Redox nanoreactor dendrimer boxes: *in situ* hybrid gold nanoparticles *via* terthiophene and carbazole peripheral dendrimer oxidation[†]

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 π -Conjugated dendrimer-protected gold nanoparticles in stable colloidal form have been successfully prepared *via* simultaneous reduction of AuCl₃ with oxidative polymerization of terthiophene (PT) and carbazole (PC) peripheral functionalized polyamidoamine (PAMAM) dendrimers. The hybrid dendrimer-metal materials were characterized by UV-vis, fluorescence, and FT-IR spectroscopy. XPS and AFM analyses were also employed. The differences in gold nanoparticle (AuNP) formation between the two PAMAM derivatives were discussed. In case of PT dendrimer, AuNPs can be stabilized *in situ* to form PAMAM–PPT–AuNP hybrid materials. For the PC dendrimer, the redox reaction afforded carbazole polymerization without necessarily forming AuNPs.

Dendrimer-encapsulated metal nanoparticles (DEMNs) are hybrid nanomaterials synthesized by complexing metal ions within dendrimers followed by reduction to yield zero valent metal nanoparticles. As widely reported by Crooks et al., dendrimers are well-suited for hosting metal nanoparticles for a number of reasons including monodispersity, stability, catalytic reactivity, and solubility.1 Of special interest are polyamidoamine (PAMAM) dendrimers which can bind a defined number of transition metal cations, while creating an ideal environment for trapping guest species.^{2,3} They are ideal templates for stabilizing metal oxide or metal nanoparticles.⁴ Furthermore, the nanoparticle size, composition, and structure can be controlled by taking advantage of the dendrimer structure and generation. In the past few decades, several methods for making gold nanoparticles (AuNPs) by chemical reduction of precursors have been developed. The most popular method used for a long time was the citrate reduction of HAuCl₄ in water.⁵ Recently, electroactive groups such as pyrrole,⁶ aniline,⁷ thiophene,^{8a} EDOT,^{8b} and others have been utilized together with the HAuCl₄ precursor. In principle, they can be oxidatively polymerized to form π -conjugated polymers while simultaneously forming the reduced AuNPs.

Polymers of thiophene and carbazole have been of high interest due to their electrochemical⁹ and electrochromic properties.¹⁰ For example, electropolymerization of terthiophene leads to the formation of highly electrochromic and conducting polythiophenes.¹¹ On the other hand, polycarbazole is well-known as a hole transport material.¹² Electrochemically polymerized carbazoles show interesting properties *via* formation of π -conjugated species at the 3,6 linkages. The radical cations generated during polymerization are responsible for coupling-propagation, whereas distinct redox states lead to electrochromic effects.¹³

Herein we report the *in situ* synthesis of hybrid AuNPs inside the redox dendrimer nanoreactor boxes based on PAMAM dendrimers with terthiophene (PT) and carbazole (PC) groups on the periphery. The formation of these hybrid DEMNs consisting of AuNPs protected with PAMAM (inner shelf) and π -conjugated species (outer shelf) is described. Energy transfer properties between the nanoparticle-thiophene and carbazole peripheral groups are also reported. Atomic Force Microscopy (AFM), FT-IR, and X-ray photoelectron spectroscopy (XPS) were utilized to further differentiate AuNP formation in PT and PC dendrimer derivatives. Unlike previously reported DEMNs, no external reducing agent was required for AuNP formation.

The starting materials, ethyl 2-(2,5-di(thiophen-2-yl)thiophen-3-yl) acetate¹⁴ and methyl-3,5-bis[4-(9*H*-carbazol-9-yl)butoxy]benzoate,¹⁵ were prepared according to literature. Hydrolyzation of both compounds was performed using KOH in THF/MeOH, followed by reaction with excess pentafluorophenol in the presence of dicyclohexylcarbodiimide/dimethyl aminopyridine (DCC/DMAP) in THF. The active ester perfluorophenyl-3,5-bis(4-(9*H*-carbazol-9-yl) butoxy) benzoate (**3**) and perfluorophenyl-2-(2,5-di(thiophen-2-yl) thiophen-3-yl)acetate (**4**) were obtained in 68% and 10% yield



Fig. 1 Electroactive groups (terthiophene, T and carbazole, C) of peripheral modified PAMAM dendrimers used in this study.

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respectively. Amidation reactions of **3** and **4** with PAMAM were accomplished in THF/DMF to obtain PC (85%) and PT (83%) (Fig. 1). NMR and IR were used to confirm the structures as described in the ESI[†].

The attempt to prepare AuNPs encapsulated in PT and PC dendrimers was initiated by adding aliquots of AuCl₃ (1 × 10^{-3} M) in MeOH into a solution containing PT or PC (1 × 10^{-6} M) in toluene. These solutions were then stirred to incorporate AuCl₃ into the dendrimer templates. The reduction to zero valent AuNPs simultaneous with the oxidative chemical polymerization to form polycarbazole (PPC) or polyterthiophene (PPT) in the periphery of the dendrimers is then expected, *i.e.* PT \rightarrow PPT and PC \rightarrow PPC.

In a typical procedure, PT was reacted with 55 equiv. of the Au precursor. Upon adding the AuCl₃ solution into the PT solution, the color of the solution changed immediately from pale yellow to blue. After 30 min, a dark blue solution was observed. The blue color is probably due to the initial electron transfer from the terthiophene to Au³⁺ (metal to ligand charge transfer or MLCT) or blue color generated by the plasmon band (440-490 nm). It has been reported that polyelectrolyte complex (PEC) with water-soluble terthiophene derivative also changed in color successively after addition of Au3+.8a A similar procedure was also employed for the PC. From the initial experiment, using 55 equiv. of gold precursor, no color change was observed. Therefore, a larger ratio of AuCl₃ to PC was employed. When 110 equiv. of gold precursor were used, the color changed from pale yellow to deep yellow and the color was found to be stable in the media even after several weeks. The fact that a higher ratio of AuCl₃ to PC was needed may be due to the higher oxidation potential (monomer) (0.8-1.0 mV) for the carbazole compared to terthiophene at about 0.22 V.17a The formation of DEMNs in PT in particular can be tracked by monitoring the change in UV-visible absorbance at various time intervals (Fig. 2a). The main absorption band at 345 nm is attributed to the terthiophene unit. The observed peaks at 320 nm and at 850 to 1000 nm corresponds to the π - π * and polaron- π , π - π , and polaron– π^* transitions, respectively. The peak shift from 345 nm to 320 nm is due to presence of MLCT transition which was highest at the initial mixing of the solutions. This peak gradually decreases with time. After vigorous stirring for 30 min, the absorption band of PPT and the surface plasmon band of AuNPs appeared at 410-550 nm. However, it may be difficult to totally distinguish the AuNP surface plasmon band due to some overlap between the AuNP and PPT peaks.18 Nevertheless, one interesting evidence is the coincident decrease of the 320 nm region due to Au3+ to thiophene MLCT, increase at the 500 nm for AuNP and PPT, and decrease in polaron band with time (Fig. 2a). The latter indicates strong evidence of Au⁰ formation since an electron charge transfer mechanism from the polaron of the π -conjugated PPT species occurs only on the surface of Au⁰ nanoparticles when present.¹⁶

The UV-vis spectrum for PC (1×10^{-6} M) to PPC conversion is shown in Fig. 2b. The absorbances at 333 and 346 nm which are characteristic of the carbazole group were observed.¹⁷ After mixing the PC solution with 110 equiv. of AuCl₃ for 30 min, a peak at 315 nm increased and a slight hypsochromic shift is observed.¹⁹ On the other hand, the π - π * transition of carbazole was red shifted and an absorption tail extending into the visible range centered at 385 nm on the PPC is observed. This indicated the formation of higher π -conjugated species. However, this spectrum seemingly lacked the characteristic surface plasmon band at the 500 nm region.



Fig. 2 UV-vis absorption spectra of (a) PT at different time (0–30 min) and (b) PC after adding AuCl₃ 30 min. Dendrimer PT and PC show their characteristic absorption bands at 345, 333 and 346, respectively.

The steady state fluorescence emission spectra of solutions of PT, PPT-AuNPs, PC and PPC-AuNPs (or Au³⁺) are shown in Fig. 3. Without AuNPs, the terthiophene modified PAMAM dendrimer, PT, exhibited a strong characteristic emission of terthiophene with the emission maximum at 433 nm and one shoulder around 415 nm upon excitation at 345 nm (in Fig. 3a) while the carbazole modified PAMAM dendrimer, PC, showed a characteristic emission at 356 and 365 nm upon excitation at 333 nm (in Fig. 3b).^{17b} The emission of PPT was quenched dramatically in the PPT-AuNPs hybrid due to a highly efficient energy transfer between PPT and AuNPs²⁰ and perhaps some self-quenching with formation of conjugated polymer species.^{17b} These were confirmed by the observation of a new peak at 545 nm with PPT. This is due to the AuNPs quenching for the PT. For the PC, a decrease in emission was also observed and a new peak at 510 nm was observed. However, this most likely represented an Au3+-MLCT quenching effect for the PC dendrimer because of the absence of the plasmon band from the UV-vis absorbance spectrum.

The preparation of the hybrid nanoparticles was also monitored by FT-IR spectra (see ESI†). The characteristic peaks were observed at 1636 and 1690, corresponding to the two amide bands of PAMAM. The =C-H in-plane and out-of-plane vibrations of the substituted terthiophene ring are assigned to 1240 and 825 cm⁻¹, respectively. These two bands disappeared for the DEMNs which formed upon the oxidation of terthiophene, PT by α - α' coupling to form PPT with Au³⁺ to Au⁰ conversion. The PAMAM characteristic peaks were also observed for the PC and in addition, 1230, 1325, 1450, and 1533 cm⁻¹



Fig. 3 Steady-state fluorescent spectra of PT and PC 10^{-6} M before and after mixing with AuCl₃ in toluene. ET mechanism was proved by quenching phenomena and new peaks of AuNPs.

peaks representing the carbazole aromatic (C–H), (C–N)_{ring} and carbazole (C=C)_{ring} vibrations (see ESI[†]).^{17a} We also observed the disappearance of the =C–H in-plane and out-of-plane vibrations of PC at 1325 and 847 cm⁻¹ or wavenumber, respectively with complexation. In general, both the loading of metal ions and the presence of nanoparticles shifted the amide vibration to longer cm⁻¹.

The formation of the hybrid materials was also examined by XPS. A solution of the AuNP-PPT dendrimer complex was solution cast on planar Si wafer. The Au⁰ spectra based on Au 4f_{7/2} and Au 4f_{5/2} doublet appeared at 84.4 and 88.1 eV, respectively (Fig. 4a). These features were in agreement with results reported for self-assembled alkanedithiol,²¹ alkanethiols on AuNPs and/or bulk gold substrates²² as well as for bulk gold.²³ Interestingly, the higher binding energy for Au 4f5/2 also provides additional evidence for an Au⁰ and PPT bipolaron charge transfer.¹⁶ However, it was hard to detect AuNPs from the AuCl₃ and PC procedure in toluene. This implies that the carbazole-modified dendrimer PC was not able to fully convert a majority of the Au³⁺ precursor to AuNPs. Although UV-vis and fluorescence support the formation of a conjugated PPC, the MLCT was primarily with Au³⁺ species. The fact that no distinct plasmon band was observed with the UV-vis spectra also supports this fact. However, the formation of Au⁰ clusters is still possible. Thus compared to PC, the PT was a more effective oxidant to form AuNP DEMNs while simultaneously forming the conjugated polythiophene, PPT, in the outer shelf.24



Fig. 4 (a) High-resolution XPS of the Au $4f_{7/2}$ and Au $4f_{5/2}$ doublet at 84.4 and 88.1 eV for the PPT–AuNPs and (b) AFM image (2 × 2 μ M) of PPT–AuNPs on mica substrate.

The particle morphology and distribution of the dendrimers before and after treatment with AuCl₃ were also studied by AFM (Fig. 4b and ESI[†]). A droplet of a 10⁻⁶ M toluene solution was cast on mica and the solution was allowed to evaporate with spin-coating. Shown in Fig. 4b is the AFM image of an array of PPT–AuNPs on a mica substrate. The image demonstrates the near uniform distribution of the particles which tends to form aggregates if higher concentrations were used. Some aggregation was also observed with the PT alone (see ESI[†]). It is believed that the use of toluene as a solvent is one reason for aggregation between the dendrimers on the hydrophilic mica substrate.²⁵ Detailed cross-sectional measurements performed on a large number of isolated features revealed an average height of 2.4 ± 1.0 nm for the PT alone and after the formation of the hybrid AuNP–PPT, a more uniform and twice higher average height ~5.2 ± 0.2 nm of particles was observed (Fig. 4b).

Surprisingly, when we investigated the AFM of PC dendrimers alone, we observed nano ring structures with different sizes together with some individual dendrimers on mica substrate (see ESI⁺). These structures are comparable to the results obtained by Nolte and coworkers²⁶ on the formation of ring liked structures of porphyrin molecules when solutions of porphyrins were allowed to evaporate fast. After the addition of AuCl₃, much larger aggregates of the dendrimer were observed together with some individual particles. The ring structures also disappeared. However, the other supporting results indicate a poor ability to mediate AuNP reduction, although the PC to PPC oxidation (formation of more conjugated species) was confirmed by spectroscopy measurements. In addition, the PC to PPC conversion was also observed electrochemically by cyclic voltammetry and spectroelectrochemical experiments (see ESI[†]). In the future, it should be possible to test this concept with different PAMAM generations.

In conclusion, we have successfully synthesized novel hybrid materials *in situ* by using PAMAM dendrimers terthiophene (PT) precursors as a reductant for simultaneous AuNP formation and polythiophene (PPT) shell formation. While the carbazole dendrimer (PC) afforded higher conjugated carbazole species, the interaction was limited to mostly Au³⁺ MLCT interaction instead of AuNP formation. UV-vis and strong fluorescence emission quenching after treatment with AuCl₃ and the appearance of new peaks were attributed to an electron transfer mechanism from the PPT shell to

the AuNPs as well as MLCT transitions. In case of PT dendrimer, AuNPs can be stabilized by the thiophene to construct core–shell AuNPs–polythiophene hybrid materials while the PAMAM in PC dendrimer stabilized Au³⁺ but only in the periphery and was not as effective as the PT in forming and stabilizing AuNPs.

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