

Electronic Supplementary Information

Plasmonic hybrid nanotubes of fullerene C₆₀-polythiophene-silver or gold nanoparticle: fabrication and enhancement of the Raman scattering

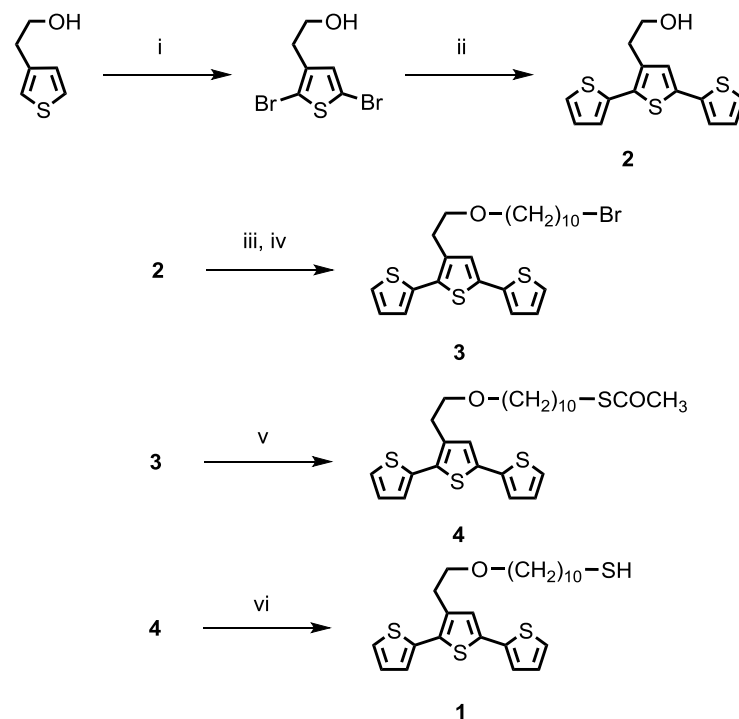
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- 1) Synthesis of terthienyl-thiol (1) and terthienyl C₆₀ (2-C₆₀).
- 2) Synthesis of silver and gold nanoparticles.
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(1) Synthesis of terthienyl-thiol (1) and terthienyl C₆₀ (2-C₆₀).

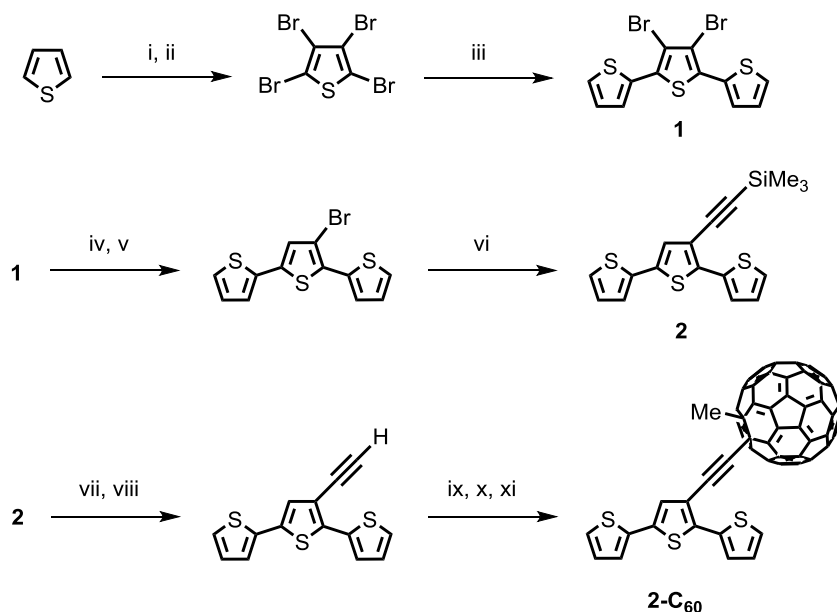
Terthienyl-thiol (**1**) and terthienyl C₆₀ (**2-C₆₀**)^(Reference 14 of the main text) were synthesized according to Schemes S1 and S2.



Scheme S1. Reagents and conditions: (i) *N*-bromosuccinimide, toluene, room temp., 5 h. (ii) 2-tributylstannylthiophene, Pd(PPh₃)₄, toluene, 95 °C, 34 h. (iii) NaH, THF, room temp., 1 h. (iv) Br-(CH₂)₁₀-Br, THF, reflux, 5 h. (v) CH₃COSK, THF, reflux, 4 h. (vi) LiAlH₄, THF, room temp., 1 h.

1: ¹H NMR (400 MHz, CDCl₃) δ 1.26-1.35 (m, 12H, CH₂), 1.33 (t, *J* = 7.2 Hz, 1H, -SH), 1.53-1.63 (m, 4H, CH₂), 2.51 (dt, *J*₁ = 7.2 Hz, *J*₂ = 7.2 Hz, 2H, -CH₂-SH), 3.02 (t, *J* = 6.8 Hz, 2H, Th-CH₂-), 3.44 (t, *J* = 6.8 Hz, 2H, -O-CH₂-), 3.66 (t, *J* = 6.8 Hz, 2H, -CH₂-O-), 7.01 (dd, *J*₁ = 3.6 Hz, *J*₂ = 5.2 Hz, 1H, Th-H), 7.07 (dd, *J*₁ = 3.6 Hz, *J*₂ = 5.2 Hz, 1H, Th-H), 7.08 (s, 1H, Th-H), 7.15 (dd, *J*₁ = 0.8 Hz, *J*₂ = 4.0 Hz, 1H, Th-H), 7.16 (dd, *J*₁ = 0.8 Hz, *J*₂ = 4.0 Hz, 1H, Th-H), 7.21 (dd, *J*₁ = 1.2 Hz, *J*₂ = 5.2 Hz, 1H, Th-H), 7.31 (dd, *J*₁ = 1.2 Hz, *J*₂ = 5.2 Hz, 1H, Th-H); ¹³C NMR (100 MHz, CDCl₃) δ 24.6, 26.2, 28.3, 29.0, 29.4, 29.4, 29.5, 29.7, 29.8, 34.0, 70.4, 71.1, 123.6, 124.4, 125.5, 126.2, 126.7, 127.5, 127.8, 130.6, 135.3, 135.5, 136.4, 137.1; MS (EI) *m/z* 464 (M⁺).

The cyclic voltammogram of **1** in 0.1 M Bu₄NPF₆-CH₂Cl₂ showed the oxidation peak at *E*_p = +0.96 V (vs. Ag/0.1 M AgNO₃).



Scheme S2. Reagents and conditions: (i) Br₂, CHCl₃, room temp., 4 h. (ii) reflux, 24 h. (iii) 2-tributylstannyl thiophene, Pd(PPh₃)₄, toluene, 110 °C, 72 h. (iv) *n*-BuLi, THF, room temp., 20 min. (v) H₂O. (vi) trimethylsilylacetylene, Pd(PPh₃)₄, CuI, piperidine, reflux, 45 h. (vii) Bu₄NF, THF, room temp., 30 min. (viii) H₂O. (ix) *n*-BuLi, THF, -78 °C, 1 h. (x) C₆₀, *o*-dichlorobenzene, room temp., 30 min. (xi) CH₃I, *o*-dichlorobenzene, room temp., 1 h.

2-C₆₀: ¹H NMR (400 MHz, CD₂Cl₂) δ 3.46 (s, 3H, CH₃), 6.97-7.01 (m, 2H, Th-H), 7.18 (dd, *J*₁ = 0.8 Hz, *J*₂ = 3.2 Hz, 1H, Th-H), 7.22 (dd, *J*₁ = 0.8 Hz, *J*₂ = 5.2 Hz, 1H, Th-H), 7.25 (dd, *J*₁ = 0.8 Hz, *J*₂ = 5.2 Hz, 1H, Th-H), 7.32 (s, 1H, Th-H), 7.49 (dd, *J*₁ = 0.8 Hz, *J*₂ = 3.2 Hz, 1H, Th-H); ¹³C NMR (100 MHz, CD₂Cl₂) δ 33.7, 62.1, 78.0, 81.6, 92.9, 117.8, 125.0, 125.9, 126.5, 126.7, 127.8, 128.0, 128.6, 134.9, 135.1, 135.2, 135.9, 136.6, 140.2, 140.6, 140.8, 142.0, 142.2, 142.5, 142.6, 142.7, 142.7, 143.1, 143.1, 143.5, 143.7, 145.1, 145.2, 145.5, 145.7, 145.9, 145.9, 146.0, 146.1, 146.4, 146.7, 146.8, 146.9, 147.0, 148.4, 153.3, 157.4; MS (FAB) *m/z* 1006 (M⁺).

(2) Synthesis of silver nanoparticles (1-AgNP) and gold nanoparticles (1-AuNP).

Typical procedure for the preparation of 1-AgNP is as follows. To a vigorously stirred solution of AgBF_4 (115 mg, 0.59 mmol) in 50 mL of MeOH was added thiol **1** (275 mg, 0.59 mmol). NaBH_4 (134 mg, 3.5 mmol) in 15 mL of H_2O was then added. The mixture was stirred for 30 min at room temperature. After the reaction, the filtrate was evaporated in vacuo to yield 1-AgNP. Purification of 1-AgNP was repeated until no free thiol remained, as detected by TLC, ^1H and ^{13}C NMR spectroscopy.

Typical procedure for the preparation of 1-AuNP is as follows. To a vigorously stirred solution of $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (124 mg, 0.30 mmol) in 50 mL of MeOH was added thiol **1** (139 mg, 0.30 mmol). NaBH_4 (68.0 mg, 1.8 mmol) in 15 mL of H_2O was then added. The mixture was stirred for 30 min at room temperature. After the reaction, the filtrate was evaporated in vacuo to yield 1-AuNP. Purification of 1-AuNP was repeated until no free thiol remained, as detected by TLC, ^1H and ^{13}C NMR spectroscopy.

(3) Fabrication of hybrid nanotubes.

3.1) 2-C₆₀-PT-NT

The electrochemical synthesis was performed by attaching the alumina membrane (Whatman Anodisc; pore diameter of about 200-250 nm, thickness of 60 μm) to a Pt electrode, another Pt electrode was used as the counter electrode, and $\text{Ag}/0.1 \text{ M AgNO}_3$ was used as the reference electrode. The electrolysis solution contains 2-C₆₀ (5 mM) in 0.1 M Bu_4NPF_6 -*o*-dichlorobenzene (1 mL). A voltage of 1.03 V was applied for 60 min. After the electrochemical synthesis, removal of the alumina membranes with 1 M NaOH led to the release of 2-C₆₀-PT-NT.

3.2) Ag-C₆₀-PT-NT and Au-C₆₀-PT-NT.

The electrochemical synthesis was performed by attaching the alumina membrane (Whatman Anodisc; pore diameter of about 200-250 nm, thickness of 60 μm) to a Pt electrode, another Pt electrode was used as the counter electrode and $\text{Ag}/0.1 \text{ M AgNO}_3$ was used as the reference electrode. The electrolysis solution contains 2-C₆₀ (3.5 mg) and 1-AgNP (10 mg) or 1-AuNP (10 mg) in 0.1 M Bu_6NPF_6 -*o*-dichlorobenzene (1 mL). A voltage of 1.03 V was applied for 60 min. After the electrochemical synthesis, removal of the alumina membranes with 1 M NaOH led to the release of Ag-C₆₀-PT-NT or Au-C₆₀-PT-NT.

3.3) 1-PT-NT

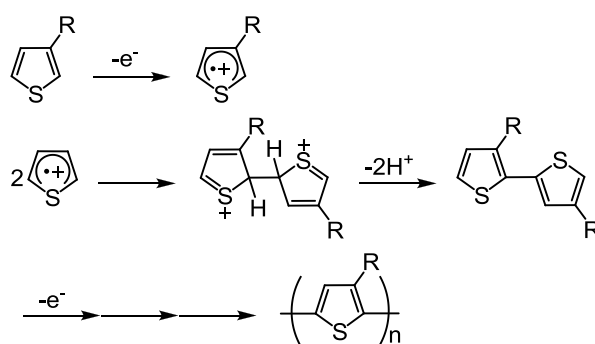
The electrochemical synthesis was performed by attaching the alumina membrane (Whatman Anodisc; pore diameter of about 200-250 nm, thickness of 60 μm) to a Pt electrode, another Pt electrode was used as the counter electrode, and Ag/0.1 M AgNO_3 was used as the reference electrode. The electrolysis solution contains **1** (30 mM) in 0.1 M $\text{Bu}_4\text{NPF}_6\text{-CH}_2\text{Cl}_2$ (1 mL). A voltage of 0.93 V was applied for 60 min. After the electrochemical synthesis, removal of the alumina membranes with 1 M NaOH led to the release of **1-PT-NT**.

3.4) 1-Ag-PT-NT

The electrochemical synthesis was performed by attaching the alumina membrane (Whatman Anodisc; pore diameter of about 200-250 nm, thickness of 60 μm) to a Pt electrode, another Pt electrode was used as the counter electrode, and Ag/0.1 M AgNO_3 was used as the reference electrode. The electrolysis solution contains **1-AgNP** (30 mg) in 0.1 M $\text{Bu}_4\text{NPF}_6\text{-CH}_2\text{Cl}_2$ (1 mL). A voltage of 0.82 V was applied for 60 min. After the electrochemical synthesis, removal of the alumina membranes with 1 M NaOH led to the release of **1-Ag-PT-NT**.

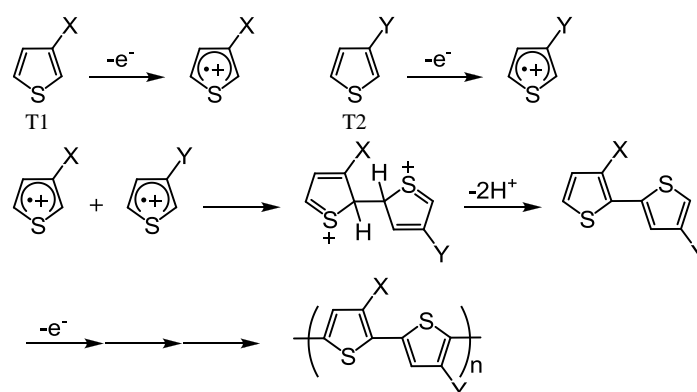
3.5) General remarks for the formation of the hybrid nanotubes.

It has been known that the mechanism for electropolymerization of thiophenes involves formation of the radical cations of thiophenes (Scheme S3).^(Reference S1) The first step (thiophene oxidation) is slow; the radical-radical coupling, deprotonation, and subsequent oxidation are fast. Reference S1: G. G. Wallace, G. M. Spinks, L. A. P. K.-Maguire and P. R. Teasdale, *Conductive Electroactive Polymers*, CRC Press, **2009**.



Scheme S3. Mechanism for electropolymerization of thiophenes.

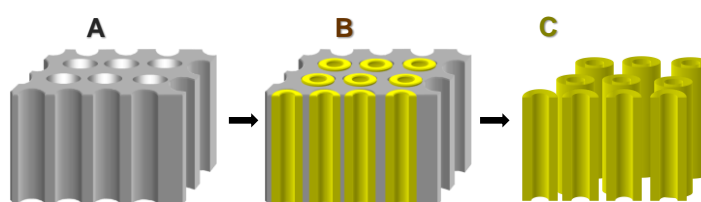
The mechanism for the electrocopolymerization of **1-AgNP** (or **1-AuNP**) and **2-C₆₀** is complex, because the electrocopolymerization contains two different monomers. One possible mechanism is shown in Scheme S4.



Scheme S4. Mechanism for electrocopolymerization of thiophenes. **1**-AgNP and **1**-AuNP are indicated as T1. **2**-C₆₀ is indicated as T2.

The growth mechanism of the polythiophene NTs, although not completely understood, is briefly suggested as follows.^(Reference S2) It has been proposed that a mechanism based on electrostatic and solvophobic interactions between the cationic sites of the polymer and the anionic sites on the pore walls explain the NT growth in the alumina template pores. These interactions induce the polymer to nucleate and preferentially grow along the pore wall to form tubular structures. Reference S2: (a) C. R. Martin, *Science*, 1994, **266**, 1961; (b) C. R. Martin, *Acc. Chem. Res.*, 1995, **28**, 61; (c) J. C. Hulteen, C. R. Martin, *J. Mater. Chem.*, 1997, **7**, 1075; (d) R. Xiao, S. II. Cho, R. Liu, S. B. Lee, *J. Am. Chem. Soc.*, 2007, **129**, 4483; (e) S. I. Cho, S. B. Lee, *Acc. Chem. Res.*, 2008, **41**, 699.

The preparation of the hybrid NTs is illustrated in Chart S1 (*vide infra*) and Scheme S5.



Scheme S5. A: bare porous alumina membrane. B: the hybrid NTs-deposited nanopores of the alumina membrane (Nanotube Membrane). C: the hybrid NTs are formed from the dissolution of the alumina membrane.

(4) Figures S1-S6

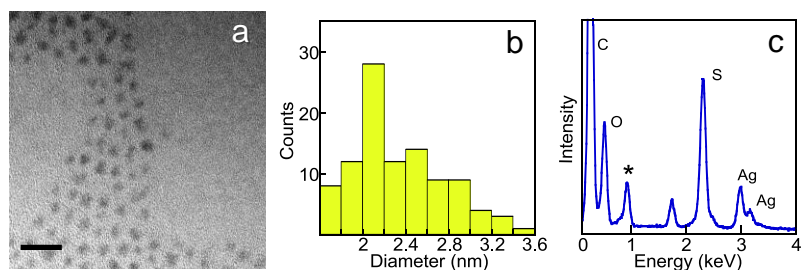


Fig. S1 (a) TEM image [scale bar = 10 nm], (b) size distribution, and (c) EDX spectrum of **1-AgNP**: the peak indicated by asterisk is due to the supporting copper grid.

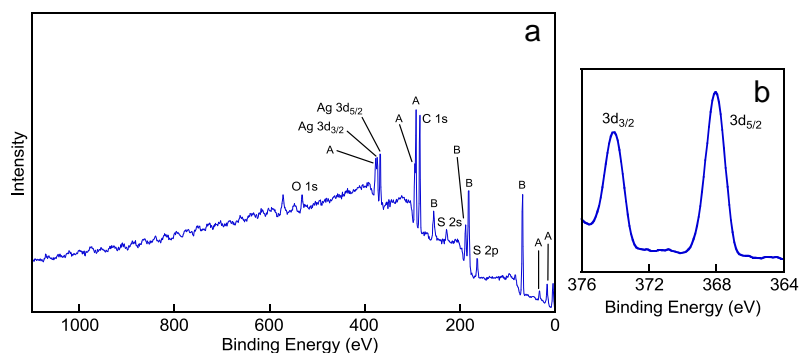


Fig. S2 (a) XPS survey spectrum obtained from **1-AgNP** using KBr (A and B peaks correspond to K and Br, respectively.), and (b) The Ag 3d XPS spectrum.

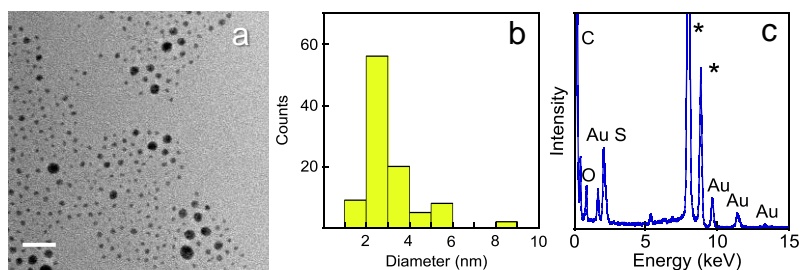


Fig. S3 (a) TEM image [scale bar = 20 nm], (b) size distribution, and (c) EDX spectrum of **1-AuNP**: the peak indicated by asterisk is due to the supporting copper grid.

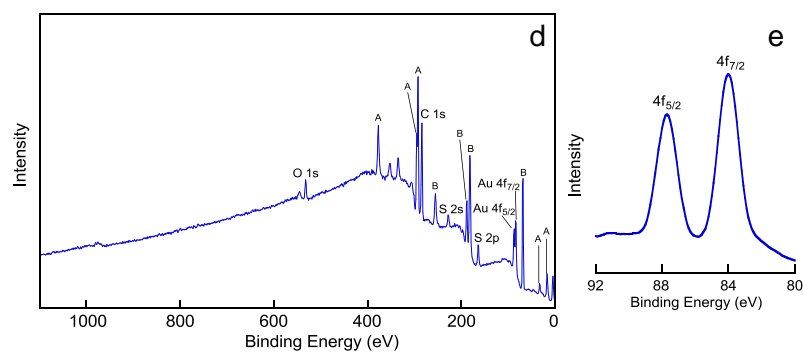


Fig. S4 (d) XPS survey spectrum obtained from 1-AuNP using KBr (A and B peaks correspond to K and Br, respectively.), and (e) The Au 4f XPS spectrum.

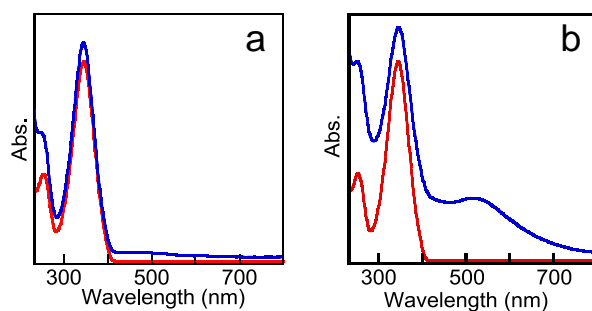


Fig. S5 (a) UV-vis spectra of **1** (red line) and 1-AgNP (blue line) in CH_2Cl_2 , and (b) UV-vis spectra of **1** (red line) and 1-AuNP (blue line) in CH_2Cl_2 .

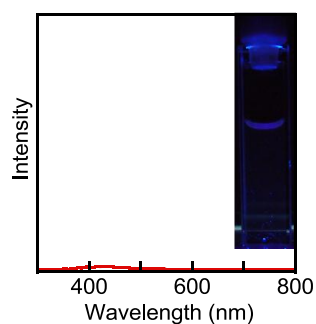


Fig. S6 PL spectrum of 2-C₆₀-PT-NT in *o*-dichlorobenzene. Inset: photograph of 2-C₆₀-PT-NT in *o*-dichlorobenzene under 365 UV light.

(5) Charts S1-S3

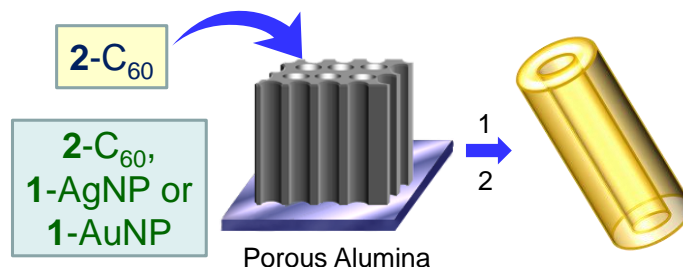


Chart S1. Our method for the fabrication of the hybrid nanotubes. 1: Electropolymerization. 2: Dissolution of porous alumina. In our hybrid NTs, the Ag NPs or Au NPs are confined as components of the wall thickness of the NTs.

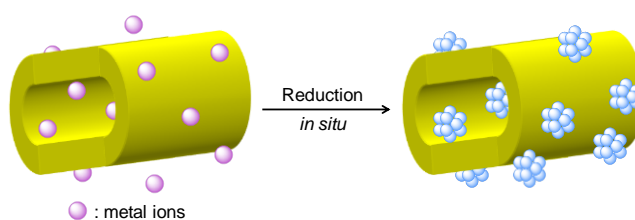


Chart S2. General method for the deposition of metal NPs either inside or outside of the NTs. [\(Reference 12 of the main text\)](#) Metal NPs are deposited in situ by the reduction of metal ions.

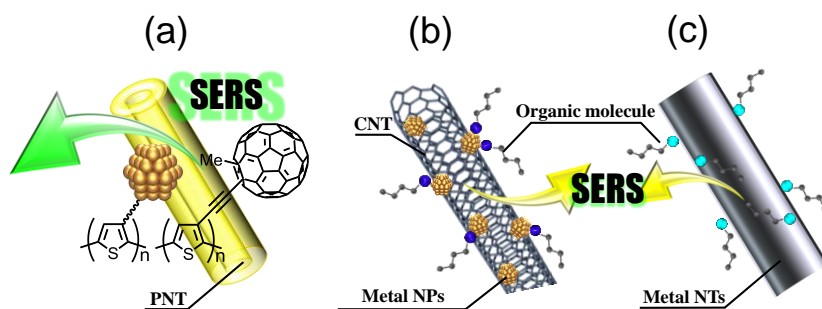


Chart S3. Schematic illustration of SERS detection for (a) our SERS-active hybrid NTs (SERS effect of nanotube itself). Schematic illustration of SERS detection for molecules adsorbed on rough metal surfaces of (b) metal NP-deposited carbon NTs [\(References 4b of the main text\)](#) and (c) gold NTs [\(Reference 4d of the main text\)](#).