Electronic Supplementary Information

Title: Study of Electronic Interactions and Photo-Induced Electron Transfer Dynamics in a Metalloconjugated Polymer-Single-Walled Carbon Nanotube Hybrid by Ultrafast Transient Absorption Spectroscopy

Authors: Haiting Shi,[a,†] Lili Du,[a,†] Wenjuan Xiong,[a] Mingjie Dai,[b,c] Wai Kin Chan,[a,*] and David Lee Phillips[a,*]

[a.] Department of Chemistry, the University of Hong Kong, Hong Kong S.A.R., China.

[b.] Wyss Institute for Biologically Inspired Engineering, Harvard University, Boston, Massachusetts 02115, USA.

[c.] Department of Systems Biology, Harvard Medical School, Boston, Massachusetts 02115, USA

[†]These co-authors contributed equally to this work.

Contents:

Reagents and Materials.

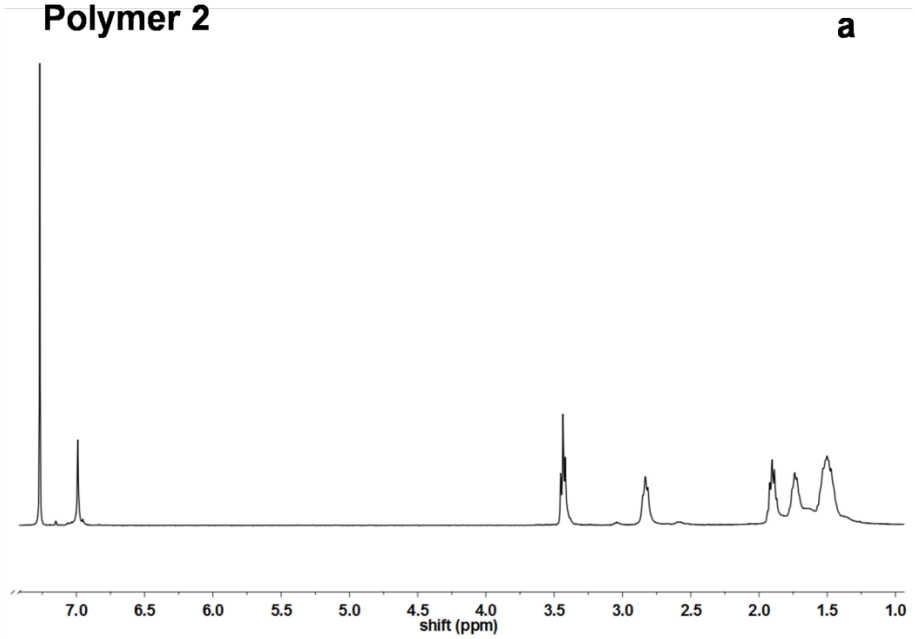
i-PrMgCl·LiCl (1.3M in THF), 1,3-bis(diphenylphosphino)propane nickel (II) chloride, 2,2':6',2''-terpyridine, *N*-ethylmorpholine, ruthenium trichloride hydrate, and 18-crown-6 were used as received. SWCNTs with diameter of around 1.5 nm (produced by chemical vapour deposition method) were purchased from NanoLab Inc. 2,5-Dibromo-3-(6-bromohexyl)thiophene[1] and (4–ethynylphenyl)-2,2':6',2''-terpyridine[2] were synthesized by previously reported procedures.

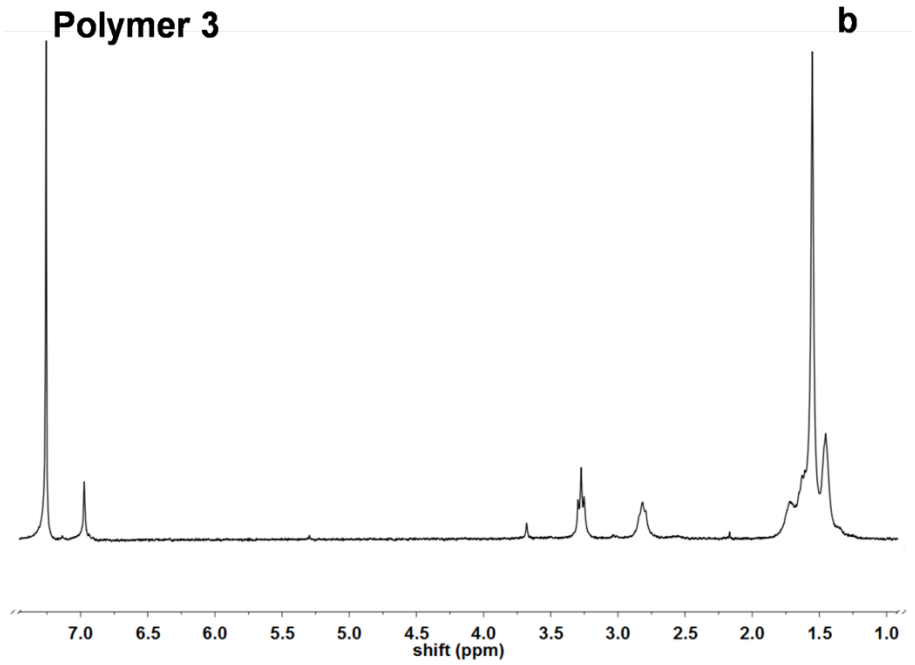
Instrumentations.

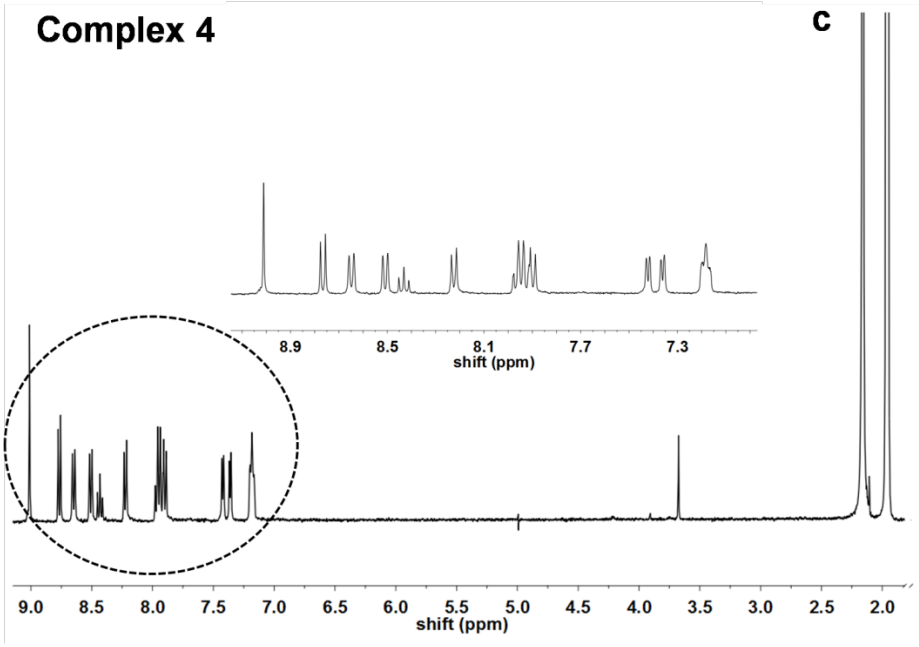
^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance-400 NMR (400 and 100 MHz respectively) and Bruker DPX-300 (300 and 75 MHz respectively) NMR spectrometers. UV−visible absorption spectra were recorded on a Varian Cary 50 UV−vis spectrometer. Mass spectra were collected on a Finnigan MAT-95 mass spectrometer. TEM images and Energy-dispersive X-ray spectroscopy (EDX) data were collected with a FEI Tecnai G2 F20 Transmission Electron Microscope. Molecular weights were determined against polystyrene standards using a Waters GPC system equipped with two Styragel HR3 and HR4 columns (25 °C), 996 photodiode array, and 2410 refractive index detectors. HPLC grade THF was used as the eluent with a flow rate of 0.8mL/min. Cyclic voltammetry was performed on an eDAQ EA161 potentiostat. A 3 mm glassycarbon electrode was used as the working electrode, a platinum foil was used as the reference electrode, and a platinum wire was used as the auxiliary electrode. 0.1 M Tetrabutylammonium hexafluorophosphate was used as supporting electrolyte and degassed HPLC grade DMF was used as the solvent.

Femtosecond Transient Absorption (fs-TA) Experiments. The fs-TA experiments were performed with the experimental setup and methods described previously[3,4]. Fs-TA spectra were collected using a femtosecond regenerative amplified Ti:sapphire laser system in which the amplifier was seeded with the 120 fs laser pulses from an oscillator laser system. The laser probe pulse was produced by utilizing ~5 % of the amplified 800 nm laser pulses to generate a white-light continuum (430-800 nm) in a sapphire crystal.

The probe beam was split into two parts before traversing the sample. One probe laser beam passed through the sample while the other probe laser beam went into the reference spectrometer in order to monitor the fluctuations in the probe beam intensity. The sample solution was excited with a 400 nm pump beam (the second harmonic of the fundamental 800 nm from the regenerative amplifier). The samples were contained in a 2 mm path-length cuvette at 400 nm (absorbance = 1) throughout the data acquisition.


Polymer 2
a
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
shift (ppm)


Polymer 3
b
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
shift (ppm)



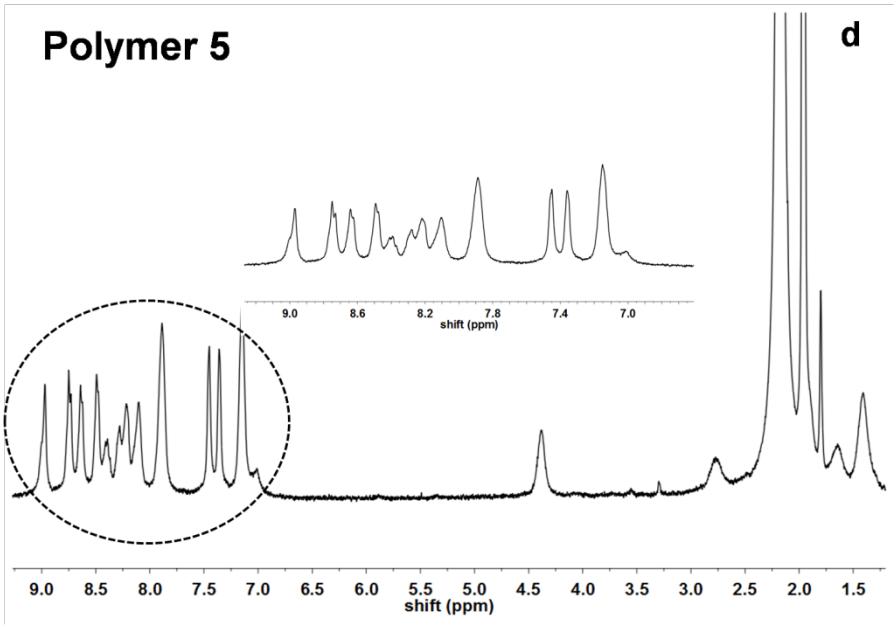


Figure S1. ^{1}H NMR spectra of (a) polymer **2**, (b) polymer **3**, in $CDCl_3$, and (c) complex **4**, (d) polymer **5** in CD_3CN.

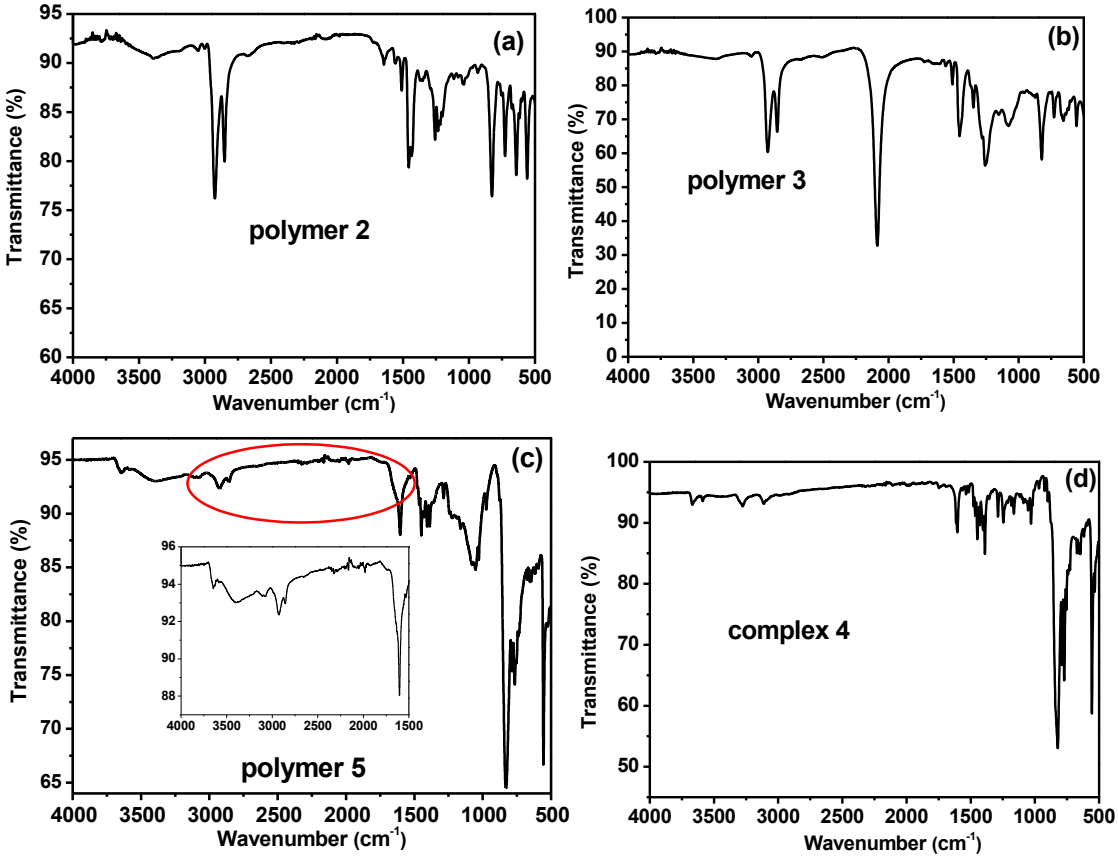


Figure S2. FTIR spectra of (a) polymer **2** (b) polymer **3** (c) polymer **5** and (d) complex **4**.

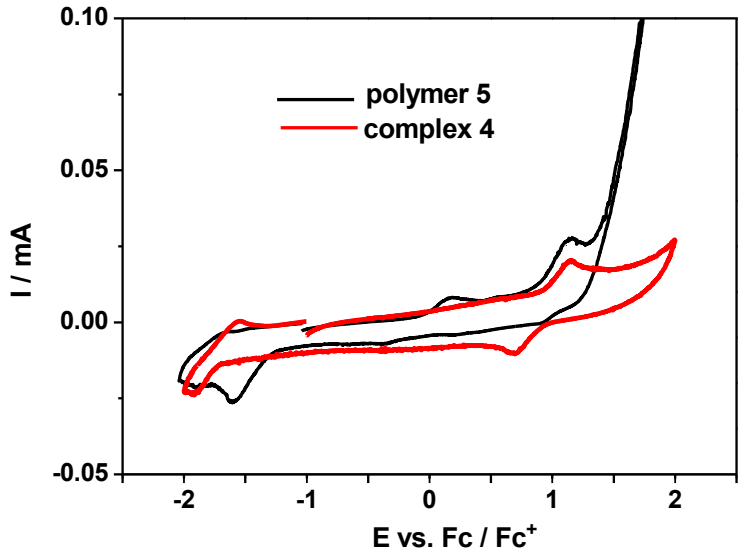


Figure S3. Cyclic voltammograms of complex **4** and polymer **5** measured in DMF solution. Scan rate = 100 mV/s.

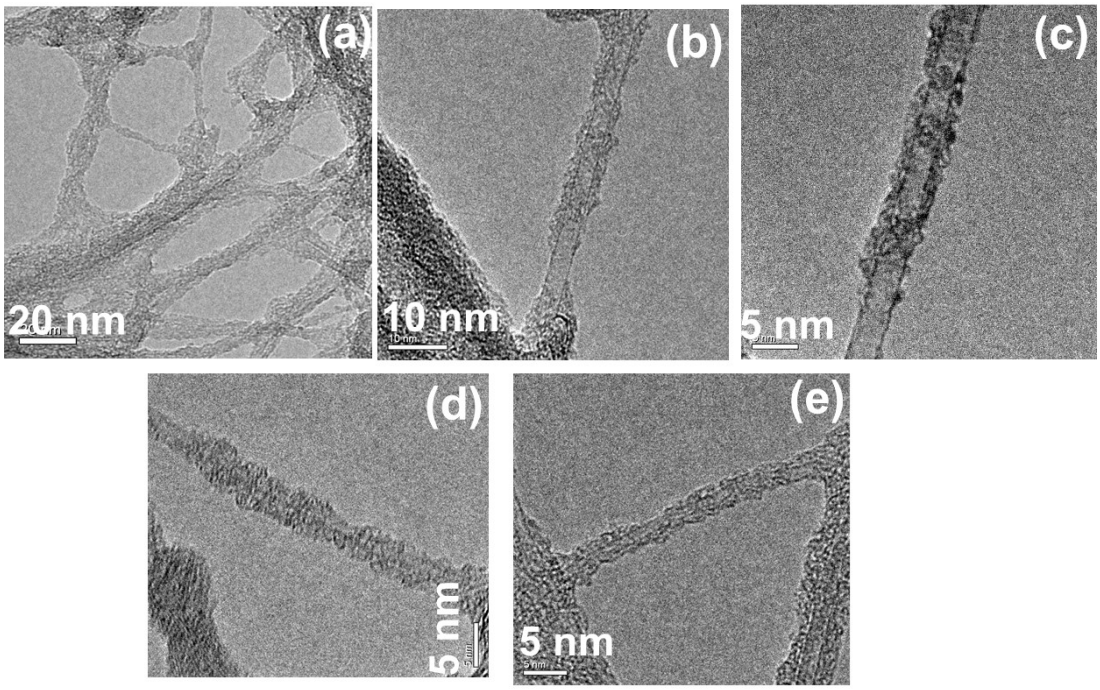


Figure S4. TEM images of (a) SWCNTs functionalized with polymer **5**, (b) and (c) individual SWCNT with large diameter and (c) and (d) with smaller diameter coated by polymer **5**.

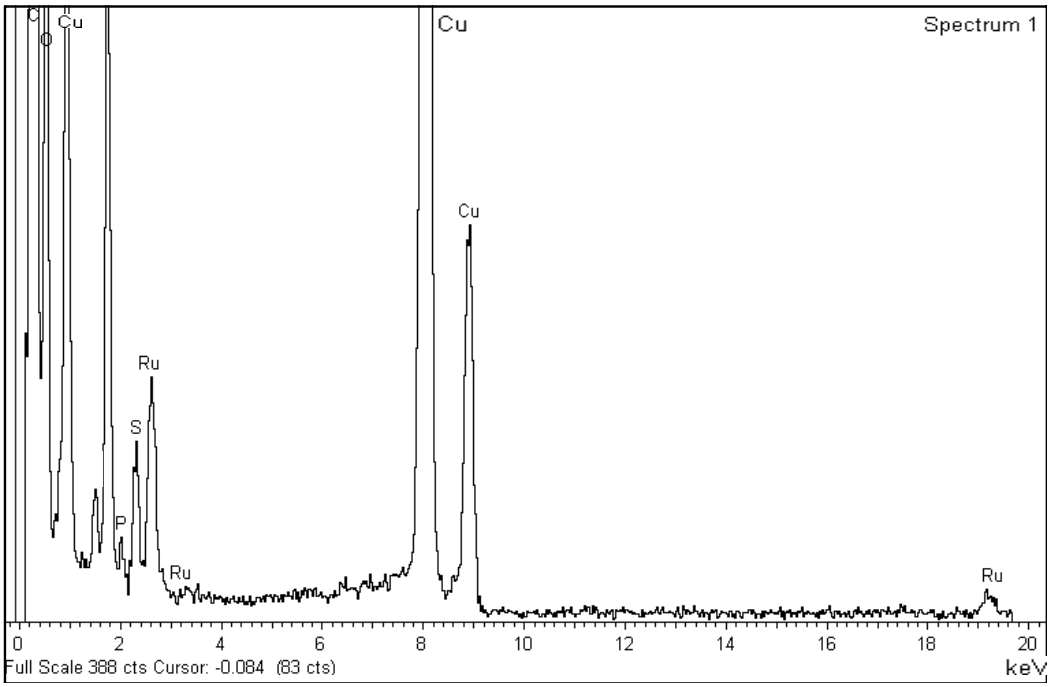


Figure S5. EDX spectrum of polymer **5**/SWCNT hybrid.

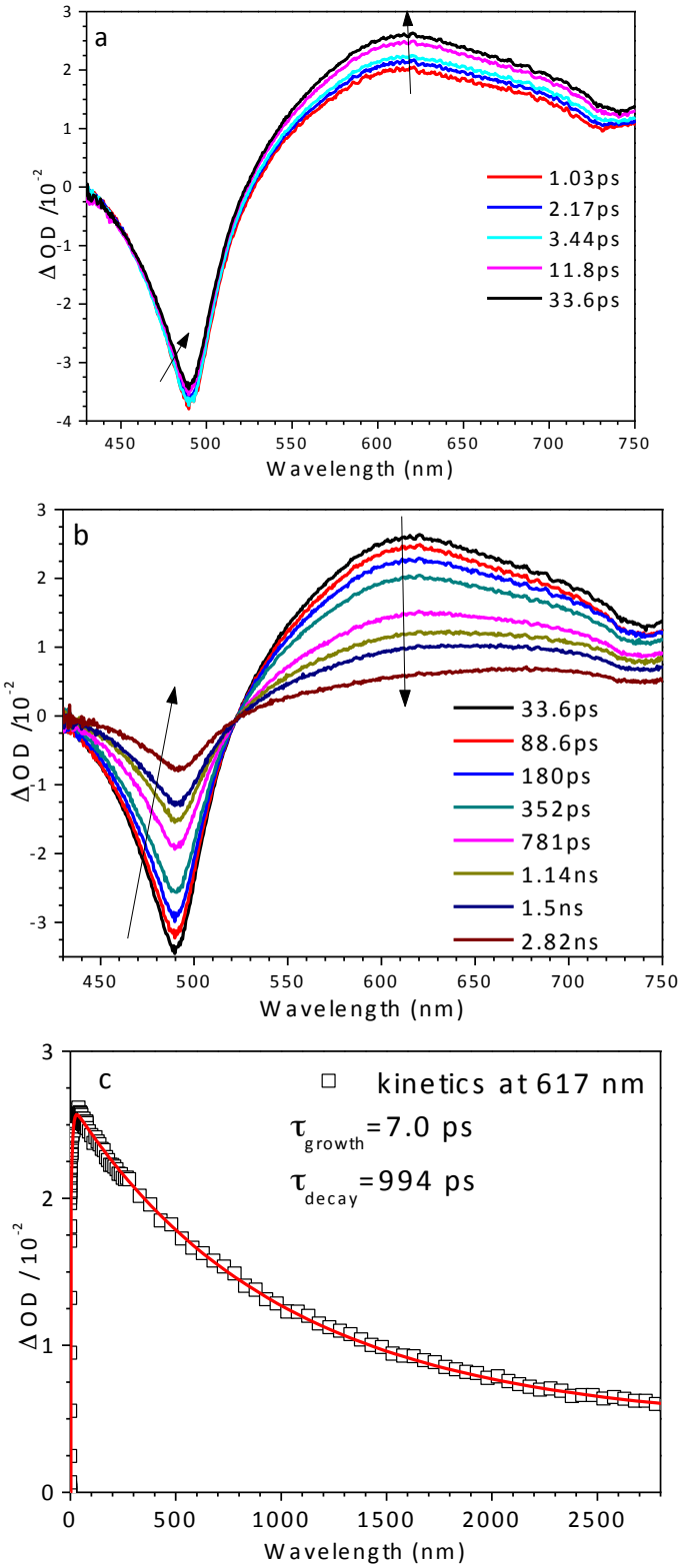


Figure S6. (a, b) fs-TA spectra of complex **4** in DMF solution acquired after 400 nm irradiation. The kinetics of the decay of the absorption bands at 617 nm is displayed in (c). The solid lines indicate the fitting of the experimental data points.

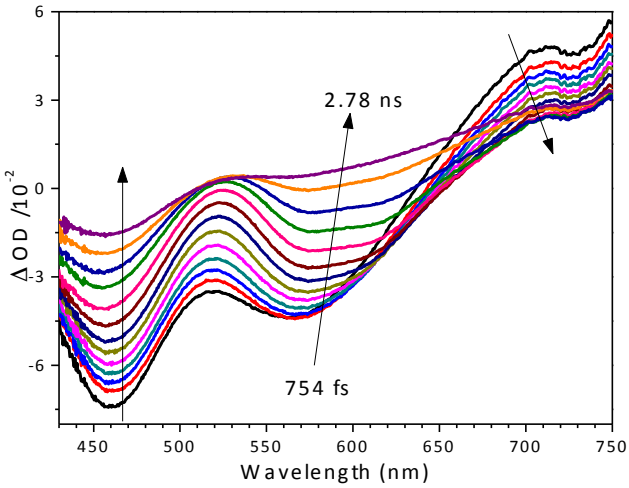


Figure S7. fs-TA spectra of polymer **2** in CH_2Cl_2 solution (excited at 400 nm).

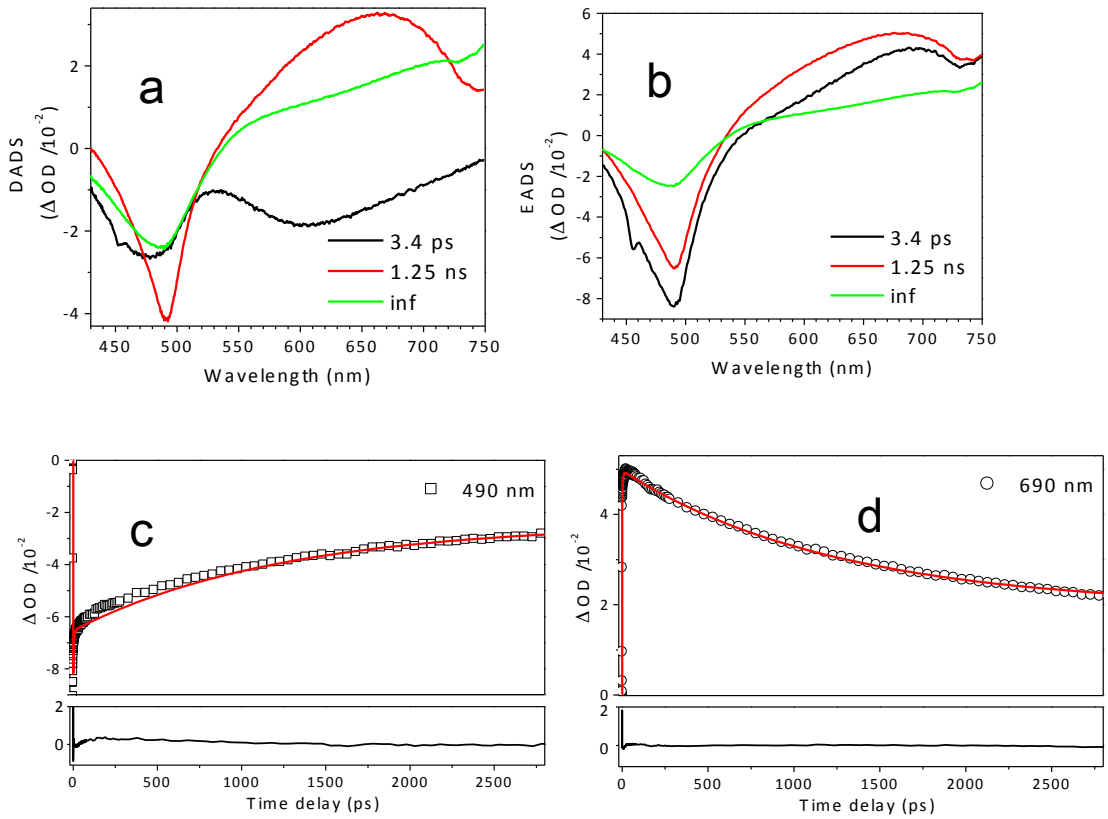


Figure S8. (a) DADS and (b) EADS derived from the global fitting analysis of the TA results for the polymer 5. The asterisk represents the solvent effect. (c,d) Selected fitting trace at 490 nm and 680 nm with fitting error showing below.

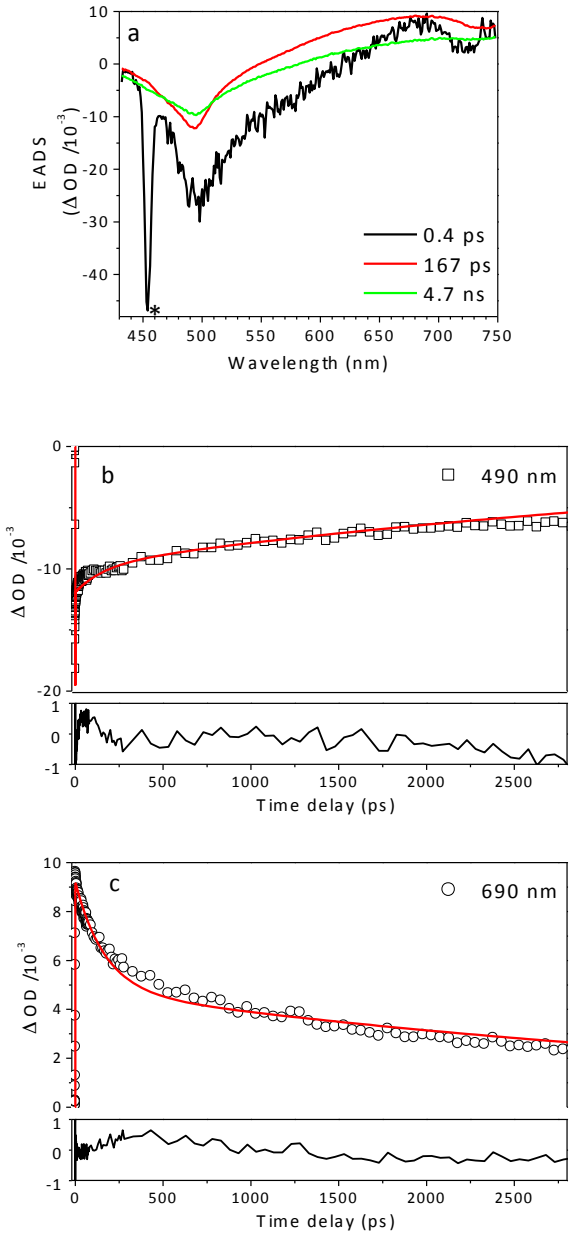


Figure S9. (a) EADS derived from the global fitting analysis of the TA results for the polymer 5/SWCNT system. The asterisk represents the solvent effect. (b,c) Selected fitting trace at 490 nm and 680 nm with fitting error showing below.

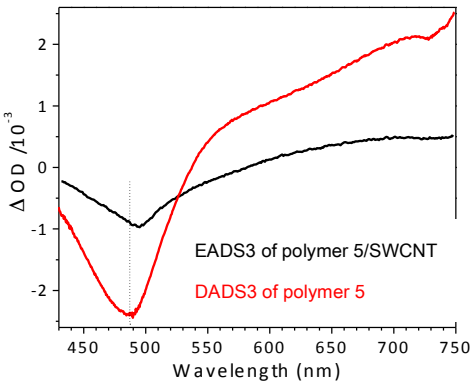


Figure S10. Comparison between the EADS3 of polymer **5**/SWCNT hybrid (shown in Figure S8) and the DADS3 of polymer **5** (shown in Figure S9).

References

1. J. De Girolamo, P. Reiss and A. Pron, *J. Phys. Chem. C,* 2007, **111**, 14681-14688.
2. F. Schlutter, A. Wild, A. Winter, M. D. Hager, A. Baumgaertel, C. Friebe and U. S. Schubert, *Macromolecules,* 2010, **43**, 2759-2771.
3. L. Du, M.-D. Li, Y. Zhang, J. Xue, X. Zhang, R. Zhu, S. C. Cheng, X. Li and D. L. Phillips, *J. Org. Chem.* 2015, **80**, 7340-7350;
4. L. L. Du, R. X. Zhu, J. D. Xue, Y. Du and D. L. Phillips, *J. Raman Spectrosc.,* 2015, **46**, 117-125.