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# Preparation, single-molecule manipulation and energy transfer investigation of a polyfluorene-*graft*-DNA polymer

Mikael Madsen[a], Rasmus S. Christensen[a], Abhichart Krissanaprasit[a], Mette R. Bakke[a], Camilla F. Riber[b], Karina S. Nielsen[a], Alexander N. Zelikin[b] and Kurt V. Gothelf*[a],[b]

**Abstract:** Conjugated polymers have been intensively studied due to their unique optical and electronic properties combined with their physical flexibility and scalable bottom up synthesis. While the bulk qualities of conjugated polymers have been extensively utilized in research and industry, the ability to handle and manipulate conjugated polymers at the nanoscale lacks significantly behind. Here we extend the toolbox for controlled manipulation of conjugated polymers through the synthesis of a polyfluorene-DNA graft type polymer (**poly(F-DNA)**). The polymer possesses the characteristics associated with the conjugated polyfluorene backbone, but the protruding single-stranded DNA provides the material with an exceptional addressability. This allows us to demonstrate controlled single polymer patterning, as well as energy transfer between two different polymer-DNA conjugates. Finally, we demonstrate highly efficient DNA directed quenching of the polyfluorene fluorescence.

Conjugated polymers (CPs) are intriguing molecules with a wide variety of applications. They can be produced at low cost, and their physical properties such as band gaps, solubility and optical behavior can be tuned by rational chemical design of the polymer structure.[1] Their semi-conducting behavior and spectacular optical properties have allowed them to find use in various devices including field effect transistors (FETs), polymer solar cells (PSCs), and polymeric light emitting diodes (PLEDs).[2] Polyfluorenes (PFs) are one type of CP that has gained particular interest due to their high stability, great quantum yields and blue light emission.[3] PFs have therefore become a favorite candidate for use in optoelectronic devices and mainly PLEDs.[4]

The success of PFs and other conjugated polymers in such devices is attributed to the bulk polymer properties prevailing in thin films. Extensive research has evolved around understanding and tuning the performance of CP thin films through calculations and thin film characterization.[5] Arguably, it would be of great value to know the behavior of individual polymer molecules and how it translates into the observed output of thin film devices. The study of individual CP molecules is however extremely challenging, and although single molecule fluorescence spectroscopy and STM studies have provided valuable insight, the ability to investigate and utilize single molecule CPs remains underdeveloped.[6],[7]

In an attempt to overcome this, our group recently presented a platform for positioning individual alkoxy-*p*-phenylene vinylene polymers carrying single-stranded DNA brushes (**poly(APPV-DNA)**) in designed patterns on DNA nanostructures, and we further showed that we could switch the polymer conformation in a controlled fashion *via* strand displacement reactions.[8] We envisioned that this platform could be of great use for studying the optical properties of individual CP molecules, as well as the interaction between different types of dyes and CPs at the single molecule level. The **poly(APPV-DNA)** of our previous studies, however, contains inherent defects which limit the conjugation length, while photooxidative degradation of the polymer upon irradiation tends to impede optical studies preventing us from investigating effects such as hybridization-controlled quenching.[9] The fact that we only had access to one type of CP-DNA conjugate further excluded the possibility of investigating inter-polymer energy transfer. To meet these challenges, we have prepared a polyfluorene-*graft*-DNA polymer (**poly(F-DNA)**) that provides continuous conjugation, improved stability and good fluorescence quantum yield. The results on the quenching and energy transfer studies, along with details on the synthesis and single molecule immobilization of **poly(F-DNA)** are outlined below.

The **poly(F-DNA)** is a graft type polymer based on a polyfluorene backbone carrying linkers that are functionalized with single-stranded DNA. To obtain polymers carrying a large number of DNA strands, we followed an approach where DNA is synthesized directly onto the polymer by solid phase oligonucleotide synthesis. To realize this for a polyfluorene type construct, we chose a target structure based on repeating fluorene units carrying protected hydroxyl linkers. This was obtained through the synthesis of a fluorene based monomer (**1**) carrying 2-tetrahydropyranyl (THP) protected triethylene glycol linkers in two steps from fluorene (Scheme S1 and S2).

Polymerization of the monomer, **1**, was carried out through a Yamamoto-type reaction. After precipitation from a MeOH/Acetone (4:1) mixture, polymers with $M_N$ values of 42, 33, and88 kDa and dispersities in the range of 1.5-1.8 as measured by SEC-MALS (Size exclusion chromatography coupled to a multiangle light scattering detector, Table S1 and figure S13) were obtained for the three batches of polymers used in this study. To facilitate immobilization of the polymers for solid phase DNA synthesis, a fraction of the THP groups were removed using dilute TsOH in a chloroform/MeOH mixture. The partial deprotection served to maintain masked hydroxyl groups for oligonucleotide synthesis as well as to keep the polymers soluble. The exposed hydroxyl groups were functionalized by reaction with 2-cyanoethyl *N,N*-diisopropylchlorophosphor-

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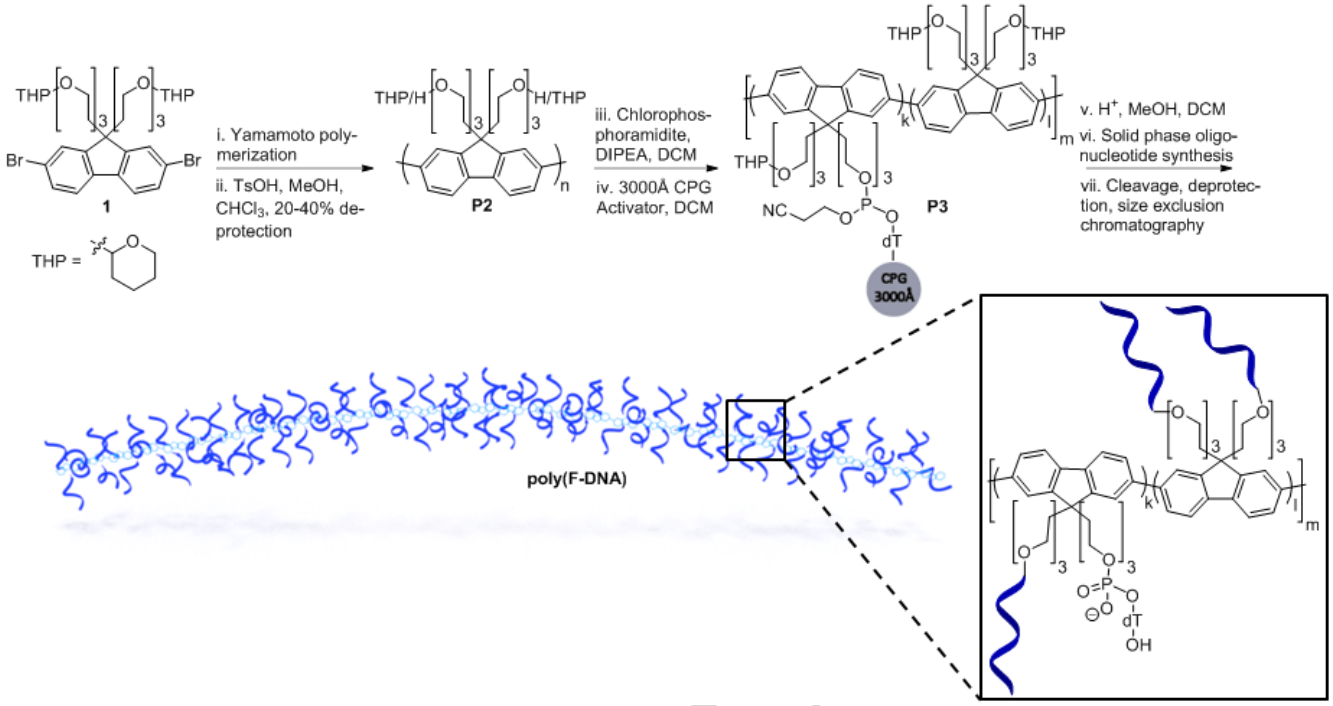


**Scheme 1.** Synthesis of **poly(F-DNA).** Yamamoto polymerization of **1** followed by partial removal of THP protecting groups affords the hydroxyl functionalized polyfluorene, **P2**. Reaction of **P2** with 2-cyanoethyl *N,N*-diisopropylchlorophosphoramidite affords the polymer phosphoramidite intermediate that is immediately immobilzed by reaction with the dT modified 3000Å CPG beads in the presence of ETT (5-ethylthio-1H-tetrazole). Deprotection of remaining THP groups allows for oligonucleotide synthesis onto the polymer. **poly(F-DNA)** is obtained after cleavage and deprotection in AMA followed by size exclusion chromatography. Further details regarding synthetic procedures are provided in the supporting information.

amidite, and the phosphoramidite of the polymer was directly used for immobilization on hydroxyl functionalized 3000 Å CPG beads. After removal of the remaining THP protecting groups, solid phase oligonucleotide synthesis was performed. Subsequent cleavage in AMA (1:1 mixture of ammonium hydroxide and 40% aqueous methylamine) and size exclusion chromatography afforded **poly(F-DNA)** (Scheme 1). Compared to the methods we have previously used for synthesis of polymers with DNA brushes, the formation of the reactive phosphoramidite was here performed on the polymer and not on the solid support. Both strategies were investigated, and apparently indifferent CP-DNA conjugates were obtained through both routes. However, higher yield was observed when the phosphoramidite was formed on the polymer prior to immobilization on the solid support. Key to obtaining **poly(F-DNA)**, was also the use of THP as the hydroxyl protecting group. This protecting group possessed the desired stability under the highly alkaline conditions used during fluorene alkylation and allowed deprotection under mild, acidic conditions after polymerization.

The obtained **poly(F-DNA)** features absorption from single-stranded DNA with $\lambda_{max}$ around 260 nm and from the polyfluorene with $\lambda_{max}$ at 395 nm. It furthermore shows bright blue fluorescence with maximum intensity at 420 nm. The material is readily soluble in buffers such as TAE (Tris-acetate-EDTA) and TEAA (triethylammonium acetate volatile buffer), and it shows great fluorescence quantum yields of ~ 0.58 in TAE and ~ 0.44 in TEAA buffer respectively (Figure S11-12).

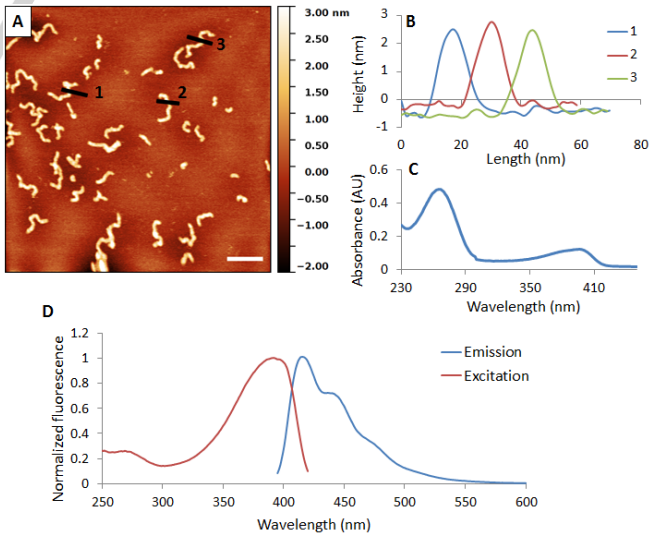


**Figure 1.** Characterization of **poly(F-DNA). A)** Topography AFM image of a fraction containing medium size **poly(F-DNA)** carrying a 10mer DNA sequence. Scale bar = 100 nm. **B)** Height profile for poly(F-DNA) showing heights between 2 and 3 nm. **C)** UV-vis absorption spectrum for **poly(F-DNA)** carrying 15T oligonucleotides. **D)** Excitation (red line, λ(em) = 430 nm ) and emission (blue line, λ(exc) = 385 nm) spectra for **poly(F-DNA).**

To further characterize the polymers, tapping mode atomic force microscopy (AFM) in liquid was performed. In AFM topography imaging, the polymers are observed as elongated structures with occasional presence of multi-polymer structures (Figure S15). Heights between 2 and 3 nm depending on imaging conditions (Figure 1A and B), are typically observed for the structures. The fractions expected to contain the largest polymers as obtained from size exclusion chromatography mainly contain polymers of lengths larger than 100 nm as observed from AFM (Figure S15). SEC-MALS analysis of the isolated fractions shows a clear difference in size between the polymers from the different fractions (Table S2). To estimate the amount of DNA attached to the backbone, a literature value for the extinction coefficient of water soluble polyfluorenes was used.[10] This approach suggests that the polymers typically carry between 0.8 and 1 DNA strands per monomer unit (Table S3).

One of the long-term goals motivating the development of polymers carrying DNA brushes was to enable characterization of intra- and intermolecular energy transfer for individual polymers positioned in controlled conformations at the nanoscale. To realize this, we wanted to establish a method to position **poly(F-DNA)** in controlled patterns on DNA nanostructures. DNA nanostructures have been successfully used for precise nanoscale positioning of various nanoobjects such as gold nanoparticles, carbon nanotubes and biomolecules as well as for templating the formation of polymers.[11] This success can be attributed to the unique spatial addressability that these kinds of structures provide. In structures formed by the DNA origami method all staple strands can be extended and addressed individually providing a spatial resolution of as low as 2-3 nm.[12] In an approach inspired by our previous work, we constructed 2D rectangular DNA origami structures carrying patterns composed of extended staple strands.[8] We then synthesized **poly(F-DNA)** with DNA sequences complementary to the extended staple strands. By mixing the polymer with the nanostructure, we expected that the polymer would align along the pattern of complementary single-stranded DNA directed by DNA-hybridization. To verify that we could indeed position **poly(F-DNA)** in desired patterns on DNA nanostructures, we showed that **poly(F-DNA)** efficiently aligned in 90 degree curves and U-shape patterns as visualized and analyzed by liquid phase AFM (Figure S4).

To move forward in the direction of creating nanoscale circuitry, we wanted to enable the positioning of multiple polymer components on DNA origami. We therefore designed a construct that would allow positioning of **poly(F-DNA)** as well as **poly(APPV-DNA)** along individual tracks on a single nanostructure. The construct was based on a flat rectangular DNA origami structure with linear patterns of extended single-stranded DNA on both planes of the flat structure (Figure 2). For ease of visualization we decided to place the two tracks so that the polymers would form a cross upon immobilization. The sequences of the tracks were designed to align **poly(APPV-DNA)** along the longest axis of the nanostructure, whereas **poly(F-DNA)** would align along the shorter axis. To test the binding specificity, the polymers were individually mixed with the DNA origami construct and characterized by AFM. We observed highly specific binding to the desired track for each polymer, and

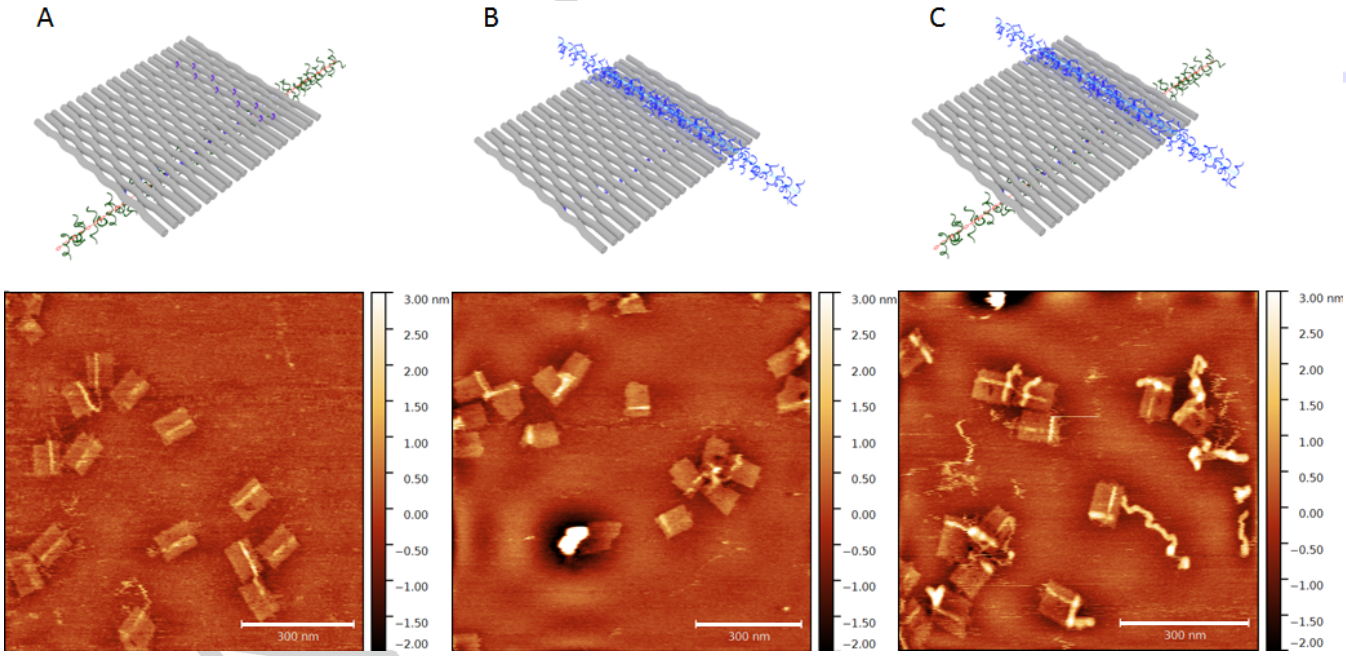


**Figure 2.** Immobilization of **poly(F-DNA)** and **poly(APPV-DNA)** in designed patterns on rectangular DNA nanostructures. **A)** Illustration (top) and AFM topography image (bottom) for immobilization of **poly(APPV-DNA)** with sequence complementarity to the longitudinal track. Scale bar = 300 nm **B)** Illustration (top) and AFM topography image (bottom) for immobilization of **poly(F-DNA)** along the short axis of the rectangular DNA nanostructure. Scale bar = 300 nm **C)** Illustration (top) and AFM topography image (bottom) for both polymers positioned on each side of the flat nanostructure in a cross type architecture. Scale bar = 300 nm. In general, **poly(F-DNA)** is observed as higher contrast structures than **poly(APPV-DNA)** allowing distinction between the two different types of polymers.

when both polymers were mixed with the construct, efficient formation of well-formed cross structures was observed (Figure 2). When using the two different polymer-DNA conjugates in combination it is noticed, that **poly(F-DNA)** generally appears with brighter height contrast than **poly(APPV-DNA)**.

In our initial attempts to investigate inter-polymer energy transfer between **poly(F-DNA)** and **poly(APPV-DNA)** on DNA nanostructures no efficient energy transfer was observed (data not given). We expect this to be caused by a lack of physical inter-polymer contact combined with difficulties eliminating background signals from non-bound polymers. Therefore, in an attempt to induce significant physical interaction between the two materials, we moved on to investigate the energy transfer between the two polymers when directly co-localized by DNA hybridization. We investigated the emission of **poly(APPV-DNA)** upon excitation of **poly(F-DNA)** in a set-up where the two different conjugates carried complementary DNA sequences. As a control, the same experiment was carried out with non-complementary sequences on the polymers.

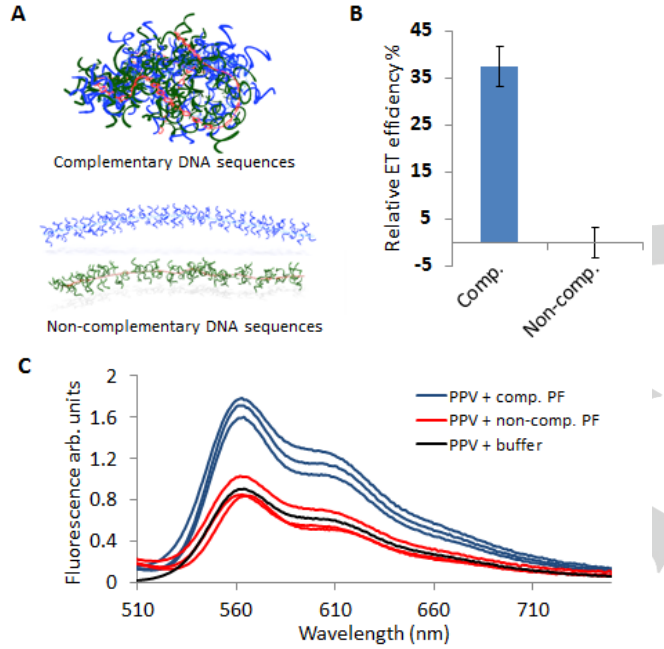


**Figure 3.** Energy transfer between **poly(F-DNA)** and **poly(APPV-DNA)**. **A)** Illustration: Sequence complementarity leads to formation of complexes between **poly(F-DNA)** and **poly(APPV-DNA)** *via* hybridization (top). Without complementarity of the DNA sequences, the two polymers exist separately in solution (bottom). **B)** Quantification of ET from **poly(F-DNA)** to **poly(APPV-DNA)**. Error bars denote 1 standard deviation from the mean derived from triplicates. **C)** Fluorescence spectra showing the APPV emission upon addition of non-complementary **poly(F-DNA)** (red line), complementary **poly(F-DNA)** (blue line), and buffer (black line) to **poly(APPV-DNA)**. Spectra are normalized at **poly(APPV-DNA)** maximum intensity before addition of **poly(F-DNA)** or buffer.

The two polymers were mixed in 200 mM NaCl solution, and in the case of sequence complementarity, significant energy transfer was observed (Figure 3), and a relative energy transfer efficiency of around 37% was calculated (Equation S1). We assume that soluble multi-polymer particles are formed bringing the two different polymers into very close proximity. Without sequence complementarity between the DNA on the two polymers, no significant ET was observed upon mixing in solution (Figure 3B and C). The energy transfer is most likely not taking place between individual polymers, and a lot of efforts remain in order to realize nanoscale optical circuitry based on individual CPs. The ability to have two conjugated polymers physically interact in this hybridization-controlled fashion is an important step on the way. Further control experiments and data concerning energy transfer are provided in the supporting information (Figure S8-10).

Single molecule fluorescence spectroscopy studies have shown that intramolecular energy transfer of excitons can take place over significant distances along the backbone of conjugated polymers until a defect site is reached.[6] This also implies that a single quencher molecule should potentially be able to quench the emission from an entire polymer molecule leading to so-called super quenching. Fan *et al.* elegantly showed that gold nanoparticles (GNPs) could quench cationic fluorene based polymers in a hyperefficient manner with Stern-Volmer constants ($K_{SV}$) approaching $10^{11}$ $M^{-1}$.[13].

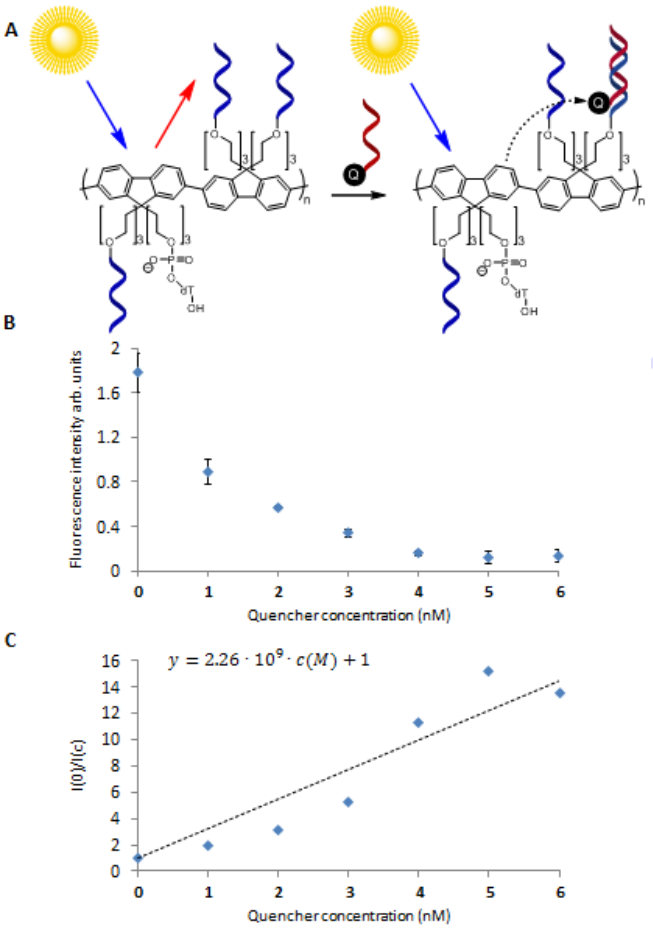


**Figure 4.** Quenching studies with **poly(F-DNA)**. **A)** Illustration of **poly(F-DNA)** binding to a complementary DNA strand carrying a dabcyl quencher. **B)** Data from titration with complementary quencher strand. 50 nM (5 pmol) of DNA on **poly(F-DNA)** was utilized in the experiments. Error bars denote 1 standard deviation from the mean derived from triplicates **C)** Stern-Volmer plot from the titration data.

We envisioned that using the unique addressability of **poly(F-DNA)** arising from the brush of ssDNA, we could obtain highly efficient quenching in a very controlled manner by adding complementary ssDNA carrying a quencher molecule. Using a polymer carrying brushes composed of 15T sequences and a 5'-dabcyl-15A sequence, we observed efficient quenching even at a stoichiometry of 1:50 between quencher-DNA and DNA on the polyfluorene (Figure 4). The Stern-Volmer plot showed decent linearity with a very high estimated $K_{SV}$ of ~ $2.26\times10^{9}$ $M^{-1}$ which is many orders of magnitude higher than for small molecule fluorophore-quencher pairs and only 1-2 orders of magnitude lower than the super quenching observed by Fan and coworkers where comparably very large quencher units in the form of gold nanoparticles were used. The use of a small molecule quencher reduces the likelihood of multi-chromophore quenching by one quencher and hence holds the potential to provide more sophisticated knowledge about intra-chain exciton transfer. Moreover, the highly efficient quenching provides a means of signal amplification, and suggests that **poly(F-DNA)** due to its unique addressability provides a very interesting sensing platform.

In conclusion, we have developed the novel hybrid DNA-polyfluorene material, **poly(F-DNA)**. It is composed of a polyfluorene backbone carrying a dense brush of ssDNA allowing the conjugated backbone to be addressed through DNA interactions. In this way, the fluorescence emission of **poly(F-DNA)** could be efficiently quenched upon binding to very small amounts of complementary DNA carrying a small molecule quencher. Furthermore, we were able to show controlled energy transfer between two CPs (**poly(F-DNA)** and **poly(APPV-DNA))** mediated by Watson-Crick base pairing. As these materials can also be positioned on DNA nanostructures in desired conformations and positions, we argue that this work opens up the possibility to investigate polymer-polymer interactions and intramolecular energy transfer with an unprecedented degree of control. Ongoing research seeks to shed light on this using single molecule fluorescence spectroscopy. The combined findings constitute the initial steps towards realizing our vision of nanoscale circuitry based on individual conjugated polymer molecules.

## Experimental Section

The experimental details can be found in the supporting information

## Acknowledgements

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**Keywords:** Conjugated polymers • Polymer-DNA conjugate • Self-assembly • Single molecule circuitry • Energy transfer

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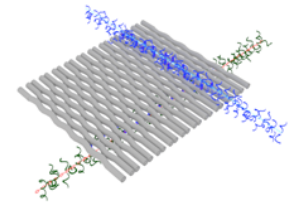
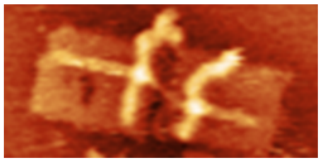
# COMMUNICATION

A graft type polyfluorene-DNA conjugate (**poly(F-DNA))** has been developed. The conjugate shows interesting features such as efficient DNA directed quenching, controlled interpolymer energy transfer and efficient single-molecule nanoscale positioning.





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