CPT (Figure S18b). Thus, H-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,82 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_{260}/A_{280} ratio, see Figure S20 for the titration results). However, the A_{260}/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 dC_{10} (A_{260}/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 dC_{10} 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 dC_{80} alone and CPT/dC_{80} (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_{260}/A_{280} = 1.06).

Finally, we find that complex formation is not complete for one monomeric equivalent of dC_{o}, 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 dC_{o}, an important excess of ssDNA needs to be added.
Leaving this solution for 1 day then leads to a narrow vibronic absorption structure with $A_0 - A_{-1} = 1.27$ (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.

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.\textsuperscript{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),\textsuperscript{52} an intermediate templating effect can be achieved, with an optical response between those of CPT/dA$_{20}$ and CPT/dC$_{20}$ (Figure S26). 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...
Figure 6. (a) TA spectra recorded following excitation at 400 nm at selected time delays with the corresponding stationary absorption (black curves) for two complexes (top, CPT/dA20; bottom, CPT/dC20) in solution at 20 °C (1.5 × 10^{-4} M on a monomeric unit basis in PBS). The features at around 740 and 860 nm are artifacts due to the white light generation near the fundamental 800 nm laser output. (b) TA dynamics at selected probe wavelengths for the three complexes (λ_t, T406, and C). Solid lines correspond to the biexponential fit. A_{ex} = 400 nm.

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[(GGAA)]_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 S3,8,3,8,3,84 (Figure 5c). P3HT-Im and P3HT-PMe3 have different cationic side groups (phosphonium and imidazole, Figure 5d), which are attached to the C_{π} position of the thiophene backbone via a six-carbon chain (without the oxygen atom present in CPT). Moreover, the methyl group from the C_{π} 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 27,28 but differ from the one of CPT, where the C=C stretching mode is split due to alk oxy substitution at the C_{π} position.86,87 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 more pronounced for both complexes of P3HT-PMe3 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 polythiophenes, with dC20 having the largest tendency to enhance backbone torsional order, its templating ability is significantly reduced with P3HT-Im and P3HT-PMe3 (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 C_{π} methyl substituent, since our MD simulations show that chalcogen interactions (involving the alkoxy 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-PMe3 with ssDNA or dsDNA.3,8,3,84 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, and a negative feature below 800 nm is attributed to ground state bleaching (GSB) and stimulated emission (SE), with the differences in band shape associated with different degrees of order in CPT as also reflected in the absorption spectra. The broad and red-shifted ESA is characteristic of delocalized excitons (as we observed for ordered CPT alone at low temperature, 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

Figure 7. (a) Dependence of the displacement (Δ) along the Cβ–Cβ and Cα–Cβ normal coordinates on the CPT/ssDNA complex, as obtained from modeling the absorption and Raman cross sections. (b) Extracted stimulated emission spectra at different time delays after photoexcitation for CPT/dC20. (c) Experimental and calculated SE spectra at 0.2 and 10 ps after photoexcitation for CPT/dC20. (d) Dependence of the displacement (Δ) along the Cβ–Cβ and Cα–Cβ normal coordinates on the delay time, as obtained from modeling the stimulated emission spectra.
resonance Raman cross sections ($\sigma_\text{R}$, section S9.1.1). The absolute $\sigma_\text{R}$’s for all the RR 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 $\sigma_\text{R}$ as a function of excitation energy. The fitting parameters are reported in Table S11. We find that the CPy−CPy 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 Cα=Cα 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 ($\lambda_{\text{tot}} = \sum \lambda_i = \sum \omega_i \Delta_i$/2)), 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 properly scaled calculated absorption (Figure 7b) and use of a similar methodology to RRIA to analyze them (Figure 7c, section S9.1.3). The earliest SE spectrum accessible within the time resolution of our TA experiment (at 200 fs) already displays a Stokes shift of 52 meV ($\sim$70% of the total Stokes shift) with respect to the absorption. Such behavior in conjugated polymers is typically related to ultrafast dynamic localization of the initial photoexcitation, caused by electronic relaxation and coupling to nuclear modes.95–97 However, the initial Stokes shift observed for CPT/dC20 is less pronounced than in other systems and (in contrast to, e.g., P3HT)98 the early emission spectrum is a mirror image of the absorption that can be reproduced with identical parameters. This points to limited (mainly electronic) relaxation within $<200$ fs, maintaining delocalization of the excited state and possibly favoring the occurrence of coherent exciton migration along the chain.95,96,97,98

At longer time delays ($>200$ fs), the SE spectrum of CPT/dC20 undergoes a red-shift of the 0−0 band (by $\sim$22 meV, leading to a total Stokes shift of 74 meV), and an increase of the vibronic band intensity ratio ($I_{0-0}/I_{0-1}$) from 1.34 at 0.2 ps to 3.41 at 10 ps (Figure 7b). Fitting of the SE spectra reveals that the geometrical relaxation of the polymer involves mainly the CPy−CPy stretch, as this exhibits the highest contribution to the SE vibronic progression and sustains the largest reduction in $\Delta$ with time (Figure 7d, Table S12). A concomitant decrease of the inhomogeneous broadening, which indicates a narrower distribution of chromophores, occurs within the first 2 ps. On the basis of previous literature about polythiophenes, this slower relaxation is ascribed to mainly incoherent exciton migration to lower energy chain segments (longer, more planar), accompanied by torsional relaxation of the backbone.13,56,99–101 Again, the effect in CPT/dC20 is weaker and faster than generally observed (e.g., the total Stokes shift for polythiophene solutions is usually twice as large and spectral relaxation proceeds up to 100–200 ps).56,98 The limited geometrical relaxation in the complex agrees with the small reorganization energy calculated by RRIA ($\sim$140 meV) and the fact that dC20 induces a more planar and tighter conformation of CPT already in the ground state, hindering large reorganization of the excited state. Moreover, exciton migration is limited to intrachain processes and likely concerns a more homogeneous distribution of chain segments with similar energy. Going to CPT/dA20, a slightly more important spectral red-shift is observed in the negative TA features (from 593 nm at 0.2 ps to 600 nm at 5 ps, vs from 591 to 594 nm in CPT/dC20), as predicted by the higher reorganization energy in the more flexible complex. This is still much less than the red-shift of the TA bands observed for random-coiled CPT alone at 55 °C (40 nm shift over 100 ps),55 suggesting that even for CPT/dA20 the excited-state relaxation is restricted by the complexation with ssDNA.

## 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 approach-

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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 intrachain exciton delocalization, favoring (possibly coherent) molecular assemblies with conjugated polymers.

**EXPERIMENTAL SECTION**

**Materials.** CPT (Figure 1) was synthesized as previously described. It has a molecular weight (Mw) of 22 kDa (Mn = 11 kDa), with a polydispersity index (PDI) of 2.0. Each monomer unit of 262.8 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-diyl] (P3HT-PMe3) and poly[3-(6′-(imidazolium)hexyl)thiophene-2,5-diyl] (P3HT-Im; Figure 5d) were synthesized as previously described. 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 polymer (monomeric concentration of 2 × 10−3 M) was prepared in water (purified through a Synergy water purification system) and stored in the freezer. Single-stranded oligonucleotides (ssDNAs) were purchased from Sigma-Aldrich. The homocytosine oligomers and their monomeric concentrations are listed in Table S2. PBS was used to dilute the CPT and ssDNA stock solutions. CPT first: 58.4 μL of CPT (2 × 10−3 M) was added to 1540 μL of PBS to obtain a final concentration of 7.3 × 10−3 M, on a monomeric basis. Then, several portions of dC (each portion corresponding to 1/4 of the total monomeric concentration of CPT) were added to the CPT solution. dC first: a volume of dC stock solution (different for each dC) was added to 1540 μL of PBS to obtain a final concentration of 7.3 × 10−3 M, on a monomeric basis. Then several portions of 14.6 μL of CPT (2 × 10−3 M, corresponding to 1/4 of the total monomeric concentration of dC) were added to the dC solution. After each addition of every titration, the solution was left to equilibrate for at least 5–10 min before recording the steady-state absorption and CD spectra. The temperature was set at 20 °C.

For the study of the pH dependence of the stability of i-motif conformation for dC20, 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 stand-alone Peltier-based 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 about 1 mm, and the pump intensity was 400 mW with the 400 nm excitation and between 200 and 330 mW for the 800 nm excitation. The probe beam consisted of a white light continuum (450–1200 nm) generated by passing a portion of the 800 nm amplified Ti:sapphire output through a 5 mm thick sapphire window. Either 720 nm low pass filters or 850 nm long pass filters were used to remove the remaining fundamental intensity from the white light, and the visible and the near-infrared (nIR) parts of the spectra were recorded separately. The probe intensity was negligible compared to the pump intensity, and the spot size was much smaller (probe energy of <5 nJ, probe diameter of about 160 μm). The probe pulses were time-delayed with respect to the pump pulses by means of a computer-controlled translation stage. The probe beam was split before the sample into a signal beam (transmitted through the sample and overlapped with the pump beam) and a reference beam. The signal and reference beams were detected separately using a pair of spectrophotographs (home-built prism spectrometers) equipped with S12 × 58 pixel back-thinned CCDs (Hamamatsu 3070—0906) and assembled by Entwicklungsbüro Streising, Berlin. The pump beam was chopped at half the amplifier frequency to improve the sensitivity of the setup. The transmitted intensity of the signal beam was recorded shot-by-shot, and it was corrected for laser intensity fluctuations using the reference beam. The single shot TA spectra were chopped at half the amplifier frequency to improve the sensitivity of the setup.
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 spectrometer, 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 featured the respective ssDNA 20mer (dC₂₀ or dA₂₀), approximately 30 000 and 54 000 water ssDNA and the polymer (10 and 30 Å, respectively). The resulting performed for each system with different initial distances between the nucleobases, i and i + 1, while $\mu_{i}$ and $\mu_{i+1}$ 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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**COMPUTATIONAL METHODS**

**MD Simulations.** For the ssDNA fragments only, the system featured the respective ssDNA 20mer (dC₂₀ or dA₂₀), approximately 5000 water molecules and 20 Na⁺ counterions for charge neutralization. The parmbsc1 force field106,107 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, in line with the ionic strength of the PBS buffer solution employed in the experiments. The ssDNA 20mers, water, and ions were described in the same fashion as in the pure ssDNA simulations. Point charges for the polymer atoms (listed in detail in Figure S1 and Tables S3 and S4) were obtained from static calculations performed on CPT tetrans, using Gaussian 09,111 and the polarizable continuum model for water.113,114 The geometry of the tetrans was optimized at the Density Functional Theory (DFT) level115,116 employing the B3LYP functional115,116 combined with the 6-31G(d,p) basis set117,118 recently used for a study of another polythiophene derivative.119 Atom types and interactions between CPT atoms were assigned according to the recently updated General AMBER force field (GAFF2120,121 with the exception of the S–C–C–S torsion angle where parameters were selected from ref 119. The simulation protocol was the same as for the pure ssDNA simulations, with the production phase amounting to a total of 1.54 μs from the two independent MD runs. All simulations were carried out with the GPU version of AMBER16.122

A simulation for CPT in aqueous solution (with approximately 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, CIᵢᵢ₊₁, is defined as

$$CI_{i,i+1} = \frac{\vec{\tau}_{i,i+1} (\vec{\mu}_i \times \vec{\mu}_{i+1})}{|\vec{\tau}_{i,i+1}|^2 + |\vec{\mu}_i|^2 |\vec{\mu}_{i+1}|^2}$$

In eq 1, $\vec{\tau}_{i,i+1}$ is the vector connecting the centers of mass of the nucleobases i and i+1, while $\vec{\mu}_i$ and $\vec{\mu}_{i+1}$ 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.

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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