

Dendron-grafted sulfur-terminated phenyleneethynylene molecular rods and blue luminescence self-assembly with Au nanoparticles†

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Dendron-grafted phenyleneethynylenes with α,ω -disulfur containing groups were newly synthesized and characterized for self-assembly with Au nanoparticles; an intense blue photoluminescence of the composite film was observed.

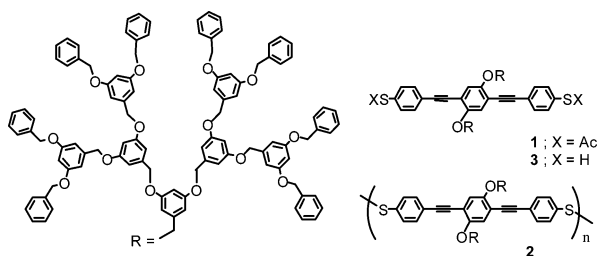
Self-assembly has been recognized as a simple and powerful methodology for the fabrication of two- or three-dimensional nanostructures.¹ Metal and/or semiconductor nanoparticle² assemblies and arrays are, in particular, one of the most promising research aspects for novel photoelectric materials,³ partly because of the variety of organic species used to construct organic–inorganic hybrid nanostructures. Many types of these nanoparticle systems have been extensively synthesized using organic surface modification^{2c} and interconnection with bifunctional molecules.⁴ Such organic modifiers/interconnectors are important due to their dramatic effect on the morphologies and functions of the nanocomposites.³ So far, several approaches have taken advantage of the uniqueness of dendrimers⁵ as the organic part by constructing dendrimer–nanoparticle composites (DNCs).⁶ Here dendrimers are used as templates (matrices),^{7,8} and ligands (stabilizers).⁹ Among their intriguing functions are a blue emission from a CdS–dendrimer nanocomposite,^{8a} and a highly efficient blue luminescence derived from dendron-encapsulated Au₈ clusters^{9g} which have been reported.

Aida and coworkers have synthesized dendron-grafted-polyphenyleneethynylenes (dend-g-PPhEs) that harvest light and convert it to blue light with a high efficiency¹⁰ (*i.e.* an antenna effect¹¹). In this context, this attractive organic blue-emitting material has prompted the author to combine a rod-type dendron-grafted conjugated system as an interconnector and nanoparticles having electroconductivity. This approach can create a new type of dendrimer–nanoparticle composite with photo-electronic properties. With this strategy in mind, the author designed dendron-grafted α,ω -sulfur terminated phenyleneethynylenes (dend-g-PhEs) (Scheme 1). Its features, due to the discrete structure relative to the dend-g-PPhEs, are as follows: (i) convenient composite synthesis using a self-assembly process and (ii) expected increasing nanoparticle density in the resulting composite. In this communica-

tion, the author reports the synthesis of the dendrimers (dend-g-PhEs) bearing α,ω -disulfur-functionalities and the self-assembly with Au nanoparticles that, when prepared as a cast film from the composite, exhibit an intense blue luminescence.

A third generation (G-3) dend-g-PhE with thioacetyl terminal groups **1** was synthesized by the etherification of dihydroxydiethynylbenzene¹⁰ with the Fréchet-type third generation poly(benzylether) dendron bromide,¹² followed by the coupling reaction of *S*-acetyl-4-iodothiophenol to form the new C–C bonds in the backbone.¹³ The chemical structure of the resulting compound **1** was confirmed by FT-IR and NMR spectroscopies and MALDI-TOF MS. **1** was then treated with sodium hydroxide in THF–H₂O at room temperature,^{13b} affording a yellow solid, which showed good solubility in common organic solvents. Gel permeation chromatography (GPC, polystyrene standard) was performed on the obtained yellow solid, affording a weight-averaged molecular weight (M_w) of 1.6×10^4 ($M_w/M_n = 1.6$), and the ¹H NMR spectrum indicated a significant peak broadening of the dendron skeleton signals. These results suggested the spontaneous oligomerization of **1** due to the formation of disulfide bonding in **2**. Dithiol conjugated compounds have been commonly known to allow spontaneous but uncontrollable oxidative oligomerization by deprotection of the terminal thiol groups to produce insoluble disulfide oligomers.^{13a,b} The good solubility of the oligomerization product most probably came from the excellent solubilizing ability of the dendrons. In fact, the author observed an insoluble oligomer product by the deacetylation of the *n*-hexyloxy side-chain analogue of the acetylated compound **1**, instead of the dendron side-chains. First (G-1) and second (G-2) generation analogues of the acetylated compound **1** instead of the G-3 side-chains were also prepared, however, the solubility gradually decreased as the generation became smaller. The G-1 analogue was hardly soluble in CHCl₃, and the oligomerized deacetylated G-2 analogue showed a slightly lower solubility than the G-3 oligomer. Isolation of the desired deacetylated monomer **3** was accomplished by a reduction of the disulfide oligomer **2** using NaBH₄ in EtOH–THF. The resulting pale-yellow solid was characterized to confirm the desired structure of **3** by NMR spectroscopies, MALDI-TOF MS and GPC analyses.

UV–visible absorption spectra (see ESI, Fig. S1, inset†) in degassed THF at room temperature showed that **1**, **2** and **3** had electronic absorption bands at around 320 and 380 nm arising from the backbone phenyleneethynylene chromophore, and at 280 nm from the dendron units. Upon excitation at 380 nm (298 K, Abs₂₈₀ = 0.05), **1** gave a blue luminescence band that peaked at 413 nm. Under irradiation at 280 nm, an almost identical emission spectrum was obtained without luminescence from the dendritic units. Thus the 280 nm excitation seemed to result in a very efficient transfer of energy from the dendron side-chains toward the conjugated backbone. Intriguingly, the luminescence of the disulfide oligomer **2** was remarkably quenched, which may be interpreted as self-quenching of the luminescence of the individual phenyleneethynylene repeating units closely arranged within the oligomer backbone. In contrast, the luminescence of the deacetylated monomer **3** was stronger than the disulfide oligomer **2**. The sharp decrease in the



Scheme 1

† Electronic supplementary information (ESI) available: UV–visible absorption and fluorescence spectra of **1**, **2** and **3** and SEM images of **3**–Au nanoparticle composite and **1**–Au nanoparticle mixture. See <http://www.rsc.org/suppdata/cc/b4/b404010d/>

luminescence intensity of the disulfide oligomer **2** is interesting in terms of switching applications induced by redox reactions.

The self-assembled nanocomposite was finally prepared *via* the ligand exchange reaction^{14b} of the hexanethiol-coated Au nanoparticle^{2c,14a} (*ca.* 2 nm mean diameter) with the deacetylated monomer **3**. In a typical experiment, the deacetylated monomer **3** (14 mg, 4.0×10^{-3} mmol) was dissolved in EtOH–THF (20/80 vol%), followed by the addition of NaBH₄ (200 eqv) in order to activate the thiol groups, and then stirred for about 30 minutes. To this suspended solution was added the hexanethiol-coated Au nanoparticles (9 mg), followed by concentration to dryness under reduced pressure after stirring at room temperature overnight. The usual work up (partition between water–CHCl₃ and reprecipitation in ethanol at –25 °C) afforded a black-ash-colored, organic-soluble solid. The ¹H NMR in CDCl₃ gave broad dendron signals, indicating that the mobility of the dendron was limited by the composite formation. Scanning electron microscopy (SEM) suggested that the Au nanoparticles are well dispersed in the nanocomposite (Fig. 1a, see also the ESI†).

A distinct observation for the nanocomposite consisting of the deacetylated monomer **3** and Au nanoparticles was a strong blue luminescence. Fig. 1b indicates three kinds of compounds emitting in the solid state. The luminescent brightness of the composite film (right) was apparently stronger than that of **1** (left) under UV_{254 nm}, 365 nm irradiation. Upon excitation at 280 nm and 380 nm, the fluorescent spectra of the composite film at 470 nm clearly indicated the antenna effect (Fig. 1c). In contrast, a simple mixing of the acetylated **1** and the Au nanoparticles gave a solid showing very little luminescence (Fig. 1b: center) in spite of showing luminescence in the THF solution, and sharp ¹H NMR signals. In addition, a specific assembled structure was not observed in the SEM images.† These results suggested that the interactive formation of the nanocomposite was responsible for the strong luminescence ability. The intensified fluorescence could be related to metal-enhanced fluorescence.¹⁵ The details are currently being examined.

In summary, the results described here suggest a new approach for the construction of a dendrimer–nanoparticle composite. Most notably, the mutual S–Au interaction constructing the nanocomposite unexpectedly afforded a strong blue luminescence. The designed sulfur-mediated self-assembly would be applicable for other quantum dots with various electro/photophysical characteristics. The synergy between the dend-g-PhE and nanoparticles is of considerable interest. The electronic properties of this novel

nanocomposite have been under investigation and will be reported elsewhere.

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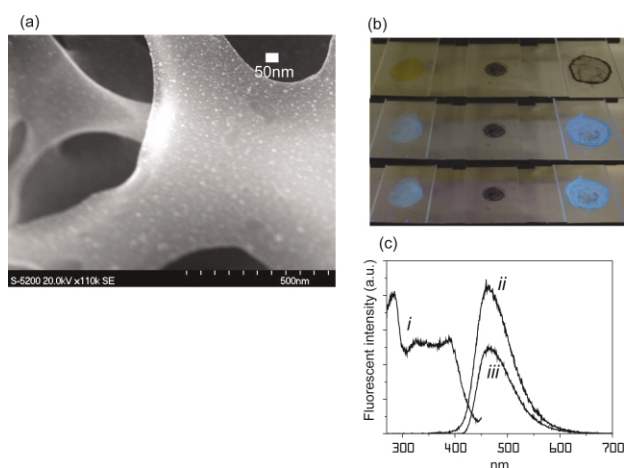


Fig. 1 (a) SEM image of **3**–Au nanoparticle composite. (b) From left to right, photograph of the cast films of **1**, **1**–Au nanoparticle mixture and **3**–Au nanoparticle composite on quartz glass. From top to bottom, under daylight, UV_(254 nm) and UV_(365 nm) lamp irradiation. (c) (i) Excitation: $\lambda_{\text{obsd}} = 470$ nm, (ii) photo-luminescence: $\lambda_{\text{exc}} = 280$ nm and (iii) $\lambda_{\text{exc}} = 380$ nm spectra of **3**–Au nanoparticle composite film.