## **Supporting Information**

# Enhancement of Photoswitchable Dielectric Property by Conducting Electron Donors on Plasmonic Core-Shell Gold-Fluorenyl C<sub>60</sub> Nanoparticles

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### **Experimental Section**

**General.** Chemicals of FeCl<sub>3</sub>·6H<sub>2</sub>O, FeCl<sub>2</sub>·4H<sub>2</sub>O, sodium oleate, 1-oleic acid, 1-octadecene, hydrogen tetrachloroaurate(III) trihydrate (HAuCl<sub>4</sub>·3H<sub>2</sub>O), sodium citrate dihydrate, hydroxylamine hydrochloride, 1-octanethiol, lithium diisopropylamide (LDA), selenium (powder), methyl iodide, diphenyl diselenide, 1,2-dibromocyclopentene, *tert*-butyllithium (*t*-BuLi) solution in pentane (1.7 M), (1*S*)-(+)-10-camphorsulfonic acid (CSA), tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>N<sup>+</sup>-PF<sub>6</sub><sup>-</sup>) were purchased from Aldrich Chemicals and used without further purification. The anhydrous grade solvent of THF was refluxed over sodium and benzophenone overnight and distilled under reduced pressure (1.0–10 mmHg).

Electron donors of tetrathiafulvalene (TTF, **2**), bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF, **6**), poly(3-hexylthiophene-2,5-diyl) (P3HT, **8**), and polyaniline (PANi, emeraidine base, **9**,  $M_w > 15,000$ ) were purchased from Aldrich Chemicals and purified by thin layer chromatography (TLC). 2,3,6,7-tetramethyltetrathiafulvalene (TMTTF, **3**) were synthesized according to the previous reported method.<sup>S1</sup>

Spectroscopy data of TMTTF: <sup>1</sup>H NMR (CDC1<sub>3</sub>)  $\delta$  1.55 (s); FT-IR (KBr)  $v_{max}$  2977 (w), 2939 (w), 2905 (s), 2845 (w), 1429 (m), 1370 (w), 1183 (m), 1089 (m), 776 (s, stretching vibrations of C–S), 747 (m), 638 (m), and 437 (s) cm<sup>-1</sup>.

Synthesis of 2,3,6,7-Tetrakis(methylseleno)tetrathiafulvalene (TMSeTTF, 4). A solution of tetrathiafulvalene (TTF, 0.75 g, 3.68 mmol) in anhydrous THF (6 mL) was added dropwise at -78 °C to a solution of lithium diisopropylamide (LDA, 1.6 g, 15.0 mmol) in anhydrous THF (200 mL) under Ar. It formed a yellowish suspension. After stirring at -78 °C for a period of 1.0 h, selenium powder (1.16 g, 14.7 mmol) was added slowly over 10 min via a pearl-shaped flask. The mixture was stirred at -78 °C for an additional 1.0 h, warmed to ambient temperature, and maintained at this temperature for another 1.0 h to result in complete consumption of the selenium powder and afforded a brownish suspension. It was cooled to -10 °C and quenched by dropwise addition of an excess amount of methyl iodide (3 mL). The mixture was then warmed to ambient temperature, stirred for 2.0 h, and diluted with ethyl acetate (150 mL) in sequence. The organic solution was washed by a dilute HCl solution, H<sub>2</sub>O, brine, and dried over MgSO<sub>4</sub>. Solvent was removed via rotary evaporation to afford orange-red solids. Purification was carried out by both column and thin layer chromatography (TLC) using silica gel (SiO<sub>x</sub>) as the stationary phase and a mixture of CHCl<sub>3</sub>-hexane (1:1, v/v) as the eluent ( $R_f = 0.55$ ) to give a yield of 73% (1.55g). Spectroscopic data: <sup>1</sup>H NMR (CDC1<sub>3</sub>,)  $\delta$  2.37 (s, -CH<sub>3</sub>); FT-IR (KBr)  $v_{max}$  2996 (w), 2915 (m), 2805 (w), 1504 (m), 1418 (m), 1266 (m), 907 (s), 855 (m), and 772 (s, stretching vibrations of C-S), 713 (w), 577 (w), and 446 (s)  $\text{cm}^{-1}$ .

Synthesis of 2,3,6,7-Tetrakis(phenylseleno)tetrathiafulvalene (TPSeTTF, 5). A similar procedure as that for the preparation of TMSeTTF, described above, was applied to generate tetraanionic TTF (TTF<sup>4-</sup>, 0.75 g, 3.68 mmol) using LDA (15 mmol) as the base. It was quenched by the dropwise addition of a diphenyl diselenide (4.8 g, 15.5 mmol) solution in THF (15 mL) at -78 °C. The mixture was stirred at the same temperature for 1.0 h, warmed up to -20 °C over another 1.0 h, and followed by slow warming to ambient temperature overnight. Resulting dark red solution was diluted with ethyl acetate (250 mL), washed thoroughly with H<sub>2</sub>O and brine, and dried over MgSO<sub>4</sub>. After evaporation of the solvent, the raw product was purified by column chromatography using silica gel (SiO<sub>x</sub>) as the stationary phase and a mixture of CHCl<sub>3</sub>–hexane (1:1, v/v) as the eluent ( $R_f = 0.75$ ) to afford tetrakis(phenylseleno)-tetrathiafulvalene (TPSeTTF) in 68% yield (2.06 g) as brown solids. Spectroscopic data: <sup>1</sup>H NMR (CDCl<sub>13</sub>)  $\delta$  7.52–7.49 (m, 8 H) and 7.31–7.25 (m, 12 H); FT-IR (KBr)  $v_{max}$  1574 (m), 1473 (m), 1436 (m), 1323 (w), 1296 (w), 1173 (w), 1064 (w), 1018 (m), 995 (m), 903 (w), em<sup>-1</sup>.

Synthesis of hexamethylenetetraselenafulvalene (HMTSF, 7). Synthesis of HMTSF was carried out according to a modified procedure of McCullough and Cowan.<sup>S4</sup> To a solution of 1,2dibromocyclopentene (2.94 g, 13 mmol) in anhydrous THF (35 mL) was added dropwise t-BuLi in pentane (15.4 mL, 1.7 M, 26 mmol) at -78 °C to give an opaque yellow solution. After stirring at -78 °C for 3.0 h, the mixture was warmed to -20 °C followed by the slow addition of selenium powder (1.03 g, 1.0 equiv., 13 mmol) over a period of 10 min via a pearl-shaped flask. After a clear solution was obtained indicating nearly full consumption of Se solids, the solution was cooled to -78 °C. The resulting mixture was added dropwise the second portion of t-BuLi in pentane (15.4 mL, 1.7 M, 26 mmol) and stirred at -78 °C for an additional 3.0 h. It was then warmed up to ambient temperature and added the second equivalent of selenium powder (1.03 g, 13 mmol). After roughly 30 min of stirring, tetrachloroethylene (1.08 g, 6.5 mmol) was added and stirred at 45 °C for a period of 2 d. It was slowly cooled to -20 °C to effect precipitation of HMTSF as pink fine crystals. They were collected via centrifuge, washed with water and hexane, and dried in vacuo to vield the product in a vield of 31% (0.95 g). Spectroscopic data: <sup>1</sup>H NMR (CDC1<sub>3</sub>)  $\delta$  2.61 (t, 4 H) and 2.33 (q, 2 H); FT-IR (KBr)  $v_{max}$ 2961 (w), 2942 (w), 2905 (m), 2845 (m), 1600 (m), 1440 (s), 1308 (s), 1229 (w), 1192 (w), 1118 (s), 1059 (w), 1016 (w), 842 (m), 732 (m), 648 (w), and 412 (s, stretching vibrations of C-Se) cm<sup>-1</sup>.

**Spectroscopic Characterization of Electron Donors.** <sup>1</sup>H NMR spectroscopy and cyclic voltammograms were applied for the characterization of electron donors synthesized in this study, as shown in Figures S1 and S2, respectively, below.



**Figure S1.** <sup>1</sup>H NMR spectra of (a) 2,3,6,7-tetramethyltetrathiafulvalene (TMTTF, **3**), (b) 2,3,6,7-tetrakis(methylseleno)tetrathiafulvalene (TMSeTTF, **4**), and (c) 2,3,6,7-tetrakis(phenylseleno)-tetrathiafulvalene (TPSeTTF, **5**).



**Figure S2.** Cyclic voltammograms of (a) hexamethylenetetraselenafulvalene (HMTSF), (b) bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF), (c) 2,3,6,7-tetrakis(phenylseleno)-tetrathiafulvalene (TPSeTTF), (d) 2,3,6,7-tetrakis(methylseleno)tetrathiafulvalene (TMSeTTF), and (e) 2,3,6,7-tetramethyltetrathiafulvalene (TMTTF). The data were collected at different voltages vs Ag/Ag<sup>+</sup> using Pt as the working and counter electrodes, Ag/AgCl as the reference electrode at a scan rate of 10 mV/s. A solution in a concentration of  $1.0 \times 10^{-3}$  M in CH<sub>3</sub>CN–CH<sub>2</sub>Cl<sub>2</sub> containing the electrolyte (*n*-butyl)<sub>4</sub>N<sup>+</sup>-PF<sub>6</sub><sup>-</sup>(0.2 M) was used for all CV measurements.

Preparation of RF-Responsive Multilayered Core-Shell Nanoparticles. Spectroscopic data: FT-IR (KBr)  $v_{max}$  2956 (w), 2918 (m), 2846 (m), 1588 (s), 1399 (s), 1261 (w), 1089 (w), 1016 (w), 970 (w), 905 (w), 810 (m), and 580 (vs) cm<sup>-1</sup>.

Preparation of  $C_{60}(>DPAF-C_9)$  (1-C<sub>9</sub>)-Encapsulated  $\gamma$ -FeO<sub>x</sub>@AuNP Yielding Trilayered Core-Shell Nanoparticles, ( $\gamma$ -FeO<sub>x</sub>@AuNP)@[C<sub>60</sub>(>DPAF-C<sub>9</sub>)]<sub>n</sub> (11-NPs). Spectroscopic data of 11-NPs: FT-IR (KBr)  $v_{max}$  2955 (m, aromatic C–H stretching), 2922 (s, aliphatic C–H stretching), 2850 (m), 1745 (m), 1676 (m, –C=O), 1636 (m), 1620 (m), 1592 (s, –C=C–), 1492 (m), 1460 (s), 1430 (m), 1383 (m), 1271 (m, asymmetric stretching vibrations of C–N–C), 1205 (s, –C-N–), 1170 (m), 1111 (m), 1077 (m), 1029 (m), 875 (w), 748 (m, C–H out-of-plan deformation), 695 (m), 617 (m), 583 (s, C<sub>60</sub>>), and 525 (s, C<sub>60</sub>>) cm<sup>-1</sup>.

Deposition of Electron Donors onto  $(\gamma - FeO_x@AuNP)@[C_{60}(>DPAF-C_9)]_n$  to Yield the Corresponding 12-NPs and 15-NPs to 21-NPs. Spectroscopic data of tetralayered (y-FeO<sub>x</sub>@AuNP)@[C<sub>60</sub>(>DPAF-C<sub>9</sub>)]<sub>n</sub>@(TMTTF)<sub>m</sub> (**12**-NPs): FT-IR (KBr) v<sub>max</sub> 2960 (w), 2920 (m), 2909 (m), 2842 (w), 1738 (m), 1668 (m), 1632 (m), 1608 (m), 1596 (s), 1488 (m), 1459 (s), 1429 (m), 1426 (m), 1380 (m), 1370 (w), 1268 (m), 1204 (s), 1183 (m), 1171 (m), 1111 (m), 1089 (m), 1076 (m), 1027 (m), 776 (s), 748 (s), 747 (m), 695 (m), 638 (m), 620 (m), 583 (s), 526 (s), and 438 (s) cm<sup>-1</sup>; (11-NPs)@(TMSeTTF)<sub>m</sub> (15-NPs): FT-IR (KBr) v<sub>max</sub> 2959 (w), 2918 (m), 2912 (m), 2848 (w), 1740 (m), 1678 (m), 1639 (m), 1622 (m), 1592 (s), 1500 (w), 1493 (w), 1460 (m), 1429 (m), 1413 (m), 1380 (w), 1271 (m), 1265 (m), 1205 (s), 1168 (m), 1114 (w), 1078 (w), 1030 (w), 903 (s), 851 (m), 811(w), 770 (s), 748 (m), 713 (w), 695 (m), 620 (m), 583 (s), 577 (w), 526 (s), and 446 (s)  $cm^{-1}$ ; (11-NPs)@(TPSeTTF)<sub>m</sub> (16-NPs): FT-IR (KBr) v<sub>max</sub> 2955 (w), 2918 (m), 2850 (m), 1748 (m), 1674 (m), 1639 (m), 1616 (m), 1592 (s), 1574 (m), 1498 (m), 1471 (m), 1463 (s), 1435 (m), 1432 (m), 1388 (m), 1271 (m), 1208 (m), 1170 (m), 1114 (m), 1073 (m), 1064 (w), 1031 (m), 1018 (m), 995 (m), 903 (w), 877 (w), 849 (m), 763 (m), 748 (m), 732 (s), 715 (w), 698 (m), 684 (s), 667(m), 620 (m), 585 (m), 525 (s), 469 (s), and 445 (m) cm<sup>-1</sup>; (11-NPs)@(HMTSF)<sub>m</sub> (18-NPs): FT-IR (KBr)  $v_{max}$  2960 (w), 2955 (m), 2945 (w), 2920 (m), 2900 (m), 2850 (m), 2841 (m), 1748 (m), 1674 (m), 1639 (m), 1616 (m), 1598 (m), 1592 (m), 1498 (m), 1463 (s), 1438 (m), 1432 (m), 1388 (m), 1305 (s), 1270 (m), 1208 (m), 1170 (m), 1116 (s), 1075 (m), 1060 (w), 1031 (m), 1018 (m), 877 (w), 844 (m), 748 (m), 732 (m), 698 (m), 648 (w), 620 (m), 585 (m), 525 (s), and 412 (m) cm<sup>-1</sup>.



**Figure S3.** Infrared (FT-IR) spectra of (a) trilayered ( $\gamma$ -FeO<sub>x</sub>@AuNP)@[C<sub>60</sub>(>DPAF-C<sub>9</sub>)<sub>x</sub>]<sub>n</sub> (**11**-NPs), (b) 2,3,6,7-tetramethyltetrathiafulvalene (TMTTF), (c) tetralayered ( $\gamma$ -FeO<sub>x</sub>@AuNP)@[C<sub>60</sub>(>DPAF-C<sub>9</sub>)<sub>x</sub>]<sub>n</sub> (**11**-NPs)@(TMTTF)<sub>m</sub>, **12**-NPs], (d) 2,3,6,7-tetrakis(methylseleno)tetrathiafulvalene (TMSeTTF), (e) tetralayered (**11**-NPs)@(TMSeTTF)<sub>m</sub> (**15**-NPs), (f) 2,3,6,7tetrakis(phenylseleno)-tetrathiafulvalene (TPSeTTF, **5**), (g) tetralayered (**11**-NPs)@(TPSeTTF)<sub>m</sub> (**16**-NPs), (h) hexamethylenetetraselenafulvalene (HMTSF, **7**), and (i) tetralayered (**11**-NPs)@(HMTSF)<sub>m</sub> (**18**-NPs).

### Dielectric (permittivity) Measurement Diagram.



Figure S4. The outline and schematic description of the dielectric measurement system.

The complex relative electric permittivity (dielectric constant and loss factor) values were measured in terms of complex reflection coefficient of electromagnetic waves in proportion to a complex scattering parameter, defined as S<sub>11</sub>. The scattering parameter S<sub>11</sub> was measured by a high-performance coaxial probe (Agilent 85070E).<sup>S5</sup> It was then converted to complex relative electric permittivity values consisting of both a real part ( $\varepsilon_r$ ' or dielectric constant) and an imaginary part ( $\varepsilon_r$ '' or loss factor) using the Nicolson-Ross algorithm.<sup>S6</sup>

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