Supporting Information

Probing Mobile Charge Carriers in Semiconducting Carbon Nanotube Networks by Charge Modulation Spectroscopy

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Abundance of SWCNT Species in the Mixed HiPco/PFO Dispersion

Table S1. Position of absorption maxima of SWCNT chiralities in the HiPco SWCNT/PFO dispersion, integrated chirality-specific molar absorptivities as determined by Streit et al.,¹ and abundance determined from $E_{11}$ peak fits of the absorbance spectrum (see Figure 1b).

| Chirality (n,m) | Absorption maximum (nm) | $\int \varepsilon_{11} (n,m) \, d\lambda$ ($10^5$ M$^{-1}$ cm$^{-1}$) | Abundance (%) |
|-----------------|-------------------------|---------------------------------------------------------------|---------------|
| (7,5)           | 1043                    | 1.67                                                          | 19.7 ± 0.7    |
| (7,6)           | 1134                    | 2.48                                                          | 21.9 ± 0.4    |
| (8,6)           | 1195                    | 1.86                                                          | 28.1 ± 0.5    |
| (8,7)           | 1283                    | 2.59                                                          | 20.0 ± 0.4    |
| (9,7)           | 1348                    | 1.85                                                          | 10.5 ± 0.5    |

Raman Spectra

Figure S1. Raman spectra of a drop-cast HiPco SWCNT/PFO film in the RBM region. Absence of any RBM peaks for excitation at 532 nm confirms a purely semiconducting network (i.e., no metallic SWCNTs).
Photoluminescence Excitation-Emission Map

Figure S2. Photoluminescence excitation-emission map of a HiPco SWCNT/PFO dispersion.

Atomic Force Micrographs of SWCNT Networks

Figure S3. AFM images (2.5 x 2.5 µm) of (a) a spin-coated (6,5) SWCNT network and (b) an aerosol-jet-printed, mixed HiPco/PFO SWCNT network. Lateral scale bars are 500 nm.
Output Characteristics of (6,5) and Mixed SWCNT Network FETs

Figure S4. Representative output curves of FETs based on (a,b) spin-coated (6,5) SWCNTs, and (c,d) an aerosol-jet-printed mixed SWCNT network.
Figure S5. Schematic charge modulation absorption spectroscopy (CMS) setup. Note that the reference transmission spectrum T was acquired with no applied bias and a chopper as reference for the lock-in amplifier.
Figure S6. Complete dataset of $V_{os}$-dependent CMS spectra ($V_{pp} = 0.2$ V, modulation frequency 363 Hz) of (6,5) SWCNT network FETs and corresponding colour plots (a,b) in hole accumulation and (c,d) in electron accumulation.
Capacitance-Voltage Sweeps of (6,5) and Mixed SWCNT Network FETs

**Figure S7.** Representative capacitance-voltage double sweeps of (a) (6,5) SWCNT FETs and (b) mixed SWCNT FETs recorded with the usual CMS settings ($V_{pp} = 0.2$ V, $f = 363$ Hz, source and drain electrodes shorted).
Comparison between Static Absorbance Bleaching and CMS Spectra of (6,5) SWCNT Networks

Figure S8. (a) Static absorbance bleaching in an electrochromic device based on a thick film of (6,5) SWCNTs. Data reproduced from Berger et al.\(^2\) (b) Difference spectra (\(\Delta V = 0.2\) V) from (a) show the decrease in exciton bleaching with increasing charge density as well as the change from negative ("charge-induced absorption") to positive ("bleaching") sign at the wavelength of trion absorption (~1165 nm). (c) CMS spectra (\(V_{pp} = 0.2\) V, modulation frequency 363 Hz) of (6,5) SWCNT network FETs for different offset voltages show identical trends compared to the spectroelectrochemical data in (b).

Additional CMS Cross-Checks, First and Second Harmonic CMS Spectra of (6,5) SWCNTs

To ensure the correct assignment of the observed transitions and to prevent misinterpretation, we performed additional cross-checks for the CMS spectra. Measurements with identical settings but under different angles of the incident light beam (sample chamber tilted from the usual configuration in which the incident light is orthogonal to the sample/substrate) were performed but did not result in any changes. Hence, any possible interference effects can be excluded.

In previous studies using the CMS method, spectral contributions of electroabsorption (EA) due to the Stark effect were identified.\(^3\),\(^4\) We investigated the possible presence of an EA response by detecting the signal at twice the modulation frequency (second harmonic detection scheme, \(2\omega\)).\(^3\)
Since the charge density modulation is linearly dependent on the electric field, charge-induced signals should not contribute to the spectra when locking onto the $2\omega$. The absence of signals in the $2\omega$ spectra (see Figure S9) suggests that there is no significant contribution of EA and that the observed CMS signals are purely charge-induced.

**Figure S9.** CMS spectra of (6,5) SWCNTs ($V_{os} = -1.0$ V, $V_{pp} = 0.2$ V) in the first ($1\omega$) and second ($2\omega$) harmonic detection. (X) and (Y) denote the in-phase (solid lines) and out-of-phase (quadrature, dashed lines) component of the signal, respectively.

**Combined vis-nIR CMS Spectra of (6,5) SWCNTs**

**Figure S10.** Combined CMS spectra of (6,5) SWCNTs in the visible and nIR spectral regions at moderate electron doping level ($V_{os} = 1.5$ V, $V_{pp} = 0.2$ V). Spectra are normalized to the $E_{11}$ bleaching signal.
**Normalized Frequency-Dependent CMS Spectra of (6,5) SWCNTs**

Figure S11. Normalized frequency-dependent CMS spectra of (6,5) SWCNTs in the hole accumulation regime (a) at moderate doping level ($V_{os} = -1.5$ V, $V_{pp} = 0.2$ V) and (b) in strong accumulation ($V_{os} = -3.5$ V, $V_{pp} = 0.2$ V).

**Gate Voltage-Dependent Linear Mobility of (6,5) and Mixed SWCNT Network FETs**

Figure S12. Gate voltage-dependent linear mobility ($V_{d} = -0.1$ V) of (a) a (6,5) SWCNT FET and (b) a mixed SWCNT FET. Arrows indicate the voltages that were probed in the frequency-dependent admittance measurements (see Figure 3c and Figure S19c).
Frequency-Dependent Capacitance of a (6,5) SWCNT Network FET

Figure S13. Frequency-dependent capacitance of a (6,5) SWCNT network FET for different gate voltages $V_g$ recorded with the usual CMS settings ($V_{pp} = 0.2$ V, source and drain electrodes shorted) show a cut-off with transit time. The slight capacitance decrease observed for all gate voltages is a result of the intrinsic frequency dependence of the PMMA/HfO$_x$ dielectric.

Phase Plot of the Frequency-Dependent Admittance of a (6,5) SWCNT Network FET

Figure S14. Phase plot of the frequency-dependent device admittance (corresponding magnitude of device admittance shown in Figure 3c) of a (6,5) SWCNT FET for different gate voltages $V_g$. 
Gate Voltage-Dependent PL of (6,5) SWCNTs

**Figure S15.** Static gate voltage-dependent PL spectra of (6,5) SWCNTs in electron accumulation. The arrow indicates the wavelength of trion emission.
Charge Modulation PL Spectroscopy Setup

Figure S16. Experimental setup for charge modulation photoluminescence (CMPL) spectroscopy. Note that the reference PL spectrum was acquired with no applied bias and by modulating the excitation beam with a mechanical chopper that served as reference for the lock-in amplifier.
Frequency-Dependent CMPL Spectra of (6,5) SWCNTs

**Figure S17.** (a) Frequency-dependent CMPL spectra of (6,5) SWCNTs in the hole accumulation regime ($V_{os} = -0.5$ V, $V_{pp} = 0.5$ V) and (b) spectra normalized to the E$_{11}$ quenching signal.

First and Second Harmonic CMS Spectra of Mixed SWCNTs

**Figure S18.** CMS spectra of mixed SWCNTs ($V_{os} = 0.7$ V, $V_{pp} = 0.2$ V) in the first (1$\omega$) and second (2$\omega$) harmonic detection. (X) and (Y) denote the in-phase (solid lines) and out-of-phase (quadrature, dashed lines) component of the signal, respectively.
Frequency-Dependent CMS Spectra of Mixed SWCNTs

**Figure S19.** (a) Frequency-dependent CMS spectra of mixed SWCNTs in the hole accumulation regime ($V_{os} = -0.8$ V, $V_{pp} = 0.2$ V). (b) Spectra normalized to the (7,6) SWCNT E11 bleaching signal. (c) Frequency-dependent magnitude of the device admittance of a mixed SWCNT network FET for different gate voltages $V_g$. The contribution scaling with modulation frequency is due to the source-to-drain capacitance.
Frequency-Dependent CMPL Spectra of Mixed SWCNTs

Figure S20. Frequency-dependent CMPL spectra of mixed SWCNTs in electron accumulation. (a) Spectra acquired at low modulated charge densities ($V_{os} = 0.5$ V, $V_{pp} = 0.5$ V). (b) Spectra normalized to the (8,7) SWCNT E_{11} quenching signal. (c) Spectra acquired at high modulated charge densities ($V_{os} = 1.0$ V, $V_{pp} = 2.0$ V). (d) Spectra normalized to the (8,7) SWCNT E_{11} quenching signal. Note that the mixed SWCNT network has a different composition (cf. Table S2 and Figures S21, S22).
Absorbance Spectra and Abundance of SWCNT Species in a Mixed Dispersion with Different Composition

Table S2. Absorption maxima of SWCNT chiralities in a different batch of the mixed HiPco/PFO dispersion, integrated chirality-specific molar absorptivities as determined by Streit et al.,\(^1\) and abundance determined from \(E_{11}\) peak fits of the absorbance spectrum (see Figure S21a).

| Chirality (n,m) | Absorption maximum (nm) | \(\int \varepsilon_{11} (n,m) \, d\lambda \) (10\(^5\) M\(^{-1}\) cm\(^{-1}\)) | Abundance (%) |
|----------------|-------------------------|---------------------------------|---------------|
| (7,5)          | 1046                    | 1.67                            | 10.7 ± 0.7    |
| (7,6)          | 1134                    | 2.48                            | 28.3 ± 0.5    |
| (8,6)          | 1196                    | 1.86                            | 12.5 ± 0.5    |
| (8,7)          | 1284                    | 2.59                            | 35.1 ± 0.5    |
| (9,7)          | 1348                    | 1.85                            | 13.5 ± 0.5    |
Electrical Characterization of Mixed SWCNT Network FETs and CMPL Spectra with Different Composition

Figure S21. (a) Absorbance spectrum of a mixed HiPco/PFO dispersion with different composition. (b-d) Representative ambipolar transfer characteristics in the linear regime ($V_d = -0.1$ V) and output curves of FETs based on random networks of mixed SWCNTs that were aerosol-jet-printed from the dispersion shown in (a).
Figure S22. (a,b) CMPL spectra of mixed SWCNT FETs with a different network composition in hole and in electron accumulation, respectively, with modulation between off- and on-state of the device. Note that the corresponding transfer curve was slightly shifted to negative voltages (onset for holes, -0.4 V; onset for electrons, 0 V). (c,d) Normalized ΔPL/PL for each chirality in the mixed SWCNT networks. Values were determined from peak fits and represent the share of mobile carrier density of this chirality and thus, the current share at varying total charge densities (offset voltages $V_{ox}$). Lines are guides to the eye.
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