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Evolution of atomically precise silver clusters to superlattices

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S. No.	Description	Page No.
1	Experimental section and instrumentation.	2
2	Photographs during synthesis.	3
3	MALDI mass spectrum, UV-VIS spectrum and TEM image of ethanol extracted clusters.	4
4	Laser dependent MALDI mass spectra of product **1**.	5
5	UV Vis spectrum and TEM image of PET protected silver NPs.	6
6	UV-Vis spectrum and TEM image of dark yellow supernatant after 2 h heating.	7
7	SEM/EDAX of product **3**.	8
8	TEM image of product **3**.	9

S1.Supplementary information 1

Experimental section

Materials

All the chemicals were commercially available and were used without further purification. Silver nitrate ($AgNO_3$, 99%), 2-phenylethanethiol (PET, 97%), tetraoctylammonium bromide (TOABr, 99%), sodium borohydride ($NaBH_4$) and trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) were purchased from Aldrich.

Instrumentation

UV/Vis spectra were measured with a Perkin Elmer Lambda 25 instrument in the range of 200-1100 nm. High resolution transmission electron microscopy of clusters was carried out with a JEOL 3010 instrument. The samples were drop casted on carbon-coated copper grids and allowed to dry under ambient conditions. Matrix-assisted laser desorption ionization mass spectrometry (MALDI MS) studies were conducted using a Voyager-DE PRO Bio-spectrometry Workstation from Applied Bio-systems. A pulsed nitrogen laser of 337 nm was used for the MALDI MS studies. The samples are mixed with DCTB matrix in 1:1 ratio and spotted on target plate and allowed to dry under ambient conditions. Mass spectra were collected in the negative ion mode and were averaged for 200 shots. Scanning electron microscopy (SEM) and energy dispersive X-ray (EDAX) analysis were done in a FEI QUANTA-200 SEM. For measurements, samples were drop casted on an indium tin oxide coated conducting glass and dried in ambient conditions.

Method of Jacobian correction

To amplify the less-intense absorption features, the data have been corrected with the Jacobian factor. For this, the experimentally obtained absorbance values as a function of wavelength [I(ω)], were converted to energy-dependent numbers [I(E)], using the expression,

$$I(E) = I(\omega)/\ \partial E/\partial \omega \propto I(\omega) * \omega^2$$

where $\partial E/\partial \omega$ represents the Jacobian factor.

S2. Supplementary information 2

Photographs during synthesis

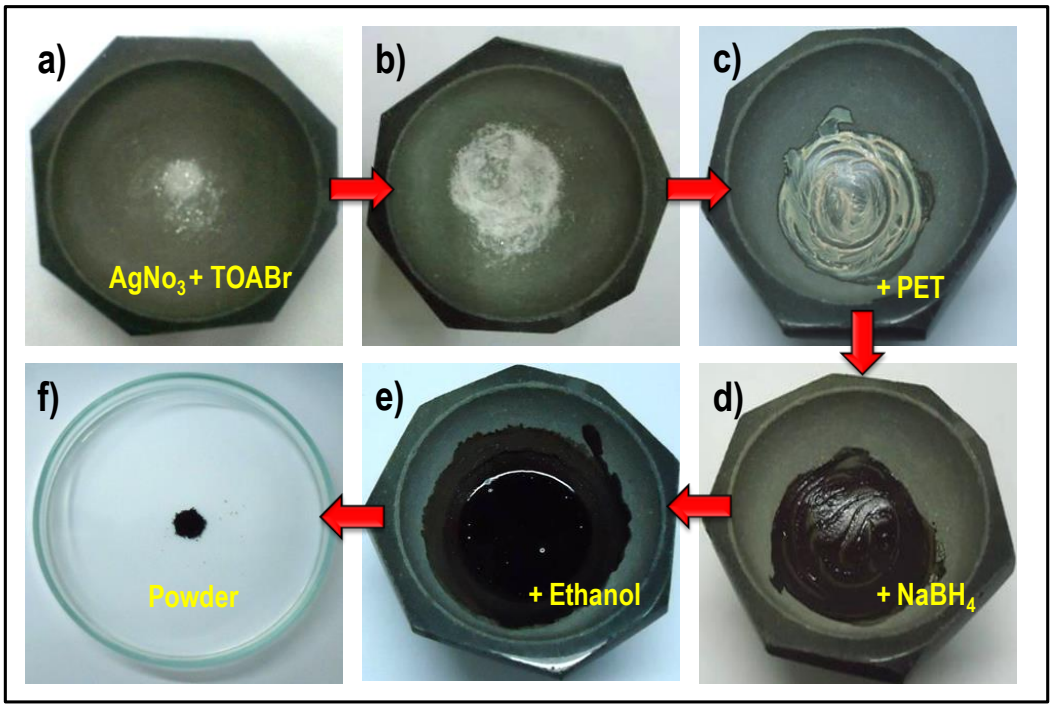


Figure S2. Photographs representing various stages during the synthesis of Ag@PET clusters. The mixture of silver nitrate and TOABr (a) was ground for 5 mins to obtain fine powder of uniform size (b). To that mixture, PET was added and ground well which shows a pale orange color, may be due to the formation of Ag (I) PET thiolate (c). Finally, $NaBH_4$(s) was added and ground uniformly (d). The final mixture was extracted with ethanol (e). This solution contains small clusters which show distinct peaks. After purification these clusters are extracted in toluene. Toluene was removed from the extract and a fine powder was obtained (f).

S3. Supplementary information 3

MALDI mass spectrum, UV/Vis spectrum and TEM of ethanol extracted clusters

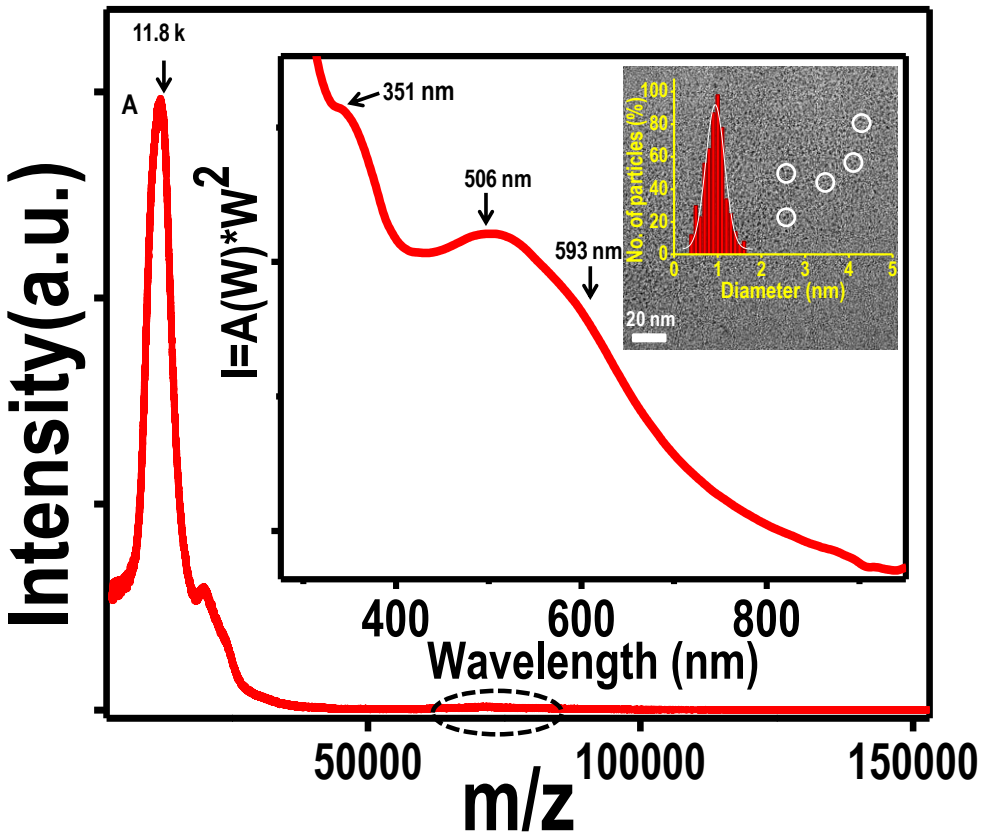


Figure S3. MALDI mass spectrum of Ag@PET clusters extracted in ethanol. Two small humps are arising at 62 and 72 k which are marked by a dotted line. Inset shows the corresponding optical absorption spectrum (corrected by the Jacobian factor). Inset of inset is TEM image and size distribution of the corresponding clusters. Some of the clusters seen are marked by white circles.

S4. Supplementary information 4

Laser dependent MALDI mass spectra of product 1

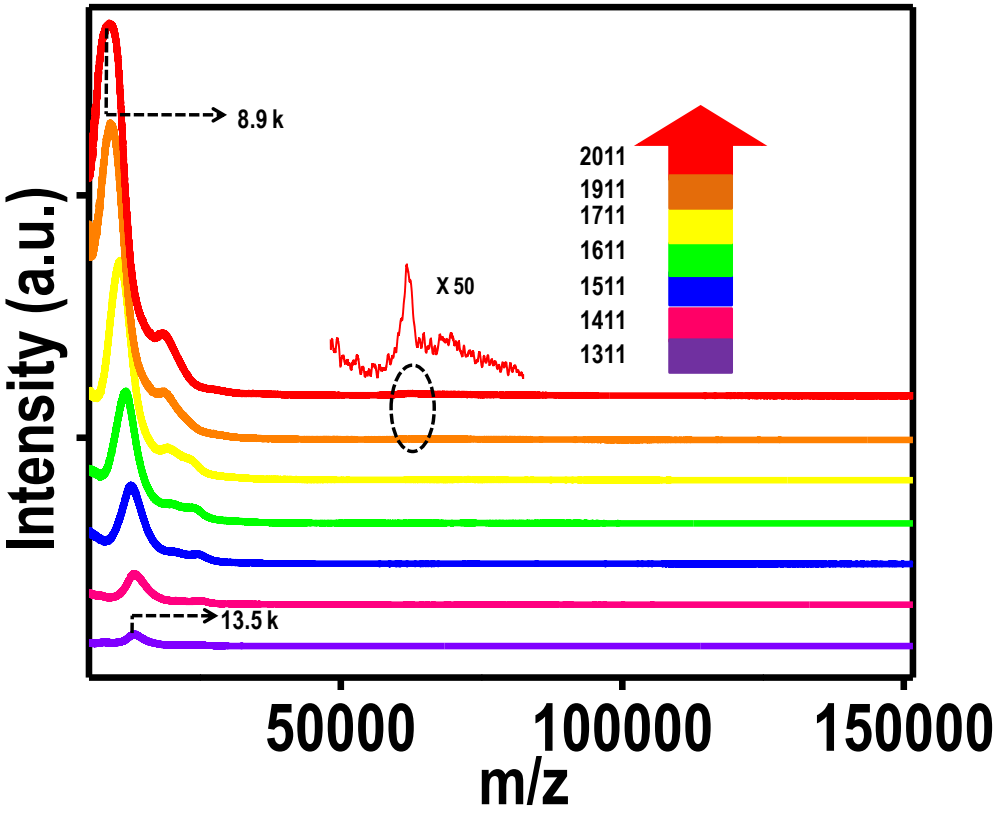


Figure S4. Laser dependent MALDI mass spectra of product **1** extracted in toluene. It shows a shift from 13.5 kDa to 8.9 kDa. This could be attributed to gradual fragmentation arising because of high laser power. The 27 k feature is due to the dimer of product **1**. A small hump near 78 k is seen at high laser power (Inset) which confirms the growth of clusters to form a stable plasmonic product **2**. This requires a higher laser power to desorb.

S5. Supplementary information 5

UV-Vis spectrum and TEM image of PET protected silver NPs

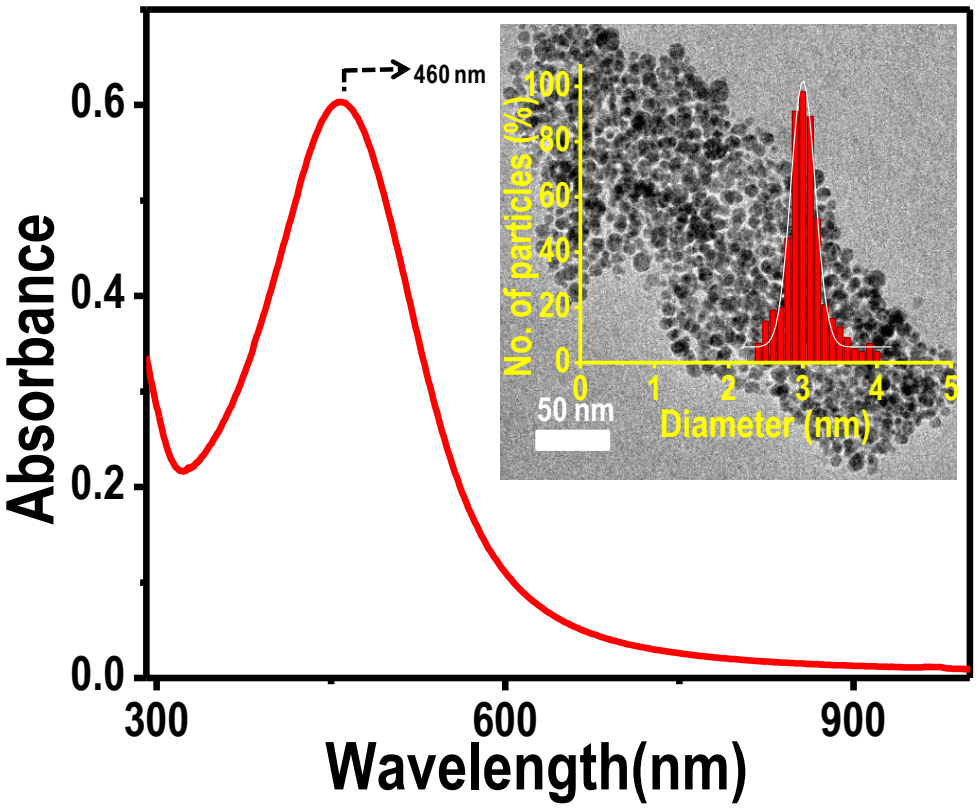


Figure S5. The UV-Vis spectrum of PET protected silver NPs showing a sharp SPR band at 460 nm. Inset shows the corresponding TEM image and size distribution.

S6. Supplementary information 6

UV/Vis spectrum and TEM image of dark yellow supernatant after 2 h heating.

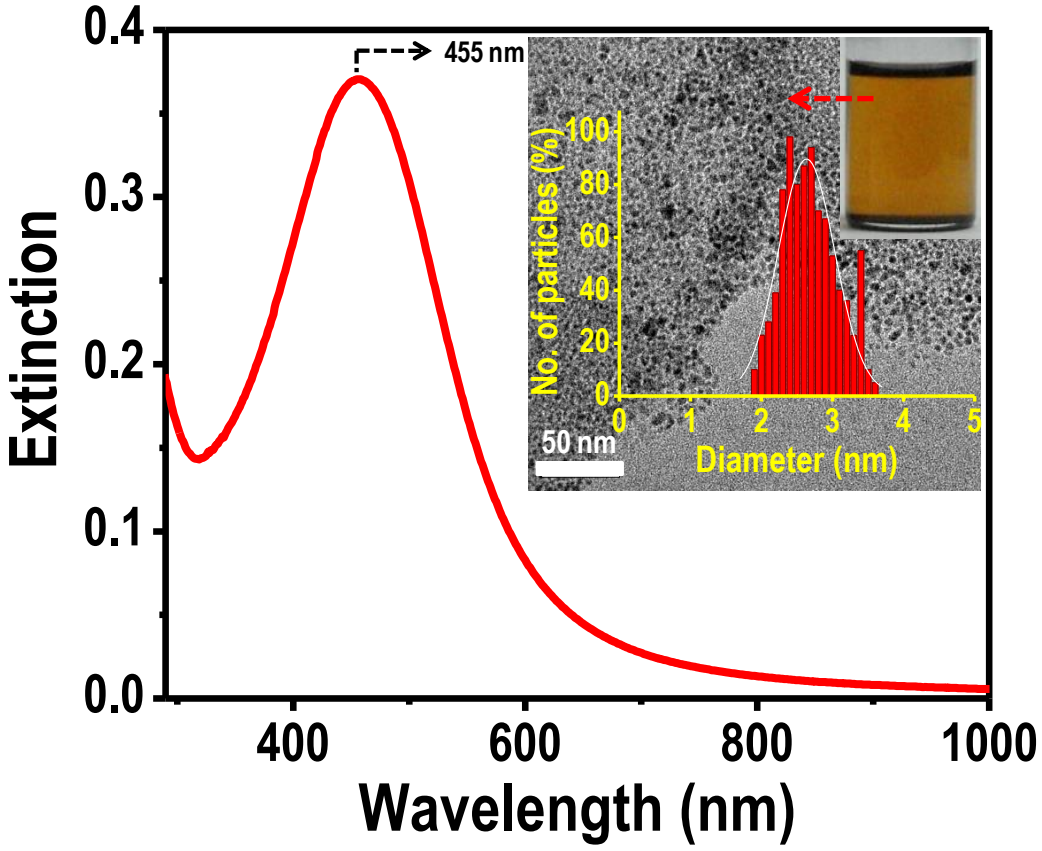


Figure S6. UV/Vis spectrum of the supernatant obtained after 2 h constant heating of product **2**. It shows a SPR band at 455 nm. Inset shows the corresponding TEM image, size distribution and photograph of the solution.

S7. Supplementary information 7

SEM/EDAX of product 3.

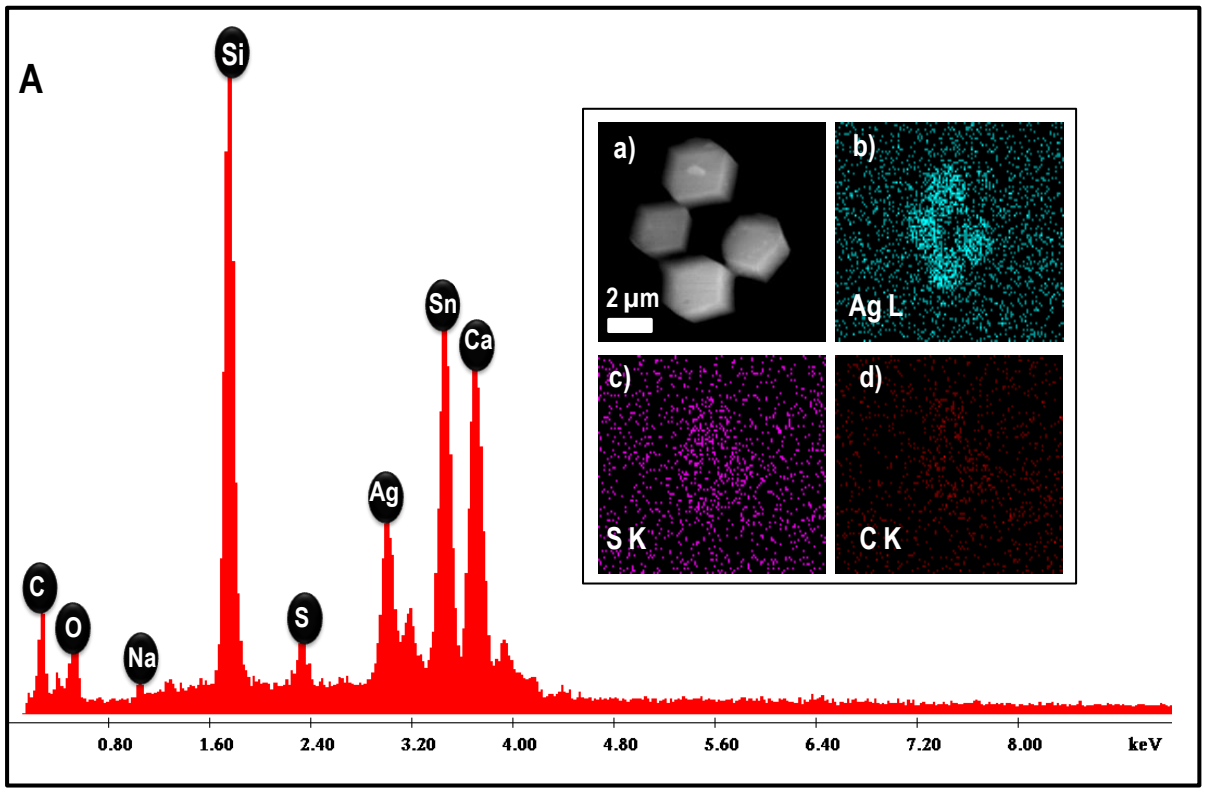


Figure S7. (A) SEM/EDAX spectrum of the SLs (taken on an ITO plate) which shows the presence of silver and sulphur with a ratio of 2.5:1 (Sn Kα, Ca Lα, Si Kα and O Kα are coming from the ITO sample plate). Insets: (a) The corresponding SEM image that shows crystals with sharp edges; (b), (c) and (d) are the elemental maps of Ag, S and C, respectively.

S8. Supplementary information 8

TEM image of product 3.

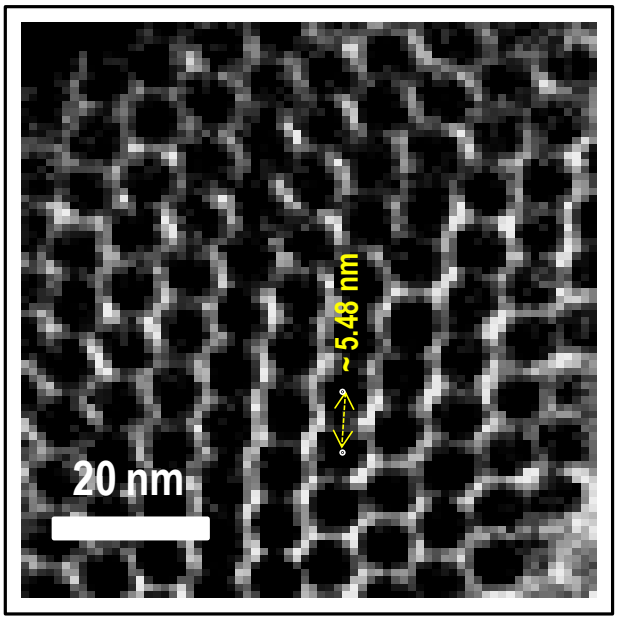
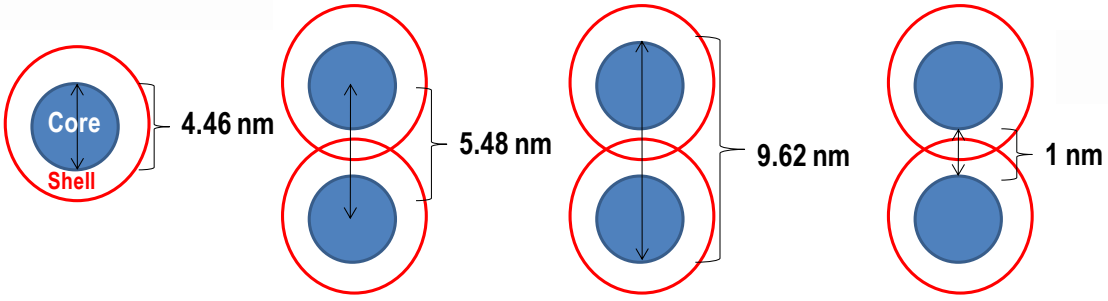
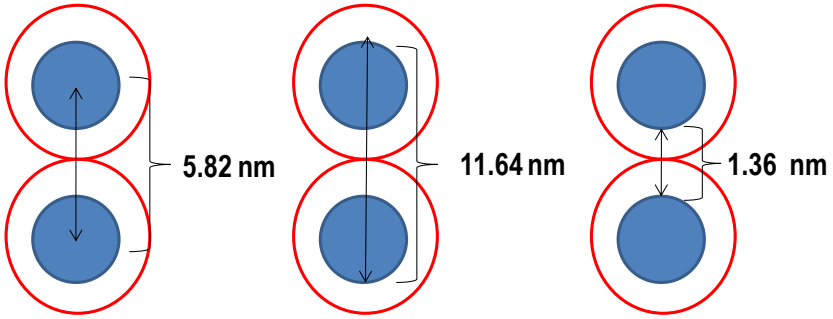


Figure S8. TEM image of product **3** showing definite periodicity and the interparticle distance is ~5.48 nm which is smaller than twice the distance of core+shell which confirms the interdigitation of monolayers. Details of the calculation of distances is below.

From TEM image



If there is no interdigitation



Here metal is considered as core and protecting ligand (PET) is considered as shell.
Chain length of PET is 0.68 nm or 6.8 A°.
Core diameter = 4.46 nm.
Core radius = 2.23 nm.
Chain length of PET = 0.68 nm.
So theoretically interparticle distance = 2 * core radius + 2 * PET chain length = 4.46 nm + 1.36 nm = 5.82 nm.
From TEM image the interparticle distance is 5.48 nm < 5.82 nm, this confirms the interdigitation of monolayers.
If there is no interdigitation, this distance between core of two particles will be twice the length of PET.