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ssDNA Templated Self-Assembly of Chromophores

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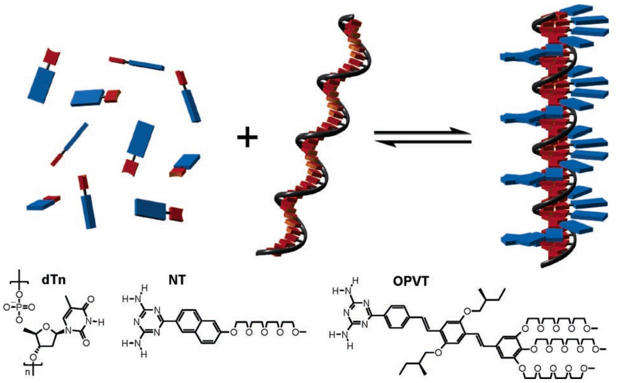
DNA is a promising building block to organize molecules in a "bottom-up" approach for construction of functional nanosized objects.[1,2] For example, organic molecules have been covalently attached to DNA for a precise nanoscale organization of chromophores.[3] Noncovalent approaches such as intercalation and groove binding have also been reported,[4] while discrete metal arrays in artificial DNA were recently constructed by using metal−ligand interactions.[5] We have similarly organized chromophores by sandwiching them between two strands of oligoadenine (**dA*n***) via hydrogen bonding.[6] We now demonstrate an approach where only a single strand of DNA templates a supramolecular strand of chromophores, yielding a new type of DNA hybrid.[7] In this hybrid construct, an oligothymine (**dT*n***, n = number of thymines) is used as the template to which a supramolecular stack of chromophores is hydrogen-bonded via the complementary diamino triazine unit. We report that, in case of **dT40**, 40 naphthalenes (**NT**) can be bound and show that this approach can be extended to organize a π-conjugated oligo(*p*-phenylene)vinylene (**OPVT**) (Scheme 1).

The two chromophores have been synthesized analogously to alkyl equipped derivatives[8] and have been fully characterized.[9] **OPVT** and **NT** are both molecularly dissolved in chloroform, giving absorption maxima at $\lambda = 403$ and 315 nm, respectively. Concentration-dependent UV−vis measurements show that **NT** is molecularly dissolved in water up to a concentration of 0.6 mM (Figure 2b). **OPVT** is aggregated at 5 μM, indicated by the blue shift in absorption to 390 nm and a red-shifted, quenched photoluminescence. Remarkably, aggregates of chiral **OPVT** do not possess preferred helical order, concluded from the lack of Cotton effect in the circular dichroism (CD) spectra.

We first studied the complexation and the stoichiometry between **NT** and **dT40**. When **NT** is added to **dT40**, the absorption spectra of **NT** revealed a red shift from 311 to 318 nm at 268 K (Figure 1b). In addition, CD spectroscopy (Figure 1a) shows an induced positive bisignate Cotton effect with a positive maximum at 269 nm and a negative maximum at 244 nm with the zero-crossing at $\lambda_{\max} = 258$ nm. In the region where only the achiral **NT** absorbs, a positive Cotton effect is present with the maximum at 327 nm, showing that **NT** binds to **dT40** and that the chirality present in the template is expressed in the supramolecular organization of the **NTs**.[10] Titration experiments at 263 K show that the absorption changes before the CD intensity increases, suggesting that the helical organization of **NT** occurs at a later stage than the binding to **dT40** (Figure 1c). The Job plot performed at 263 K clearly shows that each **NT** binds to one thymine (Figure 1d).[11]

With electrospray ionization mass spectrometry (ESI-MS), we were not able to detect the **NT**−**dT40** complexes since the detected signals could not be deconvoluted and therefore could not be assigned. Complexes of **dT10** and a number of **NT** molecules have been detected (Figure 1e). The deconvoluted mass spectrum shows **dT10** (M_{dT40} = 2978.5 g/mol) with 2−11 **NT** molecules (443.2 g/mol) bound, showing that the supramolecular complex disassembles under these mild conditions. The formation of nanodroplets could cause the formation of **dT10**−**NT** complexes with more than 10 **NT** molecules.

Scheme 1[a]



[a] Schematic representation of ssDNA templated self-assembly of chromophores (black strand, ssDNA; blue bar, chromophores; red bar, hydrogen-bonding unit) and molecular structures of **dT*n***, **NT** and **OPVT**.

The formation and the stability of the **NT**−**dT40** complex was monitored with temperature-dependent UV and CD spectroscopy measurements by cooling at 6 K/h (Figure 1f). Binding of **NT** to **dT40** is fully reversible, and the shape of the curves indicates a nucleation growth mechanism.[12,13] **NT** first binds to **dT40** (absorption at 269 nm) before **NT** is organized in a helical fashion (CD intensity at 269 nm).

When **dT40** is replaced with the noncomplementary strand **dA40**, no Cotton effect is present above 300 nm, which demonstrates that **NT** binds specifically to **dT40**. In an exchange experiment where an equivalent amount of **dA40** is added to the **dT40**−**NT** complex, the Cotton effect above 300 nm disappears and the CD spectrum of **dT40**−**dA40** arises, meaning that the stack of **NT** is replaced by **dA40** (Figure 2a). This suggests that binding occurs via hydrogen bonding and that the **dT40**−**NT** complex is less stable than **dT40**−**dA40**.

Concentration-dependent UV and CD measurements of the **NT**−**dT40** (40:1) complex show a linear relationship at low concentrations ([**NT**] < 0.6 mM) between the ln[**NT**] and T_e^{-1} (temperature at which the elongation starts), yielding an enthalpy $\Delta H_e = -68$ kJ/mol (Figure 2b). A similar linear relation has been found for dsDNA.[14] At high concentrations ([**NT**] > 0.6 mM), the T_e deviates from the straight line because **NT** itself already aggregates, showing a linear relationship between the ln[**NT**] and T_e^{-1}, with a $\Delta H_e = -26$ kJ/mol (Figure 2b).

In order to create functional materials, we also studied binding of **OPVT** with **dT*n***. Complexes of **OPVT** (0.27 mM) with **dT40** showed a Cotton effect above 300 nm, which is not present in the absence of **dT40** (Figure 3a). The positive Cotton effect at high

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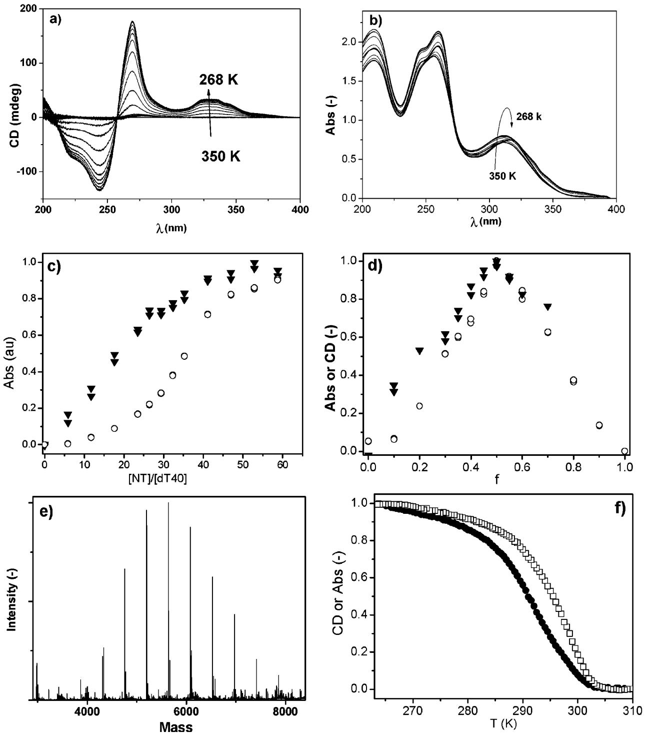

Figure 1. (a) CD and (b) absorption spectra and (f) the normalized UV (□) and CD (○) intensities at 269 nm as a function of temperature of a **NT**−**dT40** mixture ([**NT**] = 0.5 mM, [**dT40**] = 8.5 μM). (c) Titration of **NT** to **dT40**, with [**dT40**] = 8.5 μM and [**NT**] increasing from 0 to 0.5 mM, monitored at 269 nm (absorption (■), CD intensity (○)). (d) A Job plot of **NT** to **dT40** ([**NT**] + 40[**dT40**] = 1.66 mM with f = [**NT**]/1.66 mM). (e) Deconvoluted ESI-MS spectrum of [**dT10**] = 0.2 mM and [**NT**] = 2 mM.

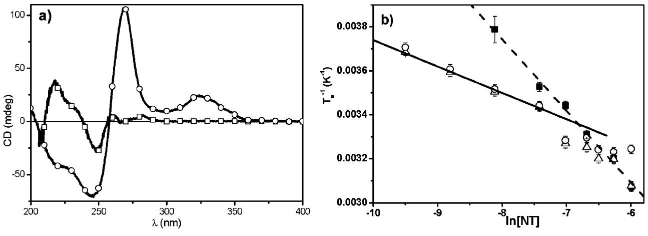

Figure 2. (a) CD spectra at 263 K of a mixture of **dT40** (12.5 μM) and **NT** (0.5 mM) (○) and of the same mixture after adding 1 equiv of **dA40** (□). (b) Plot of T_e^{-1} against ln[**NT**] of **NT**−**dT40** mixtures (40:1) (absorption (△, solid line), CD (○)) mixtures (40:1) and of **NT** alone (absorption (■, dashed line)).

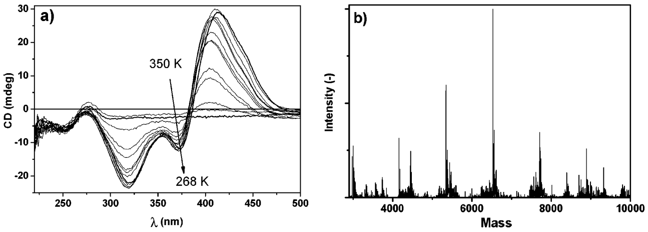

Figure 3. (a) CD spectra of an **OPVT**−**dT40** mixture ([**OPVT**] = 0.27 mM, [**dT40**] = 6.75 μM). (b) Deconvoluted ESI-MS spectrum of [**dT10-OPVT**] = 1 mM at 293 K.

wavelengths suggests a right-handed helical arrangement of **OPVT** molecules upon binding to **dT40**. Compared to a similar concentration of **NT**−**dT40** the T_e of the **OPVT**−**dT40** is higher, probably due to extended $\pi-\pi$ interactions in the supramolecular strand. With ESI-MS, up to five **OPVT** molecules bound to **dT10** were detected (Figure 3b).

In conclusion, new DNA hybrids have been constructed in which the number of chromophores is controlled by the template. Binding of chromophores to ssDNA occurs via hydrogen bonding and is stabilized by $\pi-\pi$ interactions. This approach can, in principle, be applied to any functional molecule equipped with an appropriate hydrogen-bonding moiety to create uniform well-organized nanoscale objects that are potentially useful in the emerging field of supramolecular electronics.[15]

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Supporting Information Available: Experimental methods, synthetic details, and characterization of **NT** and **OPVT** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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