Supporting Information (S.I.)

Rigid, Conjugated and Shaped Arylethynes as Mediators for the Assembly of Gold Nanoparticles

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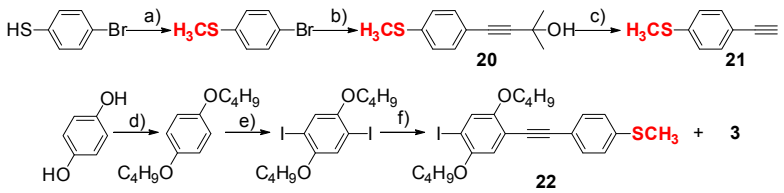
1. Additional experimental details for the synthesis of different methylthio arylethynes (MTAs)

*Synthesis of terminal function molecule **21**.* (4-ethynylphenyl)(methyl)sulfane **21** was prepared according to the procedures shown in Scheme S1. Reaction of 4-bromobenzenethiol with CH_3I afforded (4-bromophenyl)(methyl)sulfane, which was then reacted with 2-methylbut-3-yn-2-ol in Sonogashira reaction afforded **20**. The propan-2-ol group was next removed with KOH in toluene at 100 °C for 2 hr to give (4-ethynylphenyl)(methyl)sulfane (**21**).



Scheme S1. A schematic illustration for the synthesis of **21** and **22**. a) CH_3I, K_2CO_3, acetone, 50 °C, 2 hr; b) 2-methylbut-3-yn-2-ol, $PdCl_2(PPh_3)_2$, CuI, toluene, *i*-Pr_2NH, 50 °C; c) KOH, toluene, 100 °C, 2 hr; d) $CH_3(CH_2)_3Br$, K_2CO_3, acetone, 50 °C, 2 hr; e) KIO_4, I_2, CH_3COOH, H_2SO_4, H_2O, reflex; f) **21**, $PdCl_2(PPh_3)_2$, CuI, toluene, *i*-Pr_2NH, 50 °C.

*Synthesis of terminal function molecule **22**.* Normally, increasing the number of side chains decreases the transition temperatures and increases the solubility. While unsubstituted linear methylthio arylethynes (MTAs) is poor solubility, the long alkoxy side chains moieties enhances the solubility of the longer linear MTAs. 2,5-dibutoxy-1,4-diiodobenzene was generated by etherification of hydroquinone, iodination with 1,4-dibutoxybenzene. The synthesis proceeded followed by cross-coupling of **21** giving **22**. A co-product of **3** could also be produced (Scheme S1).

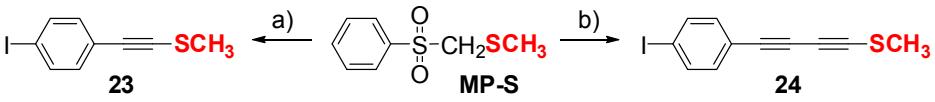
22 and **3**: To a nitrogen purged flask were added 2,5-dibutoxy-1,4-diiodobenzene (1.26 g, 2.65 mmol), $(Ph_3P)_2PdCl_2$ (91 mg, 0.13 mmol), CuI (25 mg, 0.13 mmol), diisopropylamine (5 mL), and toluene (20 mL). Then, to the above suspension was added a solution of **21** (410 mg, 2.77 mmol) in diisopropylamine (2.5 mL) and toluene (10 mL) over a period of 5 hr 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 subjected to a silica-gel chromatography (SiO_2; eluent, Hexane/CH_2Cl_2, 2: 1) to give 446 mg of **22** (33.9%) as a yellow solid. m.p. 85~87 °C, (SiO_2; eluent, Hexane/CH_2Cl_2, 1: 1) to give 350 mg of **3** (25.6%) as a yellow solid. m.p. 102~104 °C.

22: ^{1}H NMR ($CDCl_3$, 400 MHz): 1.0 (t, J = 7.2 Hz, 6H), 1.6 (m, 4H), 1.8 (m, 4H), 2.5 (s, 3H), 4.4 (m, 4H), 6.9 (s, 1H), 7.2 (d, J = 8.4 Hz, 2H), 7.3 (s, 1H), 7.4 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): 13.8 (CH_3), 13.9 (CH_3), 15.4 (SCH_3), 19.2 (CH_2), 19.3 (CH_2), 31.3 (CH_2), 31.3 (CH_2), 69.6 (CH_2), 69.8 (CH_2), 85.6 (C≡), 87.4 (C≡), 94.0 (C), 109.8 (C), 113.7 (C), 115.9 (CH), 123.9 (CH), 125.8 (CH), 131.8 (CH), 131.8 (C), 151.9 (C), 154.3 (C); MS(APCI) *m/z* (%): 494.8 (M^+,100), 368 (M^+-I, 94).

3: ^{1}H NMR ($CDCl_3$, 400 MHz): 1.0 (t, J= 7.2 Hz, 6H), 1.6 (m, 4H), 1.8 (m, 4H), 2.5 (s, 6 H), 4.0 (t, J= 6.8 Hz, 4H), 7.0 (s, 2H), 7.2 (d, J= 8.4 Hz, 4 H), 7.4 (d, J= 8.8 Hz, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): 13.9 (CH_3), 15.4 (SCH_3), 19.3 (CH_2), 31.4 (CH_2), 69.3 (CH_2), 86.1 (C≡), 94.7 (C≡), 113.9 (C), 116.9 (CH), 119.8 (C), 125.8 (CH), 131.8 (CH), 139.3 (C), 153.6 (C); IR (KBr, disk) *v*: 2953, 2922, 2853, 2204, 1590, 1505, 1486, 1431, 833, 743 cm^{-1}; MS(APCI) *m/z* (%): 515 (M^++H^+, 100), 458 (M^++H^+-C_4H_9, 25).

Synthesis of terminal functional *molecules **23** and **24***. Using methylthiomethyl phenyl sulfone (MP-S) reacted with benzaldehyde and 3-phenylpropiolaldehyde in one-pot reaction gave methylthio aryldiynes **23**, **24** in good yield, respectively (Scheme S2). This method is quite simple and does not require a tedious separation of the reaction mixture. A typical synthetic procedure is as followed: to a solution of MP-S in THF was orderly added BuLi (1.0 eq), benzaldehyde or 3-phenylpropiolaldehyde (1.0 eq), diethyl chlorophosphate $ClP(O)(OEt)_2$ (1.2 eq), and lithium diisopropylamide (LDA) (2.5 eq). After the usual workup, the residue subjected to a silica-gel chromatography to give **23** and **24** in 87.5% and 81.5% yield, respectively.



23 **MP-S** **24**

Scheme S2. A schematic illustration for the synthesis of **23** and **24**. a) BuLi, 4-iodobenzaldehyde, diethyl chlorophosphate, lithium diisopropylamide, -78 °C; a) BuLi, 3-(4-iodophenyl)propiolaldehyde, diethyl chlorophosphate, lithium diisopropylamide, -78 °C.

23 and **24:** To a solution of **MP-S** (2.0 mmol) in dry THF (25 mL) was added dropwise BuLi (2.5 M in hexane, 0.8 mL, 2.0 mmol) at –78 °C under nitrogen. The solution was stirred for 10 min. A solution of 4-iodobenzaldehyde or 3-(4-iodophenyl)propiolaldehyde (2.0 mmol) in dry THF (3 mL) was

added dropwise, and the mixture was stirred for 10 min. After diethyl chlorophosphate (2.4 mmol) was added dropwise to the reactant, the cooler was removed. The system was then allowed to warm up to room temperature naturally and stirred for 30 min. The solution was recooled to –78 °C and LDA (5.0 mmol) was added. After stirring for 30 min, the reaction was quenched with saturated NH_4Cl solution. The mixture was diluted with water and extracted with ethyl acetate (30 mL×3). The organic layer was washed (brine), dried ($MgSO_4$), filtered and evaporated. The residue was purified by silica gel column chromatography.

23, white solid; yield 70.0%; mp 56~57 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): 2.6 (s, 3H), 7.1 (d, J = 8.4 Hz, 2H), 7.6 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): 19.2 (S**C**H_3), 82.8 (C≡), 90.9 (C≡), 93.7 (C), 122.7 (C), 123.7 (CH), 137.3 (CH); MS (EI) *m/z* (%): 273.93 (M^+, 100).

24, pale yellow solid; yield 89.4%; mp 92~93 °C. ^{1}HNMR (DMSO-d_6, 400 MHz): 2.5 (s, 3H), 7.3(d, J = 8.4Hz, 2H), 7.8 (d, J = 8.4Hz, 2H); ^{13}CNMR (DMSO-d_6, 100 MHz): 18.8 (SCH_3), 75.5 (C≡), 77.1 (C≡), 78.1 (C≡), 78.5 (C≡), 97.3 (C), 120.2 (C), 134.2 (CH), 137.9 (CH); MS (EI) *m/z* (%): 298 (M^+, 100).

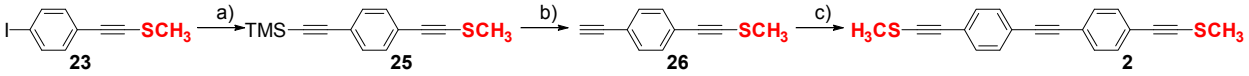
*Synthesis of compound **1***. To a nitrogen purged flask were added **21** (500 mg, 3.37 mmol), $(Ph_3P)_2PdCl_2$ (471 mg, 0.67 mmol), CuI (128 mg, 0.67 mmol), diisopropylamine (5 mL), and toluene (20 mL). After the mixture was stirred at 65 °C for 4 hr, the reaction mixture was cooled to room temperature 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 subjected to a silica-gel chromatography (SiO_2; eluent, Hexane) to give 0.84 g of **1** (85.1%) as a yellow solid. m.p. 189 ~ 190 °C. ^{1}H NMR(400 MHz, $CDCl_3$): 7.4(d, J = 8.4 Hz, 4H), 7.2(d, J = 8.4 Hz, 4H), 2.5(s, 6H); ^{13}C NMR(100 MHz, $CDCl_3$): 161.9 (C), 140.9(C), 132.7(CH), 125.7 (CH), 81.6(C≡), 74.1 (C≡), 15.2 (CH_3); MS(APCI) *m/z* (%): 326.9(M^++H^++CH_3OH, 100).

21 **1**

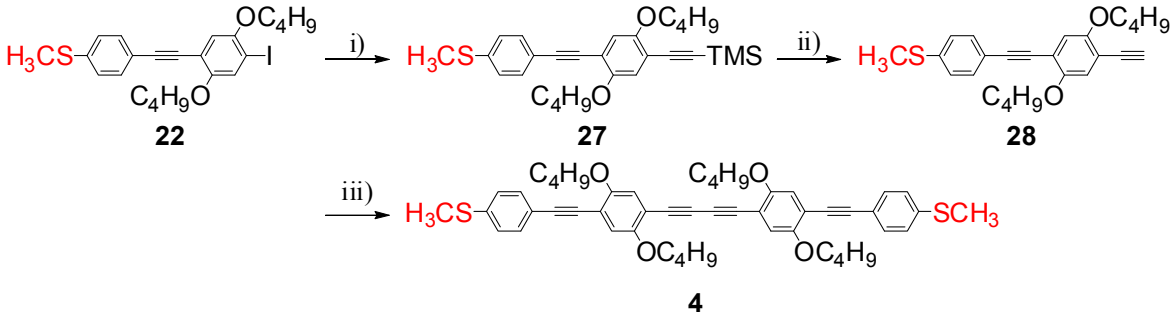
Scheme S3. A schematic illustration for the synthesis of **1**. i) $PdCl_2(PPh_3)_2$, CuI, toluene, *i*-Pr_2NH, 50°C.

*Synthesis of compound **2***. To a nitrogen purged flask were added **23** (328 mg, 1.2 mmol), $(Ph_3P)_2PdCl_2$ (168 mg, 0.2 mmol), CuI (46 mg, 0.2 mmol), diisopropylamine (5 mL), and toluene (20 mL). Then, to the above suspension was added a solution of **26** (172 mg, 1.0 mmol) in diisopropylamine (2.5 mL) and toluene (10 mL) over a period of 10 hr 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 subjected to a silica-gel chromatography (SiO_2; eluent, Hexane/CH_2Cl_2, 10: 1) to give 248 mg of **2** (78%) as a white solid. m.p. 189 ~ 190 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 2.5 (s, 6H), 7.4 (d, J = 8.4 Hz, 4H), 7.4 (d, J = 8.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): 19.4 (S**C**H_3), 83.4 (C≡), 90.8 (C≡), 91.6 (C≡), 122.5 (C), 123.4 (C), 131.2 (CH), 131.4 (CH); IR (KBr, disk) v: 2954, 2925, 2854, 2160, 1921, 1680, 1510, 1460, 1406, 1377, 1308, 837, 540 cm^{-1}; MS(APCI) m/z (%): 350.9 (M^++MeOH+H^+, 100).



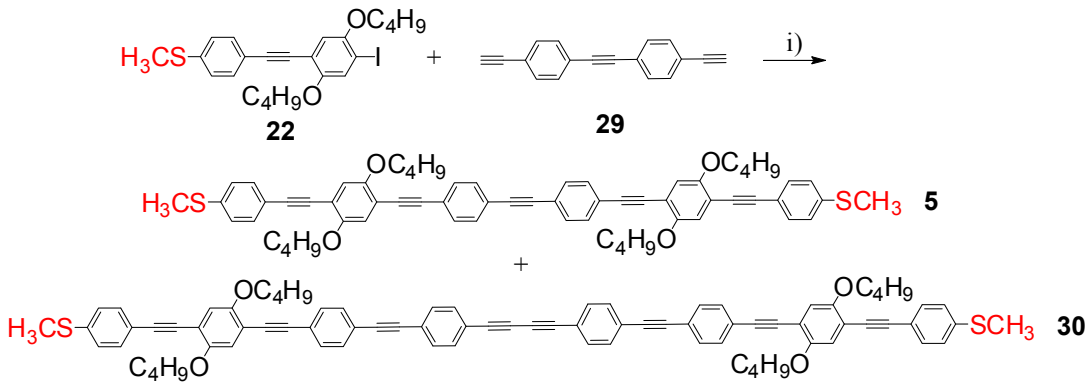
Scheme S4. A schematic illustration for the synthesis of **2**. a) TMSA, $PdCl_2(PPh_3)_2$, CuI, toluene, i-Pr_2NH, 50 °C; b) K_2CO_3, Acetone, r.t.; c) **23**, $PdCl_2(PPh_3)_2$, CuI, toluene, i-Pr_2NH, 65 °C.



Scheme S5. A schematic illustration for the synthesis of **4**. i) TMSA, $PdCl_2(PPh_3)_2$, CuI, toluene, i-Pr_2NH, 50°C; ii) K_2CO_3, Acetone, r.t.; iii) **28**, $PdCl_2(PPh_3)_2$, CuI, toluene, i-Pr_2NH, 65 °C.

Synthesis of compound 4. To a nitrogen purged flask were added **28** (370 mg, 0.94 mmol), $(Ph_3P)_2PdCl_2$ (132 mg, 0.19 mmol), CuI (36 mg, 0.19 mmol), diisopropylamine (5 mL), and toluene (20 mL). Then, the mixture stirred over a period of 10 hr at 65 °C. The reaction mixture was cooled to room temperature and filtered. The filtrate was poured into aqueous NH_4Cl, and extracted with ethyl acetate. The solvent was evaporated in vacuo, and the residue subjected to a silica-gel chromatography (SiO_2; eluent, Hexane/CH_2Cl_2, 10: 1) to give 570 mg of **4** (78%).

4: ^{1}H NMR ($CDCl_3$, 400 MHz): 1.0 (t, J = 7.2 Hz, 6H), 1.6 (m, 4H), 1.8 (m, 4H), 2.5 (s, 3H), 4.4 (m, 4H), 6.9 (s, 1H), 7.0 (s, 1H), 7.2 (d, J = 8.4 Hz, 2H), 7.4 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): 13.9 (CH_3), 15.3 (SCH_3), 19.2 (CH_2), 19.3 (CH_2), 31.2 (CH_2), 31.3 (CH_2), 69.2 (CH_2), 69.4 (CH_2), 79.2 (C≡), 79.5 (C≡), 85.9 (C≡), 95.4 (C≡), 112.3 (C), 115.1 (C), 116.7 (CH), 117.6 (CH), 119.5 (C), 125.7 (CH), 131.8 (CH), 139.5 (C), 153.3 (C), 154.9 (C).

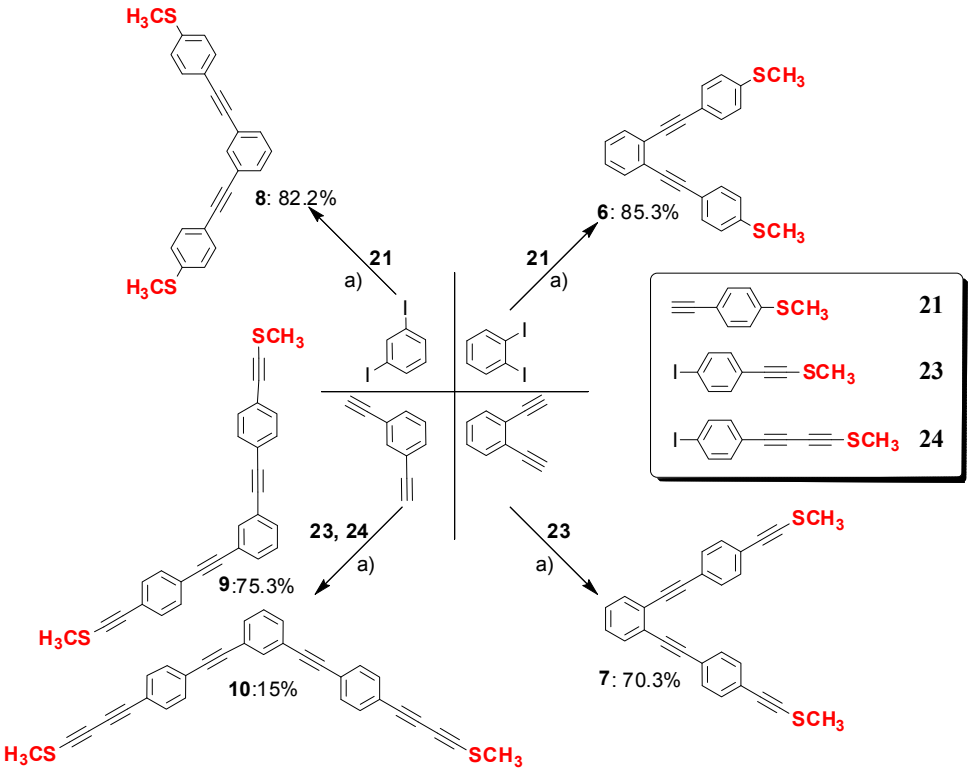


Scheme S6. A schematic illustration for the synthesis of **5**. i) $PdCl_2(PPh_3)_2$, CuI, toluene, *i*-Pr_2NH, 65°C.

Synthesis of compound ***5***. To a nitrogen purged flask were added **22** (138 mg, 0.28 mmol), $(Ph_3P)_2PdCl_2$ (39 mg, 0.056 mmol), CuI (11 mg, 0.056 mmol), diisopropylamine (5 mL), and toluene (20 mL). Then, to the above suspension was added a solution of **29** (30 mg, 0.13 mmol) in diisopropylamine (2.5 mL) and toluene (10 mL) over a period of 10 hr 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 separated by HPLC to give 2 mg of **30** (1.3%) as a yellow solid. m.p. 210 °C, to give 15 mg of **5** (11.6%) as a yellow solid. m.p. 178 °C.

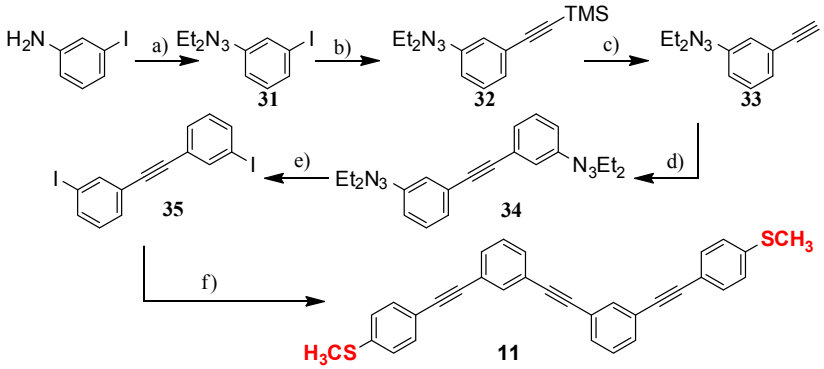
5: ^{1}H NMR ($CDCl_3$, 400 MHz): 1.0 (t, J = 7.6 Hz, 12H), 1.6 (m, 8H), 1.8 (m, 8H), 2.5 (s, 6H), 4.0 (t, J = 6.4 Hz, 8H), 7.0 (s, 4H), 7.2 (d, J = 8.4 Hz, 4H), 7.4 (d, J = 8.0 Hz, 4H), 7.5 (s, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz): 13.9 (CH_3), 15.4 (SCH_3), 19.3 (CH_2), 31.4 (CH_2), 69.4 (CH_2), 69.5 (CH_2), 86.1 (C≡), 88.2 (C≡), 91.1 (C≡), 94.5 (C≡), 94.9 (C≡), 113.7 (C), 114.5 (C), 116.9 (CH), 117.1 (CH), 119.8 (C), 122.8 (C), 123.6 (C), 125.9 (CH), 131.5 (CH), 131.5 (CH), 131.8 (CH), 139.4 (C), 153.7 (C), 153.8 (C); IR (KBr, disk) v: 2956, 2870, 2203, 1743, 1518, 1416, 1220, 1040, 857, 813 cm^{-1}; MS(APCI) *m/z* (%): 959 (M^++H^+, 100), 960(M^++2H^+, 68).

30: ^{1}H NMR ($CDCl_3$, 400 MHz): 1.0 (m, 12H), 1.6 (m, 8H), 1.9 (m, 8H), 2.5 (s, 6H), 4.0 (m, 8H), 7.0 (s, 4H), 7.2 (d, J = 8.8 Hz, 4H), 7.4 (d, J = 8.0 Hz, 4H), 7.5 (s, 16H); ^{13}C NMR ($CDCl_3$, 100 MHz): 13.9 (CH_3), 19.3 (SCH_3), 31.4 (CH_2), 53.4 (CH_2), 69.4 (CH_2), 69.5 (CH_2), 86.1 (C≡), 88.2 (C≡), 91.1 (C≡), 94.5 (C≡), 94.9 (C≡), 95.9 (C≡), 96.9 (C≡), 113.7 (C), 114.5 (C), 116.9 (CH), 117.1 (CH), 119.8 (C), 122.8 (C), 123.6 (C), 125.9 (CH), 131.5 (CH), 131.5 (CH), 131.8 (CH), 139.4 (C), 153.7 (C), 153.8 (C); MS(ESI) *m/z* (%):1182 (M^+, 20), 1183 (M^++H^+, 27), 1184 (M^++2H^+, 12).



Scheme S7. A schematic illustration for the synthesis of **6~10**. a) $PdCl_2(PPh_3)_2$, CuI, toluene, *i*-Pr_2NH, 65°C.

The synthesis of the V-shaped molecules **6~10** began with 1,2-diiodobenzene, 1,2-diethynylbenzene, 1,3-diiodobenzene, 1,3-diethynylbenzene, respectively, which cross coupling with the free alkyne in Sonogashira condition gave the **6~10** as the desired targets as shown in Scheme S7. The synthesis of the **11** started with 3-Iodoaniline as depicted in Scheme S8. Conversion of **31** into **32** is by Sonogashira coupling with TMSA. Then a TMS group was next removed with K_2CO_3 in MEOH-THF stirred at room temperature for 1 hr to give **33**. This compound was then reacted with **31** in the Sonogashira coupling conditions afforded **34**, which was then converted into iodide **35** in sealed tube. The Sonogashira coupling reaction of **35** with 2.1 equiv of **21** at 60 °C gave **11** in 78.2% yield.



Scheme S8. A schematic illustration for the synthesis of **6~10**. a) 1) $NaNO_2$, HCl, H_2O; 2) Et_2NH, K_2CO_3; b) TMSA, $PdCl_2(PPh_3)_2$, CuI, toluene, *i*-Pr_2NH, 50 °C; c) K_2CO_3, Acetone, r.t.; d) **33**, $PdCl_2(PPh_3)_2$, CuI, toluene, *i*-Pr_2NH, 65 °C; e) MeI, 135 °C; d) **21**, $PdCl_2(PPh_3)_2$, CuI, toluene, *i*-Pr_2NH, 65 °C.

*Synthesis of compound **6***. A 100 mL two-necked flask was charged with 1,2-diiodobenzene (200 mg, 0.6 mmol), $(Ph_3P)_2PdCl_2$ (85 mg, 0.12 mmol), CuI (23 mg, 0.12 mmol), diisopropylamine (5 mL), and toluene (20 mL) under nitrogen. Then, to the above suspension was added a solution of **21** (206 mg, 1.3 mmol) in diisopropylamine (5 mL) and toluene (20 mL) over a period of 10 hr 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 subjected to a silica-gel chromatography (SiO_2; eluent, Hexane/CH_2Cl_2, 50: 1) to give 195 mg of **6** (85.3%) as a yellow solid. m.p. 156~158 °C. ^{1}H NMR(400 MHz, $CDCl_3$): 7.5(dd, J = 6.0 Hz & J = 3.2 Hz, 2H), 7.5(d, J = 8.4 Hz, 4H), 7.3 (dd, J = 6.0 Hz & J = 3.2 Hz, 2H), 7.2(d, J = 8.4 Hz, 4H), 2.5(s, 6H); ^{13}C NMR(100 MHz, $CDCl_3$): 139.6(C), 131.9(CH), 131.7(CH), 127.9(CH), 125.8(CH), 125.8(C), 119.5(C), 93.4(C≡), 88.4(C≡), 15.3(CH_3); MS(APCI) *m/z* (%): 324.1(M^+-SMe, 100), 370.9(M^+, 55).

Synthesis of compound 7. A 100 mL two-necked flask was charged with **23** (630 mg, 2.3 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 1,2-diethynylbenzene (126 mg, 1.0 mmol) in diisopropylamine (5 mL) and toluene (20 mL) over a period of 10 hr 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 subjected to a silica-gel chromatography (SiO_2; eluent, Hexane/CH_2Cl_2, 6: 1) to give 293 mg of **7** (70.3%) as a white solid. m.p. 140~141 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 2.5 (s, 6H), 7.3 (dd, J = 5.8 Hz & J = 3.4 Hz, 2H), 7.4 (dd, J = 6.6 Hz & J = 1.8Hz, 4H), 7.5 (dd, J = 6.8 Hz & J = 1.6 Hz, 4H), 7.6 (dd, J = 6.0 Hz & J = 3.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 19.4 (S**C**H_3), 83.4 (C≡), 90.0 (C≡), 91.6 (C≡), 93.4 (C≡), 122.6 (C), 123.4 (C), 125.6 (C), 128.2 (CH), 131.2 (CH), 131.5 (CH), 131.8 (CH); IR (KBr, disk) *v*: 2924, 2160 , 1920, 1680, 1512, 1462, 1377, 1309, 974, 837, 540 cm^{-1}; MS(APCI) *m/z* (%): 418.4 (M^+, 100), 419.6 (M^++H^+, 33), 420.6 (M^++2H^+, 29), 421.6 (M^++3H^+, 7).

*Synthesis of compound **8***. 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 **21** (310 mg, 2.1 mmol) in diisopropylamine (5 mL) and toluene (20 mL) over a period of 10 hr 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 subjected to a silica-gel chromatography (SiO_2; eluent, Hexane/CH_2Cl_2, 50: 1) to give 303 mg of **8** (82.2%) as a yellow solid. m.p. 140~141 °C.

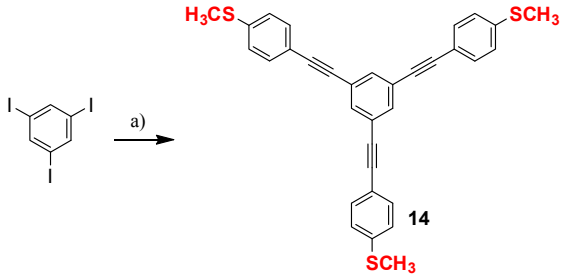
^{1}H NMR(400 MHz, $CDCl_3$): 7.7(s, 1H), 7.5(d, *J* = 8.0 Hz, 2H), 7.4(d, *J* = 8.4 Hz, 4H), 7.3(d, *J* = 8.0 Hz, 1H), 7.2(d, *J* = 8.4 Hz, 4H), 2.5 (s, 6H); ^{13}C NMR(100 MHz, $CDCl_3$): 139.6(C), 134.5(CH), 131.9(CH), 131.1 (CH), 128.5(CH), 125.9(CH), 123.7(C), 119.3(C), 89.8(C≡), 88.7(C≡), 15.4(CH_3); MS(APCI) *m/z* (%): 403.0(M^++ H^++CH_3OH, 100), 434.9(M^++H^++2CH_3OH, 27).

*Synthesis of compound **9**.* A 100 mL two-necked flask was charged with **23** (630 mg, 2.3 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 1,3-diethynylbenzene (126 mg, 1.0 mmol) in diisopropylamine (5 mL) and toluene (20 mL) over a period of 10 hr 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 subjected to a silica-gel chromatography (SiO_2; eluent, Hexane/CH_2Cl_2, 7: 1) to give 314 mg of **9** (75.3%) as a yellow solid. m.p. 178~180 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 2.5 (s, 6H), 7.3 (t, *J* = 7.8 Hz, 1H), 7.4 (d, *J* = 8.4 Hz, 4H), 7.5 (d, *J* = 8.0 Hz, 4H), 7.5 (dd, *J* = 8.0 Hz & *J* = 1.8 Hz, 4H), 7.7 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 19.4 (SCH_3), 83.4 (C≡), 89.7 (C≡), 90.3 (C≡), 91.7 (C≡), 122.5 (C), 123.5 (CH), 128.5 (C), 131.2 (CH), 131.4 (CH), 131.5 (CH), 134.6 (C); IR (KBr, disk) *v*: 2162, 1585, 1498, 1462, 1377, 1306, 833, 793, 683, 542 cm^{-1}; MS(EI) *m/z* (%): 418 (M^+, 100).

*Synthesis of compound **10**.* A 100 mL two-necked flask was charged with **24** (685 mg, 2.3 mmol), $(Ph_3P)_2PdCl_2$ (160 mg, 0.23 mmol), CuI (44 mg, 0.23 mmol), diisopropylamine (5 mL), and toluene (20 mL) under nitrogen. Then, to the above suspension was added a solution of 1,3-diethynylbenzene (126 mg, 1.0 mmol) in diisopropylamine (5 mL) and toluene (20 mL) over a period of 10 hr at 50 °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 subjected to a silica-gel chromatography (SiO_2; eluent, Hexane/CH_2Cl_2, 7: 1) to give 63 mg of **10** (15%) as a yellow solid. m.p. 185 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 2.5 (s, 6H), 7.4 (t, *J* = 8.0 Hz, 1H), 7.5 (s, 8H), 7.5 (dd, *J* = 7.6 Hz & *J* = 1.2 Hz, 2H), 7.7 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 19.0 (SCH_3), 76.3 (C≡), 76.8 (C≡), 77.8 (C≡), 78.7 (C≡), 89.6 (C≡), 91.0 (C≡), 121.8 (C), 123.3 (C), 123.7 (C), 128.6 (CH), 131.6 (CH), 132.5 (CH), 134.6 (CH); IR (KBr) *v*: 2958, 2928, 2854, 2191, 2112, 1589, 1506, 1404, 1264, 1104, 828, 792, 684 cm^{-1}.

*Synthesis of compound **11**.* A 100 mL two-necked flask was charged with **35** (665 mg, 1.5 mmol), $(Ph_3P)_2PdCl_2$ (217 mg, 0.3 mmol), CuI (58 mg, 0.3 mmol), diisopropylamine (5 mL), and toluene (20 mL) under nitrogen. Then, to the above suspension was added a solution of **21** (480 mg, 3.2 mmol) in diisopropylamine (5 mL) and toluene (20 mL) over a period of 10 hr at 60 °C by a machine. The reaction

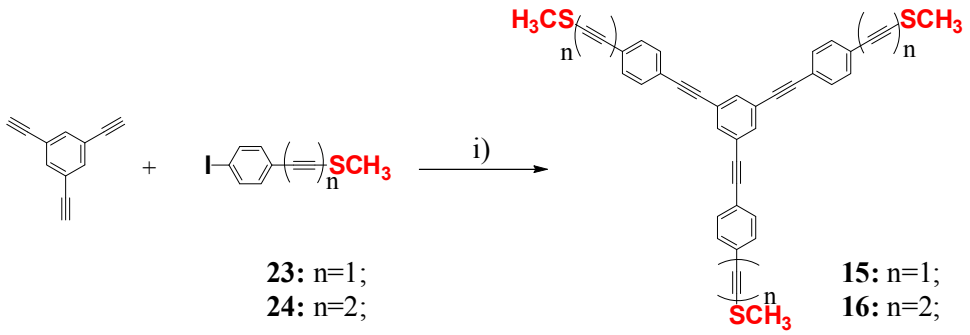
mixture was cooled to room temperature and filtered. The filtrate was poured into aqueous NH_4Cl, and extracted with ethyl acetate. The extract was then washed with brine, dried over $MgSO_4$, and filtered. The solvent was evaporated in vacuo, and the residue subjected to a silica-gel chromatography (SiO_2; eluent, Hexane/CH_2Cl_2, 25: 1) to give 570 mg of **11** (78.2%) as a yellow solid. m.p. 189~190 °C. ^{1}H NMR(400 MHz, $CDCl_3$): 7.7(s, 2H), 7.5(d, J = 8.0 Hz, 4H), 7.5(d, J = 8.4 Hz, 4H), 7.3(t, J = 8.0 Hz, 2H), 7.2(d, J = 8.4 Hz, 4H), 2.5(s, 6H); ^{13}ÇNMR(100 MHz, $CDCl_3$): 139.7(C), 134.6(CH), 131.9(CH), 131.4(CH), 131.2(CH), 128.5(CH), 125.9(CH), 123.8(C), 123.4(C), 119.3(C), 89.9(C≡), 89.1(C≡), 88.6(C≡), 15.4(CH_3); MS(APCI) *m/z* (%): 502.9(M^++H^++CH_3OH, 100), 504.0(M^++2H^++CH_3OH, 34), 505.0(M^++3H^++CH_3OH, 18);



Scheme 3.2. Synthesis of Y-shaped MTA **Y1**.

*Synthesis of compound **14***. A 100 mL two-necked flask was charged with 1,3,5-triiodobenzene (200 mg, 0.44 mmol), $(Ph_3P)_2PdCl_2$ (62mg, 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 **21** (260 mg, 1.75 mmol) in diisopropylamine (5 mL) and toluene (20 mL) over a period of 10 hr 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 subjected to a silica-gel chromatography (SiO_2; eluent, Hexane/CH_2Cl_2, 5: 1) to give 200 mg of **14** (88.5%) as a white solid.

14. White solid; yield 88.5%; mp 134~137 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): 2.5 (s, 9H), 7.2 (d, J = 8.4 Hz, 6H), 7.4 (d, J = 8.4 Hz, 6H), 7.6 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 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); IR (KBr, disk) v: 2962, 2911, 2203, 1572, 1490, 1435, 1398, 1091, 816 cm^{-1}; MS(APCI) *m/z* (%): 549.0 (M^++CH_3OH+H^+, 100), 550.1 (M^++CH_3OH+2H^+, 33), 551.1 (M^++CH_3OH+3H^+, 25).



23: n=1;
24: n=2;

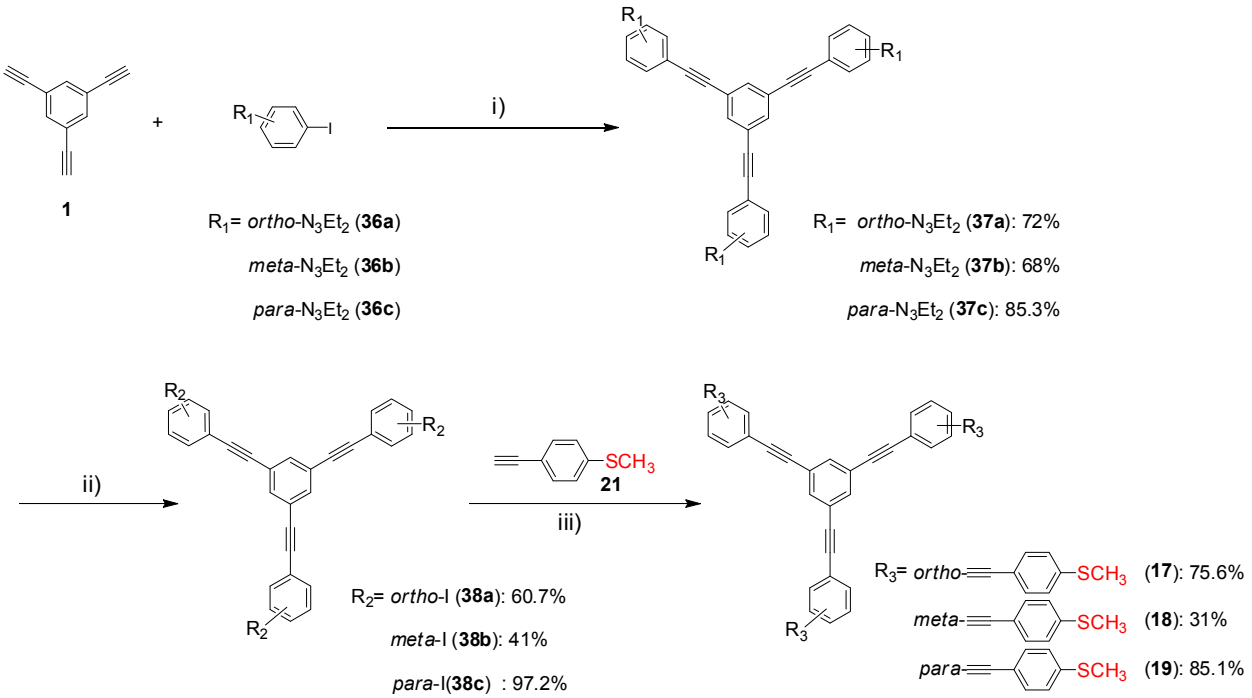
15: n=1;
16: n=2;

Scheme 3.3. Synthesis of Y-shaped MTA **Y2**, **Y3**.

*Synthesis of compound **15, 16**.* A 100 mL two-necked flask was charged with **23** or **24** (3.5 mmol), $(Ph_3P)_2PdCl_2$ (0.21 mmol), CuI (0.21 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 hr 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 subjected to a silica-gel chromatography (SiO_2) to give **15**, **16.**

15. White solid; yield 63%; mp 121~122 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): 2.5 (s, 9H), 7.4 (d, J = 8.4 Hz, 6H), 7.5 (d, J = 8.4 Hz, 6H), 7.6 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz,): 19.4 (SCH_3), 83.6 (C≡), 89.4 (C≡), 90.3 (C≡), 91.6 (C≡), 122.2 (C), 123.7 (C), 123.9 (C), 131.2 (CH), 131.6 (CH), 134.1 (CH); IR (KBr, disk) v: 2854, 2164, 1577, 1502, 1377, 835 cm^{-1}; MS(APCI) *m/z* (%): 612.0 (M^++MeOH+H^+, 100), 622.0 (M^++MeOH+2H^+, 54), 623.0 (M^++MeOH+3H^+, 23), 624.0 (M^++MeOH+4H^+, 10);

16. Yellow solid; yield 45.1%; mp 96~97 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): 2.5 (s, 9H), 7.5 (s, 12H), 7.6 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 19.3 (SCH_3), 76.7 (C≡), 77.2 (C≡), 78.1(C≡), 78.9 (C≡), 90.4(C≡), 90.5 (C≡), 122.3(C), 123.6 (C), 124.1 (CH), 131.9 (CH), 132.8 (CH), 134.6 (C); IR (KBr, disk) v: 2925, 2854, 2192, 2110, 1628, 1579, 1505, 1311, 876, 832 cm^{-1}; MS(APCI) *m/z* (%): 692.9 (M^++CH_3OH+H^+, 100), 694.0 (M^++CH_3OH+2H^+, 44), 551.1 (M^++CH_3OH+3H^+, 27).



Scheme 3.4. Synthesis of Y-shaped MTA **Y4**, **Y5**, **Y6**.

*Synthesis of compounds **17, 18, and 19**.* The following steps were followed for the synthesis of compounds **17**, **18**, and **19**.

Step 1. A 100 mL two-necked flask was charged with **36** (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 hr 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 subjected to a silica-gel chromatography (SiO_2) to give **37**.

Step 2. A 50 mL sealed tube was charged with **37** (1.0 mmol) and methyl iodide (30 mL). The solution was kept at 135 °C for 20 hr. The reaction mixture was filtered and then evaporated. The residue subjected to a silica-gel chromatography (SiO_2) to give **38**.

Step 3. A 100 mL two-necked flask was charged with **38** (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 **21** (3.1 mmol) in diisopropylamine (5 mL) and toluene (20 mL) over a period of 10 hr 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 subjected to a silica-gel chromatography (SiO_2) to give **17~19**.

37a. ^{1}H NMR ($CDCl_3$, 400 MHz): 1.3 (t, J = 6.8 Hz, 18H), 3.8 (q, J = 7.2 Hz, 12H), 7.1 (t, J = 7.2 Hz, 3H), 7.3 (t, J = 7.2 Hz, 3H), 7.4 (d, J = 8.0 Hz, 3H), 7.5 (d, J = 8.0 Hz, 3H), 7.6 (s, 3H).

37b. ^{1}H NMR ($CDCl_3$, 400 MHz): 1.3 (t, J = 6.8 Hz, 18H), 3.8 (q, J = 7.2 Hz, 12H), 7.3 (d, J = 6.8 Hz, 3H), 7.3 (t, J = 7.6 Hz, 3H), 7.4 (d, J = 7.2 Hz, 3H), 7.6 (s, 3H), 7.7 (s, 3H).

37c. ^{1}H NMR ($CDCl_3$, 400 MHz): 1.3 (t, J = 6.8 Hz, 18H), 3.8 (q, J = 7.2 Hz, 12H), 7.5 (s, 12H), 7.6 (s, 3H).

38a. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.0 (t, J = 7.2 Hz, 3H), 7.3 (t, J = 7.2 Hz, 3H), 7.6 (d, J = 7.6 Hz, 3H), 7.9 (d, J = 8.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 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).

38b. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.1 (t, J = 7.6 Hz, 3H), 7.5 (d, J = 8.0 Hz, 3H), 7.6 (s, 3H), 7.7 (d, J = 8.0 Hz, 3H), 7.9 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 88.8 (C≡), 89.0 (C≡), 93.7 (C), 123.7 (C), 124.7 (C), 129.9 (CH), 130.8 (CH), 134.3 (CH), 137.7 (CH), 140.2(CH).

38c. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.5 (s, 12H), 7.7 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 89.5 (C≡), 90.8 (C≡), 98.7 (C), 123.1 (C), 123.8 (C), 131.5 (CH), 132.1 (CH), 134.2(CH).

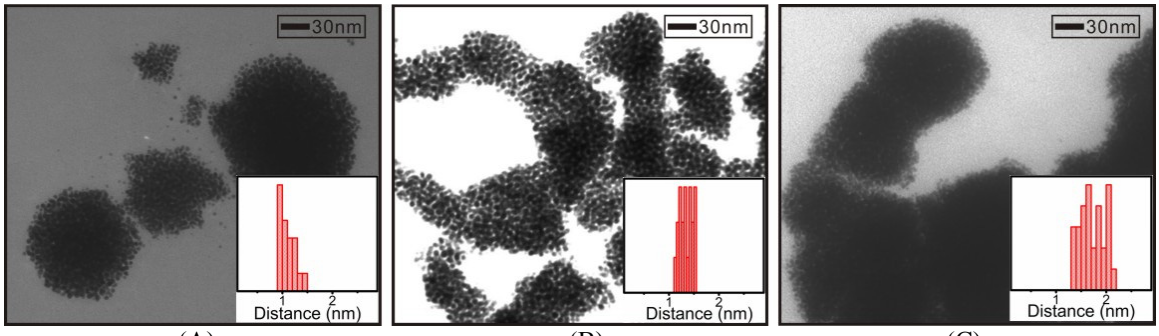
17. Yellow solid; yield 85.1%; mp 268~272 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): 2.5 (s, 9H), 7.2 (d, J = 8.4 Hz, 6H), 7.5 (d, J = 8.4 Hz, 6H), 7.5 (s, 12H), 7.7 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 15.3 (SCH_3), 89.1 (C≡), 89.5 (C≡), 90.4 (C≡), 91.4 (C≡), 119.1 (C), 122.4 (C), 123.6 (C), 123.9 (C), 125.8 (CH), 131.5 (CH), 131.6 CH), 131.9 (CH), 134.1 (CH), 139.7 (C); MS(APCI) *m/z* (%): 816.1 (M^+, 48), 817.8 (M^++H^+, 100), 818.1 (M^++2H^+, 74)).

18. White solid; yield 75.6%; mp 166~168 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): 2.3 (s, 9H), 7.1 (d, J = 8.4 Hz, 6H), 7.3 (m, 6H), 7.4 (d, J = 8.4 Hz, 6H), 7.6 (m, 6H), 7.8 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 15.0 (SCH_3), 88.2 (C≡), 89.7 (C≡), 91.8 (C≡), 94.0 (C≡), 119.1 (C), 124.2 (C), 125.1 (C), 125.7 (CH), 126.3 (C), 128.0 (CH), 128.4 CH), 131.7 (CH), 131.8 (CH), 131.9 (CH), 134.2 (CH), 139.8 (C); MS(APCI) *m/z* (%): 816.8 (M^+, 100), 817.8 (M^++H^+, 56), 818.8 (M^++2H^+, 31).

19. White solid; yield 32%; mp 192~193 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): 2.5 (s, 9H), 7.2 (d, J = 8.4 Hz, 6H), 7.4 (t, J = 7.6 Hz, 3H), 7.5 (d, J = 8.4 Hz, 6H), 7.5 (t, J = 7.2 Hz, 6H), 7.7 (s, 3H), 7.7 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 15.3 (SCH_3), 88.2 (C≡), 88.5 (C≡), 89.8 (C≡), 90.0 (C≡), 119.1 (C), 123.0 (C), 123.7 (C), 123.8 (C), 125.7 (CH), 128.6 (CH), 131.3 CH), 131.6 (CH), 131.9 (CH), 134.2 (CH), 134.6 (CH), 139.6 (C); MS(APCI) *m/z* (%): 816.8 (M^+, 100), 817.9 (M^++H^+, 58), 818.9 (M^++2H^+, 26).

2. Additional Characterization Data

Determination of average edge-to-edge interparticle distance (s):



(A) (B) (C)

Figure S1. TEM micrographs for samples from the assembly of Au NPs mediated by V(**8**), X(**12**) and Y(**14**). Insert: the distribution charts for the measured edge-to-edge interparticle distance in these assemblies. (V(**8**), 1.1 ± 0.2 nm; X(**12**), 1.3 ± 0.1 nm; Y(**14**), 1.7 ± 0.2 nm)

Determination of enhancement factors:

The SERS enhancement factor (EF) for each of the nanoparticle assemblies was also estimated based on the following relationship:

$$EF = \frac{I_{sers}}{I_{raman}} \cdot \left(\frac{d \cdot \rho_{ligand} \cdot \frac{No}{MW}}{\frac{NPs}{cm^2} \cdot \frac{ligand}{NP}}\right)$$

(I_{sers}: Raman intensity in the interparticle assembly sample; I_{raman}: Raman intensity in powder sample, d: diameter of laser beam (d = 2 μm), ρ_{ligand}: the molecular density of MTAs (1.5 g/cm^3), No: Avogadro's number, MW: molecular weight of MTAs, NPs/cm^2: the number of gold nanoparticles per cm^2, ligand/NP: the number of MTAs per gold nanoparticle in the mediated assembly (V ~ 1.4/NP, Y ~ 0.8/NP, X ~ 1.5/NP, as determined from the UV-Vis data).

Table S1. Summary of the determined enhancement factors

M.	group	**EF** (1s)	**EF** (2s)
V(**8**)	Ph-	6.06×10^4	2.24×10^4
X(**12**)	Ph-	1.13×10^4	1.18×10^4
Y(**14**)	Ph-	6.10×10^4	5.50×10^4

Note: We did not compare the I-shaped MTAs because it is difficult precipitation after assembly.

Spectrophometric determination of concentrations and molar absorptivity (ε *):*

The measurement procedure for the assessment of ligand exchange and replacement in the two-component assemble processes is as follows:

(1) After the formation of nanoparticle assembly mediated by the first ligand, the solution was centrifuged and the precipitation was collected.

(2) A 6-mL toluene and the second ligand were added into the precipitation, and the solution was then stirred overnight.

(3) For the assembly thus formed, it contained a mixture of the 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 8, 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:

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

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

Table S2. 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	$\mathbf{1.779\times10^6}$
V (**8**)	$\mathbf{0.429\times10^5}$	0.394×10^5	0.380×10^5	0
X (**12**)	0.146×10^5	0.191×10^5	$\mathbf{0.405\times10^5}$	0
Y (**14**)	0.642×10^5	$\mathbf{0.703\times10^5}$	0.324×10^5	0

Note: the unit for all entries : $M^{-1} \cdot cm^{-1}$

TEM for comparing samples from the 1- and 2-component mediated nanoparticle assembly solutions:

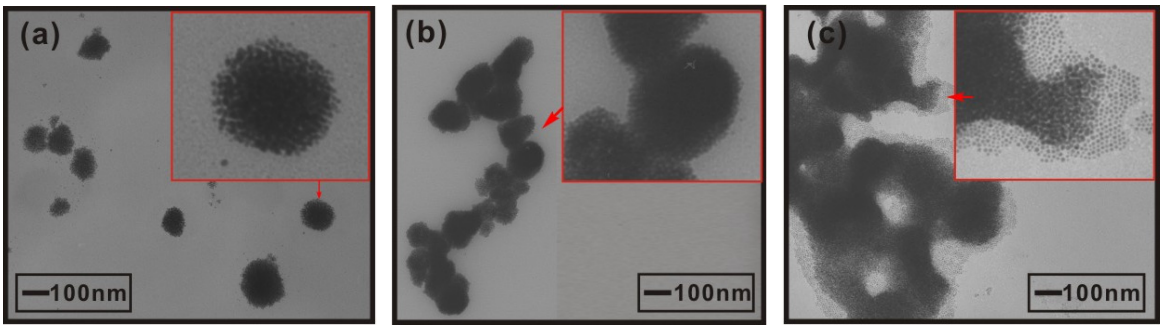


Figure S2. TEM micrographs for samples from the nanoparticle assembly solutions: (a) the assembly of Au NPs mediated by mediator V(**8**); (b) the assembly of Au NPs mediated by mediator Y(**14**); (c) the assembly in *S1* sequence upon adding Y(**14**) to the solution of V(**8**) mediated assembly (inserts: magnified views of the indicated areas).

Comparison of Raman bands:

Table S3. Comparison of Raman bands between the theoretically predicted (calculated by Gaussian 3.0) and the experimentally observed Raman spectra for powder samples of V (**8**), X (**12**), and Y (**14**) and their nanoparticle assemblies.

V			**X**			**Y**		
Ligand powder	NP assembly	Cal'd	Ligand powder	NP assembly	Cal'd	Ligand powder	NP assembly	Cal'd
996.9	996.8	1029.7	1003.1	1043.8		996.9	996.9	1023.2
1090.6	1078.1	1057.6	1025	1068.8	1052.1	1096.9	1087.5	1059.5
		1111.3	1093.8	1084.4	1110.6	1128.1	1143.8	1112
1159.4	1156.2	1146.6	1159.4	1153.1		1171.9	1168.8	1161
	1181.2	1189.8		1184.4	1175.8		1190.6	1199.3
		1239.8		1275.5	1238.4		1271.9	1239.1
		1288.4			1309.6		1309.4	1300.5
	1365.6	1363.9		1356.2	1373.6		1343.8	
	1390.6			1403.1			1371.9	1387.4
				1462.5			1456.2	
				1484.4	1485.2		1506.2	
1568.8	1568.8	1537.7		1531.2	1537		1528.4	1538.6
1593.8	1587.5	1591.7	1584.4	1587.5	1597.2	1578.1	1556.2	1600.6
	1621.9	1618.9		1708.8	1618.9	1596.9	1584.4	1619
2209.4	2206.2		2212.5	2206.2	2326.3	2212.5	2215.6	
2228.1	2240.6	2337.8				2253.1	2253.1	2346.4