Molecularly-mediated assembly of gold nanoparticles with interparticle rigid, conjugated and shaped aryl ethynyl structures[†]

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The rigidity, conjugation, and shape-persistent architectures of aryl ethynyls of V, Y, and X shapes serve as an ideal model system for defining interparticle structures, which have been demonstrated for the mediated assembly of gold nanoparticles.

The control of interparticle interactions and structures in nanoparticle assemblies using molecular or biomolecular mediators¹⁻⁶ has attracted increasing interests for the design of functional nanostructures.^{7,8} However, the understanding of such control is often hampered by the lack of well-defined mediator structures in terms of size, shape, rigidity and other properties. Arylalkynes are known to serve as intriguing building blocks for the covalent construction of molecular architectures.9 The viability of interparticle linkages via coordination of the methylthio groups of X-shaped arylethynes to gold surfaces was demonstrated recently in our laboratory.¹⁰ However, a key challenge is to determine the orientation of such interparticle shaped molecules for exploiting their unique optical and electrical properties. A relevant question is how the size, shape and number of methylthio groups of the rigid arylethynes influence the assembly of nanoparticles from both kinetic and thermodynamic perspectives, and the optical or spectroscopic properties (e.g., surface-enhanced Raman scattering (SERS)). Aryl ethynyls of different shapes serve as an ideal model system for defining interparticle structures because of their rigidity, conjugation, and shape-persistent architectures.¹⁰⁻¹³ We report herein novel findings of using rigid methylthio arylethynes with several sizes and shapes such as V(1)-, X(2)-, Y(3)-, and Y'(4) (Scheme 1) to define interparticle bridging and orientation for the assembly of gold nanoparticles. The X-shaped molecule¹⁰ is included for a detailed comparison of these structures and properties. The ability to engineer the interparticle size, shape, and structural properties would allow advanced exploitation of the nanoscale optical and spectroscopic properties.

Fig. 1 show a representative set of spectral evolution of the surface plasmon (SP) resonance band of gold nanoparticles

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Scheme 1 (A) Structures of V(1)-, X(2)-, Y(3)-, and Y'(4)-shaped aryl ethynyls (a = 1.8, b = 1.0, c = 1.5, d = 3.0, and e = 2.6 nm). (See ESI for detailed synthesis†); 1,3-diiodobenzene (DIB); 1,3,5-triiodobenzene (TIB); 1,2,4,5-tetraiodobenzene (TTIB); 1,3,5-tris-((4-odophenyl) ethynyl) benzene (TEB). (B) Schematic illustration of the molecularly-mediated assembly of nanoparticles.



Fig. 1 Spectral evolution of SP band in toluene solution with [mediator]/[AuNPs] = 2.1 for 1-(a), 2- (b), 3-(c), and 4-(d) mediated assemblies. The reactions were followed for 1 h.

(AuNPs) capped with a tetraoctylammonium (TOA⁺) bromide monolayer (5.1 \pm 0.9 nm, see ESI[†]) (525 nm in toluene solution)¹⁴ for the different mediators. The spectral evolution for the assembly mediated by **1–4** all features a decrease of the 525 nm band and an increase in the long-wavelength band region as a result of the mediated assembly.

Based on the band characteristics and the kinetics of the spectral evolution of the red-shift SP band (*e.g.*, @ 700 nm) (Fig. 2A), apparent rate constants were derived from fitting

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Fig. 2 (A) Kinetics for the absorbance at 700 nm in toluene solution with [mediator]/[AuNPs] = 2.1 for $1-(\bigcirc)$, $2-(\bigtriangledown)$, $3-(\blacksquare)$ and $4-(\blacktriangle)$ assemblies (dashed lines: 1st-order kinetic fits). (B) The red-shift $(\Delta \lambda/\lambda_0)$ (see ESI Table S1[†] for $\Delta \lambda$ and λ_0 values) as a function of the interparticle separation (s/D) as defined in the inserted scheme (dashed line: theoretical fit with eqn (1)).

the time dependence of the absorbance with an exponential growth (k, 1st-order). Under the same concentration, the resulting rate constants displayed an order of **3** (8.4 × 10^{-3} s^{-1}) > **4** (5.8 × 10^{-3} s^{-1}) > **2** (3.7 × 10^{-3} s^{-1}) > **1** (2.1 × 10^{-3} s^{-1}). Upon completion of the assembly, the peak position of the red-shift of the SP band was found to exhibit the order of **1** ($\lambda_{\text{max}} = 930 \text{ nm}$) > **2** ($\lambda_{\text{max}} = 790 \text{ nm}$) > **3** ($\lambda_{\text{max}} = 670 \text{ nm}$) > **4** ($\lambda_{\text{max}} = 602 \text{ nm}$ (see ESI†).

The SP band characteristics were further analyzed based on the correlation between the interparticle separation (s/D) and the SP band's red-shift $(\Delta \lambda / \lambda_0)$:¹⁴

$$\frac{\Delta\lambda}{\lambda_0} = C \exp\left(-\frac{1}{\tau}\frac{s}{D}\right) \tag{1}$$

(s: interparticle gap, D: particle diameter (5.1 \pm 0.9 nm), τ : decay constant, λ_0 : wavelength for SP band, $\Delta\lambda$: red-shift, C: constant). As shown in Fig. 2B, an exponential decay was evident for the interparticle spacing parameters defined by these mediator structures. In comparison with the decay constant for simulated metallic nanoparticle pairs using discrete dipole approximation method (~0.2),¹⁴ τ was found to be 0.17, consistent with the theory that both the interparticle near-field dipolar coupling potential and the intraparticle restoring potential depend on similar powers of particle radius separation distance defined by ethynyl structures. The measured average edge-to-edge interparticle distance (s, see ESI Fig. S1⁺) showed ~1.1 nm for V(1) assembly, ~ 1.3 nm for X(2) assembly and ~ 1.7 nm for Y(3) assembly, which are in good agreement with the molecular modeling results for the interparticle orientations defined in Fig. 2B.

The differences between these mediator-NP assemblies were assessed by introducing two different mediators to the solution of nanoparticles in different sequences. Following addition of the 1st mediator, the addition of the 2nd mediator in a controlled concentration ratio led to a distinct change in the SP band. The red-shift band (at 700 nm) for the V–Y (*S1* sequence), V–X (*S2* sequence), and Y–X (*S3* sequence) series was characterized by a sharp increase in absorbance before levelling off (Fig. 3A). As indicated by the ratio of the rate constants (*i.e.*, *k* (2nd) *vs. k* (1st) (*e.g.*, $k_Y/k_V = 3.5$)), the rate for the 2nd mediator was faster than that for the 1st by a factor of 2–4 (ESI Table S2†). Note that the absorbance



Fig. 3 (A–B): SP band absorbance (A) and the DLS intensity (B) in response to sequential addition of two mediators in the solution of AuNPs: V–Y (S1) and V–X (S2). ([mediator]/[Au] = 4.2(A), and 8.1(B)) (dashed lines: 1st-order kinetic fits).

decrease for Y–X (S3) was due to precipitation of the assembly. This observation was in contrast to Y(X)-V (S4) where no spectral evolution was found upon 2nd mediator addition.

The kinetic evolution was further substantiated by in situ dynamic light scattering (DLS) measurement of the diameter vs. assembly time (Fig. 3B). The further increase in size upon the addition of the 2nd mediator was evident. A close examination of the DLS data for V-Y (S1), V-X (S2), and Y-X (S3) series (see ESI Table S3[†]) and the initial stage of the 2nd mediator assembly provided some mechanistic insights into the two-mediator assembly process. For the V-Y and Y-X sequences, there was an initial size reduction (disassembly) or up-down transient within the first 1-2 min before the size increase became dominant. The rate constant for the assembly growth by the 2nd mediator was also found to be faster than that for the 1st by a factor of 2–3 (e.g., $k_{\rm Y}/k_{\rm V} = 1.8$). Based on TEM analysis of the final assembly sizes (ESI Fig. S3, S4[†]), the V(1) mediated assemblies showed individually-isolated clusters of nanoparticles ranging from 90 to 170 nm, and the addition of the 2nd mediator Y(3) appeared to lead to interconnection of the clusters into a spreading network architecture, indicative of the interconnection of the 1st mediator assemblies (V-NP) by 2nd mediator (Y).

Based on a spectrophotometric analysis of the relative changes of the constituents in the mediated assembly system (ESI Table S4 \dagger), 18–34% of V(1) were found to be incorporated into V–NP assembly, about 43% of X(2), or 11% of Y(3), were found for the 2nd mediator (X(2), or Y(3) to incorporate into the V–Y–NP and V–X–NP assemblies, and about 23% or 33% of V(1) were found to be released as a result. On average, about one mediator per NP was found (*e.g.*, 1.4 for V(1), 1.5 for X(2) and 0.8 for Y(3) per NP). The relative changes of the incorporated 2nd mediator were consistent with the released 1st mediators.

The interparticle mediators were confirmed by examining the SERS signatures of the aryl ethynyl structures in the mediators. As shown in Fig. 4, the detected spectral signatures were characteristic of the triple bond stretching ($\nu_{(C=C)}$) (~2200 cm⁻¹), and the benzene ring breathing ($\nu_{(\phi)}$) (~1600 cm⁻¹). There were clear differences in peak positions (± 1 -6 cm⁻¹), or new bands being detected in the 1400–2400 cm⁻¹ region. The data clearly revealed signatures from the mediators, including the elimination of peak splitting for



Fig. 4 Raman spectra for two sets of samples: (A) V-(a), Y-(b), and V-Y-(c) mediated assemblies; (B) V-(a), X-(d), and V-X-(e) mediated assemblies.



Scheme 2 A schematic illustration of the nanoparticle assembly by two mediators (*e.g.*, V(1) and Y(3)) in a sequential addition process, involving a partial disassembly of V-NPs and an assembly of the partially-disassembled V-NPs and NPs toward (V + Y)-NPs.

V(1) in $\nu_{(\phi)}$ mode and the shift of $\nu_{(C \equiv C)}$ band corresponding to X(2) or Y(3), demonstrating the presence of both mediators in the two-mediator assemblies. A comparison between the Raman intensities between the solid and the interparticle assembly samples yielded an estimate of 10^4 – 10^5 for the SERS enhancement factor.

As illustrated in Scheme 2, the structural evolution for the sequential addition of V(1) and Y(3) involved an initial partial disassembly as a result of the displacement of V(1) by Y(3) and a subsequent assembly by Y(3), forming an assembly with interconnected (V+Y)–NP moieties. The observed characteristics of the SP band, the assembly size, and the SERS signatures provided strong evidence for the assessment.

As supported by the DLS (Fig. 3) and the SERS data (Fig. 4), the addition of the second mediator (stronger) led to an initial partial disassembly of the first mediator (weaker) mediated assembly before the second mediator mediated assembly of them towards the formation of the V–Y, V–X, or Y–X assemblies. As such, the first mediator was not completely replaced by the second mediator, and both the first and second mediators were present in the mixed-mediator assemblies. These findings have demonstrated that the interparticle spacing and structures of nanoparticle assemblies are well defined by rigid, conjugated, and shape-persistent aryl ethynyls. It is important to note that these mediated assemblies all showed highly-clustered features with various sizes as

revealed by TEM (*e.g.*, 90–170 nm for V(1), 90–130 nm for Y(3), and 40–60 nm for X(2) assemblies (ESI Fig. S1 \dagger), which were in agreement with the optical data. Both aryl ethynyl shape- and size-determined interparticle structural effects are believed to be operative in the assembly process, the detailed understanding of which requires a more systematic tuning of the structures. A certain degree of intershell overlap is also believed to operate for the growth of larger-sized assemblies at a slower assembly rate. This type of interparticle structural control of optical and spectroscopic properties have important implications to enabling the design of a wide range of nanoparticle assembly systems for potential applications in chemical/biosensing, spectroscopic signal amplification, and microelectronics.

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