# Electronic Supplementary Information (ESI)

Molecularly-Mediated Assembly of Nanoparticles with Interparticle Rigid, Conjugated and Shaped Aryl Ethynyl Structures

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[a] Department of Chemistry, College of Chemistry and Chemical Engineering, Hunan University, Changsha, Hunan, 410082, China. [b] Department of Chemistry, State University of New York at Binghamton, Binghamton, New York 13902. USA. [c] Department of Chemistry, City University of New York, Staten Island, New York 10314, USA.

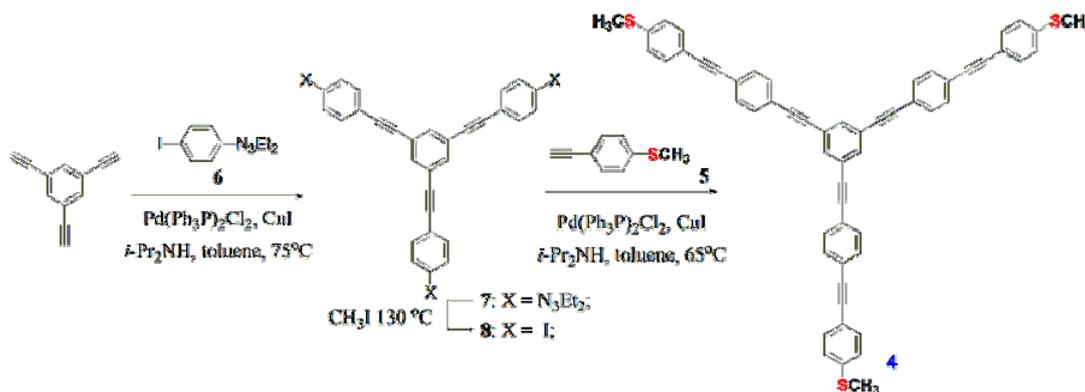## 1. Synthesis of Aryl Ethynyls:
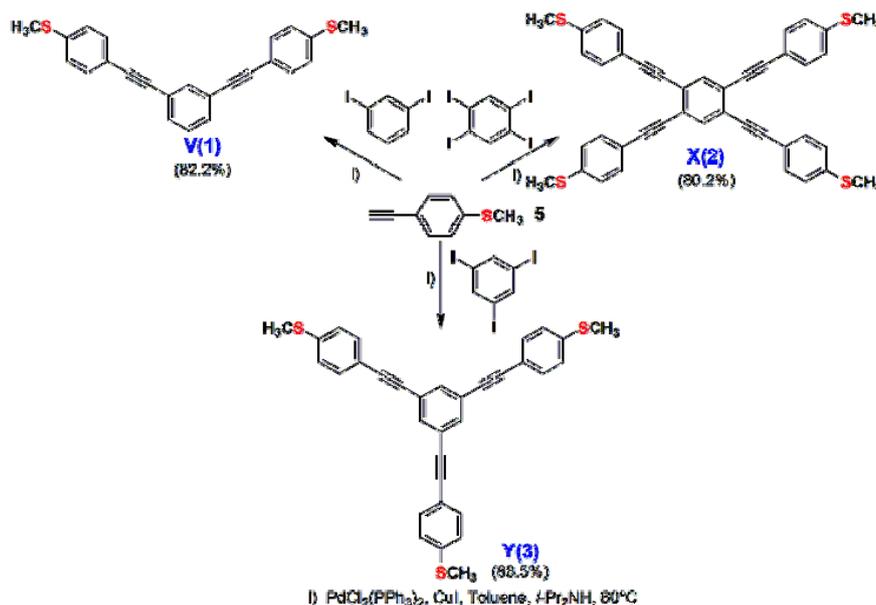
Scheme S1. Synthesis of V-, Y-, and X-shaped aryl ethynyl molecules **1**, **2**, **3** with different dimensions.

Synthesis of V (1). A 100 mL two-necked flask was charged with 1,3-diiodobenzene (329 mg, 1.0 mmol), $(Ph_3P)_2PdCl_2$ (140 mg, 0.2 mmol), CuI (38 mg, 0.2 mmol), diisopropylamine (5 mL), and toluene (20 mL) under nitrogen. Then, to the above suspension was added a solution of **5** (310 mg, 2.1 mmol) in diisopropylamine (5 mL) and toluene (20 mL) over a period of 10 h at 60 °C by a machine. The reaction mixture was cooled to room temperature and filtered. The filtrate was poured into aqueous NH_4Cl, and extracted with ethyl acetate. The extract was then washed with brine, dried over $MgSO_4$, and filtered. The solvent was evaporated in vacuo, and the residue was chromatographed (SiO_2; eluent, Hexane/CH_2Cl_2, 50 : 1) to give 303 mg of **V** (**1**) (82.2%) as a yellow solid. m.p. 120~121 °C. MS (APCI): 403.0(M^++1+CH_3OH, 100), 434.9(M^++1+2CH_3OH, 27); ^{1}H NMR(400 MHz, $CDCl_3$): 7.69(1H, s), 7.47(2H, d, J=8.00 Hz), 7.44(4H, d, J=8.40 Hz), 7.32(1H, d, J=8.00 Hz), 7.21(4H, d, J=8.40 Hz), 2.50(6H, s); ^{13}C NMR (100 MHz, $CDCl_3$): 139.61(2C), 134.46(CH), 131.91(4CH), 131.11 (2CH), 128.45(CH), 125.92(4CH), 123.68(2C), 119.28(2C), 89.80(2C≡), 88.65(2C≡), 15.38(2CH_3).

Synthesis of X (2). A 100 mL two-necked flask was charged with 1,2,4,5-tetraiodobenzene (200 mg, 0.34 mmol), $(Ph_3P)_2PdCl_2$ (48 mg, 0.068 mmol), CuI (26 mg, 0.136 mmol), diisopropylamine (5 mL), and toluene (20 mL) under nitrogen. Then, to the above suspension was added a solution of **5** (260 mg, 1.75 mmol) in diisopropylamine (5 mL) and toluene (20 mL) over a period of 10 h at 65 °C by a machine. The reaction mixture was cooled to room temperature and filtered. The filtrate was poured into aqueous NH_4Cl, and extracted with ethyl acetate. The extract was then washed with brine, dried over $MgSO_4$, and filtered. The solvent was evaporated in vacuo, and the residue was chromatographed (SiO_2; eluent, Hexane/CH_2Cl_2, 5 : 1) to give 183 mg of **X** (**2**) (80.2%) as brown solid. MS (APCI): 662.8(M^++1, 100), 694.8(M^++1+CH_3OH, 90); ^{1}H NMR(400 MHz, $CDCl_3$) 7.72(2H, s), 7.46(8H, d, J=8.40 Hz), 7.22(8H, d, J=8.40 Hz), 2.52(12H, s); ^{13}C NMR (100 MHz, $CDCl_3$): 140.05(4C), 134.62(2CH), 131.91(8CH), 125.73(8CH), 125.11(4C), 119.10(4C), 95.28(4C≡), 87.73(4C≡), 15.22(4CH_3).

Synthesis of Y (3). A 100 mL two-necked flask was charged with 1,3,5-triiodobenzene (200 mg, 0.44 mmol), $(Ph_3P)_2PdCl_2$ (62 mg, 0.088 mmol), CuI (33 mg, 0.18 mmol), diisopropylamine (5 mL), and toluene (20 mL) under nitrogen. Then, to the above suspension was added a solution of **5** (260 mg, 1.75 mmol) in diisopropylamine (5 mL) and toluene (20 mL) over a period of 10 h at 65 °C by a machine. The reaction mixture was cooled to room temperature and filtered. The filtrate was poured into aqueous NH_4Cl, and extracted with ethyl acetate. The extract was then washed with brine, dried over $MgSO_4$, and filtered. The solvent was evaporated in vacuo, and the residue was chromatographed (SiO_2; eluent, Hexane/CH_2Cl_2, 5 : 1) to give 200 mg of **Y (3)** (88.5%) as a white solid. m.p. 134~137 °C. MS (APCI): 549.0 (M^++CH_3OH+1, 100), 550.1 (M^++CH_3OH+2, 33), 551.1 (M^++CH_3OH+3, 25); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.51 (9H, s, SCH_3), 7.22 (6H, d, J = 8.4 Hz), 7.44 (6H, d, J = 8.4 Hz), 7.62 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 15.3 (SCH_3), 87.9 (C≡), 90.3 (C≡), 118.9 (C), 124.0 (C), 125.7 (CH), 131.9 (CH), 133.8 (CH), 139.8 (C).

Scheme S2. Synthesis of Y' -shaped aryl ethynyl.

Synthesis of Y' (4). Step 1. A 100 mL two-necked flask was charged with **6** (3.1 mmol), $(Ph_3P)_2PdCl_2$ (0.05 mmol), CuI (0.05 mmol), diisopropylamine (5 mL), and toluene (20 mL) under nitrogen. Then, to the above suspension was added a solution of 1,3,5-triethynylbenzene (1.0 mmol) in diisopropylamine (5 mL) and toluene (20 mL) over a period of 10 h at 75 °C by a machine. The reaction mixture was cooled to room temperature and filtered. The filtrate was poured into aqueous NH_4Cl, and extracted with ethyl acetate. The extract was then washed with brine, dried over $MgSO_4$, and filtered. The solvent was evaporated in vacuo, and the residue was chromatographed (SiO_2) to give **7**.

Step 2. A 50 mL sealed tube was charged with **7** (1.0 mmol) and methyl iodide (30 mL). The solution was kept at 135 °C for 20 h. The reaction mixture was filtered and then evaporated. The residue was chromatographed (SiO_2) to give **8**.

Step 3. A 100 mL two-necked flask was charged with **8** (1.0 mmol), $(Ph_3P)_2PdCl_2$ (0.20 mmol), CuI (0.20 mmol), diisopropylamine (5 mL), and toluene (20 mL) under nitrogen. Then, to the above suspension was added a solution of **5** (3.1 mmol) in diisopropylamine (5 mL) and toluene (20 mL) over a period of 10 h at 65 °C by a machine. The reaction mixture was cooled to room temperature and filtered. The filtrate was poured into aqueous NH_4Cl, and extracted with ethyl acetate. The extract was then washed with brine, dried over $MgSO_4$, and filtered. The solvent was evaporated in vacuo, and the residue was chromatographed (SiO_2) to give **Y' (4)**.

7. ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.33 (18H, t, J = 6.8 Hz), 3.81 (12H, q, J = 7.2 Hz), 7.10 (3H, t, J = 7.2 Hz), 7.29 (3H, t, J = 7.2 Hz), 7.44 (3H, d, J = 8.0 Hz) , 7.52 (3H, d, J = 8.0 Hz), 7.58 (3H, s).

8. ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.03 (3H, t, J = 7.2 Hz), 7.34 (3H, t, J = 7.2 Hz), 7.55 (3H, d, J = 7.6 Hz), 7.89 (3H, d, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 91.2 (C≡), 92.9 (C≡), 101.2 (C), 123.8 (CH), 127.9 (CH), 129.2 (C), 129.8 (CH), 132.6 (CH), 134.3 (C), 138.8 (CH).

Y' (4). Yellow solid; yield 85.1%; mp 268~272 °C. ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 2.51 (9H, s, CH_3), 7.21 (6H, d, J = 8.4 Hz), 7.45 (6H, d, J = 8.4 Hz), 7.51 (12H, s), 7.66 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 15.28 (SCH_3), 89.1 (C≡), 89.5 (C≡), 90.4 (C≡), 91.4 (C≡), 119.1 (C), 122.4 (C), 123.6 (C), 123.9 (C), 125.8 (CH), 131.5 (CH), 131.6 CH), 131.9 (CH), 134.1 (CH), 139.7 (C); MS (APCI): 816.1 (M^+, 48), 817.8 (M^++1, 100), 818.1 (M^++2, 74)) ; IR (KBr disk): 2918 (Aro. C-H), 2205(C≡C), 1575, 1508, 1085, 835, 817 cm^{-1}.

2. Synthesis of Au@TOA nanoparticles

The synthesis of gold nanoparticles (Au NPs) capped with a tetraoctylammonium (TOA^+) bromide monolayer (Au@TOA) followed the reported procedure [Fink, J.; Kiely, C. J.; Bethell, D.; Schiffrin, D. J. *Chem.*

Mater. **1998**, *10*, 922]. Briefly, $AuCl_4^-$ was first phase transferred to toluene by TOA^+Br^- (phase-transfer reagent and template agent), followed by adding an excess of aqueous reducing agent, $NaBH_4$. The reaction was then allowed to continue under stirring at room temperature for 1 hour. The aqueous phase of the resulting solution was removed, and further treated with drying agent to remove trace water. The resulting toluene solution contained gold nanoparticles capped with TOA^+Br^- (Au@TOA). The average size of the particles is shown to be 5.1 ±0.9 nm.

3. Additional Experimental Data:

The surface plasmon (SP) resonance band of gold nanoparticles (Au NPs) capped with a tetraoctylammonium (TOA+) bromide monolayer (5.1 ±0.9 nm) is 525 nm in toluene solution. 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. Table S1 shows the red shift of surface plasmon (SP) resonance band after gold nanoparticles assembled with different mediators.

Table S1. λ_{max} of surface plasmon (SP) resonance band assemblies of gold nanoparticles mediated by methylthio arylethynes: V (**1**)-, X (**2**)-, Y (**3**)-, and Y′ (**4**)

UV-Vis.	V (**1**)	X(**2**)	Y (**3**)	Y' (**4**)
SP band λ_{max}	930 nm	790 nm	670 nm	602 nm
$\Delta\lambda$	405 nm	265 nm	145 nm	77 nm

(A) (B) (C)
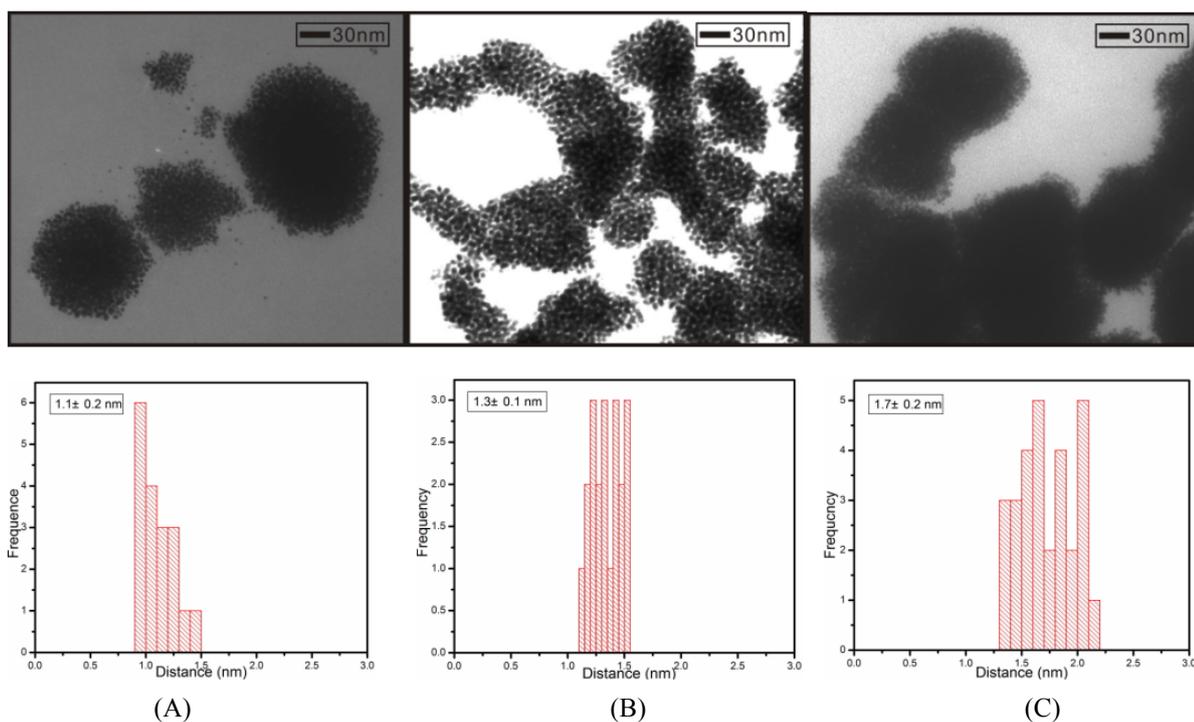
Figure S1. Top panel: TEM micrographs for samples from the assembly of Au NPs mediated by V(**1**), X(**2**) and Y(**3**). Bottom panel: the distribution charts for the measured edge-to-edge interparticle distance in these assemblies.

The measured average edge-to-edge interparticle distance values, ~1.1 nm for V(**1**) assembly, ~1.3 nm for X(**2**) assembly and ~1.7 nm for Y(**3**) assembly, are in good agreement with the molecular modeling results for the interparticle orientations defined by models in Figure 2B. Based on the models, a sum of the molecular dimension and the Au-S bond distance (~0.25 nm) would yield an interparticle edge-to-edge distance of 1.5 nm for X (**2**) and 2.0 nm for Y (**3**), respectively. For V(**1**), the interparticle edge-to-edge distance (1.2 nm) was conisdered to be defined by a combination of the flxible molecular linker (V) position and the minimum molecular capping (TOA) interdigitation).

Several sequences for introducing two different mediators to the solution of nanoparticles: adding Y (**3**) to the solution of V (**1**) mediated assembly (*S1*); adding X (**2**) to the solution of V (**1**) mediated assembly (*S2*); adding X (**2**) to the solution of Y (**3**) mediated assembly (*S3*), and adding V (**1**) to the solution of Y (**3**) (or X (**2**)) mediated assembly (*S4*).

Table S2. Summary of rate constants derived from kinetic fitting of SP band and DLS data.

Group	Mediator	k (s^{-1}) (from SP)	$(k_{2nd})/k_{1st}$	k (s^{-1}) (DLS)	$(k_{2nd})/k_{1st}$
S1 （**V+Y**)	V(1st)	5.04×10^{-3}	3.53	2.47×10^{-4}	1.78
	Y(2nd)	1.78×10^{-2}		4.40×10^{-4}	
S2 （**V+X**)	V(1st)	4.70×10^{-3}	1.72	2.47×10^{-4}	2.86
	X(2nd)	8.10×10^{-3}		7.07×10^{-4}	
S3 （**Y+X**)	Y(1st)	5.11×10^{-3}	5.18	4.05×10^{-4}	1.97
	X(2nd)	2.64×10^{-2}		7.97×10^{-4}	

Note: [mediator]/[Au] = 4.2 for SP measurement, and 8.1 for DLS measurement.

Table S3. Summary of the assembly sizes determined from the DLS data.

Mediators	Assembly size (1st)	Assembly size (2nd)
V (1st) – Y (2nd)	207 (nm)	688 (nm)
V (1st) – X (2nd)	199 (nm)	596 (nm)
Y (1st) – X (2nd)	321 (nm)	595 (nm)
X	243 (nm)	-

(A) (B) (C)
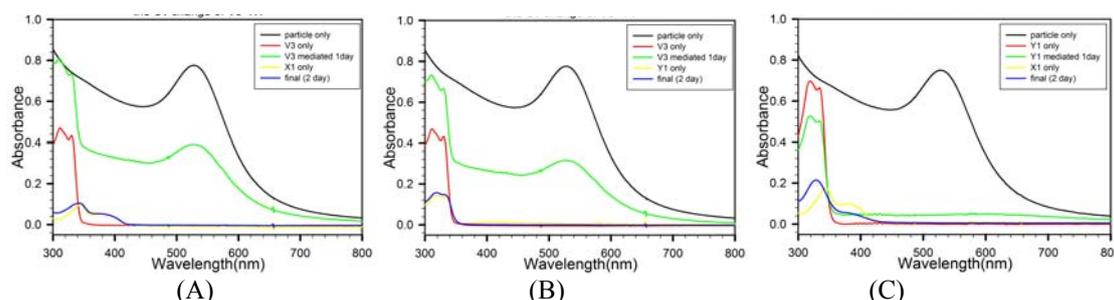
Figure S2. UV-Vis spectra for (A) Y (2nd) + (V (1st) + Au NPs); (B) X (2nd) + (V (1st) + Au NPs); and (C) X (2nd) + (Y (1st) + Au NPs) systems. The absorbance changes for the SP band at 520 nm and the band at 300-350 nm region characteristic of the 1st and the 2nd mediator aryl ethynyl molecules.

The measurement procedure is as follows: (1) After the formation of nanoparticle assembly mediated by the first ligand in toluene, the solution was centrifuged and the precipitation was collected. (2) 6 mL toluene and the second ligand were added to the precipitation, and the solution was then stirred overnight. (3) For the assembly thus formed, it contained mixed mediator ligands (1st and 2nd). The number of ligand molecules adsorbed onto the Au nanoparticles was determined by measuring the change of the absorbance for the corresponding bands in Figure S2, from which the change of the concentration of the molecules in the solution before and after the assembly was estimated based on solving the following equations involving the absorbance data for the two mediator molecules:

$$\begin{cases} A_{\lambda a(nm)} = A_{\lambda a(nm)}^{1st\ mediator} + A_{\lambda a(nm)}^{2nd\ mediator} \\ A_{\lambda b(nm)} = A_{\lambda b(nm)}^{1st\ mediator} + A_{\lambda b(nm)}^{2nd\ mediator} \end{cases}$$

$$\Rightarrow \begin{cases} A_{\lambda a(nm)} = \varepsilon_{\lambda a(nm)}^{1st\ mediator} \cdot b \cdot c^{1st\ mediator} + \varepsilon_{\lambda a(nm)}^{2nd\ mediator} \cdot b \cdot c^{2nd\ mediator} \\ A_{\lambda b(nm)} = \varepsilon_{\lambda b(nm)}^{1st\ mediator} \cdot b \cdot c^{1st\ mediator} + \varepsilon_{\lambda b(nm)}^{2nd\ mediator} \cdot b \cdot c^{2nd\ mediator} \end{cases}$$

The calculated results are summarized in Table S2, which used the ε values for different molecules at different wavelengths obtained from standard solutions of the corresponding molecules or nanoparticles (Table S3).

Table S4. summary of the concentration changes determined from UV-Vis data

1st ligand	2nd ligand	1st mediator			2nd mediator			
		$C_a^{initial}$	C_a^{final}	ΔC_a	$C_b^{initial}$	C_b^{final}	ΔC_b	$C_a^{released}$
V	Y	11.31	9.28	2.03	2.47	2.19	0.28	0.47
V	X	11.31	7.51	3.80	3.41	1.93	1.48	1.27
Y	X	10.11	7.05	3.06	4.53	2.17	2.36	1.35

Note: *a: first ligand; b: second ligand. $\varepsilon_{Au}^{525nm}=0.1779\times10^6$ M$^{-1}\cdot$ cm^{-1}. All concentration in μM.

An analysis of the relative changes in absorbance values for the spectrophotometric bands corresponding to the constituents in the mediated assembly was also performed to determine the ratio of the mediators vs. Au NPs and the competitive interparticle binding between two mediators in the above 1st - 2nd mediator assembly systems. Considering the V - Y system as an example, the V (1st)-NP assembly was first separated out from the solution by centrifugation, and was then re-dispersed in a fresh solution for further reacting with Y (2nd). In each step, the changes in concentration for each of the mediators were determined. As shown in S.I. **Table S4**, 18~34% of V (**1**) were found to be incorporated into the V-NP assembly. For the addition of the 2nd mediator (X (**2**), or Y (**3**)), about 43% of X (**2**), or 11% of Y (**3**), were found to be incorporated into the V-Y-NP and V-X-NP assemblies, respectively. As a result of the incorporation of X (**2**) or Y (**3**) into the assemblies, about 23% or 33% of V (**1**) were found to be released, respectively. In the case of Y-NP assembly, 30% of Y (**3**) was incorporated into the assembly. In the case of the 2nd mediator being X (**2**), about 52% of X were incorporated into the Y-X-NP assembly, and ~44% of Y (**3**) were released as a result of the incorporation of X (**2**) into the Y-X-NP assembly. On average, the ratio of the mediator vs. Au NPs was found to be one mediator per nanoparticle for these mediators (e.g., 1.4 for V (**1**), 1.5 for X (**2**) and 0.8 for Y (**3**) per Au NP). In addition, the relative changes of the incorporated 2nd mediator were found to be quite consistent with the released 1st mediators.

Table S5. Summary of ε values for different molecules at the indicated different wavelengths which were determined by standard calibration curves. The data in bold font are those ε values at the maximum absorbance for each of the molecules measured.

M.	λ(312 nm)	λ(319 nm)	λ(344 nm)	λ(525 nm)
Au NPs	1.863×10^5	1.813×10^5	1.679×10^5	**1.779×10^6**
V	**0.429×10^5**	0.394×10^5	0.380×10^5	0
Y	0.642×10^5	**0.703×10^5**	0.324×10^5	0
X	0.146×10^5	0.191×10^5	**0.405×10^5**	0

Note: the unit for all entries : M$^{-1}\cdot$ cm^{-1}
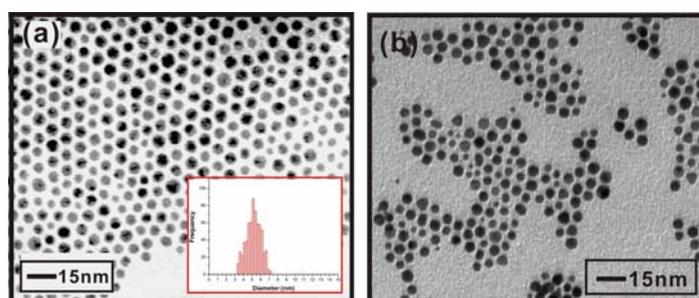
Figure S3. TEM micrographs for (a) as-synthesized Au nanoparticles capped with TOA$^+$Br$^-$ (insert: size distribution, 5.1 ± 0.9 nm); (b) Au nanoparticles in a after ligand exchange with decanethiols.
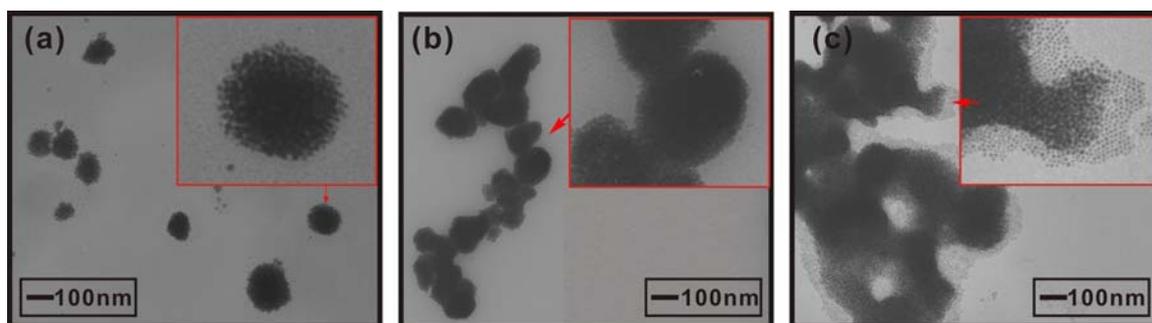
Figure S4. TEM micrographs for samples from: (a) the assembly of Au NPs mediated by mediator V (**1**); (b) the assembly of Au NPs mediated by mediator Y (**3**); (c) the assembly upon adding Y (**3**) to the solution of V (**1**) mediated assembly (inserts: magnified views of the indicated areas).