# Electronic Supplementary Material (ESI) for Nanoscale. This journal is © The Royal Society of Chemistry 2020

 Contents

 I. Physical measurements

 II. Synthesis and Computational details

 III. Characterization

 Figure S1. a) Au<sub>30</sub> kernel of 1. b) Diagram of linear "RC≡C-Au-C≡CR" staples fixed at the Au<sub>30</sub> kernel of 1.

 Figure S2. The arrangement of linear "RC≡C-Au-C≡CR" staples in 2

 Figure S3. The experimental absorption (black) in comparison with the calculated (red) spectra of (a) 1 and (b) 2.

 a.u., arbitrary unit.

 Figure S4. The plot of the projected density of states (PDOS) of (a) 1 and (b) 2.

## I. Physical measurements

UV-Vis-NIR absorption spectra were recorded on Cary 5000. Mass spectra were recorded on Bruker MicroFlex MALDI-TOF-MS using DCTB (Trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenyldide-ne] malononitrile) as a matrix.

**X-ray Crystallography.** Intensity data of compounds **1** and **2** were collected on a Rigaku SuperNova Dual system (Cu K $\alpha$ ) at 100 K. Single black block-like crystal specimens of **1** (approximate dimensions: 0.08 mm × 0.12 mm × 0.2 mm) and **2** (approximate dimensions: 0.03 mm × 0.05 mm × 0.09 mm) were used as supplied, respectively. Absorption corrections were applied by using the program CrysAlis (multi-scan). For cluster **1**, the structure was solved using the SHELXT program, and by using *Olex2* (Dolomanov et al., 2009) as the graphical interface. The space group *P*-1 was used for cluster **1**, and *P*2<sub>1</sub>/*n* for cluster **2**. The models were refined with ShelXL 2014/7 (Sheldrick, 2015) using full matrix least squares minimisation on *F*<sup>2</sup>. The diffuse electron densities resulting from the residual solvent molecules were removed from the data set using the *Olex2* solvent mask. Constraints (afix 66, dfix, flat etc.) have been applied to the alkynyl ligands of the structure, due to geometric requirements of the ligands. In addition, the atomic displacement parameters (ADPs) of bonded C-atoms and F-atoms were restrained to be similar using RIGU command and a few select ISOR commands.

## II. Synthesis and Computational details

**Materials and reagents.** 3-Fluorophenylacetylene (3-F-C<sub>6</sub>H<sub>4</sub>-C=CH, 98%), 2-(Trifluoromethyl)phenylacetylene (2-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-C=CH, 97%) were purchased from Adamas; 2-(Trifluoromethyl)-phenylacetylene (2-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-C=CH, 97%) was purchased from BokaChem; Chloroauric acid hydrate (HAuCl<sub>4</sub> H<sub>2</sub>O, 97%) was purchased from Tuosi; sodium borohydride (NaBH<sub>4</sub>, 98%) and other reagents employed were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All reagents were used as received without further purification. Me<sub>2</sub>SAuCl was prepared from dimethyl sulfide and HAuCl<sub>4</sub> according to literature.<sup>1</sup>

### AuC=CR (R= C<sub>6</sub>H<sub>4</sub>-2-CF<sub>3</sub> or C<sub>6</sub>H<sub>4</sub>-3-F)<sup>2</sup>

To 30.0 mL acetone solution containing Me<sub>2</sub>SAuCl (590.0 mg, 2.0 mmol) and HC=CR (R= C<sub>6</sub>H<sub>4</sub>-2-CF<sub>3</sub> or C<sub>6</sub>H<sub>4</sub>-3-F) (2.1 mmol), 294.0  $\mu$ L of NEt<sub>3</sub> (212.5 mg, 2.1 mmol) was added under stirring. The mixture was stired for 2 h at room temperature in air in the dark. Then the solution was evaporated to dryness to give a yellow solid, which was washed with water and dried in a vaccum desiccator at room temperature to give AuC=CR.

Synthesis of Au<sub>42</sub>(C=CC<sub>6</sub>H<sub>4</sub>-2-CF<sub>3</sub>)<sub>22</sub> (1). A freshly prepared solution of NaBH<sub>4</sub> (1.14 mg in 1.0 mL of ethanol) was added dropwise to a chloroform/methanol (V: V = 5: 1, 6 mL) suspension containing AuC=CC<sub>6</sub>H<sub>4</sub>-2-CF<sub>3</sub> (0.1 mmol) under vigorous stirring, which was followed by addition of trimethyl amine (20 uL). The color changed from orange to pale brown and finally dark brown. The reaction continued for 20 h at room temperature in the dark. Then the solvents were removed by rotary evaporation, and the obtained product was dissolved in the mixture of CH<sub>2</sub>Cl<sub>2</sub>: EtOH (V: V = 1: 1, 2 mL). After centrifugation, the supernatant solution was subjected to the diffusion of n-hexane to afford block dark crystals within 2 weeks in 6% yield (1.6 mg, based on Au).

Synthesis of Au<sub>50</sub>(C=CC<sub>6</sub>H<sub>4</sub>-3-F)<sub>26</sub> (2). Cluster 2 was prepared with the same procedure as 1 with AuC=CC<sub>6</sub>H<sub>4</sub>-3-F instead of AuC=CC<sub>6</sub>H<sub>4</sub>-2-CF<sub>3</sub>. The yield is 5% (1.3 mg) based on Au.

### **Computational details**

Time-dependent DFT calculations of the UV-vis absorption were performed with the quantum chemistry program Gaussian 09.<sup>3</sup> To save computational time, we replaced R group ( $R=C_6H_4$ -2-CF<sub>3</sub> or C<sub>4</sub>H<sub>4</sub>-3-F) with H. In calculations, the 6-31G(d) basis set is used for C, H and F, and LANL2DZ for Au.<sup>4-5</sup> Geometry optimizations were done with the functional of B3LYP. Time-dependent DFT calculations were done with the functionals of Perdew–Burke–Ernzerhof (PBE).<sup>6</sup> Sixty singlet states are chosen in the calculations of the UV-vis absorption spectra for two clusters. All transitions together with their oscillator strengths were then convoluted with a Gaussian line shape of 0.17 eV broadening to make the whole optical-absorption spectrum.

The theoretical results calculated by Gaussian were post-processed to facilitate comparison to experimental ones, for instance, the calculated spectra of cluster **1** and cluster **2** were stretched and shifted, respectively. Different scales are used for showing theoretical and experimental results in the UV spectra (Figure S3). The projected density of states (PDOS) analysis of the title clusters were performed with the Multiwfn software.<sup>7</sup>

#### **III.** Characterization

Figure.



**Figure S1.** a)  $Au_{30}$  kernel of **1**. b) Diagram of linear "RC=C-Au-C=CR" staples fixed at the  $Au_{30}$  kernel of **1** (R = C<sub>6</sub>H<sub>4</sub>-2-CF<sub>3</sub>, aromatic groups were omitted for clarity).



Figure S2. The arrangement of linear "RC $\equiv$ C-Au-C $\equiv$ CR" staples in 2 (R = C<sub>6</sub>H<sub>4</sub>-3-F).



**Figure S3.** The experimental absorption (black) in comparison with the calculated (red) spectra of **1** (a) and **2** (b). a.u., arbitrary unit. Different scales are used to show the theoretical and experimental results in the UV spectra.



Figure S4. The plot of the projected densities of states (PDOS) of 1 (a) and 2 (b).

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