Supporting Information

Helical Polycarbodiimide Cloaking of Carbon Nanotubes Enables Inter-Nanotube Exciton Energy Transfer Modulation

Januka Budhathoki-Uprety†, Prakrit V. Jena†, Daniel Roxbury†, and Daniel A. Heller‡, †*

†Memorial Sloan Kettering Cancer Center, New York, New York 10065, United States
‡Weill Cornell Medical College, New York, New York 10065, United States
*Correspondence to: hellerd@mskcc.org

1. Supporting Figures

![Morphology characterization of polycarbodiimide-SWCNT complexes. A–C) Atomic force microscopy (AFM) height images of Methoxy-PEG-Poly-4-SWCNT, Amine-Poly-5-SWCNT, and Carboxy-Poly-7-SWCNT. D) Transmission electron microscopy (TEM) images of polycarbodiimide-SWCNTs.](image-url)

Figure S1
Figure S2. Near-infrared photoluminescence excitation/emission (PL) plots showing normalized emission intensity from polycarbodiimide-SWCNTs and surfactant (SDS)-suspended SWCNTs.
**Figure S3.** A) PL Intensity change as a function of (n, m) species of polycarbodiimide-SWCNTs in inter nanotube exciton energy transfer (INEET) and its reversal upon addition of amine-functionalized free polymer (from Figure 3). B) Nanotube (n, m) species-dependent PL intensity change upon initiating EET (from Figure 3), and C) upon EET reversal (also from Figure 3). The change shows apparent mod-dependent behavior.
Figure S4. A) nIR fluorescent images of Polycarbodiimide-SWCNTs immobilized on glass surfaces showing discrete fluorescent nanotubes (left and middle panels). Dilute solution of specified polymer-SWCNTs were placed on 35 mm glass bottom petri dishes for 10 seconds and excess solution was removed prior to imaging the nanotubes on the surface. Right panel shows nIR fluorescent aggregates of Polycarbodiimide-SWCNTs formed upon mixing the two nanotube-complexes in solution. Carboxy-Poly-6-SWCNTs solution was added to Amine-Poly-5-SWCNTs (1:1), mixture was allowed to stand for 10 sec, and excess solution was removed from the surface prior to imaging nanotubes. B) Height projection nIR image of polycarbodiimide-SWCNTs aggregates, generated by 3D deconvolution of a stack of height cross-sections acquired at 10 µm steps.
Figure S5. Photoluminescence of nanotubes undergoing INEET. A) Photoluminescence excitation/ emission (PL) plots of Amine-Poly-5-SWCNTs, Carboxy-Poly-6-SWCNTs, and a 1:1 mixture of the two. After mixing and incubation of the mixture for 40 hours, emission peaks in the short wavelength excitation/long wavelength emission range (circled and numbered 1 and 2) were enhanced. B) Spectra showing distinct enhancement of emission peaks (at 1200 nm and 1280 nm) upon excitation of the polycarbodiimide-SWCNTs mixture at 551 nm. Emission peaks resulting from EET in the experiment were compared with the spectra constructed by mathematical addition of individual amine and carboxylic acid polymer-encapsulated SWCNT. The spectra were extracted from the PL plots shown in A. C) PL plot from mathematical addition of individual amine and carboxylic acid polymer-SWCNTs, and D) An expanded region in PL plot of the mixture in A.
Figure S6. A) The kinetic data from Figure 4B was fit with a logistic function (of the form $y = \frac{A_1 - A_2}{1 + (x/x_0)^p} + A_2$) to obtain the parameters in the accompanying table. B) The curves of peaks P1 and P5 fit the classical solutions for the reactant and product, respectively, in a consecutive series of first order chemical reactions.

$P1 \rightarrow \text{Intermediates} \rightarrow P5$

$P1 = \exp(-k_1t)$

$P5 = 1 + \frac{k_1 \exp(-k_1t) - k_2 \exp(-k_2t)}{k_2 - k_1}$
2. Supporting Methods

2.1. Chemicals

Reagents were purchased from Sigma-Aldrich, Milwaukee, WI, Acros Organics, and Fisher Scientific, Fair Lawn, NJ, and used as received. Neutral silica gel (Ultrapure 60–200 µm, 60 Å, Acros Organics) was used in column chromatography purification of monomers. Anhydrous and inhibitor-free tetrahydrofuran (THF) was used for click chemistry.

2.2. Material characterization

NMR data were recorded on a Bruker Advance III Ultrashield Plus 500 MHz spectrometer at room temperature. The chemical shift values were reported relative to TMS (δ = 0.00 ppm) as an internal standard. Fourier transform infrared (FTIR) spectra were acquired using a Bruker Optics Tensor 27 FTIR spectrometer using ATR cell (Pike technologies) or NaCl disc. Wavenumbers in cm⁻¹ are reported for characteristic peaks. High resolution mass spectra (HRMS) were obtained on a Waters LCT-Premier XE mass spectrometer by electrospray ionization. Size exclusion chromatography (SEC) was performed on a Viscotec GPCmax system (Malvern Instruments) equipped with ViscoGEL columns (I-MBMMW-3078 and I-MLBW-3078 in series) connected to a Viscotec TDA 305 triple detector array at 30 °C using THF as an eluent to determine relative molecular weights of the polymers. Polystyrene standards were used for the calibration of the instrument. Polymer samples were dissolved in THF, and the solutions were filtered through 0.45 µm PTFE filters prior to injection. The flow rate was 1.0 mL/min, and injector volume was 100 µL. OmniSEC software was used to calculate the molecular weight. The polymer-SWCNTs zeta potential measurements were carried out in a Zetasizer Nanoseries ZS (Malvern Instruments).

2.3. Synthesis and characterization of compounds

Urea derivatives (1 and 2), monomers (3 and 4), and corresponding polymers (Poly-1 and Poly-2) were prepared following a previously reported procedure¹ and briefly described below. Molar ratio of monomer to catalyst was limited to 25:1 (Poly-1) or 32:1 (Poly-2) to obtain low molecular weight polymers to improve aqueous solubility.

\[
\text{H} \quad \text{N} \quad \text{N} \\
\text{O} \\
\text{1-(3-ethylphenyl)-3-propylurea, 1.} \quad \text{3-Amino phenylacetylene (1.0 g, 8.53 mmol, 1.0 equiv) was diluted in anhydrous dichloromethane (25 mL) and added to n-propylisocyanate (0.87 g, 10.24 mmol, 1.2 equiv) in dichloromethane (10 mL), stirred at low temperature, and kept cold in an ice bath. The reaction mixture was allowed to warm to room temperature followed by reflux overnight. The solvent was removed in a rotary evaporator and crude white solid was purified by recrystallization in ethanol at 4°C and dried to obtain white crystalline solid 1. ¹H NMR (500 MHz, CDCl₃, δ ppm): reference TMS = 0 ppm, δ = 7.99 (s, 1H), 7.39 (s, 1H), 7.26 (d, 1H), 7.15–7.08 (m,} \]
(2H), 6.02 (s, br, 1H), 3.11–3.07 (m, 2H), 2.99 (s, 1H), 1.45–1.38 (m, 2H), 1.45
(7.5 Hz, 3H). \(^{13}\)C\ NMR (125 MHz, CDCl\textsubscript{3}, \(\delta\) ppm): reference CDCl\textsubscript{3} = 77.23 ppm, \(\delta\) = 156.9, 139.4, 129.1, 126.6, 123.4, 122.8, 120.7, 83.5, 77.3, 42.0, 23.4, 11.4. HRMS (ESI) [M+H]\(^+\) m/z calcld for C\textsubscript{12}H\textsubscript{13}N\textsubscript{2}O, 203.1184; found, 203.1187.  

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\begin{align*}
&\text{1-phenyl-3-(prop-2-yn-1-yl)urea, 2. Propargyl amine (0.60 g, 10.89 mmol,} \\
&\text{1.1 equiv) was diluted in anhydrous dichloromethane (20 mL) and added to} \\
&\text{phenylisocyanate (1.18 g, 9.90 mmol, 1.0 mol equiv) in dichloromethane (20 mL),} \\
&\text{stirred at low temperature, and kept cold in an ice bath. The reaction mixture} \\
&\text{was then allowed to warm to room temperature. A white precipitate resulted} \\
&\text{shortly after mixing with phenylisocyanate. The reaction mixture was allowed} \\
&\text{to stir for 3 hours. The white solid was then separated and purified by} \\
&\text{recrystallization in dichloromethane at 4°C to obtain white crystalline solid 2.} \\
&\text{\(^1\)H NMR (500 MHz, DMSO-d\textsubscript{6}, \(\delta\) ppm): reference DMSO-d\textsubscript{6} = 2.50 ppm,} \\
&\text{\(\delta\) = 8.56 (s, 1H), 7.40 (d, \(J\) = 7.65 Hz, 2H), 7.23 (t, \(J\) = 7.60 Hz, 2H),} \\
&\text{6.91 (t, \(J\) = 7.35 Hz, 1H), 6.45 (t, \(J\) = 5.60 Hz, 2H), 3.90 (dd, \(J\) = 5.70 Hz, 2.45 Hz, 2H),} \\
&\text{3.09 (t, \(J\) = 2.45 Hz, 1H). \(^{13}\)C NMR (125 MHz, DMSO-d\textsubscript{6}, \(\delta\) ppm): reference DMSO-d\textsubscript{6} = 39.51 ppm,} \\
&\text{\(\delta\) = 154.7, 140.1, 128.6, 121.4, 117.8, 82.1, 72.9, 28.7. HRMS (ESI) [M+H]\(^+\) m/z calcld for C\textsubscript{10}H\textsubscript{11}N\textsubscript{2}O,} \\
&\text{175.0871; found, 175.0863.}
\end{align*}
\]

\[
\begin{align*}
&\text{3-ethyl-N-((propylimino)methylene)aniline, 3. Triethyl amine} \\
&\text{(2.07 g, 20.51 mmol, 2.5 equiv) was added to a suspension of} \\
&\text{dibromotriphenylphosphorane (4.15 g, 9.84 mmol, 1.2 mol equiv) in} \\
&\text{dichloromethane (2 mL) and stirred at low} \\
&\text{temperature under inert atmosphere. After stirring the mixture} \\
&\text{for 5 minutes, compound 1 (1.66 g, 8.20 mmol, 1.0 equiv) was} \\
&\text{added and the reaction mixture was stirred until reaction completion. The} \\
&\text{dehydration of the urea derivative into carbodiimide monomer was monitored} \\
&\text{by the formation of a very strong FTIR signal at ~2120-2140 cm}^{-1}. \\
&\text{Upon completion of the reaction, hexane was added to precipitate side products.} \\
&\text{The monomer compound was then extracted from solid by hexanes. Crude} \\
&\text{monomer was further purified by column chromatography on silica gel using} \\
&\text{ethyl acetate:hexanes (1:2) and dried under reduced pressure to obtain 3 as a colorless} \\
&\text{oil. \(^1\)H NMR (500 MHz, CDCl\textsubscript{3}, \(\delta\) ppm): reference TMS = 0 ppm, \(\delta\) = 7.20 (m,} \\
&\text{3H), 7.07–7.04 (m, 1H), 3.39 (t, \(J\) = 6.8 Hz, 2H), 3.07 (s, 1H), 1.73–1.1.69 (m, 2H),} \\
&\text{1.01 (t, \(J\) = 7.4 Hz, 3H). \(^{13}\)C NMR (125 MHz, CDCl\textsubscript{3}, \(\delta\) ppm): reference CDCl\textsubscript{3} = 77.23 ppm,} \\
&\text{\(\delta\) = 141.3, 129.5, 128.4, 127.1, 124.3, 123.3, 120.9, 83.2, 77.7, 48.7, 24.9, 11.6. FTIR} \\
&\text{(thin film, cm}^{-1}): \text{characteristic absorption from} \\
\text{terminal alkyne group and monomer; 3290 (terminal alkyne), 2123 (vs, carbodiimide). HRMS (ESI)} \\
\text{[M+H]\(^+\) m/z calcld for C\textsubscript{12}H\textsubscript{13}N\textsubscript{2}, 185.1079; found, 185.1071.}
\end{align*}
\]
The same procedure as described in the synthesis of compound 3 was employed. 

\[ ^1H \text{NMR} (500 \text{ MHz, CDCl}_3, \delta \text{ ppm}): \text{reference TMS} = 0 \text{ ppm, } \delta = 7.31-7.28 \text{ (m, 2H), 7.16-7.14 \text{ (m, 3H), 4.08 (d, } J = 2.45 \text{ Hz, 2H), 2.44 (t, } J = 2.50 \text{ Hz, 1H).} \]

\[ ^{13}C \text{NMR (125 MHz, CDCl}_3, \delta \text{ ppm): reference TMS} = 0 \text{ ppm, } \delta = 139.5, 139.0, 125.5, 124.0, 79.0, 73.5, 36.0. \]

**FTIR (thin film, cm\(^{-1}\)):** characteristic absorption from terminal alkyne group and polymer backbone; 3302 (terminal alkyne), 2119 (vs, carbodiimide). 

**HRMS (ESI) [M+H] \[^+\] m/z calcld for C\(_{10}\)H\(_9\)N\(_2\), 157.0766; found, 157.0761.

**Synthesis of polymers.** Polymers were synthesized following the reported procedure\(^1\). All manipulations for polymerization were performed at room temperature inside an MBraun UNIlab drybox under inert atmosphere. Briefly, the catalyst, \(R\)\(-\)BINOL-titanium(IV)-diisopropoxide\(^2\), either neat or dissolved in chloroform (0.2 mL) was added to the monomer (500 mg) at room temperature and under inert atmosphere. The reaction mixture turned to dark red and solidified to an orange red solid (ca. 24 h). The completion of the polymerization process was confirmed by disappearance of IR signals from carbodiimide (~ 2140 – 2120 cm\(^{-1}\)) and formation of new IR absorption at ~ 1619 – 1640 cm\(^{-1}\) of the polymer backbone. The solid polymer was dissolved in chloroform, precipitated in methanol, separated, and dried to obtain light yellow solid.

**Poly-1.** \(R\)-BINOL-titanium(IV)-diisopropoxide catalyst (0.06 mmol, 30 mg) was added to the stirring monomer 4 (2.17 mmol, 339 mg) at room temperature. The mixture turned to a dark viscous liquid and solidified within an hour. After 48 hours, the orange-red solid was dissolved in chloroform (2 mL) and precipitated into methanol-hexane mixture. Light yellow solid was separated, re-dissolved in chloroform, re-precipitated, and dried to obtain Poly-1 as light yellow solid (84% yield). FTIR (thin film, cm\(^{-1}\)): characteristic absorption from terminal alkyne group and polymer backbone; 3304 (terminal alkyne C–H), 2123 (alkyne triple bond, C≡C), 1631 (imine in polymer backbone, C=N). \(M_n = 36, 608, \text{ PDI} = 1.35. \)

\[ ^1H \text{NMR} (500 \text{ MHz, CDCl}_3, \delta \text{ ppm): reference TMS} = 0 \text{ ppm, } \delta = 7.28-6.84 \text{ (br), 5.35–5.29 (br), 4.20 (br), 3.14 (br), 2.07–0.75 (br).} \]

**Poly-2.** The same procedure as described for Poly-1 was employed for the synthesis of Poly-2. Molar ratio of monomer 3 to catalyst was 25:1. FTIR (thin film, cm\(^{-1}\)): characteristic absorption from terminal alkyne group and polymer backbone, 3298 (terminal alkyne C–H), 2107 (w, alkyne triple bond, C≡C), 1619 (imine in the polymer backbone, C=N). \(M_n = 13, 346, \text{ PDI} = 1.29. \)

\[ ^1H \text{NMR} (500 \text{ MHz, CDCl}_3, \delta \text{ ppm): reference TMS} = 0 \text{ ppm, } \delta = 7.15–6.49 \text{ (br), 3.45 (br), 3.19 (br), 3.03(br), 2.53 (br), 1.01–0.30 (br).} \]
Figure S7. FTIR spectra of polymers, Poly-1 (top) and Poly-2 (bottom).
**Figure S8.** $^1$H NMR spectra of polymers, Poly-1 (top) and Poly-2 (bottom).

**Synthesis of azides.**

![Chemical reaction diagram](image)

Azide compounds 5 and 6 were synthesized and characterized following literature procedures.\(^{3,4,4b}\)

To a solution of 2-chloroethanamine hydrochloride (3.0 g, 25.86 mmol) in water (20 mL), sodium azide (5.04 g, 77.58 mmol) was added and the mixture was heated at 80 °C for 12 hours. The mixture was concentrated in a rotary evaporator (approx.10 mL). Upon cooling to room temperature, diethyl ether (30 mL) was added. The mixture was quenched by adding solid NaOH (1.0 g) while stirring the mixture below 10 °C using an ice bath. The organic layer was separated and the aqueous solution was extracted with diethyl ether (3 x 30 mL). The combined organic layer was washed with brine (20 mL), dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated in a rotary evaporator to yield 5 as a colorless volatile oil (1.55 g, 70% yield). $^1$H NMR (500 MHz, CDCl$_3$, δ ppm): reference TMS = 0 ppm, δ = 3.37 (t, J = 5.7 Hz, 2H), 2.88 (t, J = 5.7 Hz, 2H), 1.95 (br. 2H). $^{13}$C NMR (125 MHz, CDCl$_3$, δ ppm): reference TMS = 0 ppm, δ = 54.6, 41.3. FTIR (thin
film, cm$^{-1}$): characteristic absorption from azide group; 2109 (s). **HRMS (ESI)** [M+H]$^+$ m/z calcd for C$_2$H$_7$N$_4$, 87.0671; found, 87.0671.

**$^1$H NMR** (500 MHz, CDCl$_3$, $\delta$ ppm): reference TMS = 0 ppm, $\delta$ = 10.16 (s, 1H), 3.98 (s, 2H). **$^{13}$C NMR** (125 MHz, CDCl$_3$, $\delta$ ppm): reference CDCl$_3$ = 77.36 ppm, $\delta$ = 174.6, 50.3. **FTIR** (thin film, cm$^{-1}$): characteristic absorption from the azide group; 2109 (s). **HRMS (ESI)** [M-H]$^-$ m/z calcd for C$_2$H$_2$N$_3$O$_2$, 100.0147; found, 100.0147.

**Coupling of azides to Poly-1 and Poly-2 via ‘Click’ chemistry to prepare Poly-3–7.** To the stirring polymer solution in tetrahydrofuran under inert atmosphere, azide compound, synthesized or purchased, (1.5 mol equiv per alkyne unit), triethyl amine or 1,8-diazabicyclo[5.4.0]undec-7-ene (6.0 mol equiv per alkyne unit) and Cul (10 mol %) were added. The reaction mixture was stirred overnight under an argon atmosphere. Coupling of small molecules azides to alkyne side chains in polymers was monitored by FTIR analysis. Upon completion of the reaction, the resulting polymer was washed with THF and/or diethyl ether, separated by filtration and dried under reduced pressure. FTIR analysis of final polymers showed full conversion of all alkyne repeat units in click reaction. Limited solubility of final polymers posed difficulty in GPC measurements. Amine-Poly-5, and Amine-Poly-7 were acidified with a few drops of dilute HCl to increase water solubility. Carboxy-Poly-6 was treated with a few drops of saturated solution of NaHCO$_3$. Acidic and basic polymer solutions were then filtered through centrifugal filters (Amicon Ultracel®, MWCO 3K Da, Merck Millipore Ltd) to remove residual small molecules and washed with water until free from free acid or base as tested with litmus paper. The polymers were then used to suspend SWCNTs.

Concentration of nanotubes in polycarbodiimide-SWCNT suspension was calculated according to references 11 and 12 in the main text.

**Hydroxy-PEG-Poly-3; FTIR** (NaCl, thin film, cm$^{-1}$): 3453 (br), 2876, 1640, 1593, 1461, 1353, 1252, 1105.

**Methoxy-PEG-Poly-4; FTIR** (NaCl, thin film, cm$^{-1}$): 3457, 2877, 1638, 1458, 1351, 1249, 1103, 949.

**Amine-Poly-5; FTIR** (NaCl, thin film, cm$^{-1}$): 3370, 2929, 2864, 1446, 1344, 1286.

**Carboxy-Poly-6; FTIR** (NaCl, thin film, cm$^{-1}$): 3422, 1638, 1386, 1220, 1106.

**Amine-Poly-7; FTIR** (NaCl, thin film, cm$^{-1}$): 3401, 3117, 2925, 2859, 1646, 1449, 1358, 1323, 1274, 1205, 1105.
3. Photoluminescence Excitation/Emission Contour Plots.

Photoluminescence excitation/emission (PL) plots were constructed using a home-built apparatus consisting of a tunable white light laser source, inverted microscope, and InGaAs nIR detector. The laser was a SuperK EXTREME supercontinuum white light laser source (NKT Photonics) with a VARIA variable bandpass filter accessory capable of tuning the output 500 – 825 nm with a bandwidth of 20 nm. A longpass dichroic mirror (900 nm) was used to filter the excitation beam. The light path was shaped and directed into the back of an inverted IX-71 microscope (Olympus) where it passed through a 20x nIR objective (Olympus) and illuminated the sample in a 96-well plate (Greiner). Emission from the nanotube sample was collected by the 20x objective and diverted, via a long-pass dichroic mirror (875 nm), matched to the f/# of the spectrometer using several lenses, injected into an Isoplane nIR spectrograph (Princeton Instruments) with a slit width of 410 µm, and dispersed by a grating of 86 g/mm and 950 nm blaze wavelength. The light was collected by a PloNIR InGaAs 640 x 512 pixel array (Princeton Instruments).

Excitation, emission, and wavelength corrections and calibrations were performed as follows. The power at each excitation wavelength was measured at the objective with a PM100D power meter (Thorlabs) from which a power spectrum was constructed and used to correct the emission intensities for non-uniform excitation. A HL-3-CAL-EXT halogen calibration light source (Ocean Optics) was used to correct for non-uniformities in the emission path arising from grating, detector, and lens inefficiencies. A Hg/Ne pencil style calibration lamp (Newport) was used to calibrate emission wavelengths ranging from 950 – 1350 nm.

Acquisition was conducted in semi-automated fashion controlled by Labview code which iteratively increased the excitation laser source from 491 – 824 nm in steps of 3 nm and saved the data in ASCII format. Using a center wavelength of 1135 nm, the emission spectra range was 915 – 1354 nm with a resolution of 0.7 nm. Background subtraction was conducted using a well filled with DI H₂O. Following acquisition, the data was processed with a Matlab code to correct for non-uniform excitation and non-linear detector efficiencies. After chiralities were assigned to the nanotube peaks in the PL plots, the intensity contours were smoothed with a Gaussian filter and saved.

References

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