Supplementary Material (ESI) for Soft Matter

Supporting Information:

Redox Nanoreactor Dendrimer Boxes: *In-Situ* Hybrid Gold Nanoparticles via Terthiophene and Carbazole Peripheral Dendrimer Oxidation

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Experimental Section

General Information: Commercially available reagents were used without further purification unless noted otherwise. Solvents were purified by common methods. The starting materials ethyl- 2-(2,5-di(thiophen-2-yl)thiophen-3-yl)acetate,[14] and methyl-3,5-bis[4-(9*H*-carbazol-9-yl)butoxy]benzoate[15] were prepared according to literature procedures. ^{1}H and ^{13}C NMR spectra were recorded with a General Electric QE-300 spectrometer operating at 300 MHz. Absorption and fluorescence spectra were recorded with a Agilent 8453 UV-visible spectrometer and a Perkin Elmer LS 45 luminescence spectrometer, respectively. All FTIR measurements were performed using a Digilab FTS 7000 step scan spectrometer. The spectra was obtained using the ATR technique drop cast on Si wafer. Morphology studies by SEM was performed using a JSM 6330F (JEOL) instrument operating at 15 kV. X-ray photoelectron spectroscopy (XPS) was carried out on a Physical Electronics 5700 instrument with photoelectrons generated by the nonmonochromatic Al Kα irradiation (1486.6 eV). Photoelectrons were collected at a takeoff angle of 45° using a hemispherical analyzer operated in the fixed retard ratio mode with an energy resolution setting of 11.75 eV. The binding energy scale was calibrated prior to analysis using the Cu $2p_{3/2}$ and Ag $3d_{5/2}$ lines. Charge neutralization was ensured through cobombardment of the irradiated area with an electron beam and the use of the nonmonochromated Al Kα source. Atomic force microscopy (AFM) imaging was examined in ambient conditions with a PicoSPM II (PicoPlus, Molecular Imaging) in the Magnetic AC mode (MAC mode) using a magnetic field to drive a magnetically coated cantilever in the top-down configuration. Type II MAC levers with a spring constant of 2.8 nN/M with about 10 nm tip radius were used for all scans.

3,5-Bis[4-(9H-carbazol-9-yl)butoxy]benzoic Acid (1):

A mixture of methyl-3,5-bis[4-(9*H*-carbazol-9-yl)butoxy]benzoate (3.00 g, 4.91 mmol) and KOH (2.76 g, 49.12 mmol) in tetrahydrofuran/methanol (30 mL/60 mL) was refluxed with vigorous stirring for overnight. After cooling to room temperature, the mixture was concentrated to dryness under reduced pressure. The residue was acidified to pH 2-3 with HCl, and then the precipitate was filtered and washed with ether to give **1** as a white solid (2.76 g, yield 94 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (d, J = 7.8 Hz, 4H, Ar$H_{\mathbf{CBz}}$), 7.84-7.39 (m, 8H, Ar$H_{\mathbf{CBz}}$), 7.24-7.17 (m, 4H, Ar$H_{\mathbf{CBz}}$), 7.16 (s, 2H, Ar*H*), 6.57 (s, 1H, Ar*H*), 4.40 (t, J = 6.3 Hz, 4H, NCH_2CH_2), 3.94 (t, J = 6.0 Hz, 4H, OCH_2CH_2), 2.08 (m, 4H, $NCH_2CH_2CH_2$), 1.84 (m, 4H, $OCH_2CH_2CH_2$) ppm.

2-(2,5-Di(thiophen-2-yl)thiophen-3-yl)acetic acid (2).

A mixture of ethyl-2-(2,5-di(thiophen-2-yl)thiophen-3-yl)acetate (3.40 g, 10.18 mmol) and KOH (5.71 g, 101.79 mmol) in tetrahydrofuran/methanol (55 mL/110 mL) was refluxed with vigorous stirring for overnight. After cooling to room temperature, the mixture was concentrated to dryness under reduced pressure. The residue was acidified to pH 2-3 with HCl , then extracted with ether. The combined organic layer was dried with anhydrous $NaSO_4$. After removal the solvent, the residue was dried to give **2** as a yellow solid (2.70 g, 81 % yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.00 (m, 7H, Ar$H_{\mathbf{3t}}$), 3.78 (s, 2H, ArCH_2COOH) ppm.

Perfluorophenyl-3,5-bis(4-(9H-carbazol-9-yl)butoxy)benzoate (3).

A mixture of compound **1** (0.20 g, 0.34 mmol) and pentafluorphenol (0.08 g, 0.42 mmol) were allowed to react in 20 mL of dry THF in the presence of dicyclohexylcarbodiimide (DCC) (0.10 g, 0.50 mmol) and *p*-(dimethylamino)pyridine (DMAP) (0.06 g, 0.49) for 2 days. After separation of dicyclohexylurea by filtration, the solvent was removed by rotary evaporation. The resulting residue was purified by column chromatography on silica gel (CH_2Cl_2/*n*-hexane (v:v/1:1)). The compound **3** was obtained as an orange crystal (0.15 g (68%)). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (d, J = 7.5 Hz, 4H, Ar$H_{\mathbf{CBz}}$), 7.50-7.40 (m, 8H, Ar$H_{\mathbf{CBz}}$), 7.24-7.20 (m, 4H, Ar$H_{\mathbf{CBz}}$), 6.63 (s, 1H, Ar*H*), 6.62 (s, 1H, Ar*H*), 6.61 (s, 1H, Ar*H*), 4.38 (t, J = 6.6 Hz, 4H, NCH_2CH_2), 3.94 (t, J = 6.0 Hz, 4H, OCH_2CH_2), 2.08 (m, 4H, $NCH_2CH_2CH_2$), 1.85 (m, 4H, $OCH_2CH_2CH_2$) ppm.

Perfluorophenyl-2-(2,5-di(thiophen-2-yl)thiophen-3-yl)acetate (4)

Compound **4** was prepared by the same procedure of **3** by using compound **2** (0.20 g, 0.65 mmol), pentafluorphenol (0.15 g, 0.82 mmol), dicyclohexylcarbodiimide (DCC) (0.20 g, 0.98 mmol) and *p*-(dimethylamino)pyridine (DMAP) (0.12 g, 0.98) in 20 mL of dry THF . After purification by column chromatography on silica gel (CH_2Cl_2/*n*-hexane (v:v/1:1)), compound 4 was obtained as an orange crystal(0.03 g (10%)). δ 7.49-7.10 (m, 7H, Ar$H_{\mathbf{3t}}$), 4.17 (s, 2H, ArCH_2COOAr) ppm.

2-(3,5-Bis(4-(9H-carbazol-9-yl)butoxy)phenyl)acetoyl-Functionalized Dendrimer (PC).

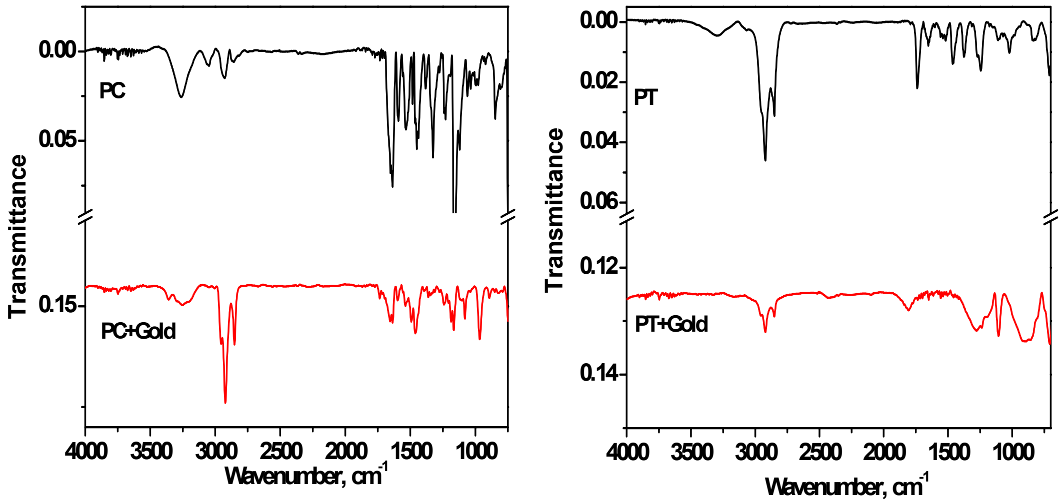
PAMAM-$(NH_2)_{64}$ (18.40 mg, 1.3 μmol) with 64 primary amine groups was dissolved in a mixture of 10 mL of dried THF and 10 mL of dried DMF. To this solution was slowly added with a solution of perfluorophenyl 3,5-bis(4-(9H-carbazol-9-yl)butoxy)benzoate (**3**) (74.00 mg, 97.5 μmol) in a dropwise fashion. After the addition was completed, the reaction mixture was refluxed for 2 days, yielding an orange solution. The solvent was removed by rotary evaporation. The obtained crude product was washed with diethyl ether twice and recrystallized from CH_2Cl_2/MeOH to afford pure **5** as a yellow solid (42 mg, 85%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (br s, 184H, Ar$H_{\mathbf{CBz}}$), 7.34-7.15 (m, 552H, Ar$H_{\mathbf{CBz}}$), 6.75 (br s, 138H, Ar*H*), 6.30 (br s, 46H, ArCON*H*CH_2), 4.10 (br s, 184H, NCH_2CH_2), 3.57 (br s, 184H, OCH_2CH_2), 3.49-2.11 (m, 1138H, CH_2CH_2NHCO,

$\mathrm{NC}\mathit{H}_2\mathrm{CH}_2\mathrm{N}$ and $\mathrm{CH}_2\mathrm{N}\mathit{H}_2$), 1.78 (br s, 184H, $\mathrm{NCH}_2\mathrm{C}\mathit{H}_2\mathrm{CH}_2$), 1.55 (br s, 184H, $\mathrm{OCH}_2\mathrm{C}\mathit{H}_2\mathrm{CH}_2$) ppm. A total of 46 carbazole units were attached out of 64 amine sites (85%) available as determined by NMR. UV-vis (Toluene): λ_{max} = 332 and 345 nm.

2-(2,5-Di(thiophen-2-yl)thiophen-3-yl)acetoyl-Functionalized Dendrimer (PT).

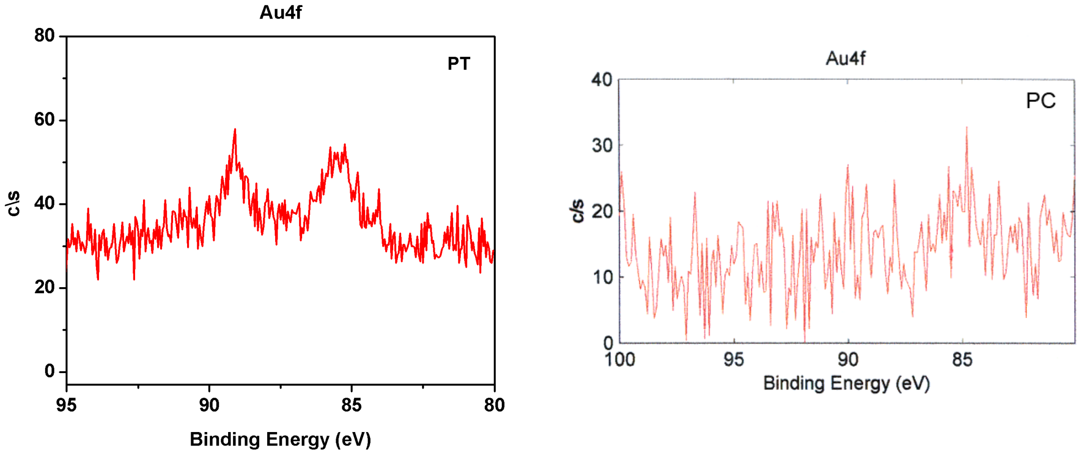
Dendrimer **6** was synthesized by using the same methodology as dendrimers **5** with PAMAM-$(\mathrm{NH}_2)_{64}$ (12.20 mg, 0.0009 mmol) with 64 primary amine groups and perfluorophenyl-2-(2,5-di(thiophen-2-yl)thiophen-3-yl)acetate (4) (30.00 mg, 0.0635 mmol) in a mixture of 10 mL of dried THF and 10 mL of dried DMF. Dendrimer **6** was obtained as a yellow solid (21 mg, 83%). ^{1}H NMR (300 MHz, CDCl_3) δ 8.23 (br s, 44H, $\mathrm{CH}_2\mathrm{CON}\mathit{H}\mathrm{CH}_2$), 7.54-7.15 (m, 308H, $\mathrm{Ar}\mathit{H}_{3t}$), 3.75 (br s, 88H, $\mathrm{ArC}\mathit{H}_2\mathrm{CONH}$), 3.43-2.39 (m, 1160H, $\mathrm{CH}_2\mathrm{C}\mathit{H}_2\mathrm{NHCO}$, $\mathrm{NC}\mathit{H}_2\mathrm{CH}_2\mathrm{N}$ and $\mathrm{CH}_2\mathrm{N}\mathit{H}_2$) ppm. A total of 44 carbazole units were attached out of 64 amine sites (83%) available as determined by NMR. UV-vis (Toluene): λ_{max} = 344 nm.

FT-IR Spectra



SI Figure 1. FT-IR ATR spectra of PAMAM dendrimers functionalized with 10^{-6} M of terthiophene (PT) and carbazole (PC) dendrons before and after mixing with AuCl_3 in toluene – drop cast on Si wafer.

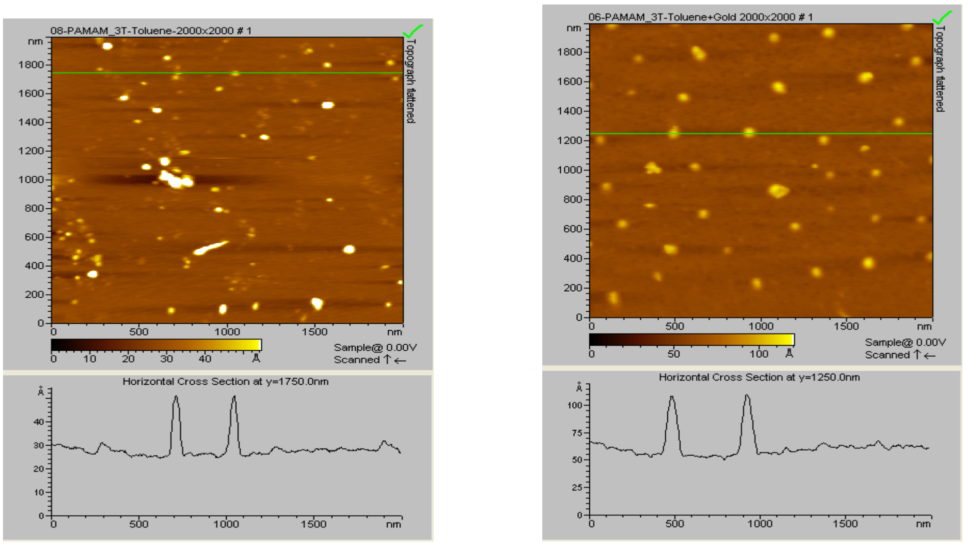
XPS Characterization.



(a) (b)

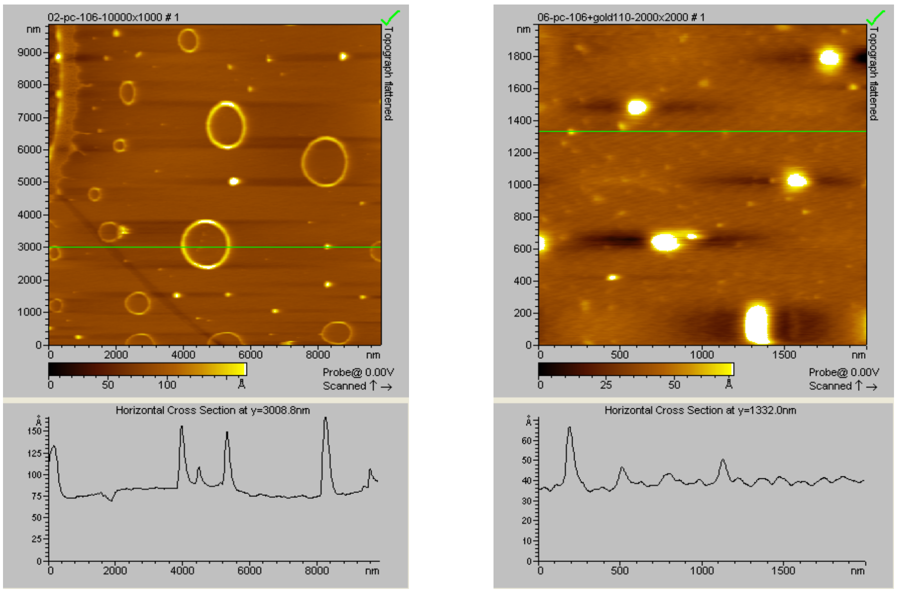
SI Figure 2. High-resolution XPS of the informative elements for the structure determination of (a) PPT-AuNPs and (b) PPC-AuNPs. Au^{o} formation was confirmed for the PPT-AuNPs whereas none with PPC.

Atomic Force Microscopy.



(a) **(b)**

SI Figure 3. AFM image (2 x 2 μM) of PT (a) and PPT-AuNPs (b) on mica substrate.

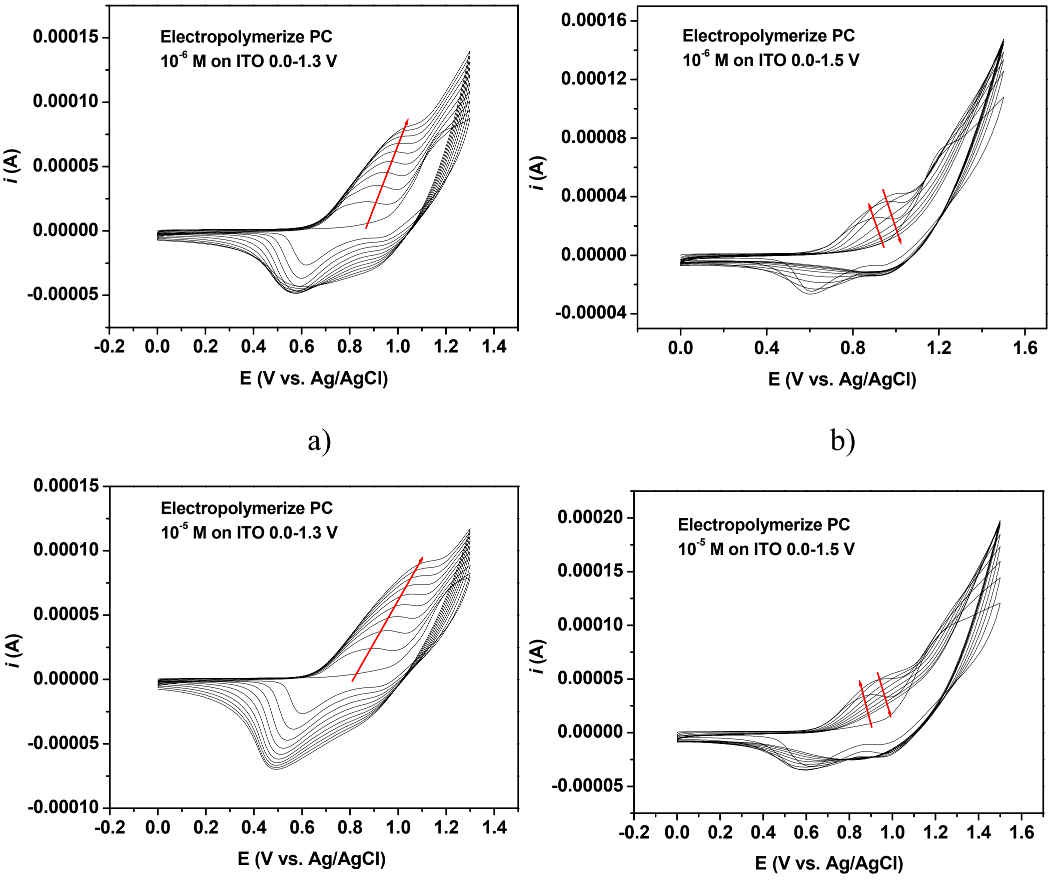


(a) **(b)**

SI Figure 4. AFM image (2 x 2 μM) of PC (a) and PPC-AuNPs (b) on mica substrate.

Electropolymerization of PC.

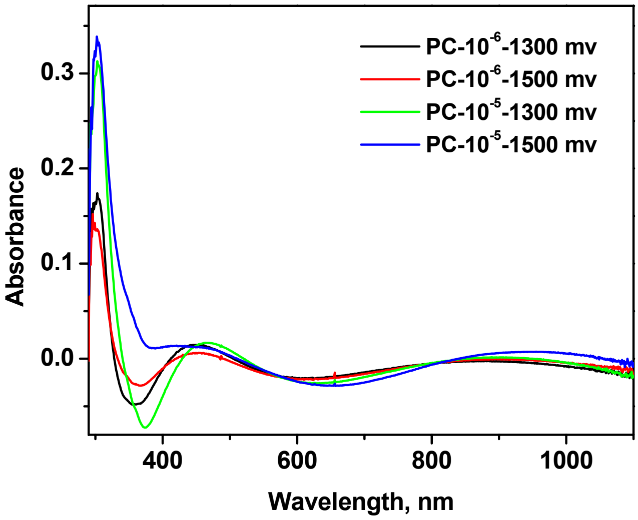
The electopolymerization of PC was done at a scan rate of 50 mV/s against Ag/AgCl reference electrode and platinum counter electrode. At the low potential application (1.3 V), a good trend of increasing oxidation potential onset was observed with increasing of cycles but the CV curves shifted to higher anodic potential (E_{pa}) and the reduction peaks shifted to lower cathodic potential (E_{pc}). Degradation was observed after applying a higher potential (1.5 V) which may come from the lack of availability of more mobile electroactive monomers. Moroever, the UV-vis spectra revealed the formation of less conjugated polycarbazole species (predominantly dimerization).



a) b)

c) d)

SI Figure 5. Cyclic voltammograms of the electrochemical cross-linking/deposition of PC at a scan rate of 50 mV/s, 10 cycles: (a) conc. 10^{-6} M, potential window from 0-1.3 V, (b) conc. 10^{-6} M, potential window from 0-1.5 V, (c) conc. 10^{-5} M, potential window from 0-1.3 V, (d) conc. 10^{-5} M, potential window from 0-1.5 V.



SI Figure 6. Spectroelectrochemical analysis performed in 0.1 M $TBAPF_6/CHCl_3$ on ITO substrate in the present of different concentrations and potential windows of PC