

Self-Assembled One-Dimensional Arrays of Gold–Dendron Nanocomposites

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Gold–dendron nanocomposites have been prepared by using poly(oxymethylphenylene) dendrons (PPD) of generations (G) 1–4 functionalized with a thiol group at the focal point as capping ligands. The mean particle size was 1.5 and 1.4 nm for G1 and G2, respectively, with 12 and 18% of relative standard deviation, and the particle size increased for higher generations with a remarkable broadening of the size distribution. For G1 and G2, spontaneous formation of one-dimensional arrays has been reproducibly observed on carbon film, with 2.5 and 2.3 nm of line spacing for G1 and G2, respectively.

Formation of size-controlled nanoparticles and their regular assemblies (superlattices) are important subjects for applications in electronic and optical devices, because physical properties of the superlattices strongly depend on the size of component nanoparticles, interparticle distances, and dimension of the superlattice.^{1,2} Two-dimensional (2D) and three-dimensional (3D) superlattices have been prepared by self-assembly of monodispersed nanoparticles,^{3–5} by the Langmuir–Blodgett method,⁶ or by electrophoretic deposition,⁷ and their optical and electron transport properties have been investigated.² In contrast, one-dimensional (1D) arrays of nanoparticles have been prepared with the help of some appropriate templates, such as DNA strand,^{8–10} other linear polymers,¹¹ or lithographically patterned substrates.¹² In these systems, the nanoparticles are passivated with an isotropic rigid capping layer, e.g., alkanethiols,⁴ sulfonated triphenylphosphine,^{5,11} or other ligands.^{13,14} Recently, Schmid and co-workers have developed some new methods for the formation of quasi 1D assemblies making use of polymer bundles formed at water–dichloromethane interface¹⁵ or fractionation of monolayered nanoparticles on water subphase.¹⁶

On the other hand, dendrimers^{17–19} or dendrons^{20,21} have recently been used for encapsulating metal or semiconductor nanoparticles. Unlike linear ligands, dendrimers and dendrons form a loosely packed capping layer around nanoparticles. In addition, the dendrimers are flexible molecules and can take various conformations. The flexible nature of dendrimers may provide unique assembling properties. Recently, Kim et al.²⁰ prepared Au/poly(oxymethylphenylene) dendron (PPD) nanocomposites by using Fréchet-type PPD with a thiol group at the focal point and methoxy phenylene groups at the terminals. They reported that the particle size becomes minimum at G2 (2.4 nm) where the highest monodispersity was observed. However, no regular assembly has been observed.

In this Letter, we report that 1D self-assemblies are reproducibly observed for the Au/PPD nanocomposites by using PPD thiolates but not modified on the terminal phenylene groups (Scheme 1).

The PPDs were synthesized according to Fréchet's method.²² The focal point was functionalized with a thiol group by reacting PPD bromide with thiourea (1.25 equiv) in refluxing THF/ethanol (1/1, v/v) for 4 h. The product was purified with silica gel column chromatography. The purity of the PPD thiol was verified by TLC, ¹H NMR (Bruker DPX-400, 400 MHz), and MALDI-TOF mass spectra (Applied Biosystems Voyager DE).

The Au/PPD nanocomposites were prepared by applying Brust's two-phase method.²³ Typically, 2 μ mol (0.7 mg) of HAuCl₄ was extracted from the aqueous solution to toluene (5 cm³) with 6 μ mol (3.3 mg) of tetraoctylammonium bromide. To the organic phase, PPD G1–G4 (5 μ mol) dissolved in toluene (5 cm³) was added with vigorous stirring. The color has changed from orange to colorless or light yellow. Subsequently, aqueous NaBH₄ (0.8 mg in 10 cm³ water) was added under vigorous stirring. The color has immediately changed to brown (G1 and G2) or brownish red (G3 and G4). The sample was continuously stirred for another 12 h.

UV–visible absorption spectra of as-prepared samples were recorded on a JASCO V-570 spectrophotometer using a quartz cell of 1 cm path length. Subsequently, the nanocomposites were purified with a silica gel column using methylene chloride as an elution solvent. After the purification, the sample was dried, then redispersed in toluene, and finally deposited on copper grids coated with amorphous carbon film. The deposited samples were observed by TEM either with a Hitachi H-9000 NAR (300 kV) or with a Hitachi H-1250ST (1 MV). The direct magnification was 1.5×10^5 and 3.5×10^5 , respectively.

Figure 1 displays UV–vis absorption spectra of Au/PPD nanocomposites of different generations. For G3 and G4 a weak absorption band is visible at around 520 nm, which can be assigned to surface plasmon resonance (SP) band of metallic Au nanoparticles.²⁴ Meanwhile the SP band is almost absent for G1 and G2, suggesting that the particle size is smaller than 2 nm.²⁵ No absorption band for aggregates which should appear at longer wavelengths was observed;²⁶ thus regular assembly is not formed in solution.

However, once deposited on carbon film, the nanocomposites can form a regular assembly. Figure 2 compares low-magnifica-

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SCHEME 1: Molecular Structure of Thiol-Substituted PPD of Generations 1–4

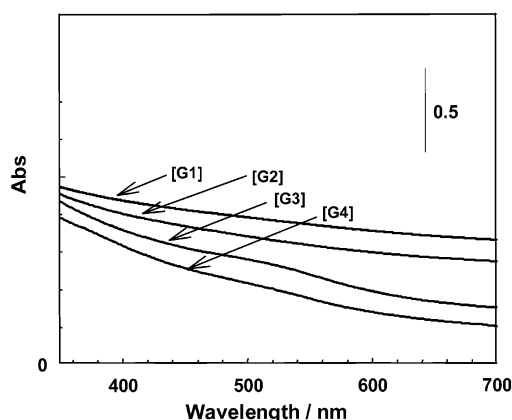
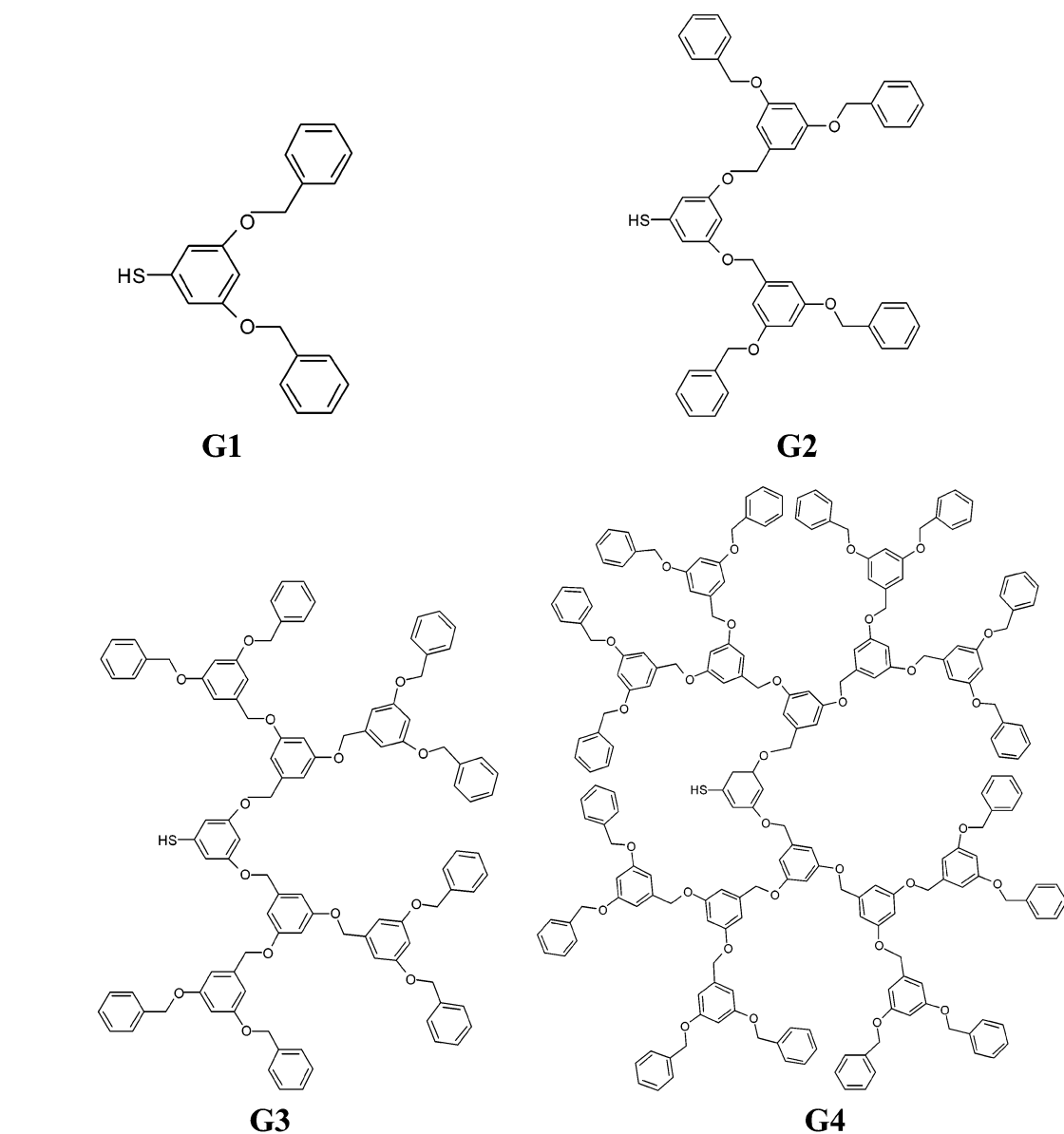


Figure 1. UV-vis absorption spectra of Au/PPD nanocomposites for different generations of PPD. $[\text{Au}] = 2 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{PPD}] = 5 \times 10^{-4} \text{ mol dm}^{-3}$. Optical pass length = 1 cm. Each spectrum is vertically shifted for easy to compare.

tion TEM images and the size distributions of Au/PPD nanocomposites for different generations of the dendron. For G1 (Figure 2a) the mean particle size (d) is 1.5 nm with the standard

deviation (σ) of 0.17 nm ($\sigma/d = 11.6\%$). For the G2 system (Figure 2b), d (1.4 nm) is almost the same as that for G1, but σ slightly increased to 0.25 nm ($\sigma/d = 18.1\%$). For higher generations both d and σ remarkably increased with increasing generation (Figure 2c,d). More intriguingly, stripe structure was reproducibly observed for G1 and G2. The stripes extended over $100 \times 100 \text{ nm}^2$ for G2 (Figure 2e), but a smaller area for G1. However, such a regular structure was not found for the nanocomposites bearing PPD G3 nor G4.

Figure 3 shows HRTEM images of the regular arrays of Au/PPD G2 nanocomposites. Although the contour of each particle is vague, one can find that the nanocomposites are aligned parallel to the direction OA (indicated in the figure), whereas no regularity is found along the direction OB. Accordingly, the stripe-structured assembly can be attributed to a 1D array of the nanocomposites. The interparticle distance along OA is widely distributed from ≈ 0 (almost touching) to 2.0 nm. By contrast, the spacing between the parallel lines passing through the centers of the particles along the direction OA is almost constant at 2.3 nm, as marked in the figure. The line spacing was very similar (2.5 nm) for Au/PPD G1 nanocomposite system (not shown).

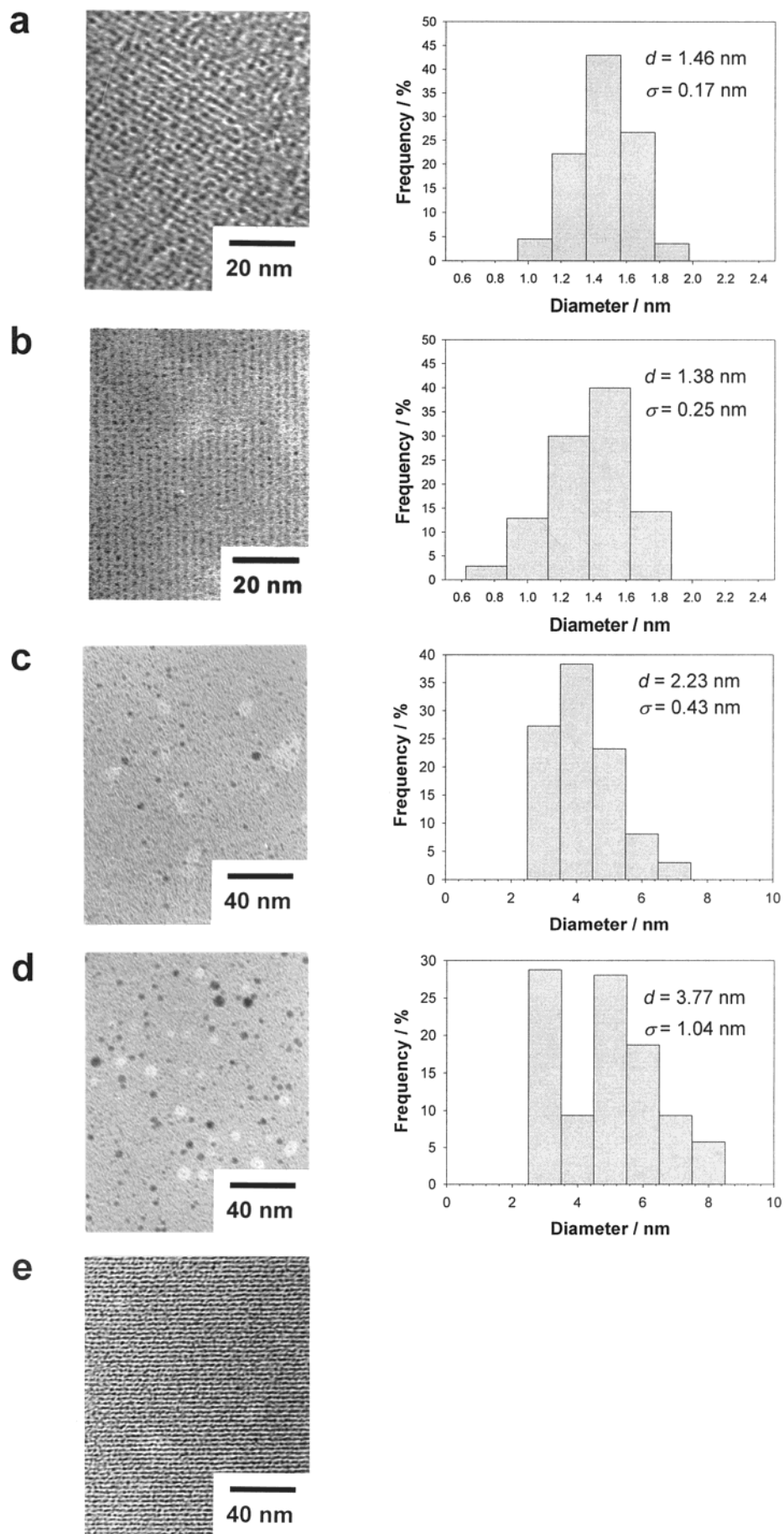


Figure 2. Low-magnification TEM images and size distributions of Au/PPD nanocomposites for different generations of PPD: (a) G1 (b) G2, (c) G3, (d) G4, (e) large-area image of sample (b). Stripe structure is found for G1 and G2 systems.

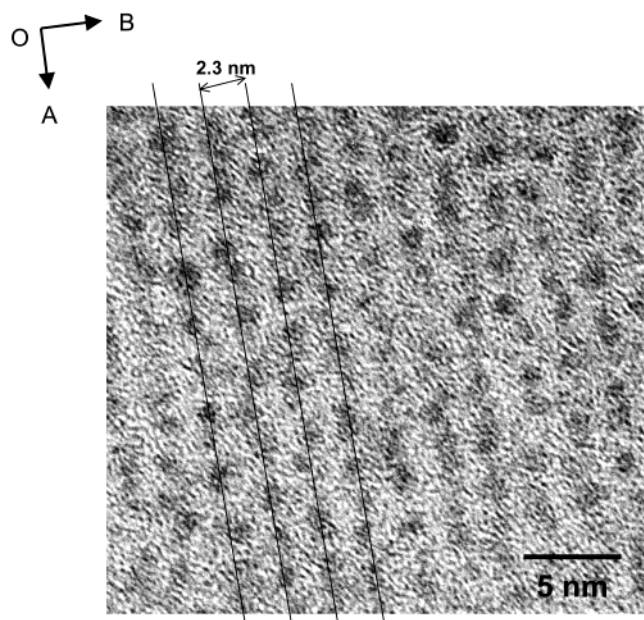


Figure 3. HRTEM image of Au/PPD G2 nanocomposites showing an alignment parallel to the direction OA, but no regularity along the direction OB.

Recently, Zhang et al. observed 1D arrays of PPD thiols in the self-assembled monolayer (SAM) on the Au plate.²⁷ The STM images revealed a stripe structure whose width increased with the increasing generation of the dendron: 2.3, 3.1, and 4.0 nm for G1, G2, and G3, respectively. In our nanocomposite systems, the line spacing is 2.5 and 2.3 nm for G1 and G2, respectively. Obviously, the different values for the same PPD stem from different origins. In the SAM, the line spacing would correspond to the distance between two terminal phenylene groups at the furthest sides from each other, because the dendron molecules stand vertically on the Au substrate.²⁷ In the nanocomposite systems, the line spacing may correspond to the sum of the particle size and twice the distance between the nanoparticle surface and the terminal phenylene groups of PPD if interdigitation of the dendron molecules does not occur. Taking the mean particle size into account, the interparticle edge-to-edge distance is calculated to be 1.0 and 0.9 nm for G1 and G2, respectively. These distances are much shorter than twice the focal-point-to-terminal distance of PPD molecules calculated from a MOPAC simulation, 1.4 and 1.8 nm for G1 and G2, respectively. This strongly suggests that interdigitation of adjacent PPD molecules is taking place between the adjacent lines. However, the reason the line spacing is not significantly different for G1 and G2 is not yet clear. On the other hand, no formation of 1D arrays for G3 and G4 PPD is probably due to large polydispersity in the size of nanocomposites. Molecular structure suggests that the thiol group at the focal point is progressively concealed from the surface with increasing generation of the dendron, thus ligation of the thiol group to the metal particle would be retarded and the particle size can be less controlled.

Although the structure of the 1D assembly in the Au/PPD (G1 and G2) nanocomposite systems is different from that in the SAM, both results can demonstrate that the dendron molecules have a strong tendency to crystallize. The driving force of 1D assembly is presumably an intermolecular π - π stacking interaction of thiol-terminated PPD, as in the case of the pyridine derivative system in which 2D superlattices have been observed.¹⁴ The contribution of electronic interaction for the 1D assembly can be supported also from the fact that

methoxy-terminated PPD do not provide 1D arrays.²⁰ On the other hand, the reason for the formation of 1D arrays and not 2D superlattices is not completely understood at the present. However, we believe that the formation mechanism would be closely related to the molecular structure of the dendron molecules and their electronic interaction. As shown in Scheme 1, PPDs are bulky and flexible molecules since their phenylene groups can take various conformations. Due to the flexibility, in the course of the deposition process two adjacent ligand molecules on a given pair of nanocomposites would readily deform. In this pair, the electronic state would not be isotropic. Due to the bulkiness of PPD molecules, this deformation would propagate to all ligand molecules on this pair, which may facilitate the electronic interaction in one direction. However, further investigation is necessary to verify this speculation.

In conclusion, we have found the spontaneous formation of 1D array Au/PPD nanocomposites by using thiol-derivatized poly(oxyethylphenylene) dendrons of generations 1 and 2. The formation of 1D arrays in a larger area would provide more elaborate nanoelectronic systems.

References and Notes

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