Electronic Supplementary Information for:

“Sergeants-and-soldiers” principle in the synthesis of intrinsically chiral Au_{13} clusters

Katsuya Mutoh, Sonomi Kawakita, Teppei Yahagi, Takuya Nakashima*

Department of Chemistry, Graduate School of Science, Osaka Metropolitan University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

E–mail: takuya.nakashima@omu.ac.jp

Experimental Procedures

General. Electrospray ionization mass (ESI-MS) spectrometry was conducted with a JEOL AccuTOF LC-plus 4G. Absorption spectra were measured using a JASCO V-670 spectrophotometer, with a 1 cm quartz cuvette. Circular dichroism (CD) spectrum was recorded with a JASCO J-725 spectropolarimeter. The anisotropy g_{abs}-value was derived from the equation $g = \theta\,[\mathrm{mdeg}]/(32980\cdot\mathrm{Abs})$ using CD (θ: ellipticity) and absorbance (Abs) data. Chemicals and Solvents were purchased from Fujifilm Wako Pure Chemical Industries, Sigma-Aldrich Japan, and Tokyo Chemical Industry Co., Ltd. All commercially available reagents were used as received.

Synthesis of $[Au_{13}(R\text{-}DIPAMP)_x(DPPE)_{5-x}Cl_2]^{3+}$ clusters. The synthesis of a series of ***R*0–*R*5** clusters was performed through a previously reported method[S1] with changing the ratio of the gold complexes, $Au_2(DPPE)Cl_2/Au_2(R\text{-}DIPAMP)Cl_2$ being Achiral/Chiral (A/C) = 5/0, 4/1, 3/2, 2/3, 1/4 and 0/5. Briefly, in the standard condition, the mixture of the gold complex (total = 0.025 mmol) was dissolved in dichloromethane (17 mL). To the mixture, $NaBH_4$ (0.125 mmol) in ethanol (0.5 mL) was added and the solution was stirred at room temperature for 3 h. The solvent was removed by evaporation and the residue was suspended in dichloromethane. The unsolved solid was removed by centrifugation. The collected solution was evaporated to give a black solid. The solid was dissolved in ethanol (3 mL) and 12 M HCl aq. (0.06 mL) was added dropwise. The mixture was stirred at room temperature for 1 day in the dark. The solvent was removed by evaporation. The resultant solid was washed with acetone followed by redispersion in methanol. The re-dispersed solutions were subjected to a reverse phase column chromatography (Wakosil 100C18, Wako-Fuji Film) using methanol solution containing 0.5vol% trifluoroacetic acid (TFA) and 0.5vol% diethylamine (DEA) as an eluent to remove larger agglomerates.

HPLC analysis. HPLC separation was conducted with LaChrom Elite system (Hitachi, pump; L-2130, detector; L2455). A preparative reverse phase column (InertSustain C30, GL Science) was employed and a linear gradient elution condition was carried out using optimized mobile phases composed of methanol containing TFA (0.2vol%) and DEA (0.2vol%) (solvent A), and water (solvent B). The flow rate was set to 5 mL/min. For a conventional separation, the column was eluted using a linear gradient (A/B, v/v) from 60/40 to 80/20 over the initial 20 min, followed by isocratic elution with A/B = 80/20 until all fractions were collected.

DFT calculations. All calculations were carried out using Gaussian 09 suite of programs version C.02.[S2] DFT calculations were performed for the models of $[Au_{13}(R\text{-}DIPAMP)_x(DPPE)_{5-x}Cl_2]^{3+}$ ($x = 0 \sim 5$) using B3LYP functional. Relativistic effective core potential LANL2DZ was used for gold atoms and the basis sets of other atoms were 6-31G**. For simulating ECD spectra, 250 excited states were solved to cover the spectrum in the energy range up to about 300 nm.

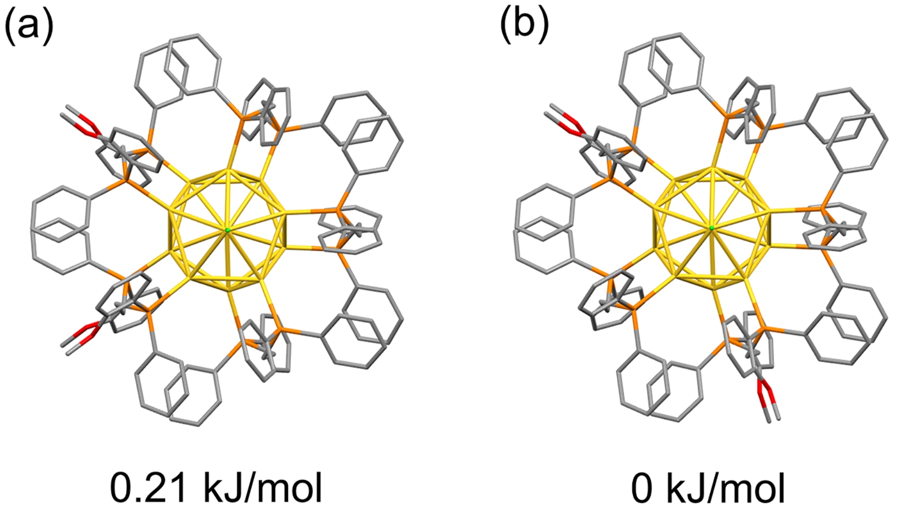

Fig. S1 The optimized structures of the structural isomers for ***R*2**: (a) with two DIPAMP ligands introduced adjacent to each other and (b) with DIPAMP ligands positioned apart, along with their relative energies calculated using the DFT method.

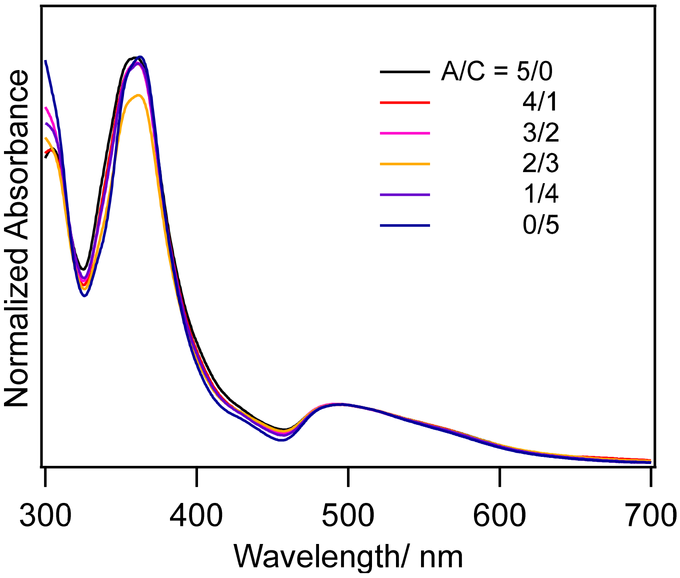

Fig. S2 Absorption spectra of unseparated Au_{13} clusters prepared with different A/C ligand ratio.

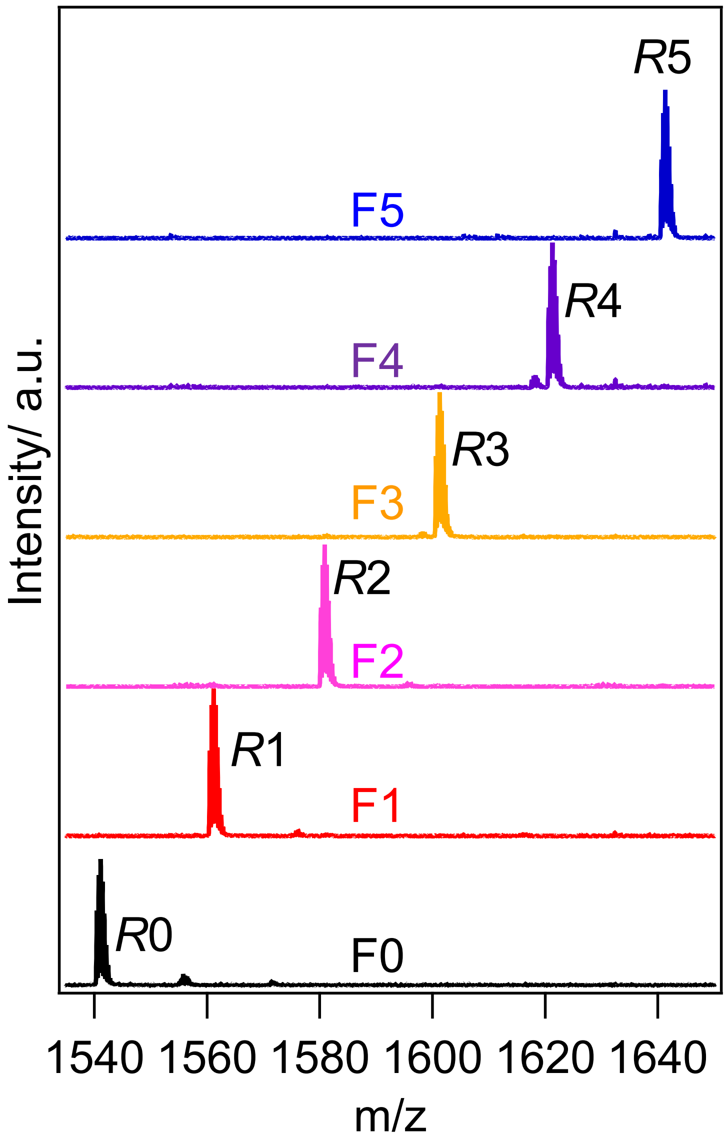

Fig. S3 ESI-MS spectra for the collected eluents in the HPLC separation experiment.

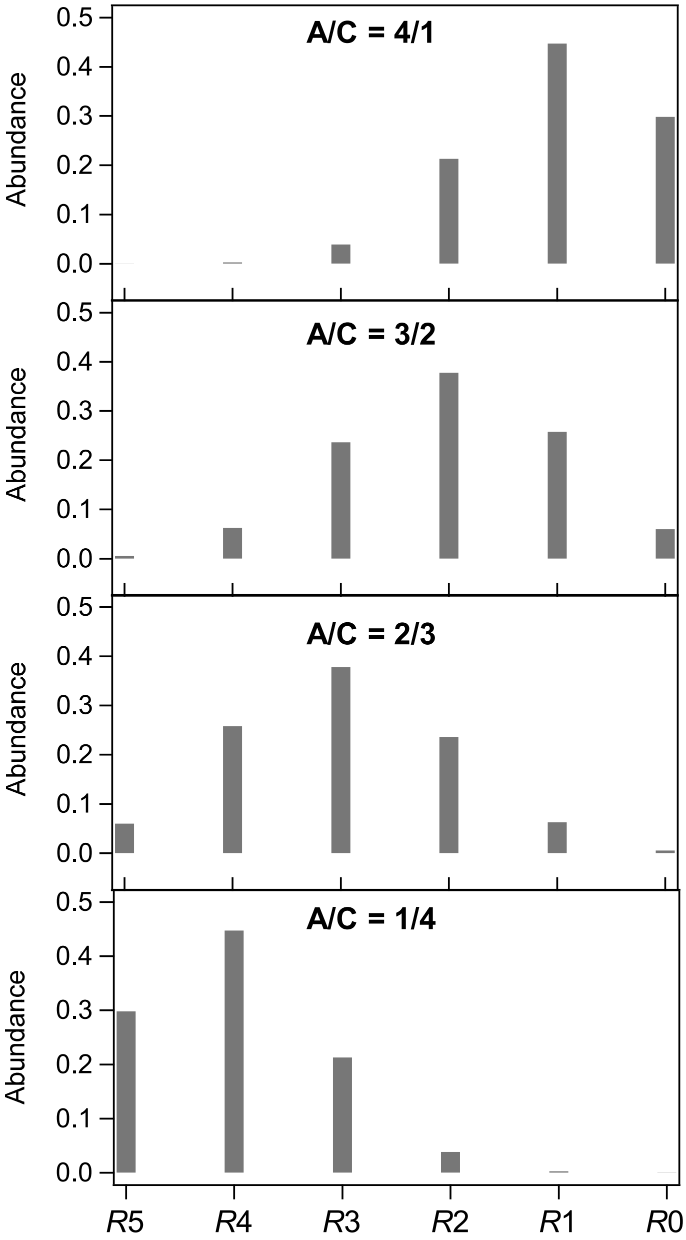

Fig. S4 Estimated abundance ratios of ***R*0**–***R*5** assuming the random incorporation of *R*-DIPAMP and DPPE in an Au_{13} cluster.

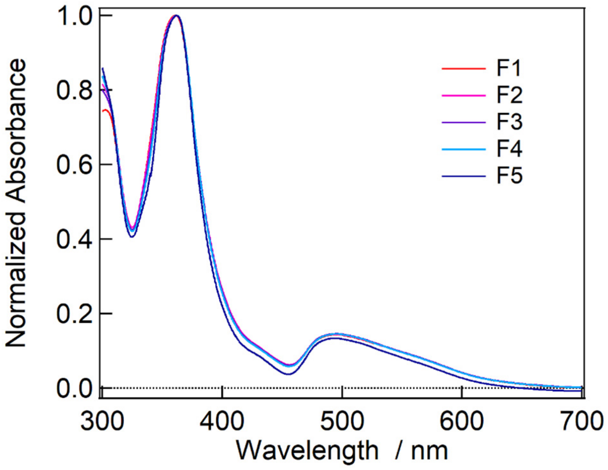

Fig. S5 Normalized absorption spectra of **F1**–**F5**.

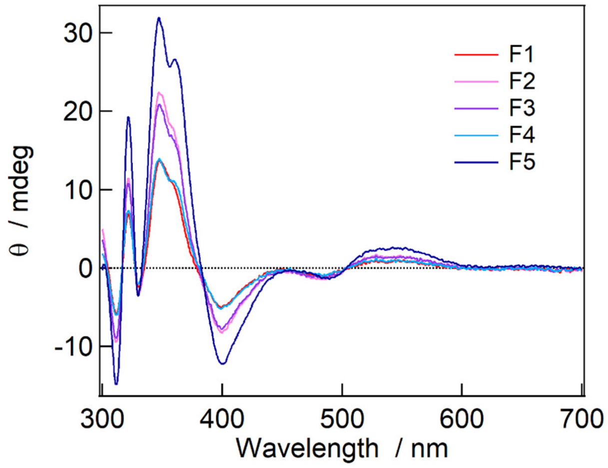

Fig. S6 CD spectra of **F1**–**F5**. **F1**–**F5** contain different concentrations of ***R*1**–***R*5**, respectively.

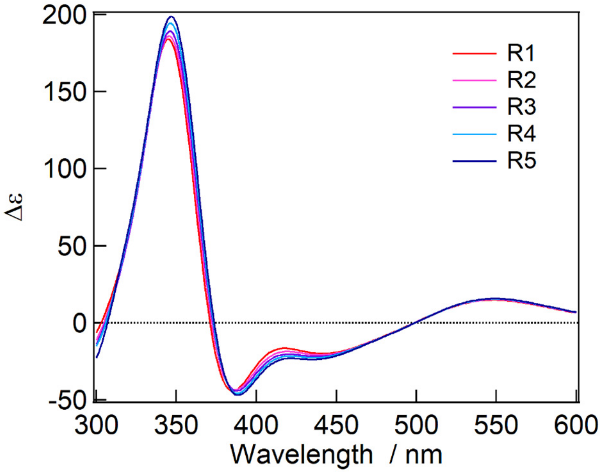

Fig. S7 Calculated CD spectra of **R1**–**R5**.

References

S1. Y. Shichibu and K. Konishi, *Small*, 2010 **6**, 1216−1220.

S2. Gaussian 16, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.