

## Electronic Supplementary Information

### Redox-active $\pi$ -conjugated polymer nanotubes with viologen for encapsulation and release of fluorescent dye in the nanospace

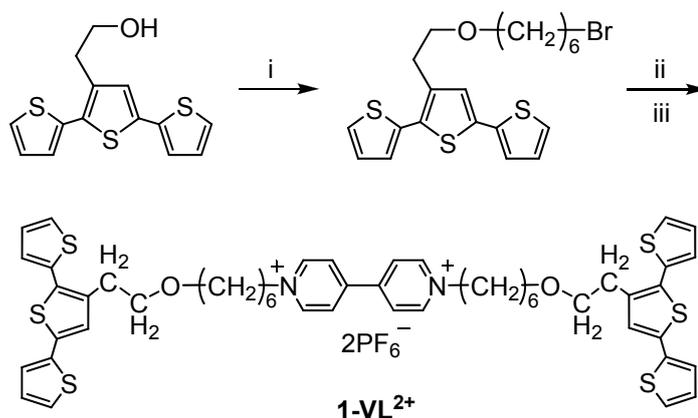
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- 1) Terthiophene (**1-VL<sup>2+</sup>**) and protective ligand ( $\text{SF}^-$ ) for Au nanoparticles ( $\text{SF}^-$ -AuNPs).
- 2) Synthesis and characterization of water-soluble gold nanoparticles ( $\text{SF}^-$ -AuNPs).
- 3) TEM image of  $\text{SF}^-$ -AuNPs, and TEM image and EDX spectrum of  $\text{SF}^-$ -AuNP@**1-VL<sup>2+</sup>**-PT-NTs.

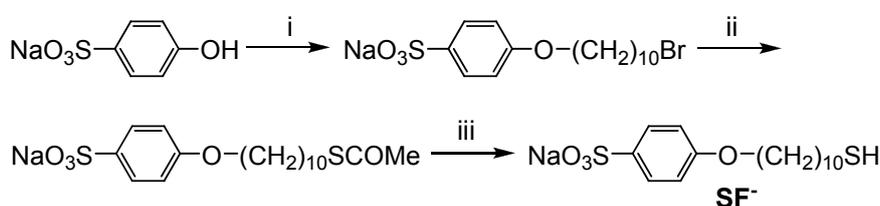
#### 1) Terthiophene (**1-VL<sup>2+</sup>**) and protective ligand for Au nanoparticles ( $\text{SF}^-$ -AuNPs).

New terthiophene (**1-VL<sup>2+</sup>**) and protective ligand ( $\text{SF}^-$ ) for Au nanoparticles ( $\text{SF}^-$ -AuNPs) were synthesized according to Scheme S1-S2.



**Scheme S1.** Reagents and Conditions: (i)  $\text{Br}(\text{CH}_2)_6\text{Br}$ , NaH, THF, reflux, 5 h; (ii) bipyridine, MeCN, reflux, 7 h; (iii)  $\text{KPF}_6$ , MeCN, room temp., 3 h.

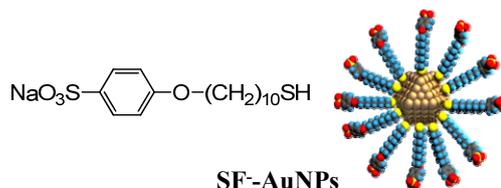
**1-VL<sup>2+</sup>** : <sup>1</sup>H-NMR (CD<sub>3</sub>CN-*d*<sub>3</sub>) δ 1.29-1.40 (m, 8H, CH<sub>2</sub>), 1.44-1.56 (m, 4H, CH<sub>2</sub>), 1.88-1.98 (m, 4H, CH<sub>2</sub>), 2.92 (t, *J*=6.5 Hz, 4H, CH<sub>2</sub>), 3.40 (t, *J*=6.2 Hz, 4H, CH<sub>2</sub>), 3.64 (t, *J*=6.5 Hz, 4H, CH<sub>2</sub>), 4.52 (t, *J*=7.5 Hz, 4H, CH<sub>2</sub>), 7.02 (dd, *J*=3.6, 5.1 Hz, 2H, Ar-H), 7.10 (dd, *J*=3.6, 5.2 Hz, 2H, Ar-H), 7.17 (s, 2H, Ar-H), 7.20 (dd, *J*=1.1, 3.6 Hz, 2H, Ar-H), 7.22 (dd, *J*=1.2, 3.6 Hz, 2H, Ar-H), 7.31 (dd, *J*=1.1, 5.1 Hz, 2H, Ar-H), 7.43 (dd, *J*=1.2, 5.2 Hz, 2H, Ar-H), 8.30 (d, *J*=6.8 Hz, 4H, Ar-H), 8.80 (d, *J*=6.8 Hz, 4H, Ar-H). <sup>13</sup>C NMR (CD<sub>3</sub>CN-*d*<sub>3</sub>) δ 26.3, 30.0, 30.5, 31.8, 63.0, 70.8, 71.1, 125.0, 126.1, 127.2, 127.6, 128.1, 128.1, 128.9, 129.3, 131.3, 135.8, 136.0, 137.5, 138.4, 146.4, 150.7; MS (FAB) Exact mass calcd. for C<sub>50</sub>H<sub>54</sub>O<sub>2</sub>N<sub>2</sub>S<sub>6</sub> (-2PF<sub>6</sub>): 906.2510. Found: 906.2515.



**Scheme S2.** Reagents and Conditions: (i) Br(CH<sub>2</sub>)<sub>10</sub>Br, NaOH, EtOH-H<sub>2</sub>O, 50 °C, 18 h, (ii) MeCOSK, MeCN, reflux, 15 h; (iii) HCl, MeOH, reflux, 1h.

**SF<sup>-</sup>** : <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>) δ 1.17-1.44 (m, 16H, CH<sub>2</sub>), 1.69 (q, 2H, CH<sub>2</sub>), 2.21 (t, 1H, SH), 3.94 (t, 2H, CH<sub>2</sub>), 6.83 (d, 2H, Ar-H), 7.49 (d, 2H, Ar-H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ 23.7, 25.5, 27.7, 28.4, 28.6, 28.7, 28.9, 33.4, 67.4, 113.2, 126.9, 140.9, 158.6.

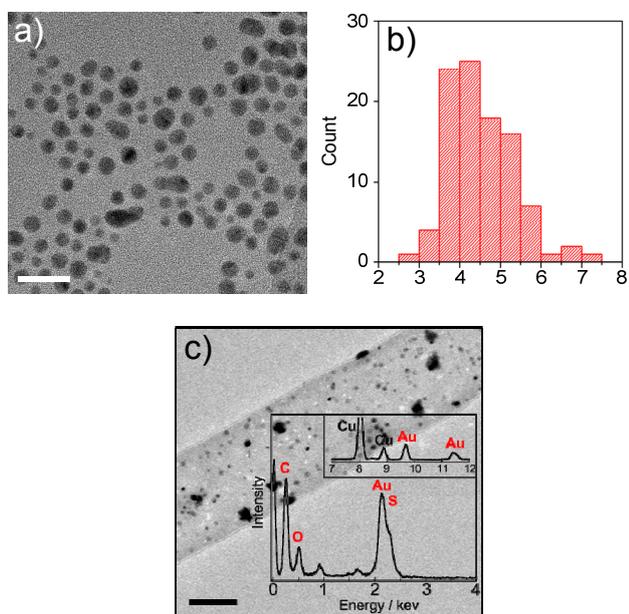
## 2) Synthesis and characterization of water-soluble gold nanoparticles (SF<sup>-</sup>-AuNPs).



Typical procedure for the preparation of SF<sup>-</sup>-AuNPs is as follows. To a vigorously stirred solution of HAuCl<sub>4</sub>·4H<sub>2</sub>O (82 mg, 0.20 mmol) in 10 mL of H<sub>2</sub>O was added thiol SF<sup>-</sup> (74 mg, 0.20 mmol) in 30 mL of MeOH. NaBH<sub>4</sub> (76 mg, 2.0 mmol) in 8 mL of H<sub>2</sub>O was then added. The mixture was stirred for 1 h at room temperature. After the reaction, the filtrate was evaporated in vacuo to yield SF<sup>-</sup>-AuNPs. Purification of SF<sup>-</sup>-AuNPs was repeated until no free thiol remained, as detected by TLC, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.

The particle size and size distribution of SF<sup>-</sup>-AuNPs were analyzed with transmission electron microscopy (TEM). The core size and size distribution of SF<sup>-</sup>-AuNPs are shown in Fig. S1. The X-ray photoelectron spectroscopy (XPS) spectrum of SF<sup>-</sup>-AuNPs shows the Au 4f binding energies at 84.1 and 87.8 eV, corresponding to the Au<sup>0</sup> state.

3) TEM image of SF<sup>-</sup>-AuNPs, and TEM image and EDX spectrum of SF<sup>-</sup>-AuNP@1-VL<sup>2+</sup>-PT-NTs.



**Fig. S1.** (a) TEM image and (b) size distribution ( $4.6 \pm 0.5$  nm) of SF<sup>-</sup>-AuNPs. Scale: 20 nm. (c) TEM image of SF<sup>-</sup>-AuNP@1-VL<sup>2+</sup>-PT-NTs. Scale: 100 nm. Inset: its EDX spectrum, Cu peaks are from the supporting copper grid.