



Nanocrystallinity and direct cross-linkage as key-factors for the assembly of gold nanoparticle-superlattices

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Nanocrystallinity and direct cross-linkage as key-factors for the assembly of gold nanoparticlesuperlattices

M. Boterashvili, T. Shirman, R. Popovitz-Biro, Qiang Wen, M. Lahav* and M. E. van der Boom*

We report here how the crystallinity of AuNPs and the choice of binding sites of molecular cross-linkers control their aggregation.

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Received 21st April 2016, Accepted 18th May 2016 **superlattices†** M. Boterashvili,‡^a T. Shirman,‡^a R. Popovitz-Biro,^b Qiang Wen,^a M. Lahav*^a and

key-factors for the assembly of gold nanoparticle-

Nanocrystallinity and direct cross-linkage as

M. E. van der Boom*^a

15 DOI: 10.1039/c6cc03352k

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We report here how the crystallinity of AuNPs and the choice of 20 binding sites of molecular cross-linkers control their aggregation. The combination of different binding moieties (*N*-oxides, Ar_F-I) and the reactivity of the particles' facets allow control over the organization and crystallinity of the AuNP assemblies.

- 25 Nanoparticle-based superlattices are one of the most fascinating classes of materials with high technological potential and their formation attracted much interest.¹ Gaining control over the assembly processes requires a fundamental understanding of the interactions that drive the formation of these structures.
- 30 The challenge is to predict and control how specific interactions would lead to targeted structures. The assembly of NPs into ordered arrays can be induced:¹ (I) via the manipulation of interparticle-interactions by evaporation of the solvent or gentle destabilizing of the colloidal solution.² The main forces respon-
- 35 sible for such superlattice formation are van der Waals interactions between NP cores or capping ligands. (II) Utilizing of specific noncovalent interactions between capping ligands (*e.g.* hydrogen bonding, halogen bonding, antibody-antigen, DNA recognitions and metallic complexation).³ (III) Utilization of 40 cross-linkers that can directly bind between the NPs. Many
- examples are based on the use of dithiols, however the fast aggregation of the AuNPs hampers often the formation of ordered structures.⁴
- The size, shape and the morphology of NPs are important parameters that determine their optical, electronic, and chemical properties.⁵ These parameters are also known to affect the structure of ordered arrays.^{2,6} The effect of NP nanocrystallinity on the structure of superlattices is also of much interest. For

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example, Klabunde and co-workers reported the formation of face-centered cubic (fcc) type superlattices with single-crystalline AuNPs, while hexagonal close-packed (hcp) type superlattices were obtained with defective AuNPs.^{6d} In another report, Pileni showed that single-crystalline and poly-crystalline AuNPs spontaneously separate in solution as the single-crystalline NPs form a superlattice.⁷

In this work, we show how to control the level of organization of AuNP assemblies: superlattices, amorphous aggregates or separate nanoparticles. The crystallinity of AuNPs capped with dodecylamine (DDA) was used to control their reactivity towards cross-linkers to form organized assemblies. Our strategy involves the utilization of single-crystalline (SC_{Au}) and multiple-twinned (MT_{Au}) AuNPs and symmetrical and asymmetrical cross-linkers having two binding sites: pyridine-*N*-oxide **Q4** and/or Ar_F-I (Scheme 1).

Both binding sites have not been well-explored for reactions with NPs,⁸ and their orthogonal reactivity towards the Au surfaces is reflected in the formed aggregates. The interactions of these moieties with the surface of the SC_{Au} and MT_{Au} AuNPs are significantly slow, therefore allowing the formation of ordered structures. We observed three levels of AuNP-arrangement: (I) superlattices obtained with cross-linker 1 having two pyridine-*N*-oxides, regardless of the crystallinity of the AuNPs. (II) Amorphous or crystalline structures obtained when one of the pyridine-*N*-oxides is substituted by Ar_{F} -I (2): single-crystalline AuNPs react with 2 to afford a superlattice, whereas the use of polycrystalline AuNPs results in amorphous aggregation. (III) The use of only Ar_{F} -I moieties (3) results in relatively small amorphous structures with SC_{Au} AuNPs. No aggregation occurred with MT_{Au} AuNPs.

The reaction between the NPs and the cross-linkers (1-4) 50 were carried at room temperature by addition of 1–4 dissolved in small quantities in DCM (1) or THF (2–4) to a solution of NPs in THF. The reaction between both SC_{Au} and MT_{Au} and 1 resulted in highly ordered structures.

Transmission electron microscopy (TEM) images taken after 55 one day revealed the formation of large ordered arrays of NPs

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[‡] These two authors contributed equally to this paper.



- with the nanocrystallinity of the individual particles controlling their packing (Fig. 1A–D and Fig. S2, ESI[†]). Fast Fourier transform (FFT) analysis of the TEM images confirmed the formation of ordered structures (Fig. 1E and H). Profile analysis reveal *d*-spacings of 5.7 nm and 6.0 nm for the SC_{Au}/1 and
- 30 **MT_{Au}/1**, respectively, due to superlattice formed by the individual metal cores (Fig. 1F and G). The spacing is in a good agreement with NP (5.2 ± 0.3 nm) and the cross-linker (1; 1.2 nm) dimensions. A dampening of the surface plasmon resonance (SPR) band accompanied by a slight band broad-
- ening is observed by UV/Vis spectroscopy (Fig. S3A and B, ESI[†]). A striking different behavior was observed upon reaction of both SC_{Au} and MT_{Au} with the symmetrical cross-linker 3 having two Ar_F-I moeties. Formation of small amorphous aggregates were observed even after 8 days (Fig. 1I and J). Differences
 between SC_{Au}/3 and MT_{Au}/3 are also reflected in the UV/Vis spectra. Dampening of the SPR band for SC_{Au}/3 accompanied
- by a small red shift (~ 6 nm) and peak broadening (Fig. S3C, ESI[†]) is observed. No significant changes in the optical spectra for **MT_{Au}/3** were observed (Fig. S3D, ESI[†]).
- The reaction between SC_{Au} and the asymmetric cross-linker 2 having both *N*-oxide and Ar_F -I moeties resulted in formation of ordered structures after one day as also observed for $SC_{Au}/1$ and $MT_{Au}/1$. The order in these assemblies is apparent from TEM imaging and FFT analysis (Fig. 2A, C, D and Fig. S4A and
- B, ESI[†]). This aggregate is less ordered than the in the case of the symmetric (I) ligand, as can be seen from the fact that the FFT shows arcs with 6-fold symmetry and not sharp spots. No aggregation was observed in the reaction between MT_{Au} and cross-linker 2 (Fig. 2B and Fig. S5, ESI[†]). Aging of the reaction solutions resulted in densely ordered aggregates (SC_{Au}/2) after
- eight (Fig. S4C and D, ESI[†]) and ten days (Fig. 2E, G and H).



Fig. 1 TEM analysis of assemblies obtained upon reaction of AuNPs with the symmetrical cross-linkers 1 or 3 for 1 day (1; A–D) or 8 days (3; I and J). (A) $SC_{Au}/1$, (B) $MT_{Au}/1$, (C) and (D) are higher magnification images of the areas marked in A and B, respectively. (E and H) Fast Fourier transform (FFT) patterns obtained from images C and D, respectively. (F and G) Profile analysis taken from the areas marked in C and D, respectively. (I) $SC_{Au}/3$ and (J) $MT_{Au}/3$. Inset I: Scale bar = 20 nm. The direction of the intensity profile in F and G is indicated by the white arrow in C and D, respectively.

One or two layers of ordered NPs sheets were observed (Fig. 2A), while in Fig. 2E more layers were added in the third dimension and the aggregate is much thicker. Smaller amorphous aggregates were observed for $MT_{Au}/2$ (Fig. 2F and J). Profile analysis for $SC_{Au}/2$ indicated a *d*-spacing of 7.26 nm (Fig. 2I). HR-TEM analysis and the corresponding FFT patterns show translational alignment among neighboring particles, and some degree of orientational order (Fig. S6, ESI†),^{6c} This interparticle lattice continuation of the Au 111 planes might result from coalescence of the 2-coated AuNP upon aging. The addition of the cross-linker 2 to the solutions of SC_{Au} and MT_{Au} NPs resulted in a dampening of the SPR band over time (Fig. S7A and S8A, ESI†). This effect was more pronounced for $SC_{Au}/2$ and is accompanied by a small red shift of ~5 nm and band broadening.

To explore the nature of the Ar_{F} -I interaction with the surface of the AuNPs, we reacted both SC_{Au} and MT_{Au} with the F, Cl and Br analogues of cross-linker 2. No aggregation was observed with these systems demonstrating the role of the Au···I interaction in driving the assembly of these DDA-capped AuNPs with cross-linker 2 (Fig. S7B, S8B and S9, ESI[†]).

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Fig. 2 TEM analysis of assemblies obtained upon reaction of AuNPs with the asymmetrical cross-linker 2: SC_{Au}/2: (A and C) 1 day, (E) 10 days, (C) is a 25 high magnification image of the area marked in A. (D) Fast Fourier transform (FFT) patterns obtained from image A. MT_{Au}/2: (B) 1 day. (F and J) 8 days. (G) Higher magnification image of the area marked in E. (H) Fast Fourier transform (FFT) pattern obtained for the image in E. (I) Profile analysis taken from the area marked in G. The direction of the intensity profile in I is indicated by the white arrow in G. 30

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In addition, we found that the non-fluorinated derivative of cross-linker 2, also did not induce NP aggregation (Fig. S10, ESI[†]). Our findings are in agreement with those of Blakey et al. who demonstrated recently that iodoperfluorobenzene and derivatives thereof form metal---iodine charge transfer complexes with AuNPs. Fluorine substitution of the arene is not required in that system, but it increases the relative strength of the interaction.^{8d}

40 In contrast to the Ar_F-I moiety, the N-oxide group might act as an electron donor to the surface (δ^{\dagger}) of the DDA-capped AuNPs. The symmetrical cross-linker 1 forms ordered assemblies regardless of the crystallinity of the AuNPs. In contrast, the symmetrical cross-linker 3 neither induces the formation of

- 45 such ordered systems nor the formation of large aggregates. From the dampening of the SPR bands, it can be concluded that for all systems a capping layer exchange occurred. The formation of only small aggregates with SCAu/3 and the lack of aggregation with MT_{Au} and 3 indicates that these AuNPs having
- 50 terminal Ar_F-I groups do not readily assemble. Binding of the first Ar_F-I moiety of cross-linker 3 to the AuNP surface can result in deactivation of the second para Ar_F-I. Similar observations were reported by Blakey et al.^{8d}

Interestingly, the asymmetric cross-linker 2 only generated 55 crystalline assemblies with SCAu and induces amorphous aggregates with MT_{Au}. These differences are due to the preferential 1

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binding of the Ar_F-I moieties to specific crystal facets on the AuNP surface. The preferential binding of adsorbates to different facets is known,⁹ and has been observed for C₆F₅I, *p*-C₆F₄I₂ and o-C₆F₄I₂ with AuNPs.^{8d} These propensity of the different AuNP facets to undergo charge-transfer with the Ar_F-I moieties is an important parameter to induce order with such crosslinkers.

In conclusion, the structure of AuNP assemblies can be controlled by the crystallinity of the individual DDA-capped AuNPs and the design of the cross-linkers. The symmetrical crosslinker (1) having two N-oxide moieties forms organized assemblies with both types of AuNPs. However, different facets of the AuNPs can exhibit different reactivity as expressed with cross-linkers (2, 3) having an Ar_F-I moiety: a higher level of NP organization was observable for SCAu compared to MTAu. The use of the asymmetrical crosslinker (2) having both N-oxide and Ar_F-I moieties results in organized assemblies (SC_{Au}) and amorphous aggregates (MT_{Au}). For 3, with SC_{Au} relatively small aggregates were observed, and no aggregation was achieved with MT_{Au}. For the cross-linkers demonstrated, the N-oxide moiety has a larger contribution to the formation of organized AuNPs, where as the reactivity of facets is clearly expressed by using Ar_F-I moieties. The observed reactivity of the singlecrystalline and multiple-twinned AuNPs with the cross-linkers illustrates the importance of nanoparticle crystallinity com-25 bined with molecular design to control the assembly of such systems.

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