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A DNA–Fullerene Conjugate as a Template for Supramolecular Chromophore Assemblies: Towards DNA-Based Solar Cells

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Abstract: *A fullerene was covalently attached to a* $(dA)_{20}$ *template that serves as structural scaffold to self-assemble an ordered and mixed array of ethynyl-pyrene- and ethynyl-Nile-red-nucleoside conjugates. Fluorescence spectroscopy revealed evidence for energy transfer between the two different chromophores. Moreover, fluorescence quenching is significantly enhanced by the attached fullerene in mixed assemblies of different chromophore ratios. This indicates exciton dissociation by electron transfer from the photo-generated exciton on the chromophore stack to the fullerene. The fullerene–DNA-conjugate was integrated as a photo-active layer in solar cells that showed charge-carrier generation in the spectral regime of all three components of the conjugate. This work clearly demonstrates that DNA is suitable as structural element for chromophore assemblies in future organic optoelectronic devices, such as solar cells.*

Supramolecular polymerization represents a powerful bottom-up concept to achieve 2D and 3D chromophore arrangements for functional π-systems which may be employed in future organic optoelectronic devices, such as solar cells.[1] DNA as a template for such chromophore assemblies became an increasingly important tool to control shape, size, and precise arrangement.[2] To obtain best possible control, organic chromophores were initially designed as artificial DNA building blocks and thereby covalently linked to each other and to the other nucleosides by phosphodiester bridges.[3] Both the yields of automated oligonucleotide synthesis on the solid phase and solubility issues limit such covalently linked conjugates to bear only 5–10 chromophores next to each other in a row.[4] The non-covalent and thereby supramolecular oligomerization of chromophores represents an important alternative, with DNA serving as template for binding of up to 40 naphthalenes[5] or porphyrins[2e] along one sequence. We have recently shown that oligo-2′-deoxyadenosines provide an excellent template for the specific self-assembly of an ethynylpyrene-2′-deoxyuridine conjugate (Py-≡-dU) from aqueous media.[6] Thereby, the mentioned limits of covalently linked oligochromophores were overtaken. The optical properties are very similar. The only difference to the covalent systems[7] was the left-handed chirality of the non-covalent chromophore assemblies. Mixed assemblies of Py-≡-dU and the ethynyl-Nile-red-modified nucleoside (Nr-≡-dU) along $(dA)_{20}$ yielded dual emission as a result of energy transfer between the two different chromophores.[8] To develop a light-harvesting system from these assemblies for future DNA-based solar cells, we present herein the templated assembly of the two chromophore conjugates Py-≡-dU and Nr-≡-dU along $(dA)_{20}$ as a synthetic oligonucleotide, which has previously been conjugated to a fullerene, and its optical and photovoltaic properties.

We have previously studied the photophysical processes between Py-≡-dU and Nr-≡-dU in DNA double strands that were covalently modified with these two chromophores in close proximity to each other.[9] When excited at the pyrene-typical wavelength 380 nm, the lifetime of Py*-≡-dU was shortened by the presence of Nr-≡-dU as a result of energy transfer. A weak fluorescence of both Py-≡-dU* and Nr-≡-dU* was obtained. The energy transfer rate was determined to be $k = 1.69\times10^{9}\,\mathrm{s}^{-1}$.[10] On the other hand, when the doubly labelled DNA was excited at the Nile-red-typical wavelength 610 nm, the steady-state fluorescence was significantly quenched and the Nr-≡-dU* lifetime was shortened to 0.60 ns by charge separation. Thus, those studies revealed that an energy-transfer process occurs from Py-≡-dU to Nr-≡-dU, followed by a charge-transfer process in the opposite direction, from Nr-≡-dU to Py-≡-dU, leading to a charge-separated state (exciton), an important prerequisite for the work presented herein (Scheme 1).

Fullerenes are typically applied as electron acceptors and transport domains in organic solar cells.[11] To obtain charge separation after energy transfer and light-harvesting in the oligonucleotide–chromophore stacks, a fullerene was covalently attached to the $(dA)_{20}$ template. Covalent fullerene-conjugates are available,[12] but those with DNA are rare. The first example was published in 1994 by Hélène and co-workers to photoinduce DNA cleavage in a sequence specific way.[13] Since then, only a few reports appeared that apply fullerene–DNA conjugates for biological and photobiological purposes.[14] Among the various types of chemistries for fullerene conjugation[15] we chose the broadly applied phenylene-bridged malonic acid ester as the linking unit between fullerene and $(dA)_{20}$ (Scheme 2). The precursors **1** and **2** were synthesized according to the literature[15b,16] and linked by esters to obtain the modified bismalonate **3**. The subsequent coupling to fullerene in the presence of iodine and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base yields adduct

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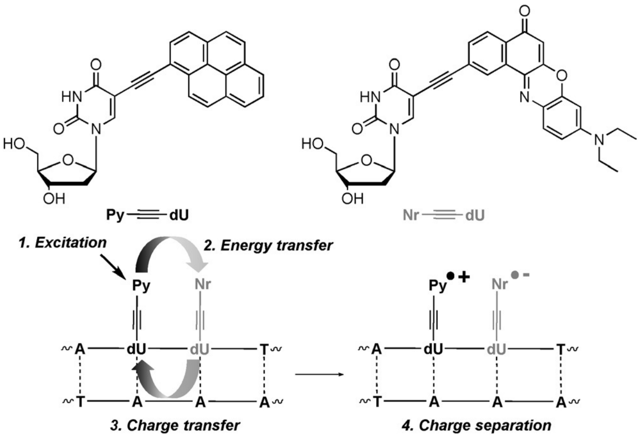
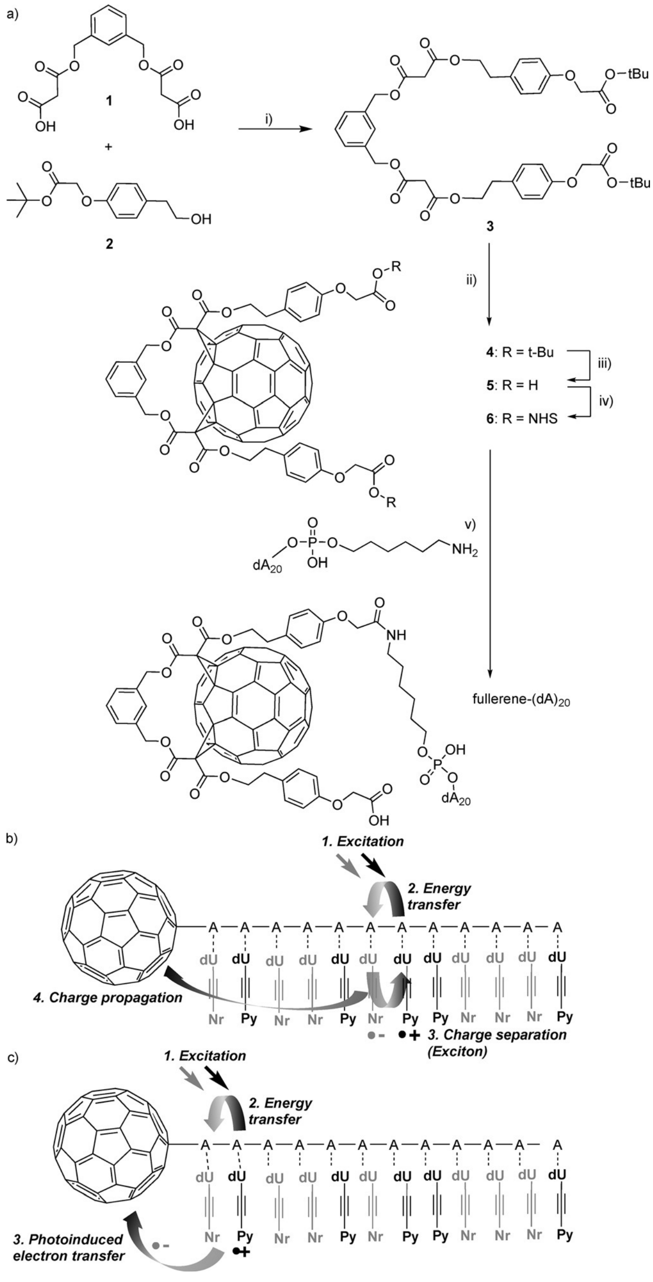


Scheme 1. Photophysical principle of the chromophore pair Py-≡-dU and Nr-≡-dU in DNA:[9] Upon selective excitation of Py-≡-dU an energy-transfer process occurs from Py-≡-dU to Nr-≡-dU, followed by a charge-transfer process in the opposite direction, from Nr-≡-dU to Py-≡-dU, leading to a charge-separated state.



Scheme 2. a) Synthesis of the fullerene–$(dA)_{20}$ conjugate i) dicyclohexyl carbodiimide, 1-hydroxybenzotriazole, 4-(*N*,*N*-dimethyl)aminopyridine in dry dichloromethane, 1 h at 0 °C, then 20 h at RT, 66 %. ii) C_{60}, DBU, iodine, in toluene, 4 h, RT, 16 %. iii) trifluoroacetic acid/dichloromethane, RT, 20 h, 99 %. iv) *N*-hydroxysuccinimide, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride in dry THF, RT, 12 h. v) DMF/carbonate buffer (pH 8.3), 0 °C, 8 h, 60 %; b),c) illustration of the Py-≡-dU and Nr-≡-dU assembly along the fullerene–$(dA)_{20}$ template and two major photophysical pathways as described in the text.

4 in moderate conversion. The carboxylic acids of **4** were converted into NHS esters (**6**) in two additional steps. As reactive counterpart, the commercially available oligonucleotide $(dA)_{20}$ contained the C6-aminolinker at the 5′-terminus that reacts with the fullerene **6** to give a covalent amide conjugate in 60 % yield. We chose this type of conjugation chemistry since the reactive precursor **6** can be obtained in nearly quantitative yield, is soluble in DMF/water mixtures and, most importantly, does not undergo side reactions with the fullerene. To our knowledge, this is the first example of a DNA–fullerene conjugate that, after ethanol precipitation, was purified by semi-preparative HPLC and identified by MALDI-TOF mass spectrometry. The UV/Vis absorption spectrum of both the single-stranded fullerene–$(dA)_{20}$ conjugate and the corresponding DNA double strand with $(dT)_{20}$ showed the presence of the fullerene by its broad band in the range between 300 and 450 nm (see Figure S2, Supporting Information). The melting temperature of the 5′-fullerene modified $(dA)_{20}$–$(dT)_{20}$ hybrid is 54.5 °C (see Figure S2, Supporting Information) and thereby 3 °C higher than that of the corresponding unmodified duplex which is in accordance with earlier reports on the stabilizing effects of fullerene modifications in DNA conjugates.[14d]

Recently, we have shown that both Py-≡-dU and Nr-≡-dU behave as derivatives of thymidine and hence selectively bind to oligo-2‘-deoxyadenosines $(dA)_n$ but not to oligothymidines $(dT)_n$ as single-stranded templates.[6,8] The chromophore-nucleoside units are π-stacked and the specifity to $(dA)_n$ templates originates presumably from hydrogen bonding similar to Watson–Crick base pairing. Moreover, we have shown that templates of the lengths $(dA)_{10}$–$(dA)_{20}$ bind nearly exactly as many Nr-≡-dU monomers as binding sites are available.[8] Herein, we rely on these properties and the similarity of the obtained optical spectra support this. The nucleosides Py-≡-dU and Nr-≡-dU were dissolved in DMSO as separate stock solutions and added in different ratios (Py-≡-dU:Nr-≡-dU = 20:0 to 0:20) to the fullerene–$(dA)_{20}$ template solution (1 μM) in water. The maximum DMSO concentration of 2 % in the final aqueous sample solution is tolerated by the double-helical conformation of DNA because it lowers the melting temperature only slightly.[17] The UV/Vis absorption spectra show bands in two different ranges, at 382 nm and 407 nm for Py-≡-dU and at 559–622 nm for Nr-≡-dU (see Figure S3, Supporting Information). With an increasing amount of Nr-≡-dU in the assembly mixtures, the pure Py-≡-dU assemblies are interrupted by Nr-≡-dU, indicated by the loss of the broad absorption at 420 nm (typical for pure Py-≡

-dU stacks).[7a] Coming from the other side, with an increasing amount of Py-≡-dU in the assembly mixtures, the pure Nr-≡-dU assemblies are also interrupted by Py-≡-dU as the absorption maximum shifts from 559 nm (typical for Nr-≡-dU stacks)[18] to 622 nm (typical for Nr-≡-dU monomers).[7b,8] Although the exact sequence of both nucleosides along the (dA)$_{20}$ template cannot be determined, the described observations contradict extensive and separate pure Py-≡-dU or pure Nr-≡-dU stacks and let us assume a well-mixed chromophore sequence for Py-≡-dU:Nr-≡-dU = 16:4 to 4:16.

An important property of the mixed Py-≡-dU:Nr-≡-dU assemblies as light-harvesting systems for optoelectronic devices is their dual-color fluorescence that arises from the energy transfer between the chromophores. To investigate the energy transfer, the Nr-≡-dU fluorescence of the mixed assemblies was recorded at the Py-≡-dU-typical excitation wavelength 380 nm with respect to direct excitation at 558 nm (Figure 1, top). Moreover, excitation spectra for the Nr-≡-dU fluorescence at 675 nm were recorded and analyzed with respect to energy-transfer-mediated (indirect) excitation at 378 nm and direct excitation at 617 nm (Figure 1, top). Primarily, quenching of both the Py-≡-dU and the Nr-≡-dU fluorescence is observed in the mixed assemblies. But more importantly, in the assemblies with mixing ratios ranging from Py-≡-dU:Nr-≡-dU = 10:10 to 4:16, the Nr-≡-dU fluorescence is more intense upon excitation at 380 nm compared to direct excitation at 558 nm. Similarly, in the excitation spectra, the contribution of Py-≡-dU excitation at 378 nm to the Nr-≡-dU fluorescence increases although the Py-≡-dU content decreases in the mixed assemblies with higher Nr-≡-dU content. Both results strongly support that energy transfer occurs between both chromophores and thus the chromophores indeed form a DNA-templated light-harvesting system.

To elucidate the impact of the covalently attached fullerene on the optical properties of the DNA-templated chromophore assemblies, the fluorescence and excitation spectra have to be compared to those obtained with the (dA)$_{20}$-templated assemblies without fullerene.[8] The quenching in the chromophore assembly along the unmodified (dA)$_{20}$–template can be explained by an energy transfer from Py-≡-dU to Nr-≡-dU, and subsequent electron transfer in the opposite direction, finally leading to a charge-separated state (exciton) as explained above.[9] The fluorescence intensities of both chromophores, Py-≡-dU at 475 nm and Nr-≡-dU at 672 nm, are significantly more quenched in the presence of the attached fullerene (Figure 1, bottom), especially in such diluted solutions (concentration of template 1 μM). Especially the quenching of up to 82 % of Py-≡-dU and up to 73 % of Nr-≡-dU fluorescence that was observed in nearly all mixed assemblies of different chromophore ratios, indicates intrachain exciton dissociation that is an electron transfer from the exciton photo-generated in the chromophore stack onto the fullerene. We assume that there is no photooxidation or photoreduction of 2′-deoxyadenosines in the templates.

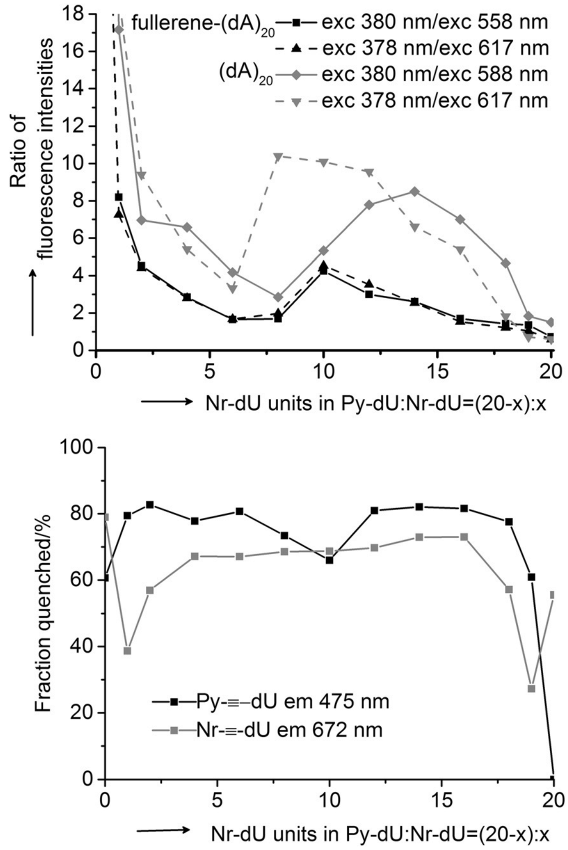


Figure 1. Top: Analysis of the Nr-≡-dU fluorescence at 672 nm in the presence of the fullerene–(dA)$_{20}$ conjugate in comparison to (dA)$_{20}$: Ratio of fluorescence intensity by indirect (energy transfer-mediated) excitation at 378 nm vs. direct excitation at 617 nm (full lines); similar ratio from excitation spectra (dashed lines). Bottom: Quenching of Py-≡-dU fluorescence at 475 nm and Nr-≡-dU fluorescence at 672 nm, both excited at 378 nm, caused by the fullerene in the template conjugate with (dA)$_{20}$ vs. the unmodified (dA)$_{20}$ template. The fractions quenched (Fq) were calculated according to Fq = 1−(fluorescence intensity along fullerene–(dA)$_{20}$/fluorescence intensity along (dA)$_{20}$). Concentration 1.25 μM template ((dA)$_{20}$ or fullerene–(dA)$_{20}$), 25 μM chromophores (x Py-≡-dU and y Nr-≡-dU, $x+y=20$), in H_2O + 2 % DMSO.

We measured lifetimes of the Nr-≡-dU* fluorescence at 672 nm by excitation of Py-≡-dU at 366 nm in the chromophore mixture Py-≡-dU:Nr-≡-dU = 8:12 assembled along (dA)$_{20}$ in comparison to the assembly along the (dA)$_{20}$-fullerene conjugate (the (dA)$_{20}$-fullerene conjugate mixture has been applied for the solar cell, see below). The major (> 91 %) lifetime component in both cases is 0.33 ns. According to our covalently P-≡-dU/Nr-≡-dU-labeled DNA reference system (see Scheme 1), in which the charge separation occurs within 0.6 ns,[9] we attribute this short lifetime component to the charge separation between Nr-≡-dU and Py-≡-dU in the non-covalent system, too. Charge separation between the chromophores in this assembly is not dependent on the attached fullerene. This rules out that charge separation primarily occurs directly between the photoexcited states of the chromophores and the fullerene (Scheme 2c). This process also seems to be very unlikely because the majority of chromophore molecules are assembled too far away from the fullerene (if an exponential dependence of the charge-transfer rate on the distance is assumed). Hence, the primary photophysical pathway (Scheme 2b) is charge separation between the chromophores (upon excitation and energy transfer) followed by charge propagation through the chromophore stack onto the fullerene yielding a long-distance charge-separated state. However, a direct electron transfer between the photoexcited chromophores and the fullerene (Scheme 2c) cannot be completely excluded for those chromophores which are assembled in the vicinity of the fullerene. That this process can occur is supported by the measured quantum yield which is 0.5% for the chromophore assembly along (dA)$_{20}$. The quantum yield of the assembly along the fullerene–(dA)$_{20}$ conjugate is too low to be measured accurately. Hence, the additional quenching of this rather small quantum-yield fraction (less than 1%) can be attributed to the direct photoinduced charge transfer from the excited chromophores to the fullerene (Scheme 2c).

Circular dichroism (CD)spectra were recorded for the different Py-≡-dU:Nr-≡-dU assemblies along the fullerene–(dA)$_{20}$ template and show two chromophore-induced CD couplets in the corresponding absorption ranges (representatively for the mixtures Py-≡-dU:Nr-≡-dU = 8:12 to 6:14 in Figure 2, all others in the Supporting Information). The Nr-≡-dU -typical CD signals consist of a positive Cotton effect followed by a negative Cotton effect with a zero crossing at approximately 560 nm, the typical absorption maximum of the Nr-≡-dU stacks. Compared with the published spectrum of a covalently attached and thereby right-handed stack of Nr-≡-dU in DNA[18] the chirality of the non-covalent assembly along fullerene–(dA)$_{20}$ is opposite, that means left-handed. Similar CD effects were also observed for Py-≡-dU but mainly in those assemblies with higher Py-≡-dU contents. With increasing amounts of Nr-≡-dU in the assemblies (starting at Py-≡-dU:Nr-≡-dU = 12:8) the CD signal of Py-≡-dU changes according to the gradual change from a pure exciton coupling to a groove binding signal.[19] Nevertheless, the helically oriented excitonic coupling that was observed for both chromophores by CD spectroscopy is an important prerequisite for efficient charge propagation within the chromophore assemblies as recently shown for chiral perylene bisimide assemblies.[20]

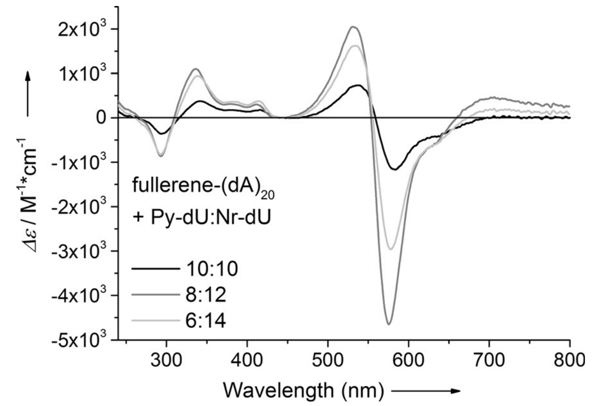


Figure 2. CD spectra of the assembled Py-≡-dU:Nr-≡-dU = 10:10 to 6:14 mixtures along fullerene–(dA)$_{20}$. Each sample: 1.25 μM template, 25 μM chromophores (*x* Py-≡-dU and *y* Nr-≡-dU, *x* + *y* = 20), in H_2O + 2% DMSO.

This charge separation on the fullerene–DNA conjugates motivated the incorporation of the fullerene–DNA conjugates into an organic solar cell with inverted device architecture depicted in the inset of Figure 3, utilizing an indium tin oxide/zinc oxide (ITO, 125 nm/ ZnO, 30 nm) cathode and a molybdenum oxide/silver (MoO_3, 10 nm/ Ag, 100 nm) anode. The photo-active layer comprised representative assemblies with a chromophore ratio Py-≡-dU:Nr-≡-dU = 8:12, exhibiting a broad spectral absorption up to 700 nm (Figure 3). According to atomic force microscopy (AFM) investigations, the fullerene–DNA conjugates formed a pinhole-free layer with a thickness of about 100 nm (see Figure S6, Supporting Information). Under 1 sun illumination (ASTM AM1.5), the devices exhibited a photo-voltage of 670 mV.

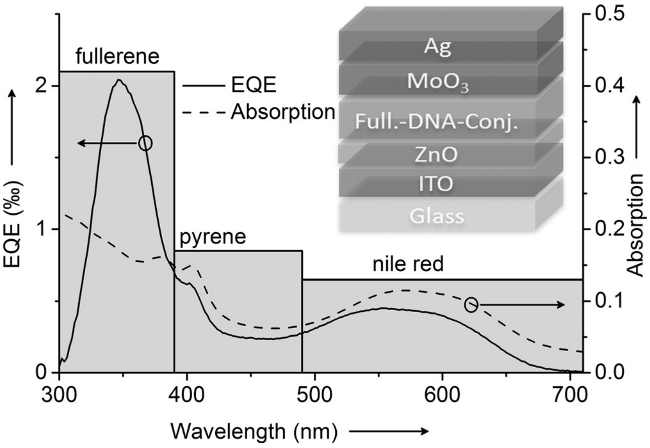


Figure 3. Absorption spectrum of a fullerene–DNA conjugate layer on glass and external quantum efficiency (EQE) of a typical solar cell. Fullerene–(dA)$_{20}$ assemblies comprising Py-≡-dU:Nr-≡-dU = 8:12 were used to form the photo-active layer. The EQE follows the characteristic shape of the absorption spectrum with an additional peak between 300 nm and 400 nm, which corresponds to the characteristic absorption of the fullerene. Inset: solar-cell device architecture.

Insight into the photovoltaic response of the device was gained by measuring the external quantum efficiency (EQE), that is, the number of photo-generated electrons extracted from the device versus the number of incident photons. Despite the excellent quenching of excited states as discussed before, the EQE is limited to a maximum of 0.2% which may well originate from the low fullerene concentration (3.5 wt% in the mixture of fullerene–(dA)$_{20}$ assembled with 8 Py-≡-dU and 12 Nr-≡-dU units) that hampers the transport of electrons to the cathode. Still, the shape of the EQE allows valuable conclusions on the working principle of the DNA–fullerene conjugates: As depicted in Figure 3, both chromophores and the fullerene contribute to the photocurrent generation according to their characteristic spectral absorption. The higher EQE in the fullerene absorption regime indicates a more efficient dissociation of photo-generated excitons on the fullerene, with the origin of its magnitude to be investigated in future devices.

In conclusion, the fullerene–(dA)$_{20}$ conjugate allows self-assembling of an ordered, π-stacked and mixed array of Nr-≡-dU and Py-≡-dU chromophores. We note that both chromophores, Py-≡-dU and Nr-≡-dU, are completely insoluble in aqueous solution in the absence of the (dA)$_{20}$ template and only very poorly soluble in the presence of the "wrong" template $(dT)_{20}$ (without attached fullerene). In both these cases, disordered aggregates of both chromophores are formed. Apparently, DNA is required as the key structural element and scaffold to precisely arrange the chromophore assemblies. The binding of Py-≡-dU and Nr-≡-dU of varying ratios along $(dA)_{20}$ yield assemblies with dual emission upon selective excitation of Py-≡-dU. Fluorescence spectroscopy revealed an energy transfer between the two different chromophores in the case of Py-≡-dU:Nr-≡-dU = 10:10 to 4:16 ratios. Moreover, fluorescence quenching is significantly enhanced by the attached fullerene in nearly all mixed assemblies of different chromophore ratios. This enhancement indicates exciton dissociation by electron transfer from the photo-generated exciton on the chromophore stack to the fullerene. The fullerene–DNA assembly with Py-≡-dU:Nr-≡-dU = 8:12 was representatively integrated as photo-active layer in solar cells. The devices reliably and reproducibly exhibited photo-voltages of 670 mV under 1 sun illumination. The external quantum efficiency measurements proved charge carrier generation on all three components of the conjugate. It is clear that the external quantum efficiency so far is too low for any real application. Based on the photophysical mechanisms (Scheme 2b) an increase of fullerene content in this DNA-based material would potentially improve the external quantum efficiency by shortening the charge propagation pathways. This work, still clearly demonstrates that DNA has a significant potential as key structural element for chromophore assemblies in functional π-systems which may be employed in future organic solar cells.

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