Spiropyran-Functionalized Polymer–Carbon Nanotube Hybrids for Dynamic Optical Memory Devices and UV Sensors

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Nanohybrids of purified semiconducting single-walled carbon nanotubes and conjugated polymers with attached spiropyran moieties are created as photoreponsive materials for optical memory devices and ultraviolet (UV) light sensors. The hybrids respond to UV light exposure in air with photoisomerization of the spiropyran groups to merocyanine, resulting in significant and persistent p-doping of the nanotubes, as confirmed by photoluminescence quenching and trion emission. The increased carrier concentration after illumination and the inherently high mobility of carbon nanotubes enable an up to two orders of magnitude increased conductivity of the nanotube/polymer hybrid networks in simple two-terminal devices operated at very low bias. The photodoping decays very slowly in the dark and increases further with every illumination dose. However, it can be completely reversed by heating for a few seconds. Thin film devices based on these photoreponsive polymer/nanotube hybrids show great potential as simple and resettable UV dosimeters and optical memory elements.

1. Introduction

Optical memory devices that can reversibly change their conductance state depending on exposure to light of a certain wavelength are of great interest for data storage,[1] radiation dosimeters,[2] and even as photogated components of neuromorphic circuits.[3] Ideally, these memory elements should be easily processable (e.g., from solution and on flexible substrates), operate at low voltages, have long retention times, allow for a large number of distinguishable conductance states to be programmed, and should be easily readable and erasable in a controlled manner.[4] A wide range of organic semiconductors has been tested and employed for this purpose, often in field-effect transistor structures.[5] The operating mechanism usually depends on photoinduced charge trapping at the interface between the semiconductor and gate dielectric, thus leading to a threshold shift and a large ratio between the channel conductance before and after irradiation.[3c,6] A second possible route is mixing the semiconductor with a photochromic molecule that can act as a charge trap in one state but not the other and thus change the effective mobility of the semiconducting layer.[1a,7] A variety of light-switchable molecules were employed in such devices, e.g., diarylethenes or azobenzene.[1a,8] Another well-known photochromic system is the spiropyran/merocyanine pair.[7d,9] Upon irradiation of spiropyran with ultraviolet (UV) light, its isomer merocyanine is formed. Merocyanine has a much higher dipole moment than spiropyran and due to its more extended π-conjugation absorbs light in the visible range.[9a] Heating as well as excitation with green–yellow light induces the reverse isomerization, which enables repeated switching between the two forms.

One desirable application of such optical memory elements is wearable UV dosimeters that can track the total exposure to harmful ultraviolet radiation.[2,10] Practical devices of this kind require mechanical flexibility and low operating voltages. Ideally, these sensors should be blind to visible light and resettable, i.e., reusable. A variety of materials and sensor concepts have been explored in recent years including photoelectric (e.g., ZnO nanowire photodetectors)[11] and again photochromic (e.g., color change of a polyoxometalates)[12] sensors.

Among them, mixed networks of single-walled carbon nanotubes (SWNTs) have been tested in photoelectric devices. Kim et al. found an increase of the resistance (by up to 50%) in a two-terminal device with a random network of SWNTs after UV exposure, which was caused by desorption of oxygen and thus decreased p-doping.[13] In general, nanomaterials such
2. Results and Discussion

Spiropyran-functionalized polyfluorene copolymers were synthesized using a method for postpolymerization functionalization of conjugated polymers by Duchateau et al.,[22] as described in detail in Figures S1–S4 and Tables S1–S3 (Supporting Information). The random copolymers consist of fluorene monomer units (n) with two spiropyran groups attached via an alkyl ester, and fluorene units (1−n) with dodecyl side chains, as shown in Figure 1a. Due to the nonconjugated linker between the spiropyran and the polymer, no direct electronic interaction is expected. The amount of spiropyran moieties is given in percent of monomer units and indicated in the polymer abbreviations. A low spiropyran content polyfluorene SP11 (11% of side chains decorated with spiropyran) and one with a higher spiropyran content of 25% (SP25) were employed. Poly(9,9-di-n-dodecyfluorenyl-2,7-diyl) (PF12) served as a reference polymer without any spiropyran.

The absorbance spectra of a thin film of SP11 polymer before and after brief illumination with ultraviolet light at the lower energy end of the UV-A range (365 nm) and after subsequent heating are shown in Figure 1b in comparison to PF12. Before illumination, the spectra look almost identical, however, after UV irradiation, the absorbance peak of the created merocyanine isomer (550–600 nm) attached to the SP11 polymer appears. The reverse isomerization and thus disappearance of the absorption peak is observed after 15 s of heating at 80 °C. Note that free merocyanine molecules (e.g., mixed into matrix polymers) have a strong tendency to aggregate through dipole–dipole interactions, which degrades their long-term switchability. The fast forward and reverse isomerization of the spiropyran (SP) and merocyanine (MC) units on the polyfluorene suggest that their switchability is not hindered substantially by the covalent attachment to the polymer backbone.

The different conjugated polymers were utilized to create hybrids with semiconducting single-walled carbon nanotubes. A direct dispersion of raw carbon nanotube powder (CoMoCAT, average nanotube diameter 0.79 nm) with SP polymer in toluene solution resulted in poor selectivity toward semiconducting nanotubes, as indicated in the photoluminescence excitation (PLE) maps, absorbance spectra, and Raman spectra (Figure S5, Supporting Information). Several different...
semiconducting and metallic nanotube species were dispersed. Such mixed dispersions are not suitable for the targeted application. To achieve nanotube/SP polymer hybrids with just one \((n,m)\) type of semiconducting nanotubes, we first created monochiral \((6,5)\) SWNT dispersions with the highly selective polyfluorene–bipyridine copolymer PFO–BPy in toluene (see Figure 2, as described previously). The corresponding PLE map, absorbance spectra, and Raman spectra of PFO–BPy-sorted nanotubes confirm the presence of only one semiconducting species, i.e., \((6,5)\) SWNTs, without any metallic impurities (Figure S5, Supporting Information). After filtration of the dispersion and thorough washing of the obtained filter cake, the \((6,5)\) SWNTs were redispersed with the tailored SP polymers (SP11, SP25) and PF12 for reference (see Figure 2) in toluene. This polymer exchange protocol was previously shown to enable efficient wrapping of \((6,5)\) nanotubes with a variety of conjugated polymers. Importantly, any remaining excess or unbound polymer is removed during a second filtration and washing step to obtain only SWNT/polymer hybrids in toluene. Note, the primary purpose of the functionalized wrapping polymer is to stabilize the nanotube dispersions sufficiently for processing and to ensure close proximity of the spiropyran moieties to the nanotubes with a controlled density.

Dispersions of these \((6,5)\) SWNT/SP hybrids aggregated and sedimented instantly upon UV irradiation, probably due to the higher polarity of the merocyanine compared to spiropyran groups (lower solubility in toluene) and the attractive dipole–dipole interaction between two MC units (H-aggregation). Similar observations were made previously for various nanoparticles functionalized with spiropyran. Hence, absorbance spectra of the hybrids before and after illumination were recorded for dropcast films (see Figure 2), which indicated that the reversible photoisomerization process of SP to MC and back was not substantially hindered by wrapping the polymer around the \((6,5)\) SWNTs. The preservation of the photoswitch-ability of spiropyran units when attached to polymers that are wrapped around nanotubes was also observed by Fong et al. for mixed SWNT dispersions. Note that the sharp peak of the \(E_{22}\) transition of \((6,5)\) SWNTs overlaps with the broad absorbance peak of the merocyanine and a difference spectrum is provided to highlight the merocyanine absorption.

Purified dispersions of hybrids of \((6,5)\) SWNTs with SP11, SP25, and PF12 in toluene were dropcast on glass and near-infrared (NIR) photoluminescence (PL) spectra (excitation at 575 nm, \(E_{22}\) transition) of the nanotubes were recorded upon stepwise UV illumination (365 nm, \(10 \times 1\) min, each \(1.27 \text{ J cm}^{-2}\)) under ambient conditions. The low spiropyran content hybrid SP11/(6,5) SWNT initially exhibited a single main excitonic emission peak \(E_{11}\) at 1006 nm with weak photoluminescence sidebands (PSBs) that are characteristic for nanotubes. Upon UV exposure, the PL intensity of \(E_{11}\) dropped and a new peak at 1174 nm corresponding to trion emission \(E_{11}\) appeared. These spectral changes increased with the total time of UV exposure but could be completely reversed again by heating the film briefly to 80 °C, as shown in Figure 3a, indicating the absence of permanent damage to the nanotubes. The high spiropyran content SP25/(6,5) SWNT hybrid showed the same general effect even more strongly. The trion emission became comparable to the exciton emission, which was severely quenched after several minutes of exposure to UV light. Again, the effects of UV exposure were completely removed by heating the film. The striking impact of UV exposure on the trion emission

Figure 2. Schematic workflow to create (6,5) SWNT hybrids with SP and PF12 by polymer exchange of PFO–BPy-sorted (6,5) SWNTs. Inset: absorbance spectra of dropcast SP11/(6,5) SWNT hybrid film before and after irradiation, showing photoisomerization of SP to MC and reversal by heating. Dashed line: difference spectra of irradiated and pristine film.
from (6,5) SWNTs with SP11 and SP25 becomes even clearer in the normalized PL spectra provided in Figure S6 (Supporting Information).

For both hybrids, the largest changes in the PL spectra were observed after the first minute of illumination. Further UV exposure still added to the effect, although less pronounced, probably approaching the maximum of possible merocyanine units. Some sample to sample variation of the achievable $E_{11}$ quenching and trion emission can be attributed to varying amounts of wrapping polymer around the nanotubes after the washing procedure. SWNT hybrids of a copolymer with only one spiropyran moiety per repeat unit also showed the same spectral changes after irradiation, although weaker than expected for the total number of spiropyran groups, suggesting a local cumulative effect (see Figure S7 in the Supporting Information).

In contrast to all of these spiropyran-functionalized hybrids, the reference sample with PF12-wrapped (6,5) SWNTs (that is, without any spiropyran moieties) did not show significant changes of the PL spectra upon equivalent UV exposure (Figure 3c). The $E_{11}$ emission exhibited a slight reduction over time, however, there were no signs of trion formation and emission. The small peak around 1130 nm corresponds to a typical photoluminescence sideband and remained constant over time. Furthermore, heating the PF12/(6,5) SWNT network did not recover the minor drop in the $E_{11}$ emission intensity, indicating irreversible photodegradation of the nanotubes or the polyfluorene (e.g., keto-defect formation).

Clearly, the presence of the spiropyran moieties is a necessary requirement for the observed cumulative irradiation effects on the photoluminescence properties of the nanotubes. The PL spectra after UV exposure show that the creation of merocyanine moieties attached to the wrapping polymer promotes exciton quenching. Charge accumulation (holes or electrons) is one of the possible causes for reduced photoluminescence from nanotubes due to Auger-like nonradiative decay. PL quenching by doping is further corroborated by the concurrent trion emission from the nanotubes. Trions are charged excitons with either an additional hole or electron, and emit at distinct lower energies compared to the corresponding excitons. Trion emission is characteristic for doped low dimensional emitters (e.g., also monolayer transition metal dichalcogenides and quantum dots) and has been observed for chemical, electrochemical, and electrostatic doping of SWNTs. There are no pronounced spectroscopic differences between positive and negative trions of (6,5) nanotubes and thus we cannot deduce directly from the spectra whether p- or n-doping of the nanotube hybrids by UV illumination takes place. However, it is usually assumed that SWNTs become easily p-doped in air, while n-doping is not possible under ambient conditions. As the trion emission coincides with the photoisomerization of spiropyran to merocyanine moieties in air, is persistent over several minutes, increases with the spiropyran content (SP11 to SP25), and is absent for irradiated PF12 hybrids, we propose that positive charges on the (6,5) nanotubes are stabilized by the created large dipoles of the merocyanine moieties. This stabilization promotes further p-doping by oxygen, leading to the observed exciton quenching and trion emission. Possibly, the local ionization potential of the (6,5) nanotubes is decreased (i.e., less negative) by the merocyanine dipoles, thus making them more likely to be p-doped. Another feasible mechanism may involve splitting of excitons that are created during illumination, followed by a stabilization of the holes by the merocyanine dipoles and quenching of the electrons due to the ambient conditions (i.e., oxygen/water).

To estimate the actual doping level after irradiation, we compare the maximum ratio of trion-to-exciton emission for the SP25/SWNT hybrid in Figure 3b ($\approx 0.45$) to PL spectra of electrostatically doped (6,5) nanotube networks in field-effect transistors with known carrier densities. From this comparison, we obtain a moderate doping level of about $1.5 \times 10^{12}$ charges cm$^{-2}$. This carrier concentration is comparable to the turn-on region of a field-effect transistor and should result in a significant increase of network conductance if the charges (holes) are mobile.

To confirm the presence of mobile charge carriers and thus effective photodoping, (6,5) SWNT hybrids with SP25 were dropcast onto interdigitated gold electrodes (channel length...
5 µm, channel width 10 mm) on glass, resulting in dense random networks. The current flow through the network (i.e., its conductivity) was continuously recorded for a constant but low bias of −0.1 V during stepwise illumination at 365 nm under ambient conditions (see schematic setup Figure 4a). PL spectra were collected 1 min after the end of each illumination step (Figure 4c,d). The purple shaded areas in Figure 4b indicate the illumination period and the red crosses mark the time when the PL spectra were recorded (excitation at 575 nm, integration time 5 s). In agreement with the data shown above, the exciton emission of the (6,5) SWNTs decreased again and trion emission rose after UV exposure. As expected, the current increased by up to a factor of 100 during illumination. The photocurrent during illumination was partially the result of exciton creation and splitting as usually expected,[32] although the applied bias was low. More strikingly, after a fast initial rise (within 2–4 s), the current continued to increase further during the entire time of illumination (1 min). After the UV light was turned off, the current only slowly decreased again, meaning that the contribution to the photocurrent by exciton splitting was small. The quenching of the E_{11} emission and the trion-to-exciton emission ratio (see Figure 4e) correlate very well with the increasing conductivity after each illumination step. Note that using two-terminal devices for monitoring network conductivity instead of a field-effect transistor geometry is not only desirable in terms of simpler device fabrication but also avoids any ambiguity regarding the mechanism, e.g., photoinduced traps within the gate dielectric.

The device current after 10 min of total illumination (≈95 µA, Figure 4e) combined with the measured trion-to-exciton emission ratio (≈0.5) and corresponding carrier density of 1.6 × 10^{12} cm^{-2} is in excellent agreement with the expected current range (60–120 µA) when assuming an effective hole mobility of 1–2 cm^2 V^{-1} s^{-1}, which is a reasonable value for a random network of (6,5) nanotubes at medium carrier densities. In the observed range of carrier concentrations from 1 × 10^{12} to 2 × 10^{12} cm^{-2}, the hole mobility will actually still increase before it reaches a maximum. Higher mobilities (5–15 cm^2 V^{-1} s^{-1}) are typically found in (6,5) SWNT network field-effect transistors in full accumulation (≈1 × 10^{13} cm^{-2}).[30d,33]

The same general behavior with a nearly linear increase of current after each illumination step was also achieved at a much lower bias of −0.01 V, as shown in Figure S8 (Supporting Information). The maximum currents were somewhat lower than expected for the observed trion-to-exciton ratios, probably due to non-negligible contact resistance between the gold electrodes and the (6,5) nanotubes.[32] A comparison of the currents measured after each 1 min exposure at lower (3 mW) and higher (14 mW) illumination powers (Figure S9, Supporting Information) showed a clear although not simply proportional dependence on the UV dose. However, the correlation of current and trion-to-exciton emission ratio was remarkably consistent for...
both data sets. Carrier concentrations of up to $2.6 \times 10^{12} \text{ cm}^{-2}$ and estimated carrier mobilities of $3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ were reached. Such high carrier mobilities enable high conductivities even at moderate carrier concentrations and thus easily measurable currents at very low applied voltages.

The low conductivity of a network of purely semiconducting nanotubes in the undoped state as achieved by presorting of (6,5) nanotubes followed by polymer exchange and the high carrier mobility in the doped state ensure a very high ratio of conductivities (almost two orders of magnitude) before and after illumination. The estimated average responsivity of the device at −0.1 V was 0.2 A W$^{-1}$, which is quite good for a simple two-terminal device at such low bias.$^{[13]}$ Note also, ambient doping of nanotubes depends on their bandgap and thus diameter. Large-diameter nanotubes (e.g., with bandgaps of 0.70–0.9 eV) become more easily p-doped in air than small-diameter nanotubes. Such unintentional doping would lead to higher off-currents without illumination, which is not desirable. The (6,5) nanotubes with their relatively large bandgap are hence a good choice both in terms of responsivity and for spectroscopic investigation.

The observed current decays after illumination in the dark were fairly slow and each additional step of irradiation boosted the total persistent current toward a not yet reached saturation level. While a complete relaxation to the current value before illumination would have required a few hours at room temperature (see below), a brief annealing step at 80 °C for 15 s completely removed all signs of p-doping and returned the device to its original or even slightly lower conductance state (see Figure 4b, red shaded area). Thus, these simple two-terminal devices with random SP/SWNT hybrid networks can act as cumulative optical memory elements or UV-radiation dosimeters that can be easily reset by heating. A direct comparison of SP25/(6,5) SWNT and PF12/(6,5) SWNT hybrids during and after continuous illumination is shown in Figure S10 (Supporting Information), including the decay of the current over 5 h. Although the conductivity of the SP25/(6,5) SWNT sample dropped by an order of magnitude in total, it still remained about 10 times higher than the initial value before illumination.

The repeatability of the current increase and slow decay for multiple illumination and heating cycles was tested for a device with a SP25/(6,5) SWNT hybrid network, as shown in Figure S11 (Supporting Information). The increase and decrease of current were reproducible over several switching cycles, although a minor baseline shift occurred. Such a shift, although not unusual, would need to be electronically compensated in practical devices after each reset. Nevertheless, the high repeatability of the isomerization of spiropyran to merocyanine and back within the SP25/SWNT hybrids is a clear advantage over spiropyran molecules mixed into a polymer matrix, which tend to aggregate upon annealing and thus very quickly lose their switchability.$^{[9b]}

To understand the kinetics of the slow current drop in the dark after repeated illumination steps better, each was fitted with two exponential decays, one with a short time constant despite a similar network density (note the current scale in Figure 5c). The increased current after illumination may again be the result of photoinduced exciton splitting and doping by oxygen in air, albeit without the stabilization effect of the merocyanine dipoles. The accompanying PL spectra, however, did not indicate significant doping. While there was some exciton quenching, no trion emission was observed.

The two types of samples are compared on the same scale in Figure 6a,b, both in terms of photoluminescence quenching and increase of current depending on stepwise illumination. The presence of the spiropyran/merocyanine groups on the wrapping polymer clearly enhances the photocurrent and its persistence over long periods of time by at least an order of magnitude.

The currents as shown in Figure 6c,d increase directly with the total illumination time. The values for the SP25/(6,5) SWNT hybrids are almost independent of whether UV exposure was applied continuously or stepwise, thus showing potential for application as a simple UV dosimeters or optical memory elements that are erasable by brief heating. A direct comparison of SP25/(6,5) SWNT and PF12/(6,5) SWNT hybrids during and after continuous illumination is shown in Figure S10 (Supporting Information), including the decay of the current over 5 h. Although the conductivity of the SP25/(6,5) SWNT sample dropped by an order of magnitude in total, it still remained about 10 times higher than the initial value before illumination.

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**Figure 5.** a) PL spectra and b) normalized PL spectra of PF12/(6,5) SWNT hybrid network upon stepwise UV (365 nm) illumination. c) Continuous current flow (i.e., conductivity) through the network during UV irradiation (purple shaded areas) with an applied bias of −0.1 V and recovery after heating at 80 °C. Red crosses indicate the times when the corresponding PL spectra were collected.
(few seconds) and one with a longer time constant (several minutes) (see Figure S12 in the Supporting Information). The latter increased with irradiation time. However, two exponential decays require a total of five fit parameters and the data points during the initial decay (up to 10 s) were not very well matched. A better fit with only three fit parameters could be obtained with a stretched exponential with \( I = I_0 \exp(-t/\tau^\beta) \), where \( I_0 \), \( \tau \), and \( \beta \) are independent fit parameters. Stretched exponentials are often used to describe bias stress behavior in organic field-effect transistors due to the relaxation of charge carriers in localized trap states.\[35\] The bias stress model assumes that the decrease of current results from trapping of mobile carriers in deep traps such that they cannot contribute to the current anymore instead of fewer charge carriers (e.g., due to reverse isomerization of the merocyanine). However, when recording PL spectra of the SP25/(6,5) SWNT hybrids over time (with or without bias) after UV illumination and using an excitation wavelength that should not induce reverse isomerization (760 nm), we also find a decrease of the trion-to-exciton emission ratio (i.e., carrier concentration) that closely resembles the measured current decrease (Figure S13, Supporting Information). We can thus assume that thermally activated reverse isomerization of the merocyanine units over time and thus reduced p-doping even at room temperature is the origin of the current decay. This notion is further corroborated by monitoring the absorbance of a dropcast SP25/(6,5) SWNT hybrid network over time after UV exposure at the wavelength of the merocyanine peak (here, 590 nm to avoid the \( E_{22} \) transition of the (6,5) nanotubes as much as possible). A similar decrease of absorbance and hence merocyanine units is observed (Figure S14, Supporting Information).

Fitting each current decay after consecutive irradiation steps for both the SP25/(6,5) SWNT and PF12/(6,5) SWNT hybrids reveals interesting differences and dependencies. While the exponent \( \beta \) is similar for both and does not change much (0.34–0.4), the fitted time constants are very different. For the SP25/(6,5) SWNT hybrid, \( \tau \) increases linearly from about 2 to 13 min with the total illumination time, while \( \tau \) of the PF12/(6,5) SWNT hybrids only varies from 3.5 to 5 min (see Figure S12e in the Supporting Information). The thermal isomerization from MC to SP is usually described as a first order process, that is, being slowed down by a solid matrix or by attaching the merocyanine to a nanoparticle.\[36\] The observed increase of the time constant with the concentration of the photogenerated merocyanine units may indicate a considerable stabilization effect, possibly due to some aggregation of adjacent MCs. The reisomerization of stacked MCs is known to be slower than that of single MC moieties\[9a\] but can be accelerated by heating, as evidenced by the complete reversal within seconds at 80 °C.
additional stabilization of the merocyanine form would be required.

So far, we have based our considerations on the assumption that oxygen must play a role in the p-doping of (6,5) SWNTs with a spiropyran-functionalized wrapping polymer. To corroborate this assumption, the devices shown in Figures 4 and 5 were encapsulated after annealing in a dry nitrogen glovebox, thus excluding air (oxygen, water) and the irradiation experiments were repeated under the same illumination conditions (Figure 7 and Figure S15 (Supporting Information)). The PL spectra of the SP25/(6,5) SWNT hybrid did not show any changes and there was no indication of trion emission or doping. While a low photocurrent (~1 μA) was still observed during illumination (as expected for exciton splitting), it dropped immediately to the initial current value in the dark. Additional steps of irradiation led to even lower photocurrents, possibly indicating some trap filling or indeed charge scattering and hence reduced carrier mobility and conductivity due to the formation of merocyanine, as observed for field-effect transistors.[90] The PF12/(6,5) SWNT hybrid showed even lower photocurrents (~60 nA) during illumination and no sign of p-doping. Indeed, the observed photocurrents are so low that we must assume that at least some photoinduced doping must have occurred in the PF12/(6,5) SWNT hybrids under ambient conditions (see Figure 5). In summary, we can conclude that the presence of oxygen/water is necessary for the photoinduced p-doping of polymer-wrapped (6,5) SWNT networks, which is further stabilized and enhanced by the presence of merocyanine moieties (see above). Encapsulation of the devices is not only not necessary but actually counterproductive. Instead, an easily produced air pocket as shown by Kim et al.[33] could protect such a device in wearable UV sensors based on SP25/(6,5) SWNT hybrid networks and provide a stable environment for reproducible measurements.

### 3. Conclusion

With this study, we have introduced nanohybrids of sorted semiconducting (6,5) SWNTs and tailored polyfluorene copolymers with photochromic spiropyran units attached to the backbone via a flexible linker as photoactive materials for optical memory elements. Simple two-terminal devices with dense networks of these hybrids show an up to two orders of magnitude increase of conductivity upon irradiation with UV-A light in air due to strongly enhanced p-doping, as confirmed by characteristic $E_{\text{g}}$ photoluminescence quenching and trion emission of the nanotubes. The UV-induced creation of merocyanine units with large dipoles stabilizes positive charges on the semiconducting nanotubes and hence increases the carrier density and conductivity of the network when operated in air. The high hole mobilities in the SWNT networks of up to 3 cm² V⁻¹ s⁻¹ lead to high currents at low voltages (~0.1 V), which persist in the dark and further increase with illumination time. The thermally activated reverse isomerization process from merocyanine to spiropyran and thus current decay is slow enough at room temperature to enable a cumulative response of the devices to the UV light doses, while still allowing them to be reset by a brief heating step. These desirable properties in combination with their solution processability and mechanical flexibility make photoresponsive polymer/SWNT hybrid networks highly interesting materials for optical memory elements and wearable UV dosimeters.

### 4. Experimental Section

**Polymer Synthesis:** All chemicals were used as obtained from commercial suppliers. 2-Bromo-9,9-didodecylfluorene,[37] 2,7-dibromo-9,9-didodecylfluorene,[38] monomers, and poly(9,9-didodecyl-fluorene-2,7-diyil)[39] (PF12, $M_w = 12.0$ kDa, $M_n = 18.0$ kDa) were synthesized using literature procedures. Spiropyran-functionalized polyfluorene copolymers (SP1, SP2) were synthesized using a method for postpolymerization functionalization of conjugated polymers[35] and is described in detail in the Supporting Information.

**Preparation of (6,5) SWNT Dispersions:** All (6,5) SWNT dispersions were prepared as reported previously[37] and used as the stock material for all experiments. Briefly, 50 mg of CoMoCAT raw material (CHASM Advanced Materials, Lot No. SG65i-L58, average diameter 0.79 nm) was exfoliated in a solution of poly([9,9-dioctylfluorenyl-2,7-diyil]-alt-(6,6-[2,2-bipyridine]) [PFO-BPy, American Dye Source, $M_w = 40 000$ g mol⁻¹]) by sheaf force mixing. Prior to dispersion, the nanotube powder was heated.
to 130 °C for at least 3 h in order to remove moisture, thus enhancing the yield and quality of the dispersions. The exfoliation was carried out using a Silverson L2/Air shear force mixer for 3 days at its maximum speed of 10 230 rpm. To maximize yield, the dispersion temperature was controlled using a chiller at ≈20 °C. The obtained mixture was centrifuged twice at 60 000g for 45 min (Beckman Coulter Avanti J26XP centrifuge) in order to separate the nonexfoliated material. The supernatant was kept and further purified by removing the free polymer by filtration through a polytetrafluoroethylene membrane filter (Merck Omnipore, JWVP, pore size 0.1 µm, diameter 25 mm). The filter cake was washed thoroughly with hot toluene at 80 °C (7 times, 5 min each) before the polymer exchange procedure. The purity of the (6,5) nanotubes was confirmed by absorbance spectra, PLE maps, and Raman spectra (see Figure S5 in the Supporting Information). The average length of the dispersed nanotubes was about 1–2 µm.

Polymer Exchange: Polymer exchange involved removing the PFO–BPY from the nanotubes and replacing it with the desired conjugated polymers: (PF12, SP11, SP25). The description for the synthesis of all conjugated polymers is provided in the Supporting Information. All polymer solutions were prepared at a concentration of 1 g L⁻¹ in toluene. The washed filter cakes obtained from the SWNT/PFO–BPY dispersion were dissolved in these polymer solutions by bath sonication. The resulting dispersions were centrifuged and filtered to remove free and excess polymer. The filter cakes were again redispersed in pure tolune.

Optical Characterization: Absorbance spectra of dispersions and films were collected using a Cary 6000i spectrometer (Varian Inc.). PLE maps were recorded with a Horiba Jobin-Yvon Fluorolog 3 spectrometer with a xenon lamp (450 W) and L2 monochromator for excitation and a cooled InGaAs diode array (800–1600 nm) for detection. Raman spectra of dropcast dispersions were collected with a Renishaw inVia Reflex confocal Raman microscope with 532 nm laser excitation.

Device Fabrication: Interdigitated electrodes with a channel length of 5 µm and channel width of 10 mm were patterned by standard double-layer resist (MicroChem LOR5B/Microscop S1813) photolithography on glass substrates (SCHOTT AG, AF32 Eco). Chromium (2 nm) and gold (30 nm) were deposited by electron-beam evaporation, followed by lift-off in N-methyl-2-pyridylidione. Prior to SWNT deposition, the substrates were cleaned by sonication in acetone and 2-propanol and a subsequent UV ozone cleaning (UV Ozone Cleaner, Ossila Ltd.). The prepared dispersions of (6,5) SWNTs were dropcast (25 µL) onto the interdigitated electrode area while heating the substrates to 80 °C to form a dense network. Device encapsulation was achieved by placing a small glass cover slip on the previously annealed devices (120 °C for 2 h under inert conditions) and sealing the edges with epoxy resin.

UV Illumination: A high power light-emitting diode (LED) with a peak wavelength of 365 nm (linewidth ~25 nm, SOLIS-365C, Thorlabs, maximum power 4.0 W) was employed with the output power set to 15 mW to achieve an irradiation of 21.2 mW cm⁻² corresponding to a dose of 1.27 J cm⁻² for 1 min exposure. The nanotube networks were illuminated for 1 min at a time for 10 cycles. Each cycle started with 1 min of illumination, followed by PL spectra collection (1 min after turning off the LED, integration time 5 s) and keeping the LED off for 2 more min before the next cycle. For continuous illumination measurements, samples were irradiated with the LED for a duration of 10 min in one step.

Device Measurements: Photoluminescence spectra were acquired using a pulsed supercontinuum laser source (Fianium Ltd., WhiteLase SC400, 20 MHz repetition rate, 6 ps pulse width, wavelength filtered at 575 nm) for excitation and an Acton SpectraPro SP2358 spectrometer with a liquid-nitrogen-cooled InGaAs line camera (OMA V:3024, Princeton Instruments) for detection. The laser was focused on the channel area using a x50 NIR-optimized objective (Olympus, numerical aperture 0.65). A dichroic long-pass filter with 875 nm cutoff wavelength was employed to block the scattered excitation light. For electrical measurements, a Keithley 2612A source meter was employed to apply a constant bias of −0.01 or −0.1 V and record the temporal changes of current. All measurements were conducted in ambient conditions.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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