

## Electronic Supplementary Information (ESI)

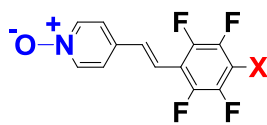
### Nanocrystallinity and Direct Cross-linkage as Key-Factors for the Assembly of Gold Nanoparticle-Superlattices

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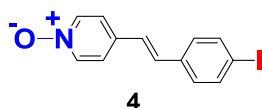
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#### Materials and Methods

Gold(III) chloride (99.9%; AuCl<sub>3</sub>; Aldrich) and 1,4-diiodotetrafluorobenzene (**3**, Apollo), were used as received. Toluene was dried and purified using an M. Braun solvent purification system. All glassware for the formation of nanoparticles (NPs) were cleaned by immersion in aqua regia (3:1 v/v, HCl/HNO<sub>3</sub>) and then washed with deionized (DI) water and triple-distilled water (TDW). *Caution: aqua regia solutions are extremely corrosive and may result in explosion or skin burns if not handled with extreme caution. It should be handled with care using appropriate personal protection.* Compounds **1**, **2** and derivatives (**2X**, X = F, Cl, Br) were prepared according to published procedures (Scheme 1).<sup>S1,S2</sup> UV/Vis spectra were recorded with a Cary 100 spectrophotometer in the double beam mode. Baseline measurements were recorded with THF. Transmission electron microscopy (TEM) samples were prepared by depositing a drop of the corresponding solution on 400-mesh formvar carbon-coated grids followed by blotting after 30 s. The samples were analyzed with a Philips (FEI Company, the Netherlands) CM-120 ST TEM operating at 120 kV. The images were recorded with a Gatan (Gatan USA) Ultrascan 1000 2k × 2k CCD camera. Data analysis was performed with DigitalMicrograph™ software V3.6.4. High-resolution TEM (HR-TEM) measurements were carried out on a Tecnai F30 UT microscope operating at 300kV (FEI Company, the Netherlands). The images were recorded with a Gatan (Gatan USA) Ultrascan 1000 2k × 2k CCD camera.

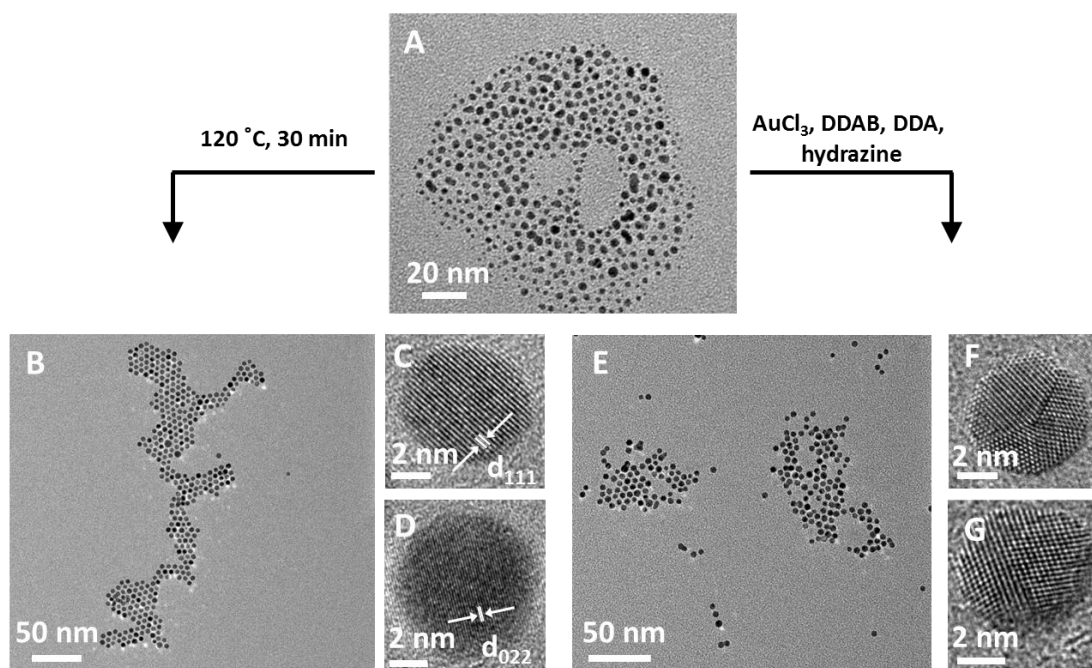


**Preparation of compound 4.** In a tri-necked round-bottom flask *E*-1-(*p*-iodophenyl)-2-(4-pyridyl)ethane (154 mg, 0.5 mmol)<sup>S2</sup> was dissolved in 10 mL CH<sub>2</sub>Cl<sub>2</sub>. Under N<sub>2</sub>, a CH<sub>2</sub>Cl<sub>2</sub> (3 mL) solution of *m*-CPBA (120 mg, 0.7 mmol) was added dropwise to the reaction flask for 15 min. at 0°C. The reaction was monitored by TLC and quenched by the addition of 0.1 mL triethylamine. The crude product was purified by column chromatography (silica, CH<sub>2</sub>Cl<sub>2</sub>:EtOH = 95:5 v/v) affording a yellow powder (68 mg, 42%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 8.23 (2 H, d, <sup>3</sup>*J* = 6.8 Hz), 7.72 (2 H, d, <sup>3</sup>*J* = 8.2 Hz), 7.40 (2 H, d, <sup>3</sup>*J* = 6.8 Hz), 7.25 (2 H, d, <sup>3</sup>*J* = 8.3 Hz), 7.11 (1 H, d, <sup>3</sup>*J* = 16.3 Hz), 6.98 (1 H, d, <sup>3</sup>*J* = 16.3 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>): δ (ppm) 139.25, 138.10, 136.36, 135.21, 132.28, 128.58, 124.42, 123.14, 94.81. HRMS (ES<sup>+</sup>) *m/z*: calc. for C<sub>13</sub>H<sub>11</sub>NOI<sup>+</sup> [M+H] 323.9885; found 323.9885. UV/Vis (acetonitrile): λ<sub>max</sub> (ε, cm<sup>-1</sup>M<sup>-1</sup>) = 353 nm (3.06 × 10<sup>4</sup>). For <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra, see Figure S11.



**Synthesis of single-crystalline DDA-capped Au NPs (SC<sub>Au</sub> NPs).** SC<sub>Au</sub> NPs were obtained by a modified published procedure.<sup>S3</sup> The AuNP seed solution was stirred for 0.5 h at 120 °C and then left to cool to room temperature. AuCl<sub>3</sub> was used as starting material instead of the reported HAuCl<sub>4</sub>·3H<sub>2</sub>O. Prior to use, SC<sub>Au</sub> NPs were diluted with THF to afford an absorption of *A* = 0.35 at λ<sub>max</sub> = 520 nm.

**Synthesis of Multiple-twinned DDA-capped Au NPs (MT<sub>Au</sub> NPs).** Multiple-twinned dodecyl amine (DDA)-capped AuNPs (MT<sub>Au</sub> NPs) were prepared in toluene according to the published seeded-growth method, using AuCl<sub>3</sub> instead of the reported HAuCl<sub>4</sub>·3H<sub>2</sub>O.<sup>S3</sup> Prior to use, MT<sub>Au</sub> NPs were diluted with THF to afford an absorption of *A* ≈ 0.35 at λ<sub>max</sub> = 519 nm, unless otherwise specified.



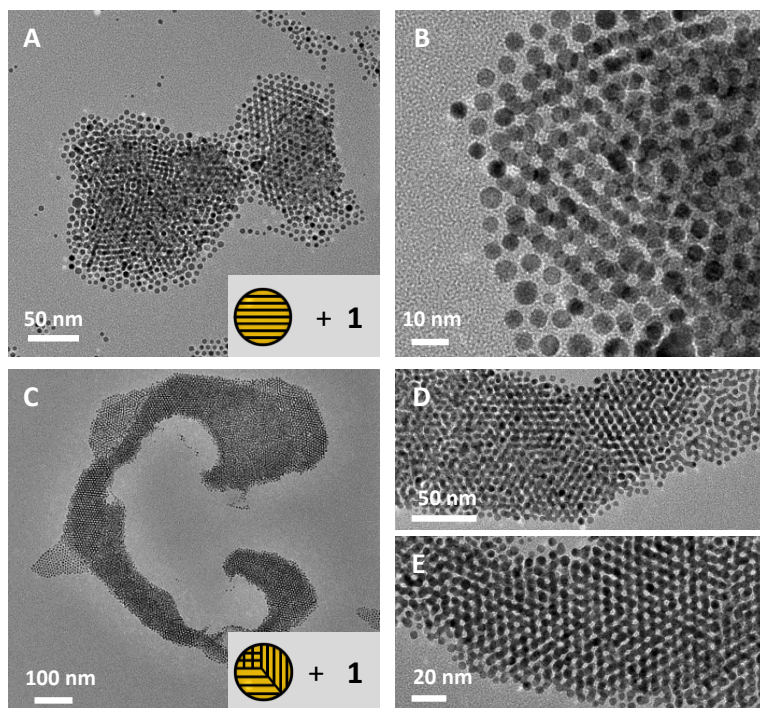
**Figure S1.** Representative TEM images of (A) as-prepared DDA-capped AuNPs (Au/DDA NPs) after reduction in the first step of synthesis (seed solution) Note that didecyldimethylammonium bromide (DDAB) is also present in the seed solution, (B-D) DDA-capped  $SC_{Au}$  NPs and (E-G) DDA-capped  $MT_{Au}$  NPs. Images C-D and F-G were obtained by HR-TEM. NP diameters:  $5.2 \pm 0.3$  nm and  $5.1 \pm 0.2$  nm, for DDA-capped  $SC_{Au}$  and  $MT_{Au}$  NPs, respectively. Analyses were performed using ImageJ on  $\sim 100$  AuNPs at different sample locations.

**Interactions between  $SC_{Au}$  and  $MT_{Au}$  NPs and cross-linker 1.** A DCM solution of compound **1** ( $185 \mu\text{L}$  or  $100 \mu\text{L}$ ,  $1 \text{ mM}$ ) was added to a THF solution of  $SC_{Au}$  or  $MT_{Au}$  NPs ( $3 \text{ mL}$ ,  $A \approx 0.65$  or  $0.35$ , respectively). THF was added to the resulting solutions up to a final volume of  $3.2 \text{ mL}$ . As a reference,  $200 \mu\text{L}$  DCM were added to the  $SC_{Au}$  or  $MT_{Au}$  NPs ( $3 \text{ mL}$ ,  $A \approx 0.65$  or  $0.35$ , respectively) solution. The reaction was monitored by UV/Vis spectroscopy and TEM analysis.

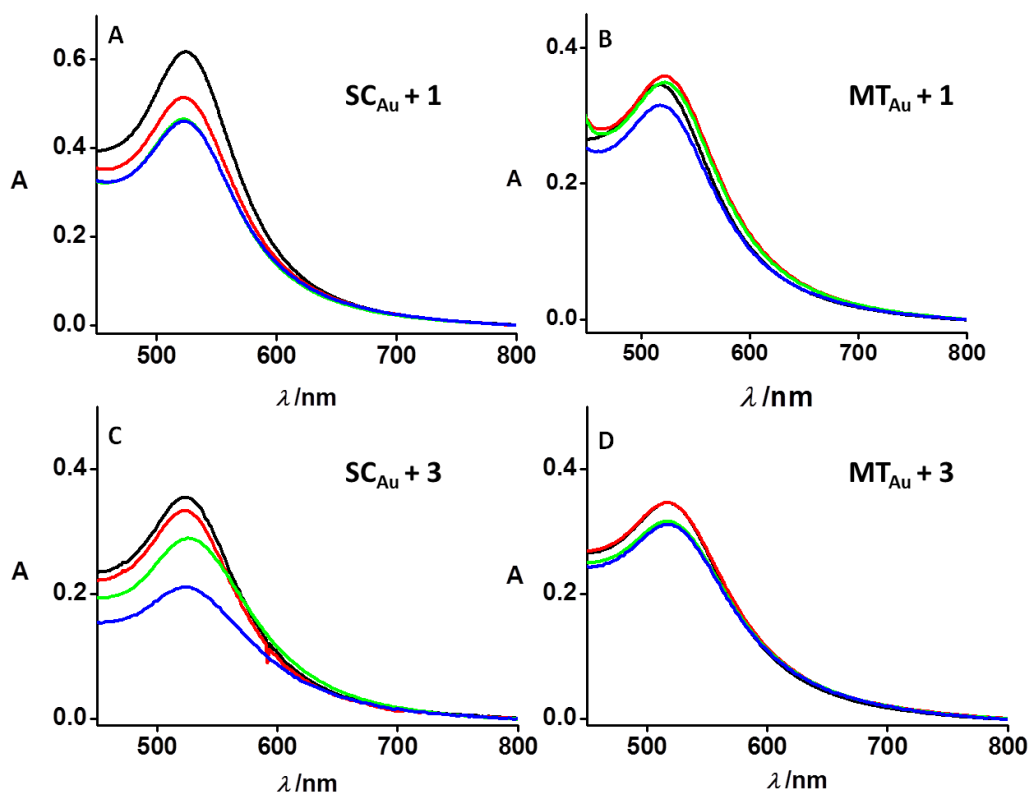
**Interactions between  $SC_{Au}$  and  $MT_{Au}$  NPs and cross-linkers 2, 2F, 3 and 4.** A THF solution of a cross-linker ( $20 \mu\text{L}$ ,  $5 \text{ mM}$ ) was added to a THF solution of  $SC_{Au}$  or  $MT_{Au}$  NPs ( $3 \text{ mL}$ ,  $A \approx 0.35$ ). THF was added to the resulting solutions up to a final volume of  $3.2 \text{ mL}$ . As a reference,  $200 \mu\text{L}$  THF were added to the  $SC_{Au}$  or  $MT_{Au}$  NPs ( $3 \text{ mL}$ ,  $A \approx 0.35$ ) solution. The reaction was monitored by UV/Vis spectroscopy and TEM analysis.

**Interactions between  $SC_{Au}$  and  $MT_{Au}$  NPs and cross-linkers 2X (X = Cl, Br).** A THF solution of a cross-linker ( $30 \mu\text{L}$ ,  $5 \text{ mM}$ ) was added to a THF solution of  $SC_{Au}$  or  $MT_{Au}$  NPs ( $3 \text{ mL}$ ,  $A \approx 0.5$ ). THF was added to the resulting solutions up to a final volume of  $3.2 \text{ mL}$ . As a reference,  $200 \mu\text{L}$  THF were added to the  $SC_{Au}$  or  $MT_{Au}$  NPs

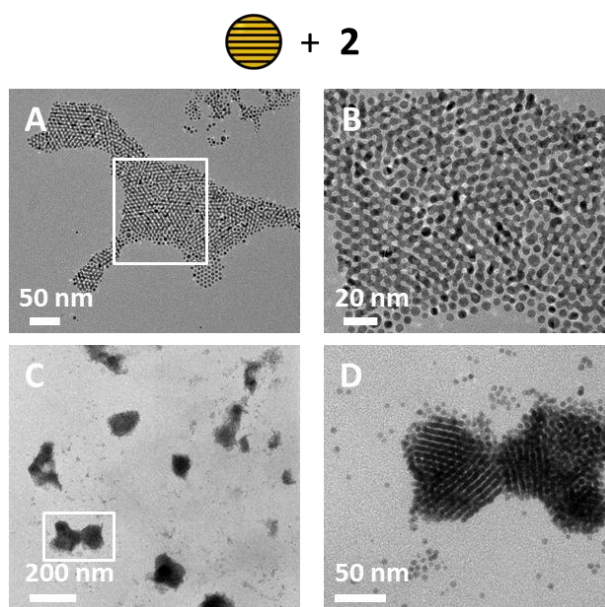
(3 mL,  $A \approx 0.5$ ) solution. The reaction was monitored by UV/Vis spectroscopy and TEM analysis.



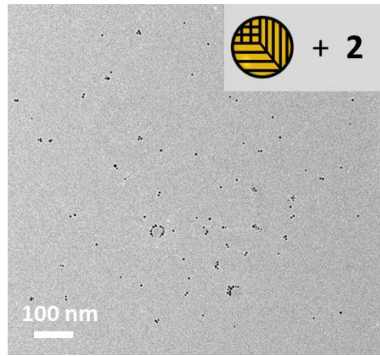
**Figure S2.** Representative TEM images of the (A-B)  $SC_{Au}/1$  and (C-E)  $MT_{Au}/1$  systems obtained upon aging of the corresponding  $SC_{Au}$  or  $MT_{Au}$  NPs with cross-linker **1** for 1 day.



**Figure S3.** Representative UV/Vis spectra monitoring the changes in surface plasmon resonance (SPR) band of (A,C)  $SC_{Au}$  NPs and (B,D)  $MT_{Au}$  upon addition of cross-linkers (A,B) **1** and (C,D) **3**. Color scheme: black, no addition of cross-linker; red, 1 d of aging; green, 5 d of aging; blue, 8 d of aging.

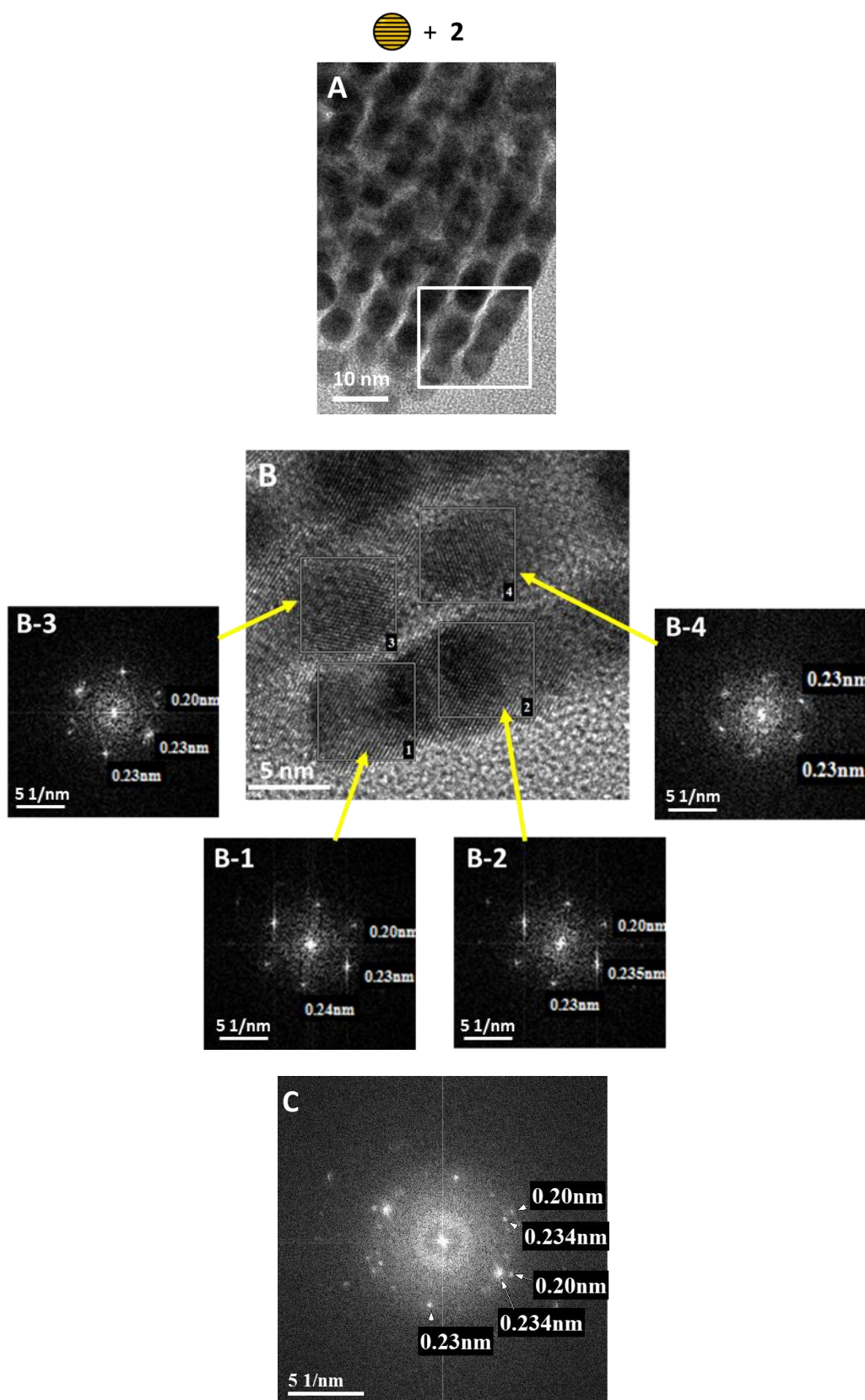


**Figure S4.** Representative TEM images of the  $SC_{Au}/2$  system aged for (A,B) 1 d or (C,D) 8 d. B and D are higher magnification images of the areas marked in A and C. Representative images of the  $SC_{Au}/2$  system aged for 10 d are shown in Figure 2.

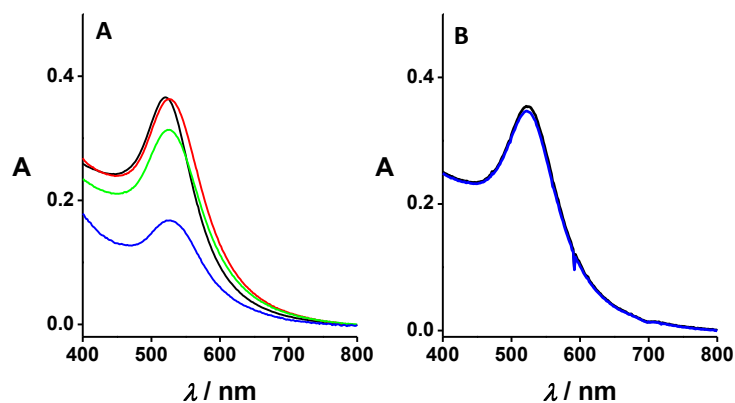


**Figure S5.** Representative TEM images of the  $\text{MT}_{\text{Au}}/2$  system aged for 1 d.

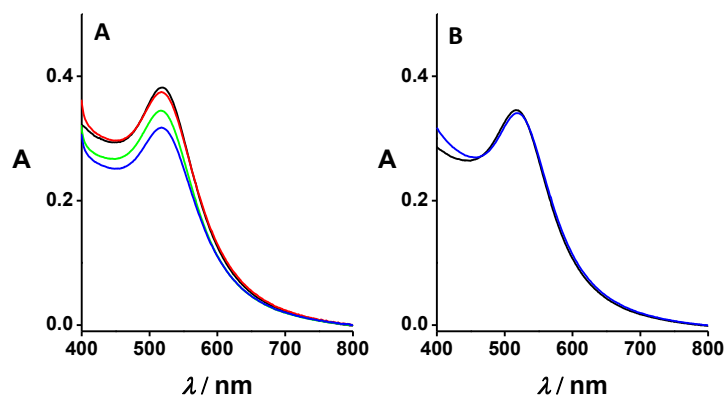




**Figure S6.** (A,B) HR-TEM images of the  $SC_{Au}/2$  system at 10 d aging time. B is a higher magnification image of the area marked in A. (B-1 to B-4) FFT of single nanoparticles according to the marked regions: (111) = 0.235 nm, (200) = 0.203 nm. (C) FFT pattern obtained for the image in B suggesting both translational and orientational order within the superlattice.

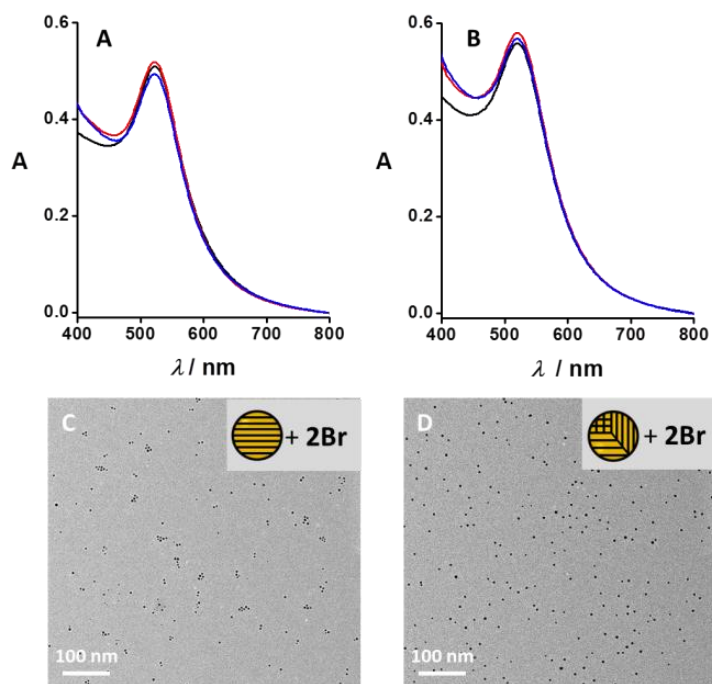


**Figure S7.** Representative UV/Vis spectra monitoring the changes in surface plasmon resonance (SPR) band of  $\text{SC}_{\text{Au}}$  NPs upon addition of cross-linker (A) **2** and (B) **2F**. Color scheme: black, before addition of cross-linker; red, 1 d of aging; green, 5 d of aging; blue, 8 d of aging.

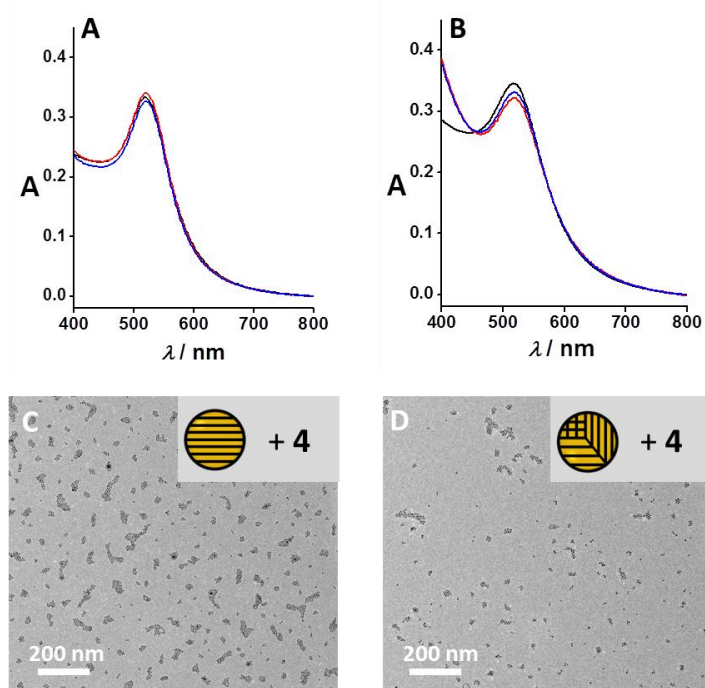


**Figure S8.** Representative UV/Vis spectra monitoring the changes in surface plasmon resonance (SPR) band of  $\text{MT}_{\text{Au}}$  NPs upon addition of cross-linker (A) **2** and (B) **2F**, respectively. Color scheme: black, before addition of cross-linker; red, 1 d of aging; green, 5 d of aging; blue, 8 d of aging.

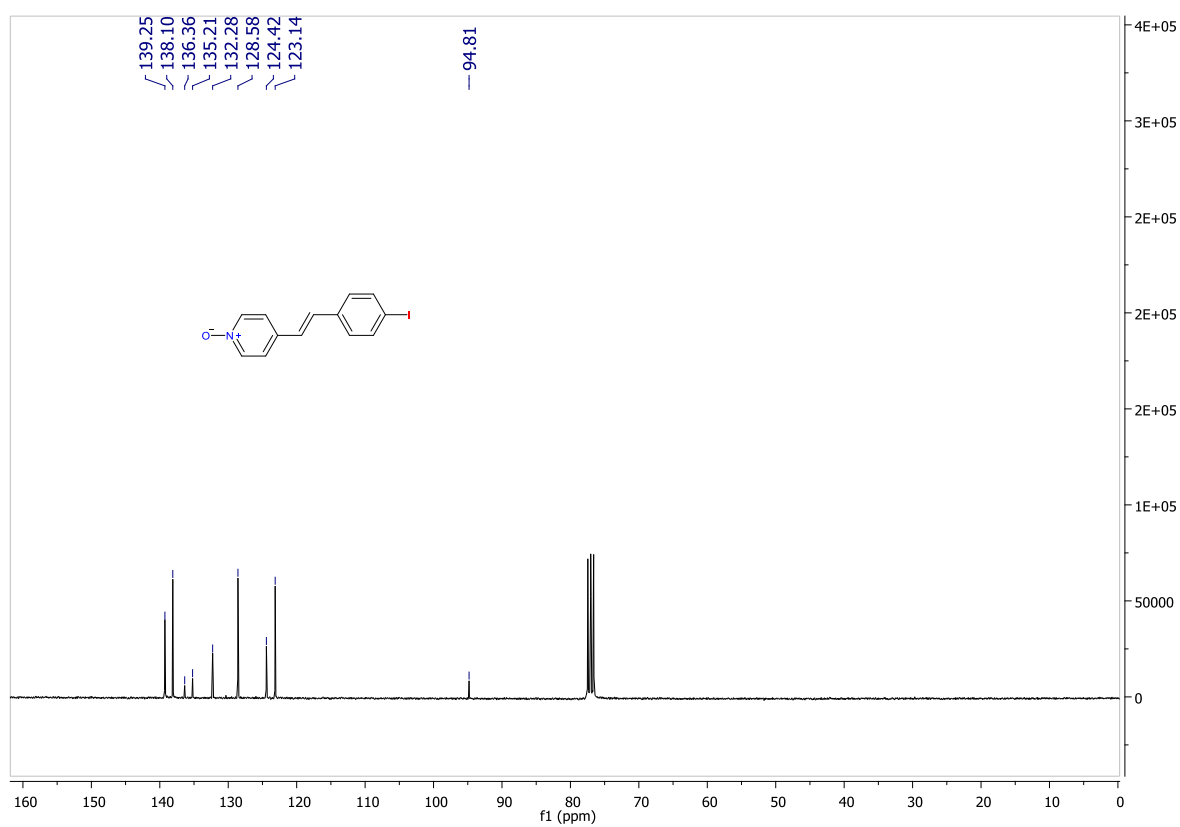
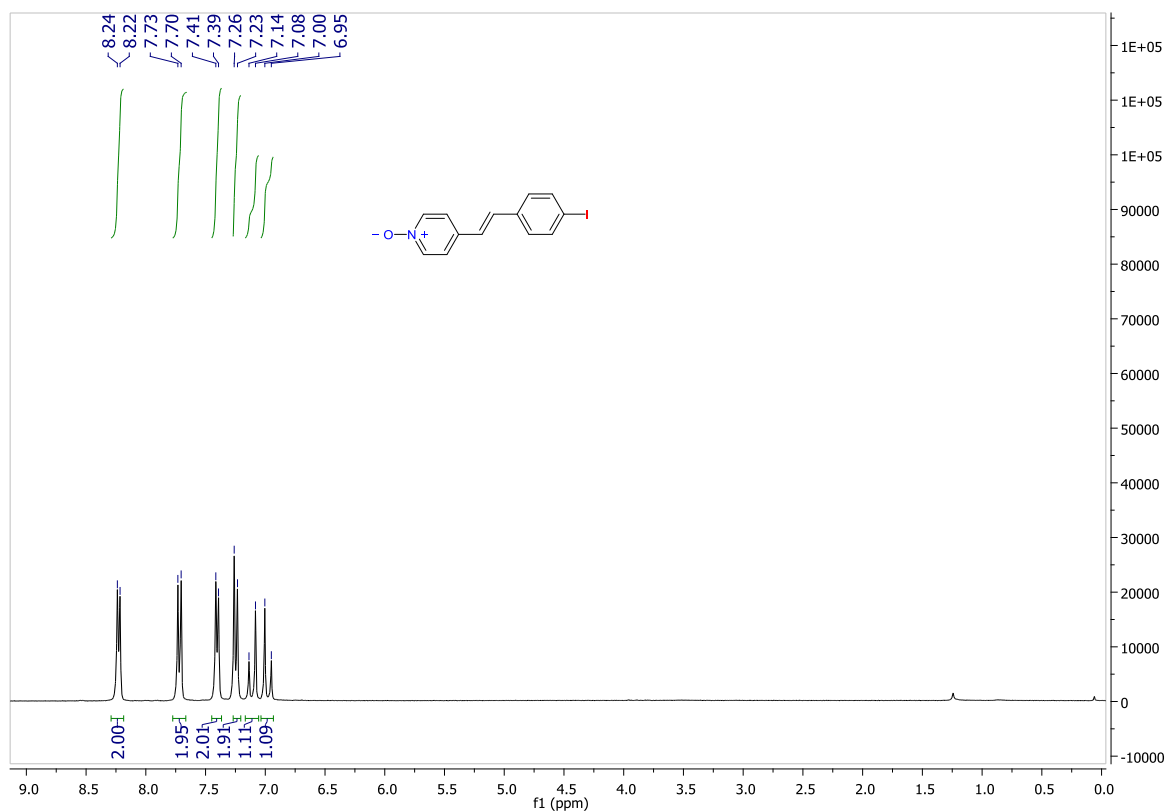




**Figure S9.** (A,B) Representative UV/Vis spectra monitoring the changes in surface plasmon resonance (SPR) band of (A)  $SC_{Au}$  NPs and (B)  $MT_{Au}$  NPs upon addition of compounds **2Cl** (blue) and **2Br** (red) aged for 14 d. The black trace is obtained for the Au NPs with no addition of the compounds. (C,D) Representative TEM images of  $SC_{Au}$  with **2Br** and  $MT_{Au}$  with **2Br** aged for 14 days.



**Figure S10.** (A,B) Representative UV/Vis spectra monitoring the changes in surface plasmon resonance (SPR) band of (A)  $SC_{Au}$  and (B)  $MT_{Au}$  NPs upon addition of non-fluorinated derivative (**4**) of cross-linker, forming  $SC_{Au}/4$  and  $MT_{Au}/4$  systems, respectively. Color scheme: black, no addition of **4**; red, 8 d of aging, blue, 15 d of aging. (C,D) Representative TEM images of  $SC_{Au}/4$  and  $MT_{Au}/4$  aged for 14 days.



**Figure S11.**  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of compound **4** in  $\text{CDCl}_3$ .

## References

- S1 M. Boterashvili, M. Lahav, T. Shirman, D. Freeman, M. E. van der Boom, *Angew. Chem. Int. Ed.*, 2012, **51**, 12268; T. Shirman, M. Boterashvili, M. Orbach, D. Freeman, L. J. W. Shimon, M. Lahav, M. E. van der Boom, *Cryst. Growth Des.*, 2015, **15**, 4756; T. Shirman, R. Kaminker, D. Freeman, M. E. van der Boom, *ACS Nano*, 2011, **5**, 6553.
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- S3 R. Klajn, K. J. M. Bishop, M. Fialkowski, M. Paszewski, C. J. Campbell, T. P. Gray, B. A. Grzybowski, *Science*, 2007, **316**, 261.