Directing energy transfer in discrete one-dimensional oligonucleotide-templated assemblies†

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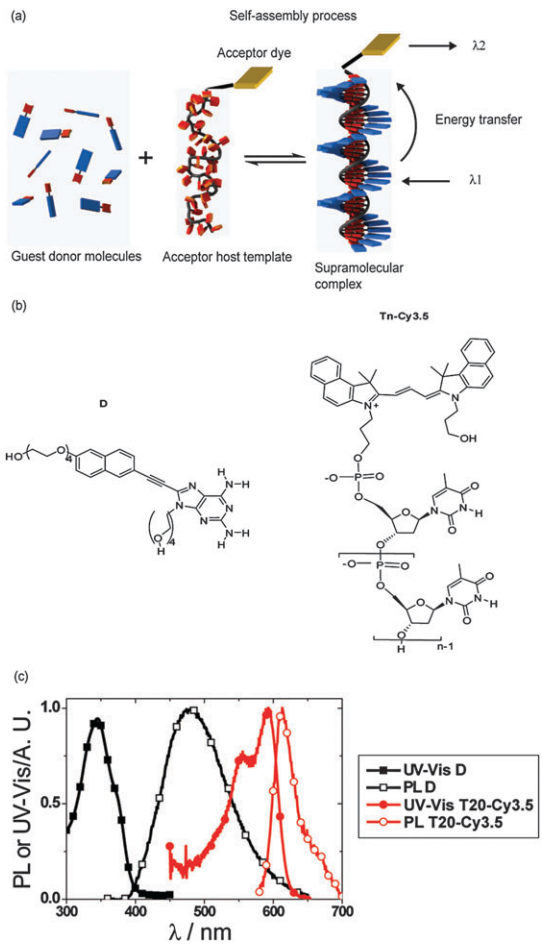
Monodisperse DNA-templated one dimensional dye assemblies have been constructed in which the energy transfer can be directed. Fluorescence experiments suggest an optimum transfer efficiency for stacks of 30 bases long.

Multichromophoric one dimensional (1D) stacks are interesting nanostructures for functional optoelectronic materials and are ideal systems for studying electron and energy transfer phenomena which are crucial processes in organic electronic devices and photosynthesis.[1–3] For these objectives, 1D assemblies of discrete size in which the position of the different chromophores is defined are desirable.[4] The use of a template is an appealing strategy to achieve such systems. DNA having a specific sequence and length is an attractive template for the construction of well-defined one dimensional supramolecular stacks.[5–7] Energy transfer processes using DNA as a template have been previously studied in systems such as hairpins[8] and molecular beacons,[9] where donors and acceptors are usually covalently linked to DNA,[10] intercalated between the base pairs of nanotags or incorporated in the base pairs.[11–13]

Previously, we have reported on the templated assembly of diaminotriazine and diaminopurine-equipped naphthalene and oligo(*p*-phenylenevinylene) guest derivatives selectively binding to an oligothymine template (**T*n***, where *n* is the number of thymines) by hydrogen bonding. In these constructs the chiral single strand DNA host templates a supramolecular strand of achiral chromophores, yielding a right-handed organization of the dye guests (Scheme 1).[14–16] We also found that for smaller template sizes the binding of the guest molecules is less efficient and more than stoichiometric amounts are needed to get a high degree of binding. We now show that these DNA-templated assemblies can be used to direct energy transfer in 1D supramolecular stacks of concrete length in which the position of the different chromophores is defined. An oligothymine template is equipped at the 5′ end with a cyanine dye (**T*n*-Cy3.5**) and energy transfer occurs between the supramolecular strand of donor diaminopurine-equipped naphthalene guest molecules (**D**) and the cyanine dye acceptor molecule (**Cy3.5**) (Scheme 1). Fluorescence measurements suggest that the energy transfer efficiency reaches a maximum at templated stacks of 30 bases (**T30-Cy3.5**).

The naphthalene guest molecule **D** shows an absorption maximum at λ_{max} = 350 nm and a broad emission band with $\lambda_{em,max}$ = 480 nm, while the cyanine dye (**Cy3.5**) has two absorption maxima at λ_{max} = 555 and 590 nm and an emission peak at $\lambda_{em,max}$ = 614 nm (Scheme 1c). The fluorescence



Scheme 1 (a) Schematic representation of the DNA templated assembly and energy transfer process. (b) Chemical structures of the donor naphthalene guest molecule (**D**) and the oligothymine template with the **Cy3.5** acceptor dye covalently attached (**T*n*-Cy3.5**). (c) Normalized fluorescence and UV-Vis spectra of donor ([**D**] = 1.6 mM) and acceptor **T20-Cy3.5** ([**T20-Cy3.5**] = 0.4 mM).

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spectrum of **D** overlaps with the absorption spectrum of **Cy3.5** permitting energy transfer from the donor to the acceptor. When **D** was added to the **T40-Cy3.5** template a similar positive Cotton-effect in the naphthalene absorption region with the zero-crossing at $\lambda_{z\text{-}c}$ = 338 nm was observed as earlier reported for the **D–T40** system indicating the formation of right-handed 1D templated stacks (ESI†).

The binding of **D** to the **T40-Cy3.5** template was further studied by temperature dependent circular dichroism (CD) spectroscopy by monitoring the Cotton-effect at λ = 354 nm (Fig. 1a).[16] The transition temperature at which the templated assembly starts is the same (T = 300 K) for both the **D–T40-Cy3.5** (Fig. 1a) and **D–T40** (ESI†) mixtures, indicating similar binding behavior. These data reveal that the covalent attachment of the **Cy3.5** dye to the oligothymine template does not influence the templated assembly process.

Fluorescence measurements were performed to further characterise the templated assemblies. Interestingly when the **T40** template was added to a solution of guest **D**, the fluorescence intensity (λ_{ex} = 400 nm, λ_{em} = 480 nm) of **D** increases, indicating enhanced emission upon binding to the DNA template. A similar behavior has recently been observed in DNA templated distyrylbenzene assemblies.[17] When the **T40-Cy3.5** template was added to **D** the fluorescence of the guest decreased while a new emission band related to the **Cy3.5** dye arose at $\lambda_{em,max}$ = 620 nm (Fig. 2). A **T40-Cy3.5** template solution having a similar concentration only gives a weak emission band when excited at λ_{ex} = 400 nm (Fig. 2b). These results suggest that energy transfer occurs from the templated assembled guests to the covalently attached **Cy3.5** acceptor.

A fluorescence spectrum of a **D–T40-Cy3.5** solution taken at 313 K showed a decrease in the acceptor emission when compared to 273 K solution (Fig. 2a). Remarkably, also the donor emission decreased (Fig. 2a). Based on the CD data (*vide supra*) it is expected that no donor guests are bound to the DNA template. Most likely at higher temperature the fluorescence of the naphthalene guest diminishes and indeed the fluorescence of a solution of **D** at 273 K is higher than at 313 K (ESI†). Therefore, when the donor molecule is excited, only emission of the donor itself is observed at 313 K. At low temperature the guest molecules are bound to the host template. In that case, energy transfer is likely to occur and indeed emission of the acceptor increases (Fig. 2). Excitation spectra reveal that the acceptor fluorescence coming from the guest donors in the **D–T40-Cy3.5** mixture increases upon lowering the temperature, while when the acceptor is not present (**D–T40** mixture) the emission hardly changes (ESI†). Time correlated single photon counting (TCSPC) experiments at different temperatures were performed to confirm the presence of energy transfer from the donor **D** to the acceptor **Cy3.5**. At 288 K where helical templated assemblies are formed, the lifetime of the **T40-Cy3.5** template probed at the acceptor emission wavelength (λ_{em} = 620 nm) showed a longer lifetime than the templated **D–T40-Cy3.5** assembly (Fig. 3a) while the lifetime of the donor emission wavelength (λ_{em} = 507 nm) has a shorter lifetime for the templated assembly revealing energy transfer from the energy donor **D** to the energy acceptor **Cy3.5** (Fig. 3b). Control measurements performed at a higher temperature where no templated assemblies are present (323 K) showed that the donor lifetime of **T40-Cy3.5** and the templated **D–T40-Cy3.5** assemblies overlap (ESI†). The lifetime of the acceptor **T40Cy3.5** in the complex **D–T40-Cy3.5** is, however, still slightly longer than the acceptor **T40-Cy3.5** template itself (ESI†) which could be due to differences in the **Cy3.5** dye surrounding caused by the guest molecules.[18]

Finally we have also investigated the energy transfer processes between **D** and **Cy3.5** attached to different length templates, ranging from 10 to 40 thymine bases (**T*n*-Cy3.5** n = 10, 20, 30, 40). An increase in the acceptor emission was found for all the different strands at a temperature where templated assembly takes place (273 K) when **D** was selectively excited at λ = 400 nm (Fig. 4a). All oligothymine strands with **Cy3.5** attached show a similar transition temperature by CD (Fig. 4b) compared to the complexes without the dye (ESI†) revealing a greater stability for the longer templated assemblies. The highest CD intensity is observed

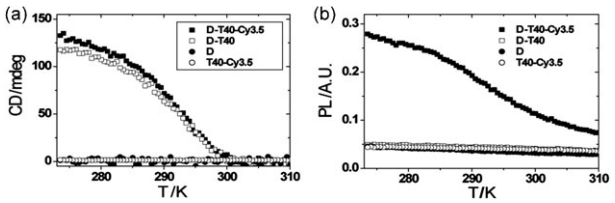

Fig. 1 (a) CD cooling curves monitored at λ = 354 nm and (b) fluorescence cooling curves (λ_{ex} = 400 nm, λ_{em} = 614 nm) of **D**, **T40-Cy3.5**, **D–T40** and **D–T40-Cy3.5** mixtures ([**D**] = 4[**T40**] = 4[**T40-Cy3.5**] = 1.6 mM).

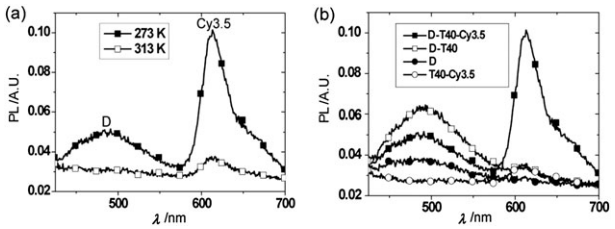

Fig. 2 (a) Fluorescence spectra of a **D–T40-Cy3.5** mixture (λ_{ex} = 400 nm) at 273 and 313 K. (b) Fluorescence spectra of **D** ([**D**] = 1.6 mM), **T40-Cy3.5** ([**T40-Cy3.5**] = 0.4 mM), **D–T40** ([**D**] = 4[**T40**] = 1.6 mM) and **D–T40-Cy3.5** ([**D**] = 4[**T40-Cy3.5**] = 1.6 mM) mixtures at 273 K in water (λ_{ex} = 400 nm).

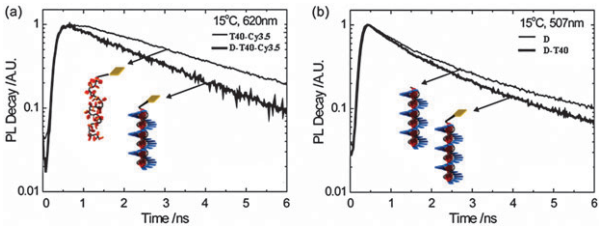

Fig. 3 Photoluminescence (PL) decay of (a) the template **T40-Cy3.5** and the **D–T40-Cy3.5** assembly monitored at the acceptor emission wavelength at 15 °C and (b) PL decay of **D** in the DNA templated assembly with and without the acceptor dye monitored at the donor emission wavelength at 15 °C.

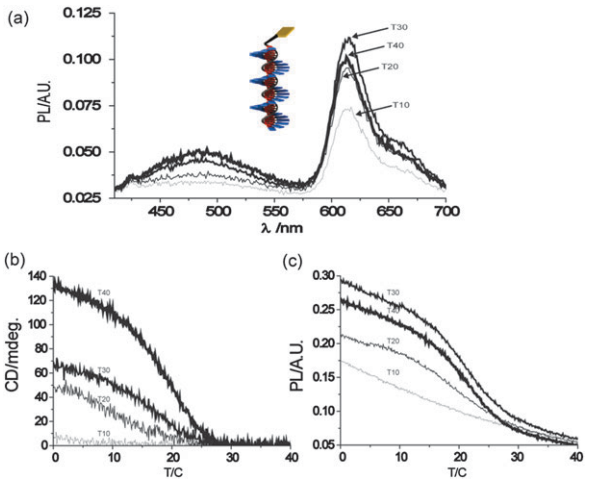

Fig. 4 (a) Fluorescence spectra of the **D–T*n*-Cy3.5** templated assemblies (λ_{ex} = 400 nm) at 273 K ([**D**] = 4[**T*n*-Cy3.5**] = 1.6 mM). (b) CD cooling curves of the **D–T*n*-Cy3.5** assemblies monitored at λ = 354 nm and (c) PL cooling curves of the **D–T*n*-Cy3.5** templated assemblies probed at the acceptor's emission wavelength (λ_{em} = 614 nm, [**D**] = 4[**T*n*Cy3.5**] = 1.6 mM).

for the **D–T40-Cy3.5** assembly which indicates that the binding of the guests is the most efficient in this case. Fluorescence measurements show an increase in the acceptor's emission upon binding **D** (Fig. 1b and Fig. 4c). Interestingly, here the highest acceptor emission is found for DNA strand having 30 bases suggesting that for this template an optimum is achieved between the average donor–acceptor distance and the binding efficiency.[15] This observation is in agreement with TCSPC measurements which will be the subject of further research.[18]

In conclusion we have constructed discrete one dimensional assemblies in which the position of the chromophores can be controlled. Energy transfer takes place in these supramolecular helical stacks between the templated assembled chromophores and the covalently linked acceptor. An optimum stack length seems to be found in the acceptor emission for a stack having 30 energy donor chromophores. Our templated multichromophoric stacks could serve as an ideal system to study fundamental issues within the nanometer dimensions like light harvesting, exciton diffusion length, energy and electron transfer processes and the conversion of light into chemical or electrical energy.

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