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Long-Lived Photocharges in Supramolecular Polymers of Low-Bandgap Chromophores

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Abstract: Photoinduced charge separation in supramolecular aggregates of π -conjugated molecules is a fundamental photophysical process, and a key criterion for the development of advanced organic electronics materials. Here, we report on the self-assembly of low-bandgap chromophores into helical one-dimensional aggregates due to intermolecular hydrogen-bonding. The chromophores confined in these supramolecular polymers show strong excitonic coupling interactions and give rise to charge-separated states with unusually long lifetimes of several hours and charge densities of up to 5 mol% after illumination with white light. Two-contact devices exhibit increased photoconductivity and can even show Ohmic behavior. Our findings demonstrate that the confinement of organic semiconductors into one-dimensional aggregates results in a considerable stabilization of charge carriers for a variety of π -conjugated systems, which may have implications for the design of future organic electronic materials.

Introduction

The self-assembly of dye molecules is a common approach for the creation of organic electronic materials with precisely tailored nanostructures.^[1] One-dimensional semiconductor nanostructures,^[2] that is, defined self-assembled structures from π -conjugated molecules with two lateral dimensions on the nanometer scale and one extended dimension, can be considered as model systems to investigate structure-property relationships in organic semiconductors under nanoscopic confinement.^[3] Such systems often exhibit remarkable photoconducting properties,^[4] and have therefore widely been investigated with respect to potential applications as defined charge percolation paths in nanoelectronic devices,^[5] photovoltaic systems,^[6] as well as materials for energy transport^[7] or sensing.^[8] Nevertheless, an improved understanding of the intricate balance between

supramolecular structure and charge transport in such well-defined one-dimensional nanostructures of self-assembled chromophores is still desirable.

A valuable strategy to achieve one-dimensional semiconductor nanostructures with a defined chromophore arrangement is based on the synergistic interplay of π - π interactions of the chromophores and hydrogen bonding between lateral substituents.^[1b, 9] Particularly promising in this regard are "infinite", resonance-enhanced strands of N-H $\cdots$ O=C hydrogen bonds, as observed in the self-assembly of oligopeptides, that can complement the π - π stacking of the chromophores and thus favor stronger electronic interactions between them along the hydrogen bonding direction. Nanowires with uniform diameters of a few nanometers can reliably be obtained by the self-assembly of a broad variety of chromophores bearing oligopeptide substituents,^[10] including oligophenylenes,^[11] oligo(p-phenylene vinylene)s,^[12] naphthalene and perylene derivatives,^[13] tetrathiafulvalene,^[14] or oligothiophene-based chromophores.^[11, 15] As illustrated by many of these examples, the intrinsic molecular chirality is translated into supramolecular helicity during self-assembly due to the preferential aggregation of the oligopeptides into β -sheet-like aggregates.^[16]

Our laboratory has established the use of π -conjugated segments with polymer-functionalized oligopeptide substituents to achieve a high degree of control over nanostructure formation by means of synergistic π - π stacking and hydrogen-bonding.^[17] The terminally attached hydrophobic polymer provides a hydrophobic medium in the bulk as well as solubility in apolar solvents. In these conditions, hydrogen bonding is strong, and one-dimensional aggregates with a high aspect ratio are formed already in dilute solution and for very short oligopeptide substituents such as dipeptides. Moreover, the combination of supramolecular helicity and the presence of the terminal polymer substituents effectively suppresses lateral aggregation, so that one-dimensional aggregates are obtained with a single, helical stack of the π -conjugated chromophores at their core.^[18] The obtained nanofibrils can hence be regarded as well-defined supramolecular polymers of the π -conjugated chromophores.^[19] We have previously employed this substitution scheme as a reliable supramolecular method to self-assemble diacetylenes and polymerize them to prepare polydiacetylenes with a well-defined helical quaternary structure,^[17b, 20] or to prepare helical supramolecular polymers from electron-rich π -systems including oligothiophenes^[17b, 18a, 21] as well as electron acceptors such as perylene bisimides.^[18a, 22] Moreover, we have recently reported that supramolecular helicity and confinement to a single stack of H-aggregated thieno[3,2-b]thiophene chromophores result in strong electronic coupling along the stack as well as the formation

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of long-lived photocharges even in the absence of a dedicated electron acceptor.^[23]

Here, we employ this approach for the first time to obtain what can be regarded as 'supramolecular low-bandgap polymers' with a defined helical secondary structure, and we demonstrate that such systems are subject to an unusual excited-state behaviour. To this end, we have prepared compounds **1** and **2** that comprise oligothiophene-based chromophores with central 2,1,3-benzothiadiazole and diketopyrrolopyrrol units, respectively (Figure 1), rendering them structurally related to segments used in recently reported low-bandgap polymers or high-performance polymer semiconductors.^[24] The corresponding quinquethiophene derivative **3** serves as a reference compound.

We demonstrate that, irrespective of the employed chromophore, all compounds self-assemble into one-dimensional aggregates with lengths of several micrometres, uniform diameters with a single, helical stack of the π -conjugated chromophores at their core, as well as strong electronic interactions of the chromophores along the central stack. We find that, upon irradiation with white light and in the absence of an external electron acceptor, these supramolecular polymers form polarons that we characterize by near-infrared (NIR) and electron spin resonance (ESR) spectroscopy. These photocharges have extraordinary lifetimes on the order of many hours so that they are accumulated to concentrations of several mol%. We demonstrate that this photocharge generation translates into macroscopic photoconductivity and charge transport properties similar to strongly doped organic semiconductors, particularly in the case of **2**.

Results and Discussion

Synthesis of the Oligopeptide-Substituted Low-Bandgap Chromophores

The preparation of the chromophores **1–3** proceeds via the chlorendylimidyl active esters of the corresponding chromophores, by analogy to a synthetic route reported by Gebbers *et al.*^[25]

To this end, the commercially available chlorendic anhydride is first converted into the hydroxylimide **4** in a yield of 87%, which is then coupled to thienylpropionic acid using ethyl-

dimethylaminopropylcarbodiimide (EDCI) and dimethylaminopyridinium toluenesulfonate (DPTS) as the coupling promoters to give **5** in a yield of 98% (Scheme 1). Bromination with *N*-bromosuccinimide (NBS) in DMF furnishes the bromothiophenylpropionate **6** in a yield of 83%, which serves as a synthetic building block for the preparation of **1** and **2**.

Moreover, the bithiophene derivative **7** is obtained by Stille coupling of **6** with 2-tributylstannylthiophene in a yield of 55%, and is converted into the corresponding bromobithiophene **8** by bromination with NBS in DMF in a yield of 69%. The latter is used as a synthetic building block in the synthetic route towards **3**.

The 4,7-di(2-thienyl)-2,1,3-benzothiadiazole **9** has been synthesized according to published procedures.^[26] Lithiation of **9** with *n*-butyllithium and subsequent reaction with tributyltin chloride affords **10**, which is directly subjected to a Stille coupling with **6** to give the bis(dithienyl)benzothiadiazol **14** in 10% yield (0.9 g) over two steps (Scheme 23).

Analogously, we have performed the stannylation of the previously described 3,6-(dithien-2-yl)-2,5-dibutylpyrrolo[3,4-c]pyrrole-1,4-dione **11** (ref. 27) to prepare **12**, followed by a Stille coupling with **6** to furnish the bis(dithienyl)dibutyl diketopyrrolopyrrol **15** in a yield of 20% (0.5 g) over two steps.

For the synthesis of the quinquethiophene reference compound, we have decided to start from the commercially available 2,5-bis(tributylstannyl)-thiophene **13** in order to avoid the stannylation of the poorly soluble 2,2':5',2''-terthiophene. The Stille coupling of **13** and **8** affords the quinquethiophene **16** in a yield of 73% (1.42 g).

The advantage of using the chlorendylimidyl active esters as temporary protecting groups lies in the combination of an excellent solubility in organic solvents and the straightforward purification by recrystallization of all intermediate products, which both facilitate performing the syntheses on a (multi)gram scale. Moreover, the active esters **14**, **15**, and **16** can be directly coupled to the free amine terminus of the poly(isobutylene)-modified L-alanyl-L-alanine **17** (obtained by solution-phase peptide coupling and deprotection reactions)^[22a] in the absence of any coupling promoters (Scheme 3), which greatly simplifies the purification of the polymer-substituted compounds **1–3** that are finally obtained by precipitation of the reaction mixtures in THF into MeOH in yields of 77% (350 mg), 79% (175 mg), and 84% (215 mg), respectively.

Figure 1. a) Molecular structures of the low-bandgap chromophores **1** and **2** with 2,1,3-benzothiazole and diketopyrrolopyrrol acceptor units (blue), respectively, as well as the quinquethiophene **3** as a reference compound, and b) schematic illustration of their self-assembly into one-dimensional helical nanowires.

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Scheme 1. Synthesis of the chlorendylimidyl active esters **6** and **8**. Reaction conditions: (i) thiophene-2-propionic acid, EDCl, DPTS, CH_2Cl_2 ; (ii) NBS, DMF, RT; (iii) 2-(tributylstannyl)-thiophene, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, DMF, 80°C .

Scheme 2. Synthesis of the chlorendylimidyl active esters **14**, **15** and **16**. Reaction conditions: (i) *n*-BuLi, -78°C , then Bu_3SnCl , -78°C ; (ii) $\text{Pd}(\text{PPh}_3)_4$, **6**, toluene, 80°C ; (iii) $\text{Pd}(\text{PPh}_3)_4$, **8**, DMF, 80°C .

Scheme 3. Synthesis of the polymer-substituted target compounds **1–3**. Reaction conditions: (i) THF, RT, over night.

Formation of One-dimensional Aggregates in Solution and in Bulk

Upon thermal annealing of dilute solutions ($c = 1 \text{ mmol/L}$) of the dipeptide-substituted chromophores **1–3** in degassed 1,1,2,2-tetrachloroethane (TCE) as a weakly polar solvent at 120°C for 2 h in an argon atmosphere and subsequent cooling to room temperature, **1–3** self-assemble into well-defined one-dimensional nanostructures. The solution-phase infrared (IR) spectrum of each of the three compounds exhibits a single amide A (N–H stretching) band at 3288, 3290, and 3291 cm^{-1} , respectively, with a full width at half-maximum (FWHM) of 48 cm^{-1} in all cases. The corresponding amide I (C=O stretching) absorptions are observed at 1631 cm^{-1} with FWHMs of 17–18 cm^{-1} (Figure 2a). These amide A and I peak positions are characteristic of amide N–H and C=O stretching vibrations in resonance-enhanced arrays of $\text{N-H}\cdots\text{O}=\text{C}$ hydrogen bonds in

extended, one-dimensional, parallel β -sheet-like aggregates.^[28] Moreover, the observed FWHM, and the absence of additional amide A bands above 3400 cm^{-1} (free N–H), above 3300 cm^{-1} (undefined, hydrogen-bonded dimers), and around 3270 cm^{-1} (antiparallel β -sheets) show that the molecules are strongly and “in-register” aggregated into well-defined, hydrogen-bonded, one-dimensional aggregates already in dilute solution. Solid samples of these aggregates have been obtained by precipitating thermally annealed solutions of **1–3** in TCE into MeOH followed by drying in high vacuum. The IR spectra obtained from these solid samples of **1–3** show exactly the same spectroscopic features as observed in dilute solution, that is, single amide A bands at 3287, 3290, and 3287 cm^{-1} with slightly larger FWHMs of 58, 58, and 49 cm^{-1} , as well as amide I absorptions at 1632, 1634, and 1630 cm^{-1} with FWHMs of 18–20 cm^{-1} , respectively (Figure 2b). These findings thus

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Figure 2. a) Solution-phase infrared (IR) spectroscopy of thermally annealed solutions of **1–3** in TCE. All IR spectra exhibit a single band at around 3290 cm⁻¹ (FWHM 48 cm⁻¹) in the amide A region, accompanied by a single amide I absorption at 1630 cm⁻¹ (FWHM 17–18 cm⁻¹), both consistent with the formation of highly ordered, parallel β -sheet-like aggregates in solution, promoted by strong hydrogen-bonding between the L-alanyl-L-alanine segments in a hydrophobic environment. For compound **2**, an additional peak is observed at 1656 cm⁻¹ corresponding to the C=O stretching vibration of the diketopyrrolopyrrol core.^[29] b) The same features are observed in the solid-state IR spectra after precipitation of thermally annealed solutions of **1–3** in TCE into MeOH and drying in high vacuum.

provide the link between our spectroscopic observations in solution and the structural characterization by AFM imaging and X-ray diffraction in the solid state (see below). The parallel β -sheet-like aggregates formed in solution are apparently sufficiently stable to endure a transfer from solution into the solid state and, in turn, the one-dimensional nanostructures observed in both solution and solid samples have the same structure.

Visualization of the aggregates of **1–3** by atomic force microscopy (AFM) height images on samples drop-cast from dilute solutions in TCE ($c = 0.01$ mmol/L) onto mica substrates reveals, in all cases, nanofibrils with lengths of several micrometres, as well as uniform widths (Figure 3a–c). While the experimentally determined apparent widths are certainly subject to AFM tip broadening and further increased by the adsorption of the attached polymer chains to the substrate, height profiles determined from the AFM images of **1–3** reveal that the nanofibrils have uniform diameters of approximately 3 nm for **1** and **3**, as well as 2 nm for **2** (Figure 3d). These heights are consistent with nanofibrils comprising

a single stack of the chromophores at their core, according to our previous in-depth structural characterization of related systems.^[17b, 18a]

Wide-angle X-ray scattering (WAXS) on solid samples of **1–3** reveals three main reflections corresponding to spacings of $d = 6.1$ – 6.3 , 4.6 – 4.7 , and 3.8 – 4.0 Å in all cases (Figure 4a). These three reflections can be assigned to, respectively, the short-range order of the attached poly(isobutylene),^[30] the intermolecular distance of the hydrogen-bonded dipeptide substituents within the nanofibrils,^[17a] and the π – π stacking distance between the chromophores.^[18a] The additional reflection at $d = 3.2$ Å in the case of the quinethiophene **3** can most likely be assigned to the length of the thiophene repeating units in the chromophore. A simple trigonometric analysis of these spacings implies that the central chromophores of **1–3** are placed at conical angles of, respectively, 60° , 58° , and 54° relative to the fibril axis if one assumes, by analogy to our previous in-depth investigation of related nanofibrils,^[18a] that the dipeptide substituents are oriented perpendicular to the fibril axis (Figure 4b). Moreover, small-angle X-ray scattering (SAXS) on solid samples of **1–3** shows single reflections corresponding to spacings of $d = 6.8$, 6.7 and 6.6 nm (Figure 4a). These values are significantly smaller than the extended molecular lengths of the molecules of about 13–14 nm and can be assigned to the centre-to-centre distance of the nanofibrils organized into a random close packing in the solid state, with the soft polymer collapsed into the space between the nanofibrils as well as within their helical grooves (Figure 4c).

Figure 3. a–c) AFM height images of thermally annealed solutions of **1–3** drop-cast from dilute solutions in TCE ($c = 0.01$ mmol/L) onto mica reveal individualized nanofibrils with uniform widths and lengths of several micrometres. d) AFM height profiles (as marked in the corresponding AFM height images) show that the nanowires have uniform heights on the order of 2–3 nm.

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Figure 4. a) Small-angle (left) and wide-angle (right) X-ray scattering (SAXS, WAXS) of solid samples of **1–3** (after precipitation of a thermally annealed solution in TCE into MeOH, dried in high vacuum). b) Proposed structure of the aggregates based on molecular modelling with MMFF geometry optimization. c) In the solid state, the nanofibrils are arranged bundles with a random-close packing of their cylindrical envelopes.

Overall, we conclude that the compounds **1–3** self-assemble into one-dimensional aggregates with a high aspect ratio, a well-defined internal geometry, and uniform lateral dimensions, irrespective of the chemical structure and symmetry of the employed chromophore

Electronic Interactions within the Supramolecular Polymers

Temperature-dependent UV/vis and circular dichroism (CD) spectroscopy prove that the hydrogen-bond-driven aggregation of **1–3** into nanofibrils is, first of all, thermally completely reversible and, secondly, results in a helical arrangement of the chromophores with strong electronic interactions between neighbours. The UV/vis spectra of the aggregates of the reference compound **3** in TCE solutions at 292 K show an absorption maximum at 387 nm, compared

to 428 nm for molecularly disperse solutions obtained by heating the solution to 373 K (Figure 5a, top). This significant (41 nm) hypsochromic shift of the absorption maximum along with the strong suppression of the 0-0 absorption peak upon aggregation indicates that the chromophores form spectroscopic H-aggregates and are clearly in the strong coupling regime according to Spano.^[31] A plot of the ratio of the main absorption in the aggregated state at 428 nm and the molecularly disperse state at 387 nm versus temperature at a cooling/heating rate of 1 K/min exhibits a significant hysteresis in the thermal aggregation and deaggregation. A sharp onset of aggregation upon cooling is observed at 323 K (50 °C), while the deaggregation upon heating occurs only gradually and at higher temperatures at an identical scanning rate (Figure 5b). A reasonable explanation for the observed hysteresis and non-sigmoidal transition is a cooperative nature of the aggregation that proceeds via a nucleation/growth process.^[32]

Moreover, molecularly disperse solutions of **3** in TCE at 373 K are CD-inactive but, upon cooling to room temperature, a well-defined bisignate CD signal appears with a zero-crossing at 387 nm, i.e., close to the wavelength of the UV/vis absorption maximum. The negative Cotton effect (Figure 5a, bottom) indicates that the chromophores are arranged into an M-helical (left-handed) supramolecular stack. Although an interpretation of the UV/vis and CD spectroscopic results is less straightforward in the cases of **1** and **2** due to the more complex absorption features of these chromophores, the results are qualitatively comparable. The main UV/vis absorption bands of **1** that are associated with a π - π^* transition and an intramolecular charge transfer between the electron-deficient benzothiadiazole and the electron-rich oligothiophene units, respectively,^[33] are shifted from 359 and 508 nm at 373 K to 365 and 513 nm in the aggregated state in TCE at 292 K (Figure 5c, top). Likewise, the major absorption band of a molecularly disperse solution of **2** ($c = 0.5$ mmol/L, TCE, 373 K) displays an absorption maximum at 585 nm with vibronic progressions, in line with previous reports on bis(bithiophene)-substituted diketopyrrolopyrrols.^[34] Upon slow cooling, however, new peaks at 523 nm and 685 nm appear, in addition to a hypsochromic shift of the main absorption at 585 nm (Figure 5d, top). Similar to **3**, the molecularly disperse solutions of **1** and **2** at 373 K are CD-inactive, while CD signals with a negative Cotton effect emerge upon aggregation by cooling to 292 K (Figure 5c–d, bottom). Hence, also **1** and **2** form M-helical cofacially stacked H-aggregates, although the simultaneous appearance of a red-shifted shoulder in the UV/vis spectra of **2** may be interpreted as a J-type transition that becomes partially allowed because of both a rotationally and laterally displaced arrangement of the chromophores within the fibrils. Most importantly, however, the temperature-dependent changes of both the UV/vis and CD spectra prove to be reversible over several heating and cooling cycles also in the case of **1** and **2**. Moreover, the observation of isosbestic points, which suggests the presence of only two spectroscopically distinguishable states, is consistent with our interpretation that the aggregation occurs under thermodynamically well-equilibrated conditions following a nucleation/growth process in all cases.^[19, 35]

In conclusion of our structural and spectroscopic investigations presented in the preceding sections, the

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Figure 5. a), c) and d) Temperature-dependent UV/vis and CD spectra of **1–3** in TCE (heating rate 1 K/min). The strong CD signal that is characteristic for helical systems slowly disappears upon going from a solution containing hydrogen-bonded aggregates at room temperature to a molecularly disperse solution at 373 K. b) Corresponding plots of the absorption ratio of **3** at 428 and 387 nm show that the onset temperature of aggregation for **3** is at about 323 K (50°C).

hydrogen-bonded aggregates of **1** and **2** can be considered to be “supramolecular low-bandgap polymers”, that is, supramolecular polymer^[19] analogues of recently reported low-bandgap polymers.^[24] These supramolecular polymers have well-defined helical secondary structures, which in turn confines their strongly electronically interacting π -conjugated repeating units to one-dimensional nanostructures.

Photocharge Generation and Macroscopic Photoconductivity

In what follows, we demonstrate that such well-defined supramolecular polymers of helically arranged chromophores with strong electronic interactions show the formation of exceptionally long-lived photocharges at low photon fluences, irrespective of the nature of the employed chromophore.^[23] This photocharge generation is even more facile in the case of the “supramolecular low-bandgap polymers” **1** and **2**. Upon irradiation with a low-power white light source (LED, 8 W, power density of 20 mW/cm², $\approx$ 0.2 suns), two additional bands emerge in the solution-phase UV/vis/NIR spectra of the supramolecular polymers from **1–3**, that is, at 956 and 1656 nm (**1**), 1033 and 1200 nm (**2**), as well as 785 and 1480 nm with a small shoulder at 1227 nm (**3**) (Figure 6a). These bands exhibit absorption intensities of

4%, 9%, and 1% relative to the main UV/vis absorptions of the respective aggregated compounds, and they are not observed at all in molecularly disperse solutions of **1–3** at 372 K, even upon intense illumination. These bands can be attributed to the optical absorptions of positively charged polarons, which we have independently confirmed by quenching experiments with hydrazine, oxidation with iodine (Figure 6b), and by electron paramagnetic resonance (ESR) spectroscopy of solutions of **1–3** in TCE ($c = 1$ mmol/L) and films (Figure 6c,d). The ESR experiments have also allowed us to quantitatively determine the photocharge concentration. Upon exposure to ambient light, spin densities of 2.6 mol% in the case of **1** and even as high as 4.8 mol% for the diketopyrrolopyrrol **2** are observed, while the quinquethiophene **3** used as a reference compound exhibits a spin density of only 0.9 mol% (Figure 6c). Comparable spin densities are also observed in vacuum-dried films of **1–3** in an argon atmosphere (Figure 6d). The remarkably high value of about one charge in every 20 repeating units of the supramolecular polymer in the case of **2** translates into a one-dimensional photocharge density of $1.04 \cdot 10^6$ cm⁻¹, which approaches the threshold concentration of about 10^7 cm⁻¹ reported for the metal-insulator transition in strongly doped organic semiconductors (in a one-dimensional system).^[36]

This remarkably high charge concentration, achieved with a low-power illumination source, can in part be explained by the extraordinary stability of the photocharges. In order to characterize their stability in more detail, we have conducted the thermal annealing of solutions of compounds **1–3** under exclusion of light, with the goal to initially suppress the light-induced formation of the polarons to a minimum; we could not completely suppress polaron formation, either due to residual illumination or a thermal pathway because of the preceding annealing step. Upon irradiation with a white light source, the polaron NIR bands rapidly increased in intensity over time, reaching saturation after tens of minutes in the case of **3** and over several hours in the case of **1** and **2** (Figure 7). In the dark, the decay of the NIR bands then proceeded over a range of several hours in all cases. Using a model-free approach we have described previously,⁵⁴ we can characterize the decay kinetics of the polaron bands assuming that it is the result of a broad distribution of simultaneous relaxation processes (Fig. S1). The mean of the apparent relaxation times and its standard deviation for the decay of the charge carriers are determined to be $\bar{\tau} = 8 (\pm 5)$ h for **1**, $25 (\pm 15)$ h for **2**, and $18 (\pm 13)$ h in the case of **3**. The large standard deviations further indicate a broad and heavily tailed distribution of relaxation times, which implies that charge generation and decay probably proceed via various, mechanistically complex pathways. Nevertheless, the apparent relaxation times are exceptionally long compared to the lifetimes usually observed for radical cation charge carriers. For instance, the lifetimes of radical cations observed in oligothiophenes, even after a photoinduced electron transfer to a strong external electron acceptor such as tetracyanoethylene^[37] or a fullerene derivative,^[38] may range up to the milliseconds regime in the best cases. The unusual stability of the polarons observed here has so far only been matched by complex electron-transfer cascade structures,^[39] leading us to assume that, by analogy to such systems, the charge

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Figure 6. a) UV/vis/NIR spectra of solutions of nanofibrils of **1–3** reveal additional peaks in the NIR region that can be attributed to the formation of positive polarons. b) UV/vis/NIR spectra of **1–3** in TCE ($c = 0.1$ mM) in the absence (grey) and presence of hydrazine (blue) or iodine (red), revealing the radical-cationic nature of the light-induced polarons. Whereas the initial polaron absorption bands disappeared upon reduction with hydrazine, they could be regenerated by the addition of I_2 . It is noted, that the absorption band of **1** at 1144 nm stems from the bipolaronic state, whereas the features marked with (*) are artefacts due to absorption by the solvent. c, d) ESR spectra of **1–3** in solution and in vacuum dried films confirm the polaron character and can be used to determine the spin density.

Figure 7. a–c) The time-dependent evolution of the NIR spectra of **1–3** in TCE upon illumination with white light shows an increase in the polaronic transitions for all compounds (top), and a decay during the subsequent placement in the dark (bottom). d–f) Plots of the intensities of the main polaron absorption of **1–3** versus time upon white light irradiation (top) and its decay in the dark (bottom).

carriers may be stabilized by their nanoscopic confinement to one-dimensional aggregates and the resulting spatial separation from the counter charges and/or their delocalization along the nanofibrils. Finally, we have investigated the macroscopic electrical properties of the supramolecular polymers **1–3** under illumination and in the dark. For this purpose, we have fabricated two-contact devices by spin-coating thermally

annealed solutions of **1–3** onto a silicon wafer (with a 300 nm SiO_2 dielectric layer), followed by vapor-deposition of gold electrodes using microstencils^[40] with a 2 μm channel length. By using microstencils with a radial placement of the devices, an approximately perpendicular orientation of the nanowires relative to the electrodes can be achieved that allows for an efficient alignment of the aggregates between the contacts.

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Figure 8. Current-voltage measurements of two-point devices before (black) and after irradiation with white light (red).

Because of the already high initial charge density, all aggregates of **1–3** show instantaneous conductivity in the dark that can be further increased by up to a factor of seven upon illumination with white light for 30 min (Figure 8).

Notably, the absolute currents observed for these devices vary up to two orders of magnitude for the different compounds. Thus, the 2,1,3-benzothiadiazol **1** and the diketopyrrolopyrrol **2** show current densities that are, respectively, four and eighty times higher than that of the quinquethiophene reference compound **3**, which matches the trend observed for the spin densities of the three compounds in ESR spectroscopy. Moreover, it is noteworthy that the diketopyrrolopyrrol **2**, under illumination and above a region of non-linear I - V dependence at an applied bias of $V \leq 20$ V typical of a contact resistance, appears to show what can be regarded as Ohmic behaviour. This has neither been observed for the measurement in the dark nor for the nanofibril samples of **1** and **3**. From the linear regime of the current-voltage curve of **2**, a lower estimate for the conductivity can be determined to be

$$\sigma = \frac{L}{A} \cdot \frac{I}{V} = 8.1 \cdot 10^{-3} \text{ a S cm}^{-1} \quad (1)$$

where L is the channel length (2 μm), I corresponds to the current (2.9 μA) measured at the applied voltage V (60 V), and $A \leq 1.2 \cdot 10^{-12} \text{ m}^2$ represents the upper boundary for the cross-section of the conducting material, assuming that the charge transport proceeds through the π -conjugated core (165 $\text{\AA}^2$) and through all nanowires in a densely packed monolayer (spacing 6.7 nm) covering the entire channel width ($W = 500 \mu\text{m}$). It should be noted, however, that charge transport *between* nanowires is certainly negligible, and that hence only a small fraction of the nanowires will in fact be in contact with both electrodes and span the whole channel without a defect. Therefore, the true conductivity should be expected to be significantly higher than the lower boundary estimate given here.

Conclusions

In conclusion, we have synthesized the novel polymer-oligopeptide-substituted chromophores **1** and **2** that have a chemical structure related to segments of low-bandgap

polymers, as well as a reference compound based on quinquethiophene **3**. All three compounds self-assemble into well-defined aggregates that can be regarded as supramolecular polymers with a defined, helical secondary structure, which places the π -conjugated chromophores into a one-dimensionally confined environment. Only in this nanoscopically confined form and independent of the nature of the chromophore, the chromophores show a remarkable photocharge generation upon illumination with a low-power white light source. The obtained photocharges have extraordinarily long average lifetimes of up to 25 h in the case of **2**. By consequence, they are accumulated to concentrations as high as several mol% that have allowed us to study their absorption even by steady-state spectroscopy. We find that the nanofibrils from the low-bandgap systems **1** and **2** exhibit an up to eighty times higher concentration of charge carriers as compared to the reference compound **3**, which corresponds to a one-dimensional charge density approaching the threshold concentration for the metal-insulator transition in a one-dimensional system. Accordingly, the low-bandgap systems **1** and **2** show macroscopic transport properties similar to strongly doped organic semiconductors as well as photoconductivity. Notably, the diketopyrrolopyrrol derivative **2** is subject to particularly high current densities and even appears to show Ohmic behaviour at higher voltages upon illumination.

The efficient generation of long-lived photocharges is a hallmark of photosynthetic systems in nature^[41] and may therefore also be relevant to the preparation of synthetic materials for solar fuel generation,^[42] photoelectrochemical water splitting,^[43] or organic photovoltaics.^[44] The photocharge density and longevity we have observed in our systems are unprecedented for regular π -conjugated chromophores such as the ones employed here, and have so far only been matched by few other synthetic systems, including certain triarylamine self-assembled into helical stacks^[45] and aggregates of π -conjugated polyelectrolytes and fullerenes.^[39] The present study thus reveals that the implementation of π -conjugated molecules into one-dimensional nanostructures appears to be a universal approach to promote the facile formation of long-lived photocharges. Nevertheless, the photocharge generation is still facilitated by a rational choice of the chromophore. Thus, the one-dimensional nanostructures of compounds **1** and **2** can be regarded as “supramolecular low-bandgap polymers” that exhibit improved photoconductivity and

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constitute promising candidates for further fundamental investigations on charge generation and transport in confined nanostructures. In particular, such systems hold great promise for further elaboration of spin-related effects such as magnetoresistance,^[46] and may contribute to an improved understanding of the supramolecular structure-property relationships in organic semiconductors.

Experimental Section

Materials and Methods

Materials. All reagents were used without further purification. Solvents were purchased as reagent grade and distilled prior to use. Compounds **4–8** (ref. 25), **9–10** (ref. 26), **11** (ref. 27) and **17** (ref. 28) were synthesized analogously to previously published methods and **13** was purchased from Sigma Aldrich.

NMR Spectroscopy and Mass Spectrometry. ¹H and ¹³C NMR spectroscopy were carried out on Bruker Avance 400 or 600 spectrometers operating at frequencies of 400.13 MHz or 600.13 MHz for ¹H nuclei, and 100.62 MHz or 150.91 MHz for ¹³C nuclei, respectively. Mass spectra were taken on an Ionspec Ultima 494 HiRes-ESI-MS, and a Bruker Daltonics Ultraflex II for MALDI-TOF.

General Preparation of Sample Solutions. In order to prepare sample solutions for use in UV/vis/NIR, IR, and CD spectroscopy, as well as AFM imaging, compounds **1–3** were dissolved in TCE (*c* = 1 mmol/L), degassed by three freeze-pump-thaw cycles, and placed in an oil bath at 120 °C in an argon atmosphere. After 2 h, the solutions were cooled to 100 °C and kept at that temperature for another 2 h, and finally left to slowly cool to room temperature overnight.

IR, UV/vis/NIR, and CD Spectroscopy. Solution-phase IR spectra were measured on a JASCO FT/IR6320 using a solution phase cuvette with KBr windows. UV/vis-NIR spectra were investigated on a JASCO V-670 or on an Ocean Optics NIR-Quest-512 spectrometer. CD spectroscopy was conducted on a JASCO J-815 spectrometer. The CD and the UV/vis-NIR spectrometers were equipped with a Jasco ETCR-762 temperature controller connected to a Jasco MCB-100 mini circulation bath for temperature dependent measurements. The UV/vis/NIR and CD spectra were recorded at concentrations of *c* = 0.1 mmol/L or *c* = 0.5 mmol/L, while time-dependent UV/vis/NIR spectroscopy and solution-phase IR were performed at a concentration of *c* = 1 mmol/L.

Time-Dependent UV/vis/NIR Absorption Spectroscopy. Solutions of **1–3** (TCE, *c* = 1 mmol/L) were degassed by three freeze-pump-thaw cycles, shielded from light with aluminum foil, and annealed as described above. A volume of 200 μL was subsequently transferred into a 4 x 4 mm quartz fluorescence cuvette (Hellma). The cuvette was placed in a four-way cuvette holder (Ocean optics, cuv-all-uv) to allow for two illumination channels: a white light source (100 W xenon short-arc lamp in a Newport Oriel Apex fiber illuminator) and an NIR source. A 1000 nm long-pass colored glass filter was employed at the NIR source to avoid excitation during the decay phase. The spectra were recorded with an Ocean Optics NIR-Quest-512 spectrometer.

AFM Imaging. AFM was measured on a Nanoscope IIIa (Veeco Instruments Inc., Santa Barbara, USA) instrument at room temperature in air using cantilevers with a resonance frequency on average of *f*₀ = 325 kHz and *k* = 40 N/m. For the preparation of AFM samples, dilute solutions (*c* = 0.01 mmol/L) of the compounds in TCE were drop-cast onto mica substrates, and gently dried in a flow of nitrogen.

SAXS and WAXS. Measurements were performed with a NanoMax-IQ camera (Rigaku Innovative Technologies, Auburn Hills, USA). The samples were kept in vacuum at room temperature during the measurements. The scattering data were presented as a function of the scattering vector modulus *q* = 4π/λ sin(θ/2), where θ is the scattering angle and λ is the photon wavelength.

ESR Spectroscopy. ESR samples of solutions (*c* = 1 mmol/L) were prepared in capillary tubes with an inner diameter of 3.0 mm placed into a standard ESR-tubes. Solid ESR samples were prepared as thin films in standard ESR-tubes by evaporating solutions (*c* = 1 mmol/L) in vacuum and filled with argon. All experiments were performed using a Bruker ESR spectrometer E500 EleXsys Series (Bruker Biospin GmbH) equipped with a Gunn diode-based microwave bridge (model SuperX) and a high-Q cylindrical cavity, model Bruker ER 4122 SHQE. The typical instrumental settings were: microwave frequency 9.40 GHz, microwave power 0.6 mW, conversion time 40.96 msec, number of points 2048, resulting sweep time 83.89 s, lock-in time constant 5.12 ms. The 100 kHz modulation amplitude was kept at 1.0 G (0.10 mT) to avoid modulation broadening. 2,2-diphenyl-1-picrylhydrazyl (DPPH) standard was used to calibrate the field and a 1 mM 4-Hydroxy-2,2,6,6-tetramethylpiperidinyloxy (TEMPOL) solution as a spin concentration standard.

Two-Point Conductivity. The electronic conductivity measurements were performed in two contacts resistance mode. Solutions of **1–3** (*c* = 1 mmol/L) in TCE were spin-coated at 4000 rpm onto a silicon wafer (with a 300 nm SiO₂ dielectric layer). The electrical contacts consisted of a 30 nm layer of gold deposited onto the deposited nanowires by thermal evaporation in a vacuum chamber at a pressure of 1 · 10⁻⁶ mbar using a micromachined stencil.^[40] The obtained gold electrodes had a channel length of 2 μm and a channel width of 500 μm. The samples were then placed into a vacuum chamber in the dark dedicated to the electrical characterization and measured at a pressure of 1 · 10⁻⁶ mbar using a Keithley 4200 data acquisition system with multiple built-in source and measure units (SMUs). The samples were connected through triax cables, in order to avoid capacitance.

Synthesis Procedures

2,5-dibutyl-1,4-bis(5-tributylstannylthiophen-2-yl)pyrrolo[3,4-c]pyrrole-3,6-dione (12**).** 3,6-dithien-2-yl-2,5-dibutylpyrrolo[3,4-c]pyrrole-1,4-dione **11** (0.9 g, 2.2 mmol) was dissolved in dry THF (60 mL) in a 100 mL pre-dried Schlenk flask. The mixture was cooled to -78 °C before slowly adding *n*-butyl lithium (3.3 mL, 6.5 mmol). The mixture was then stirred in an argon atmosphere for 30 min at a temperature of -78 °C, and for 45 min at room temperature. The dark red slurry was cooled to -78 °C, and Bu₃SnCl (2.4 mL, 8.7 mmol) was added slowly, upon which the color

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changed to yellow/brown. The solution was stirred over night at room temperature, before water and *n*-heptane were added. The organic phase was washed with water, dried over MgSO_4 , filtered, and evaporated in vacuum. The resulting purple oil was used without further purification.

(14). A dried 500 mL Schlenk flask was charged with bromothierylpropionate **6** (7.5 g, 12.5 mmol), freshly prepared 4,7-bis(5-(tributylstannyl)thiophen-2-yl) benzo[c][1,2,5]thiadiazole **10** (5.5 g, 6.3 mmol), and dry and degassed toluene (280 mL). Tetrakis(triphenyl-phosphine) palladium(0) (720 mg, 0.6 mmol, 10 mol%) was added, and the reaction mixture was stirred in an argon atmosphere for two days at 80°C. After the reaction mixture was cooled to room temperature, it was filtrated and washed once with toluene. Diisopropylether (DIPE) was added to the combined organic phases, the resulting precipitate was filtered, and washed with DIPE as well as heptane. After drying, compound **14** was obtained as a dark red powder (0.9 g, 10%). ^1H NMR (400.13 MHz, Chloroform-*d*): δ = 2.99 (4 H, t, *J* 7.2, 2 Ar-CH₂), 3.26 (4 H, t, *J* 7.5, 2 CH₂-CO), 3.98 (4 H, s, 4 CH), 6.81 (2 H, d, *J* 3.5, 2 Ar-*H*), 7.11 (2 H, d, *J* 3.5, 2 Ar-*H*), 7.19 (2 H, d, *J* 3.9, 2 Ar-*H*), 7.82 (2 H, s, 2 Ar-*H*), 8.02 (2 H, d, *J* 3.9, 2 Ar-*H*). ^{13}C NMR (151 MHz, THF-*d*): δ = 25.49, 33.02, 50.82, 80.12, 105.39, 124.87, 124.97, 126.02, 126.37, 127.32, 129.30, 132.55, 136.82, 138.82, 140.08, 142.82, 153.39, 164.14, 167.73. HRMS (APPI): calcd C₄₆H₂₂Cl₁₂N₄O₈S₅ ([M]⁺) 1343.621; found 1343.445.

(15). A dried Schlenk flask was charged with freshly prepared 2,5-dibutyl-1,4-bis(5-(tributylstannyl)thiophen-2-yl) pyrrolo[3,4-*c*]pyrrole-3,6-dione **12** (2.17 g, 3.6 mmol), bromothierylpropionate **6** (1.78 g, 1.8 mmol), as well as dry and degassed toluene (100 mL), and then flushed with argon. Tetrakis(triphenyl-phosphine)palladium(0) (104 mg, 0.89 mmol, 5 mol%) was added, and the reaction mixture was stirred for 2 d at 80°C before cooling it to room temperature. The reaction mixture was precipitated into dry *n*-hexane and collected by filtration. The collected product was washed with DIPE and heptane. After purification by column chromatography (silica gel (DCM/THF, 50:1), compound **15** was obtained as a dark blue powder (520 mg, 20%). ^1H NMR (400.13 MHz, CDCl₃): δ = 1.00 (6 H, t, *J* 7.4, 2 CH₃), 1.48 (4H, m, 2 CH₂-CH₃), 1.76 (m, *J* = 7.6 Hz, 4H, 2 N-CH₂-CH₂), 2.99 (4 H, t, *J* 7.4, 2 Ar-CH₂), 3.26 (4 H, t, *J* 7.4, 2 CH₂-CO), 3.98 (4H, s, CH), 4.10 (4 H, t, *J* 7.7, 2 N-CH₂-CH₂), 6.83 (2 H, d, *J* 3.6, Ar-*H*), 7.16 (2 H, d, *J* 3.6, Ar-*H*), 7.24 (2 H, d, *J* 3.6, Ar-*H*), 8.91 (2 H, d, *J* 4.1, Ar-*H*). ^{13}C NMR (151 MHz, THF-*d*): δ = 13.19, 20.00, 25.41, 31.77, 32.13, 41.37, 49.67, 78.97, 104.23, 107.92, 124.20, 125.17, 126.59, 127.88, 131.40, 134.53, 136.49, 138.23, 142.55, 143.41, 160.48, 163.02, 166.59. HRMS (APPI): calcd C₅₄H₃₈Cl₁₂N₄O₁₀S₄ ([M]⁺) 1453.767; found 1453.667.

(16). A dried 50 mL Schlenk flask was charged with 2,5-bis(tributylstannyl)thiophene **13** (1.00 g, 1.51 mmol), bromobithiophene **8** (2.30 g, 3.35 mmol), as well as dry and degassed DMF (20 mL). Tetrakis(triphenyl-phosphine) palladium(0) (166 mg, 0.15 mmol, 10 mol%) was added, and the reaction mixture was stirred overnight at 80°C in an argon atmosphere. The solvent was removed in vacuo, avoiding contact with air, and the resulting solid was redispersed in dry THF (20 mL), precipitated into DIPE, filtered off, and washed with DIPE. This washing procedure was repeated three times. After drying in high vacuum, compound **16** was

obtained as orange powder (1.43 g, 73%). ^1H NMR (400.13 MHz, Chloroform-*d*): δ = 2.97 (4H, m, 2 CH₂C(O)), 3.24 (4H, m, 2 CH₂-Ar), 3.97 (4H, s, 4 CH), 6.78 (2H, m, Ar-*H*), 7.00–7.07 (8H, m, Ar-*H*). ^{13}C NMR (151 MHz, THF) δ = 25.65, 33.03, 50.83, 80.14, 105.40, 124.75, 125.11, 125.48, 127.28, 132.57, 136.41, 136.93, 137.67, 142.69, 167.76, 164.15. HRMS (APPI): calcd C₄₄H₂₂Cl₁₂N₂O₈S₅ ([M]⁺) 1291.615; found 1291.382.

Bz-(T₂-Ala₂-PBI)₂ (1). PIB-Ala₂-NH₂ (**17**) (238 mg, 0.16 mmol) was dissolved in THF (100 mL), and **14** (100 mg, 0.074 mmol) was added. The reaction mixture was stirred overnight at room temperature. After reducing the volume of the solution in vacuo to about 30 mL, the crude product was precipitated into methanol (200 mL), and the resulting slurry was stirred for 1 h. The precipitate was collected by filtration, taken up in THF (30 mL), and precipitated into methanol (200 mL) two more times, to afford compound **1** as a dark-red sticky solid (0.18 g, 79%). ^1H NMR (400.13 MHz, TCE-*d*₂, 120°C): δ = 0.70–1.75 (m, 340H, aliphatic *H*), 2.67 (4H, t, *J* 7.5, 2 Ar-CH₂), 3.26 (4H, t, *J* 7.0, 2 CH₂-CO), 3.32 (4H, m, CH₂-NHC(O)), 4.39–4.48 (4H, m, C**H*), 5.77 (1H, s, 2 NH), 5.85 (1H, s, 2 NH), 6.36 (1H, s, 2 NH), 6.85 (2H, d, *J* 2.5, Ar-*H*), 7.17 (2H, d, *J* 3.4, Ar-*H*), 7.26 (2H, d, *J* 3.8, Ar-*H*), 7.89 (2H, s, Ar-*H*), 8.08 (2H, d, *J* 3.8, Ar-*H*). MS (MALDI): calcd C₁₅₄H₂₇₀N₈O₆S₅ (n=12, [M]⁺) 2488.971; found 2488.812.

DPP-(T₂-Ala₂-PBI)₂ (2). PIB-Ala₂-NH₂ (**17**) (209 mg, 0.14 mmol) was dissolved in THF (100 mL), and **15** (100 mg, 0.069 mmol) was added. The reaction mixture was stirred overnight at room temperature. After reducing the volume of the solution in vacuo to about 30 mL, the crude product was precipitated into methanol (200 mL), and the resulting slurry was stirred for 1 h. The precipitate was collected by filtration, taken up in THF (30 mL), and precipitated into methanol (200 mL) two more times, to afford compound **2** as a dark-violet sticky solid (0.22 g, 84%). ^1H NMR (400.13 MHz, TCE-*d*₂, 120°C): δ = 0.70–1.75 (m, 457H, aliphatic *H*), 2.66 (4H, m, 2 Ar-CH₂), 3.26 (4H, m, 2 CH₂-CO), 3.32 (4H, m, CH₂-NHC(O)), 4.14 (4H, m, N-CH₂-CH₂), 4.38–4.48 (4H, m, C**H*), 5.77 (1H, s, 2 NH), 5.88 (1H, s, 2 NH), 6.38 (1H, s, 2 NH), 6.87 (2H, Ar-*H*), 7.21 (2H, Ar-*H*), 7.30 (2H, Ar-*H*), 8.08 (2H, Ar-*H*). MS (MALDI): calcd C₁₇₀H₃₀₂N₈O₈S₄ (n=13, [M]⁺) 2713.239; found 2713.258.

T₅-(Ala₂-PBI)₂ (3). PIB-Ala₂-NH₂ (**17**) (0.539 g, 0.32 mmol) was dissolved in THF (250 mL), and **16** (200 mg, 0.15 mmol) was added. The reaction mixture was stirred overnight at room temperature. After reducing the volume of the solution in vacuo to about 120 mL, the crude product was precipitated into methanol (2 L), and the resulting slurry was stirred for several hours. The precipitate was collected by filtration, taken up in THF (100 mL), and precipitated into methanol (2 L), to afford compound **3** as a yellow-brown sticky solid (0.35 g, 77%). ^1H NMR (400.13 MHz, TCE-*d*₂, 120°C): δ = 0.70–1.75 (m, 393H, aliphatic *H*), 2.63 (4H, m, 2 Ar-CH₂), 3.21 (4H, m, 2 CH₂-CO), 3.30 (4H, m, CH₂-NHC(O)), 4.37–4.48 (4H, m, C**H*), 5.82 (d, 1H, 2 NH), 5.88 (d, 1H, 2 NH), 6.40 (d, 1H, 2 NH), 6.80 (m, 2H, Ar-*H*), 7.05–7.12 (m, 2H, Ar-*H*). MS (MALDI): calcd C₁₇₆H₃₁₈N₆O₆S₅ (n=13/14, [M]⁺) 2604.149; found 2604.317.

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1D matters! Low-bandgap chromophores that self-assemble into one-dimensional helical nanowires show the light-induced formation of polarons with unusual lifetimes exceeding hours. The accumulation of these charge carriers at concentrations close to the metal insulator transition is reflected by profound macroscopic charge transport properties and photoconductivity in these confined organic semiconductor systems.

Regina J. Hafner, Daniel Görl, Andrzej Sienkiewicz, Sandor Balog, Holger Frauenrath*

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Long-Lived Photocharges in Supramolecular Polymers of Low-Bandgap Chromophores