Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Noncovalent Modification of Single Wall Carbon Nanotubes (SWCNTs) by Thienothiophene Derivatives

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Materials and Experimental Procedure

All the reagents, purchased from Aldrich and Acros, were used without further purification. All the solvents used in the syntheses were technical grade. Column chromatography was performed with ≤ 0.063 µm Silica Gel for purifications. ^{1}H and ^{13}C NMR spectra were recorded on a Varian 500 and 126 MHz, respectively, spectrometer. Proton and carbon chemical shifts are reported in parts per million downfield from tetramethyl silane, TMS. The TTs, **TT-CN-TPA** and **TT-CN-TPA2** were synthesized following our previous reports.[1-3]

Synthesis of 4-(2-(4-(diphenylamino)phenyl)thieno[3,2-*b*]thiophen-3-yl)benzoic acid (TT-COOH-TPA). A mixture of TT-CN-TPA (0.2 g, 0.500 mmol) and KOH (2M, 20 mL solution) in EtOH (30 mL) was refluxed under nitrogen atmosphere for 20 h, after which the crude product was extracted with water/dichloromethane, dried over sodium sulfate, filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography eluting with *n*-hexane:CH_2Cl_2 (3:1) to obtain the title compound **TT-COOH-TPA** (0.15 g, 76%) as a greenish powder. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 5.2 Hz, 1H), 7.32 – 7.28 (m, 3H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 8.7 Hz, 2H), 7.14 (d, *J* = 7.7 Hz, 3H), 7.11-7.08 (m, 2H), 7.06 (d, *J* = 7.3 Hz, 2H), 7.01 (t, *J* = 7.3 Hz, 1H), 6.96 (d, *J* = 8.7 Hz, 2H). IR (ATR, diamond) 3531, 1586, 1480, 1326, 1275, 1181, 1033, 1017, 841, 752, 692 cm^{-1}.

Treatment of HYBRID 1 with gold nanoparticle. A mixture of a tiny piece of **HYBRID 1** film and 10 drops of AuNPs (2.4 nM)[4] were stirred in 10 ml of THF for 48 hours. Then, the mixture was filtered from gooch crucible. The filtered film was washed with THF and methanol in sonicator and dried under vacuum.

Surface Characterization

Scanning Electron Microscopy (SEM) images were recorded using Hitachi SU 500 FEG-SEM instrument. Images were obtained at 100k, 110k and 200k magnifications at 15 kV and 30 kV acceleration voltages in high vacuum.

Atomic Force Microscopy (AFM) images were collected by using Hitachi AFM5100N type instrument, which was operated under dynamic mode (DFM). In DFM mode, the tip implements intermittent contact to the sample surface to minimize the destructive lateral forces. Images were obtained by scanning 20 x 20-micron area, using SI-DF-3P2 (Hitachi) cantilever with a spring constant of 2.4 N m^{-1} at ambient temperature and humidity.

The contact angle (CA) measurements were performed using a Kürüüs DSA-100 model CA instrument, equipped with a single direct dosing system consisting of a high-performance frame grabber camera T1C (25 frames per second) and controlled by a DS3210 software, providing the static and dynamic operation mode. The CA values were determined by sessile drop technique for liquid probes of deionized water.

Transmission Electron Microscopy studies (TEM) were conducted with JEOL JEM 2100 HRTEM at 200 kV. Images were recorded by Gatan Model 833 Orius SC200D CCD Camera. Lacey carbon support film coated copper TEM grids (Electron Microscopy Sciences, LC200-Cu, 200 mesh) were used.

Computational Details

Classical molecular (MD) dynamics were used to investigate the interactions of the thienothiophene (TT) derivatives with single wall carbon nanotube (SWCNT) in solution of tetrahydrofuran (THF). To perform the MD simulations, the SWCNT in zigzag configuration with 4.5 nm was used. The structures of the SWCNT were generated by using the Python script buildCstruct, which is available at https://github.com/bio-phys/cnt-gaff.[5] General AMBER force field (GAFF)[6] parameters were used for SWCNT molecule, TT derivatives and tetrahydrofuran. Partial charges were calculated by using the geometry optimized structures of molecules, followed by restraint electrostatic potential (RESP)[7] charge calculations method with Gaussian 09 program package[8] and antechamber program.[9,10] SWCNT molecule was placed in the center of a cubic box with 8 × 8 × 8 nm^3 dimensions; either 1 or 10 thienothiophene derivatives were randomly introduced into the box. The box was filled randomly with 2000 molecules of tetrahydrofuran Packmol package.[11,12] A steepest descent minimization procedure was applied for all systems to remove all unexpected and unfavorable contacts. Linear constraint solver (LINCS) algorithm[13] was used for all bonds involving hydrogen atoms, and short-range non-bonded interactions were truncated to zero with the cutoff distance of 1.2 nm. Long-range electrostatic interactions were calculated by performing particle mesh Ewald method procedure.[14] Initial velocities were given to all particles of systems according to Maxwell–Boltzmann distribution at 300 K. V-rescale coupling algorithm was used[15] with the coupling constant of 0.1 ps to maintain constant temperature and pressure for all the simulated systems. All production runs were conducted in NPT ensemble for 50 ns at 300 K, and a time step of 2 fs for all simulations was used. Coordinates, velocities, and energies were saved for analysis every 10 ps. All simulations were performed employing Gromacs 5.0 program package.[16-18] Visual Molecular Dynamics (VMD) program was used for visualizations of the trajectory and preparation of snapshots.[19]

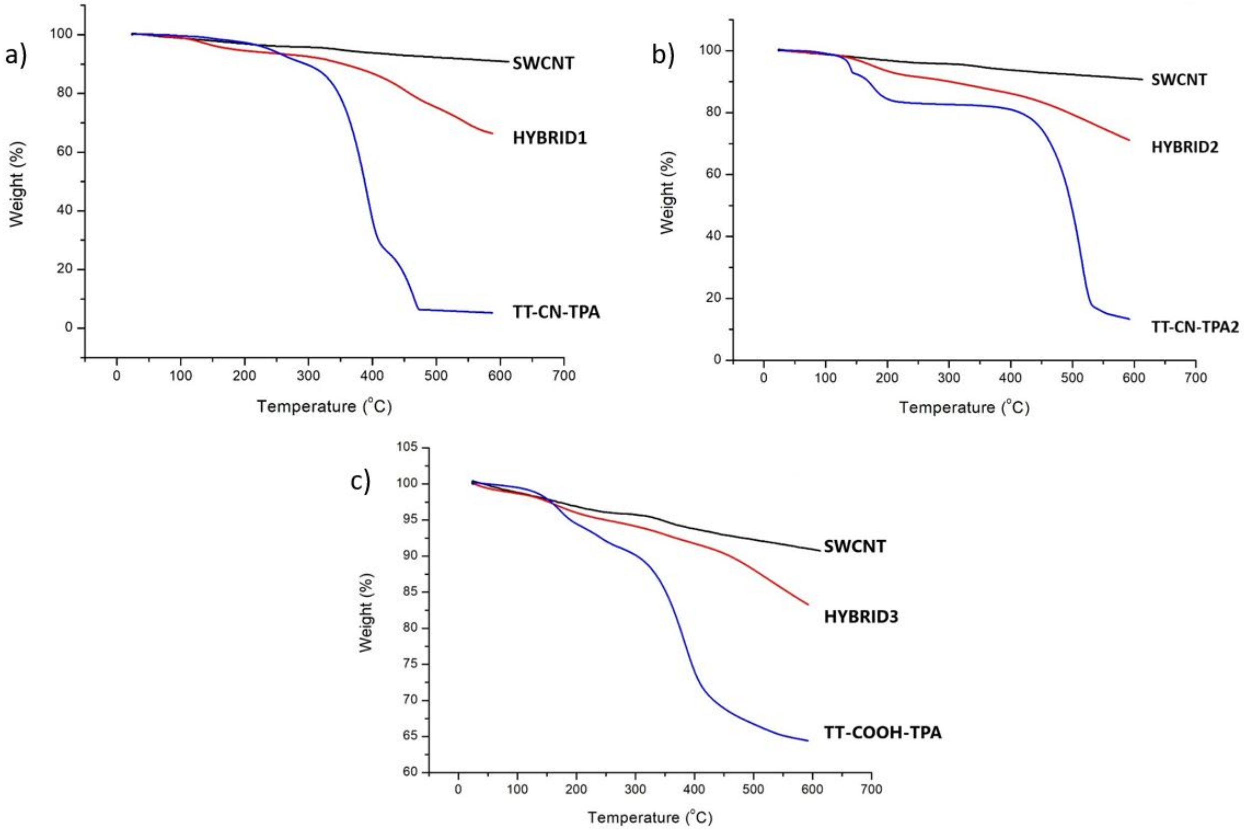


Fig. S1. TGA curves of coated SWCNTs (**HYBRID 1, HYBDRID 2, HYBRID 3**), TT derivatives (**TT-CN-TPA, TT-CN-TPA2, TT-COOH-TPA**), and the original SWCNTs.

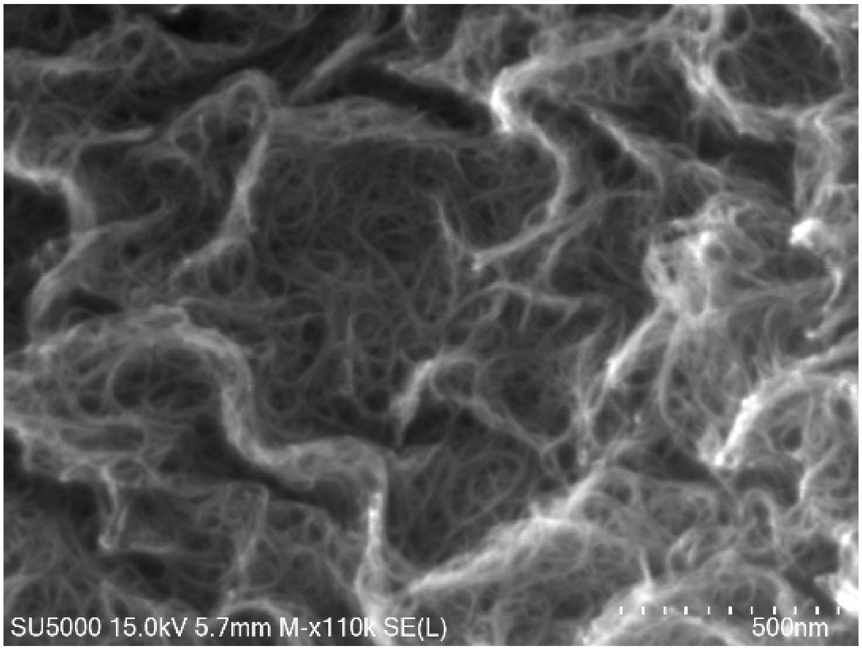
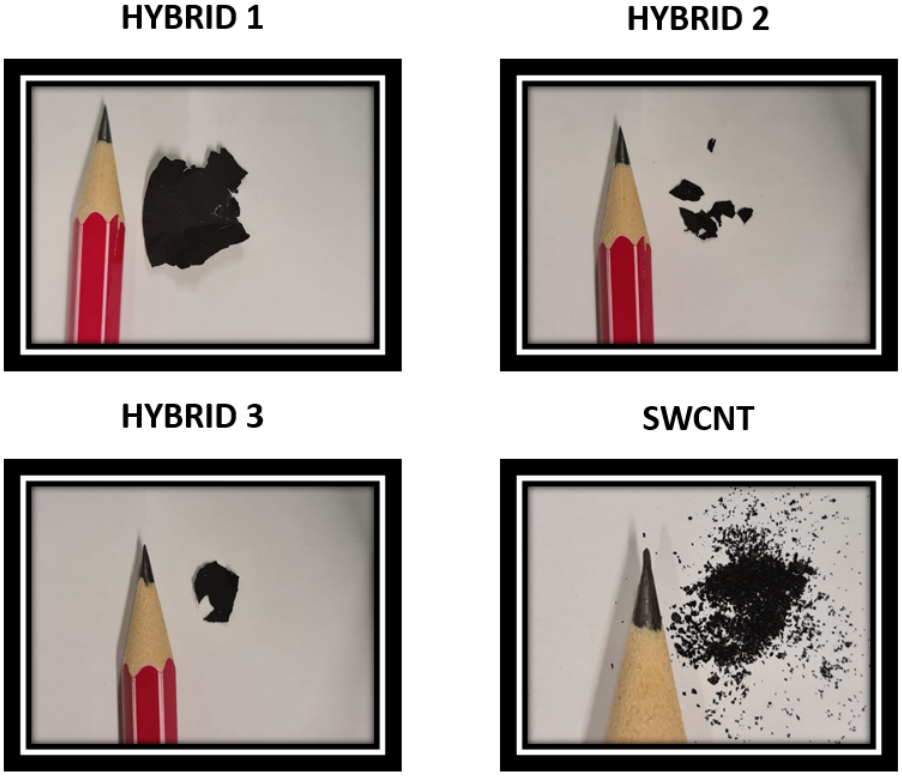


Fig. S2. Uncoated SWCNT recorded at x 110k magnification and 15 kV acceleration voltage using SU500 Hitachi FEG-SEM instrument.


HYBRID 1

HYBRID 2

HYBRID 3

SWCNT

Fig. S3. Thin film form of **HYBRID 1-3** and powder form of pristine SWCNT.

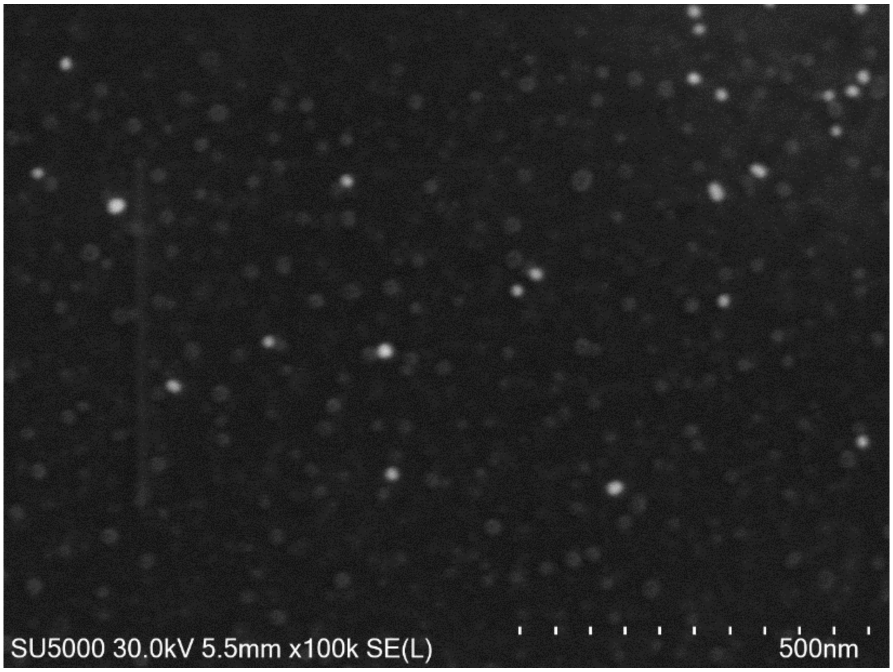


Fig. S4. SEM image of gold nanoparticles (AuNPs).

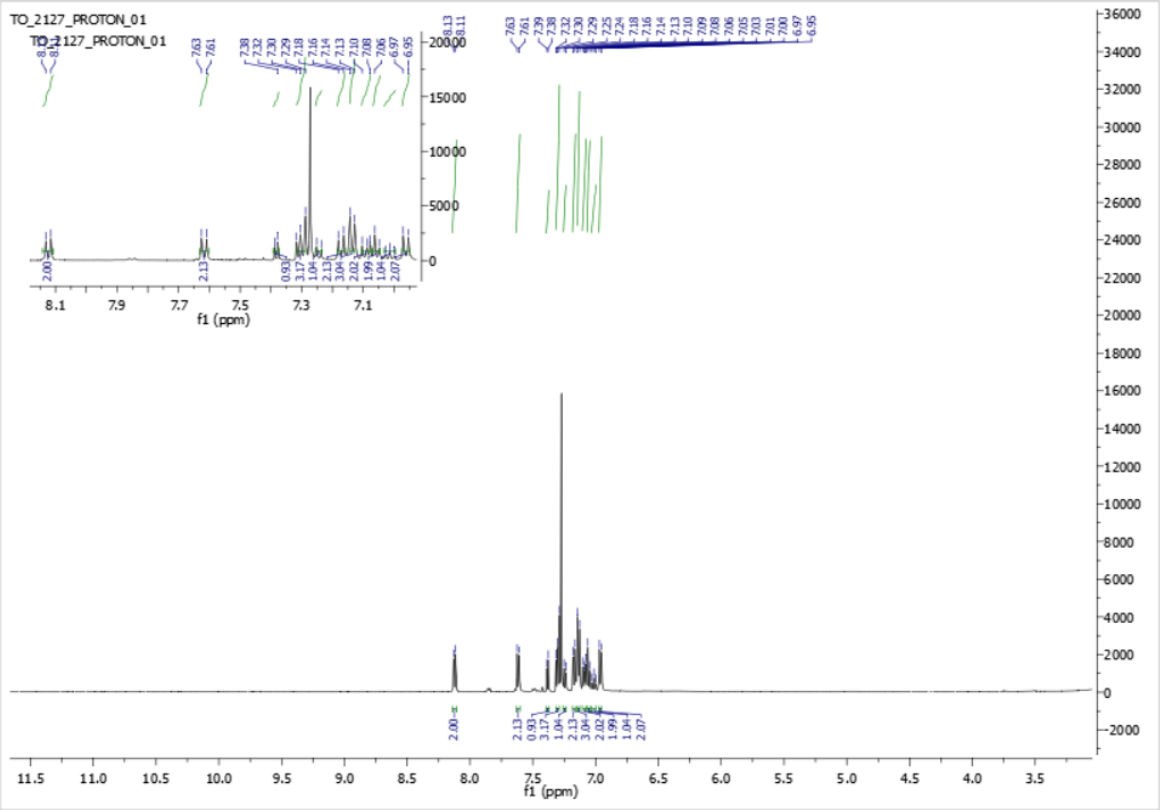


Fig.S5. ^{1}H-NMR spectrum of **TT-COOH-TPA** in $CDCl_3$.

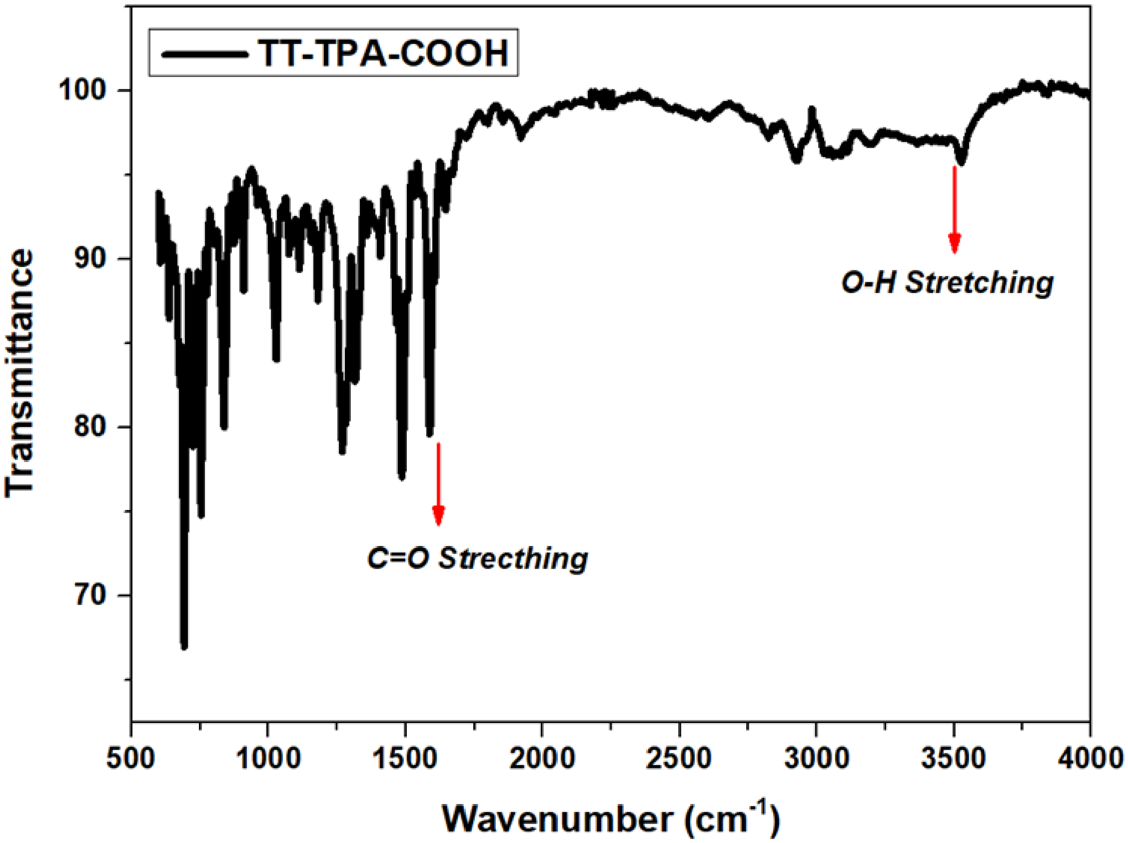


Fig. S6. FTIR spectrum of **TT-COOH-TPA**.

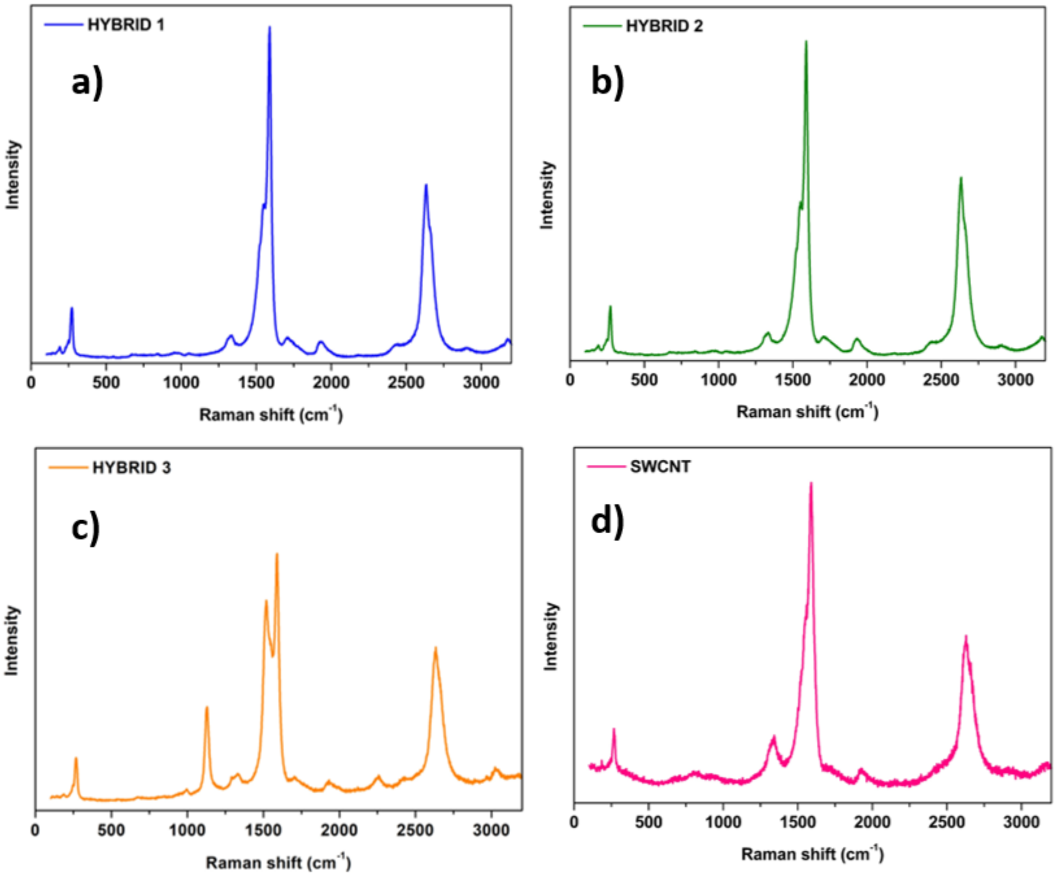


Fig. S7. Raman spectrum of **HYBRID 1-3** and **SWCNT**.

References

1. R. Isci, D. Gunturkun, A. S. Yalin, T. Ozturk, *J. Polym. Sci.* 2021, **59**, 117-123.
2. R. Isci, A. R. Varzeghani, K. Kaya, B. Sütay, E. Tekin, T. Ozturk, *ACS Sustain. Chem. Eng.* 2022, **10** (4), 1605-1615.
3. R. Isci, M. Unal, G. Kucukcakir, N. A. Gurbuz, S. F. Gorkem, T. Ozturk, *J. Phys. Chem. B* 2021, **125**, 48, 13309-13319.
4. E. Karakus, E. Erdemir, N. Demirbilek, L. Liv, *Anal. Chim. Acta* 2021, **1182**, 338939.
5. M. Vögele, J. Köfinger, G. Hummer, *Faraday Discuss.* 2018, **209**, 341-358.
6. J. Wang, R. M. Wolf, J. W. Caldwell, P. A. Kollman, D. A. Case, *J. Comput. Chem.* 2004, **25**, 1157-1174.
7. C. I. Bayly, P. Cieplak, W. Cornell, P. A. Kollman, *J. Phys. Chem.* 1993, **97**, 10269-10280.

8. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, Jr., J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03, Revision D.01*, Gaussian, Inc., Wallingford CT, 2004.
9. J. Wang, W. Wang, P. A. Kollman, D. A. Case, *J. Comput. Chem.,* 2005, **25**, 1157-1174.
10. A. Case, T. A. Darden, T. E. I. Cheatham, C. L. Simmerling, J. Wang, R. E. Duke, R. Luo, K. M. Merz, B. Wang, D. A. Pearlman, M. Crowley, S. Brozell, V. Tsui, H. Gohlke, J. Mongan, V. Hornak, G. Cui, P. Beroza, C. Schafmeister, J. W. Caldwell, W. R. Ross and P. A. Kollman, *AMBER 8*, University of California, San Francisco, 2004.
11. J. M. Martínez, L. Martínez, *J. Comput. Chem.* 2003, **24**, 819-825.
12. L. Martínez, R. Andrade, E. G. Birgin, J. M. Martínez, *J. Comput. Chem.* 2009, **30**, 2157–2164.
13. B. Hess, H. Bekker, H. J. Berendsen, J. G. Fraaije, *J. Comput. Chem.* 1997, **18** (12), 1463-1472.
14. T. Darden, D. York, L. Pedersen, *J. Chem. Phys.* 1993, **98**, 10089–10092.
15. Bussi, D. Donadio, M. Parrinello, *J. Chem. Phys.* 2007, **126**, 01410.
16. D. Van der Spoel, E. Lindahl, B. Hess, G. Groenhof, A. E. Mark, H. J. C. Berendsen, *J. Comput. Chem.* 2005, **26**, 1701– 1719.
17. E. Lindahl, B. Hess, D. Van der Spoel, *J. Mol. Mod.* 2001, **7**, 306–317.
18. J. C. Berendsen, D. Van der Spoel, R. Van Drunen, Comput. *Phys. Commun.* 1995, **91**, 43–56.

19. W. Humphrey, A. Dalke, K. Schulten, *J. Mol. Graphics* 1996, **14**, 33–38.