Supporting Information

Decorating an anisotropic Au_{13} core with dendron thiolates: enhancement of optical absorption and photoluminescence

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1. Chemicals

All commercially available chemicals were used without further purification. Tetrachloroauric acid tetrahydrate ($HAuCl_4 \cdot 4H_2O$), sodium borohydride ($NaBH_4$), potassium hydroxide (KOH), 12 M hydrochloric acid (HCl*aq*), dichloromethane (DCM), methanol (MeOH), ethanol (EtOH), toluene, *n*-hexane and Wakosil® 60 were purchased from Fujifilm Wako Pure Chemical Corporation. Cyclohexanethiol (CySH), 3,5-dibenzyloxybenzyl bromide (D1Br), 3,5-bis[3,5-bis(benzyloxy)benzyloxy]benzyl bromide (D2Br), thiourea and 2-phenylethanethiol (PhEtSH) were purchased from Tokyo Chemical Industry. Tetrahydrofuran (THF), chloroform-*d*$_1$ ($CDCl_3$) and dichloromethane-*d*$_2$ (CD_2Cl_2) were obtained from Kanto Chemical. Tetra-*n*-octylammonium bromide (TOABr) and 1,1',3,3,3',3'-hexamethylindotricarbocyanine iodide (HITCI) were obtained from Sigma-Aldrich. Acetonitrile (MeCN) was obtained from Merck. Water was Milli-Q grade (ρ > 18 MΩ·cm). $[Au_{25}(SEtPh)_{18}]^-$ was synthesized according to the reported procedure.[1]

2. Synthesis

2.1 D1SH

D1SH was synthesized by the reported procedure with modification.[2] D1Br (1 mmol) and thiourea (1 mmol) were mixed in 5 mL of EtOH/THF = 1:1 (v/v). The mixed solution was stirred for 4 h at 353 K with the connection of a balloon filled with Ar gas. Then, 1 M KOH*aq* (2 mL) was added to the reaction solution using a syringe. After further stirring for 4 h at 353 K, the solution was cooled to room temperature followed by the addition of 1 M HCl*aq* (4 mL) using a syringe and then stirring for several minutes. The obtained white suspension was transferred to a round-bottomed flask with DCM and then evaporated to remove volatile components. A crude product was extracted from the aqueous solution with DCM three times and the extract was evaporated. The obtained oil was purified by SiO_2 column chromatography (Wakosil® 60). The oil was firstly dissolved in a minimum amount of DCM and then loaded onto the SiO_2 column packed with DCM. The product was eluted with ~3 column volume of DCM. DCM solvent used for column chromatography was bubbled with Ar gas prior to the experiment. The eluted product was evaporated with *n*-hexane and dried in vacuo to give a white solid of the title compound. Yield: 91%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.45–7.32 (m, 10H), 6.60 (d, *J* = 2.3 Hz, 2H), 6.52 (t, *J* = 2.3 Hz, 1H), 5.04 (s, 4H), 3.68 (d, *J* = 7.8 Hz, 2H), 1.78 (t, *J* = 7.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.2, 143.6, 136.9, 128.7, 128.2, 127.7, 107.4, 100.9, 70.2, 29.3. Anal. Calcd. for $C_{21}H_{20}O_2S$: C, 74.97; H, 5.99; N, 0.00; S, 9.53. Found: C, 74.89; H, 6.00; N, 0.00; S, 9.37.

2.2 D2SH

D2SH was synthesized by the reported procedure with modification.[2] D2Br (1 mmol) and thiourea (1 mmol) were mixed in 5 mL of EtOH/THF = 1:1 (v/v). The mixed solution was stirred for 4 h at 353 K with the connection of a balloon filled with Ar gas. Then, 1 M KOH*aq* (2 mL) was added to the reaction solution using a syringe. After further stirring for 4 h at 353 K, the solution was cooled to room temperature followed by the addition of 1 M HCl*aq* (4 mL) using a syringe and then stirring for several minutes. The obtained white suspension was transferred to a round-bottomed flask with DCM and then evaporated to remove volatile components. A crude product was extracted from the aqueous solution with DCM three times and the extract was evaporated. The obtained oil was collected and centrifugally washed with water two times and with MeOH three times (3500 rpm). The white solid of the title compound was dried in vacuo. Yield: 84%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.44–7.31 (m, 20H), 6.69 (d, J = 1.8 Hz, 4H), 6.57 (d, J = 2.5 Hz, overlapped, 4H), 6.47 (t, J = 2.3 Hz, 1H), 5.05 (s, 8H), 4.98 (s, 4H), 3.68 (d, J = 7.8 Hz, 2H), 1.84 (t, J = 7.8 Hz, 1H). $^{13}C\{^1H\}$NMR (100 MHz, CD_2Cl_2): δ 160.6, 160.4, 144.2, 139.9, 137.4, 128.9, 128.4, 128.0, 107.6,106.8, 101.8, 101.0, 70.5, 70.3, 29.5. Anal. Calcd. for $C_{49}H_{44}O_6S$: C, 77.34; H, 5.82; N, 0.00; S, 4.21. Found: C, 77.37; H, 5.83; N, 0.00; S, 4.09.

2.3 $[Au_{23}(SCy)_{16}]$(TOA)

$[Au_{23}(SCy)_{16}]$(TOA) was synthesized by the reported procedure[3] with modifications. $HAuCl_4 \cdot 4H_2O$ (0.9 mmol) and TOABr (1.0 mmol) were dissolved in MeOH (45 mL) and stirred for ~15 min at room temperature. CySH (4.8 mmol) was added to this reddish orange solution, and the resulting pale yellow suspension was further stirred for ~15 min at room temperature. Then, ice-cooled $NaBH_4$*aq* (0.6 M, 15 mL) was added all at once and the reaction solution was stirred for 8 h at room temperature. After the stirring, the water phase was decanted and the black oil was centrifuged with an excess amount of MeOH. The obtained brown solid was centrifugally washed with MeOH three times (3500 rpm), dried in vacuo and repeatedly extracted with DCM. The DCM extract was filtered and mixed with TOABr (~10 mg) and an excess amount of *n*-hexane. The resulting powder was collected by centrifugation and then centrifugally washed with *n*-hexane once and with toluene twice. The purple precipitate of the title compound was dried in vacuo. The yield was 14%.

2.4 Ligand exchange of $[Au_{23}(SCy)_{16}]^-$ with D*n*SH.

To the DCM solution of $[Au_{23}(SCy)_{16}]^-$ (1 mM, 1 mL), a given amount of D1SH (MR = 5, 20, 50, and 100) or D2SH (MR = 5, 10, 20, 50, and 100) with respect to $[Au_{23}(SCy)_{16}]^-$ was added. The mixed solution was stirred for 6 h at 298 K. After that, MeOH was added to this solution and the DCM was evaporated. The MeOH suspension thus obtained was transferred to Eppendorf tubes. The tubes were filled with MeOH and centrifuged (14000 rpm) to precipitate ligand-exchanged products. D1S-exchanged products were further washed with MeOH by centrifugation (14000 rpm) three times. D2S-exchanged products were washed with MeOH (14000 rpm) three times and by centrifugal reprecipitation with DCM and *n*-hexane (14000 rpm). The number of washes and the ratio of DCM:*n*-hexane (v/v) were changed depending on the amount of D2SH first added: five times for 1:10 (MR = 5); five times for 1:8 (MR = 10 and 20); and five times for 1:4 (MR = 50 and 100). The sample with MR = 5 of D1SH was repeatedly extracted with the mixed solvent of DCM:MeCN = 1:10. The others were repeatedly extracted with pure MeCN. After being dried in vacuo, the ligand-exchanged products were obtained as black powders. A similar procedure was followed for ligand exchange of $[Au_{25}(SEtPh)_{18}]^-$.

3. Characterization

3.1 Nuclear magnetic resonance (NMR) spectroscopy

^{1}H (400 MHz) and $^{13}C\{^1H\}$ (100 MHz) NMR spectra were measured by a Jeol JNM-ECS400 spectrometer. The chemical shifts in the NMR charts were calibrated by the residual proton signal of the solvent: ^{1}H NMR spectra were referenced to the signals of $CDCl_3$ at 7.26 ppm and of CD_2Cl_2 at 5.32 ppm and the ^{13}C NMR spectra were referenced to the signals of $CDCl_3$ at 77.16 ppm and of CD_2Cl_2 at 53.84 ppm.[4]

3.2 Optical absorption and photoluminescence (PL) spectroscopy

Ultraviolet-visible (UV-vis) absorption spectra were measured by Jasco V-630 and V-670 spectrophotometers. PL spectra were measured by a Horiba Fluorolog-NIR spectrophotometer at room temperature. PL spectra in the range of 600–850 nm (1.46–2.07 eV) and 850–1380 nm (0.90–1.46 eV) were detected by a photomultiplier tube and an InGaAs solid-state detector cooled by liquid N_2, respectively. Toluene solutions of $[Au_{23}(SCy)_{16-x}(SDn)_x]^-$ bubbled with Ar for ~10 min were excited at 575 nm (2.16 eV). The PL QY of $[Au_{23}(SCy)_{16}]^-$ was obtained by the relative method in the range of 1.03–1.86 eV using HITCI as a standard.[5] In the same spectral range, the

PL QYs of other $[Au_{23}(SCy)_{16-x}(SD2)_x]^-$ were relatively estimated from the PL QY of $[Au_{23}(SCy)_{16}]^-$.[5] The absorbance of all the samples was ~0.1 at the excitation energy. The raw spectral data of the absorption and PL as functions of the wavelength were converted to the energy-dependent data according to the procedure reported.[6]

3.3 PL lifetime measurement

Photoluminescence lifetime spectra were measured by a Hamamatsu Photonics PLP-10 laser diode head (371 nm, FWHM = 103 ps) and a C4780 streak camera equipped with a monochromator. Emitted photons in the range of 650–850 nm (1.46–1.91 eV) were accumulated. Toluene solutions of $[Au_{23}(SCy)_{16-x}(SD2)_x]^-$ were bubbled with Ar for ~10 min prior to the measurements. The absorbance of all the samples was ~1 at the excitation wavelength.

3.4 X-ray absorption fine structure (XAFS)

XAFS of $[Au_{23}(SCy)_{16}]^-$ and $[Au_{23}(SCy)_{4.1}(SD2)_{11.9}]^-$ at the Au L_3-edge were measured in the BL01B1 beamline at the SPring-8 facility of the Japan Synchrotron Radiation Research Institute (JASRI). The incident X-ray beam was monochromatized by an Si(111) double-crystal monochromator. The X-ray energy was calibrated using Au foil. The samples of $[Au_{23}(SCy)_{16}]^-$ and $[Au_{23}(SCy)_{4.1}(SD2)_{11.9}]^-$ were diluted with boron nitride powder, ground in an agate mortar and pressed into the square pellets (5 × 10 mm). The sample pellets were wrapped with aluminum foil and mounted on a copper holder attached to a cryostat. The XAFS spectra were measured by transmission mode using ion chambers at 10 K. Data analysis was performed using the program REX2000 ver. 2.5.9 program (Rigaku Co.). First, X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) were extracted from the raw spectra by subtracting the atomic absorption background using a cubic spline interpolation. The obtained XANES spectra were normalized to the edge height. The k^3-weighted χ spectra of EXAFS in the range of $3.0\ \text{Å}^{-1} \le k \le 21.0\ \text{Å}^{-1}$ were Fourier-transformed into r space. The curve-fitting analysis on Fourier-transformed (FT)-EXAFS was performed for one Au–S and two Au–Au bonds in the range of $1.5\ \text{Å} \le r \le 3.0\ \text{Å}$. In the curve fitting analysis, the phase shifts and backscattering amplitude functions for the Au–S and Au–Au bonds were extracted from the corresponding simulation results of the FEFF8 program[7] by setting the value of the Debye–Waller (DW) factor to 0.0036. This value did not significantly affects the phase shifts and backscattering amplitude functions.

3.5 Gel permeation chromatography (GPC)

The sample containing $[Au_{23}(SCy)_{4.3}(SD1)_{11.7}]^-$ was fractionated using a high-performance liquid chromatography (HPLC) system (LC-908; Japan Analytical Industry). A preparative GPC column (T30000; YMC Co., Ltd.) was used with the system and the UV chromatogram was monitored at 300 nm. The crude mixture in toluene (10 mg/mL, 1.5 mL) was eluted using toluene as the mobile phase with a flow rate of 6 mL/min, was recycled once and then was fractionated manually (Fig. S2). Three fractions (Fr1–3) were collected, evaporated and dried in vacuo.

3.6 Mass spectrometry

Electrospray ionization (ESI) mass spectra were measured with using a Bruker compact ESI-Q-TOF mass spectrometer. $[Au_{23}(SCy)_{16}]^-$ was dispersed in DCM/MeCN = 1:1 (v/v) at a concentration of 0.1 mg/mL. The $[Au_{23}(SCy)_{16-x}(SDn)_x]^-$ samples were dispersed in DCM/MeCN = 1:9 (v/v) at a concentration of 0.2 mg/mL. The dispersions were electrosprayed (3 µL/min) in the negative ion mode. The measurement parameters for $[Au_{23}(SCy)_{16-x}(SDn)_x]^-$ are summarized in Table S1. The mass spectra were calibrated by those of $[(CsI)_nI]^-$ as an external standard.

Table S1. Parameters of Bruker compact ESI-Q-TOF mass spectrometer to obtain the mass spectra of $[Au_{23}(SCy)_{16-x}(Dn)_x]^-$.

Source	
End Plate offset voltage (V)	800
Capillary voltage (V)	4500
Nebulizer pressure (bar)	0.1
Dry gas flow rate (L/min)	2.0

Dry temperature (K)	393
Ion transfer system	
Funnel 1 RF voltage (Vpp)	400
Funnel 2 RF voltage (Vpp)	600
Hexapole voltage (Vpp)	800
isCID energy (eV)	200
Quadrupole and collision cell	
Ion energy (eV)	70
Low mass filter (m/z)	600
Collision energy (eV)	0
Collision RF voltage (Vpp)	4200
Transfer time (μs)	250
Pre-pulse storage time (μs)	15

4. Results

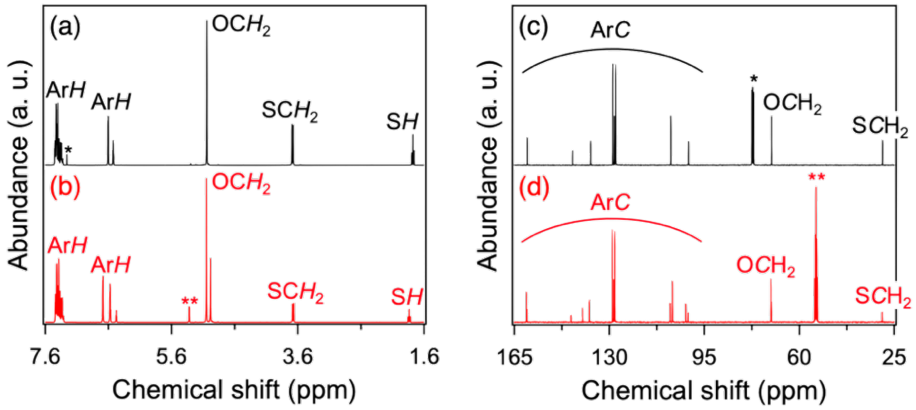

Fig. S1. ^{1}H NMR charts of (a) D1SH and (b) D2SH. ^{13}C{^{1}H} NMR charts of (c) D1SH and (d) D2SH. The assignment of peaks is also shown. * and ** indicate the residual solvent peaks of $CDCl_3$ and CD_2Cl_2, respectively.

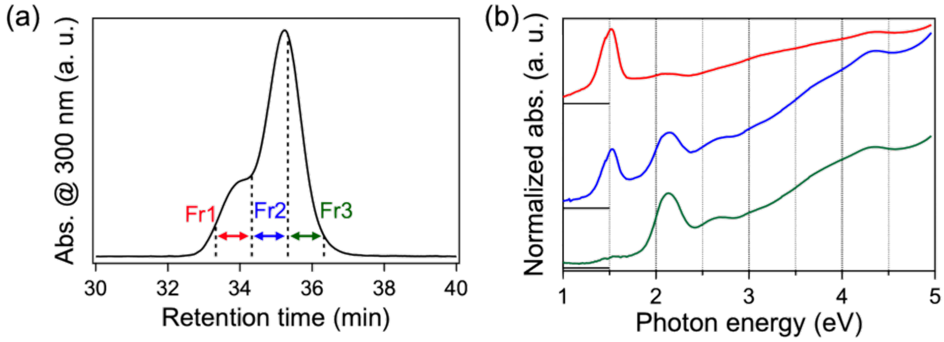

Fig. S2. (a) GPC chromatogram of the sample containing $[Au_{23}(SCy)_{4.3}(SD1)_{11.7}]^-$ and (b) UV-vis absorption spectra of Fr1 (red), Fr2 (blue) and Fr3 (green).

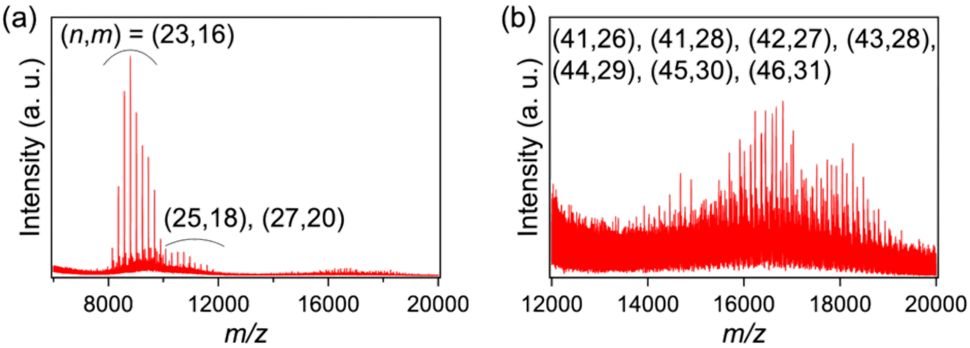

Fig. S3. (a) ESI mass spectrum of Fr1 shown in Fig. S2 and (b) its enlarged view in the high mass region. The assignments of mass peaks for $[Au_n(SCy)_{m-k}(SD1)_k]^-$ are displayed as (n, m) where $m \geq k$.

Table S2. Structural parameters of $[Au_{23}(SCy)_{16}]^-$ and $[Au_{23}(SCy)_{4.1}(SD2)_{11.9}]^-$ obtained by curve fitting analysis of Au L_3-edge FT-EXAFS and SCXRD data of $[Au_{23}(SCy)_{16}]^-$.[3]

Sample	Methods	Bonds	CN^a	r (Å)^b	σ^2 (Å^2)^c	R (%)^d
$[Au_{23}(SCy)_{16}]^-$	EXAFS at 10 K	Au–S	1.5(2)	2.320(4)	0.0037(13)	10.9
		Au–Au (short)	1.6(6)	2.711(5)	0.0035(15)	
		Au–Au (long)	1.1(8)	2.928(15)	0.0048(44)	
	SCXRD	Au–S	1.4	2.32		
		Au–Au (short)	1.6	2.71		
		Au–Au (long)	1.4	2.94		
$[Au_{23}(SCy)_{4.1}(SD2)_{11.9}]^-$	EXAFS at 10 K	Au–S	1.5(2)	2.321(4)	0.0034(12)	9.2
		Au–Au (short)	1.6(6)	2.711(5)	0.0036(16)	
		Au–Au (long)	1.2(1.0)	2.941(15)	0.0052(50)	

^{a}Coordination number, ^{b}bond length, ^{c}Debye–Waller factor, $^d R = (\sum(k^3\chi^{data}(k) - k^3\chi^{fit}(k))^2)^{1/2}/(\sum(k^3\chi^{data}(k))^2)^{1/2}$.

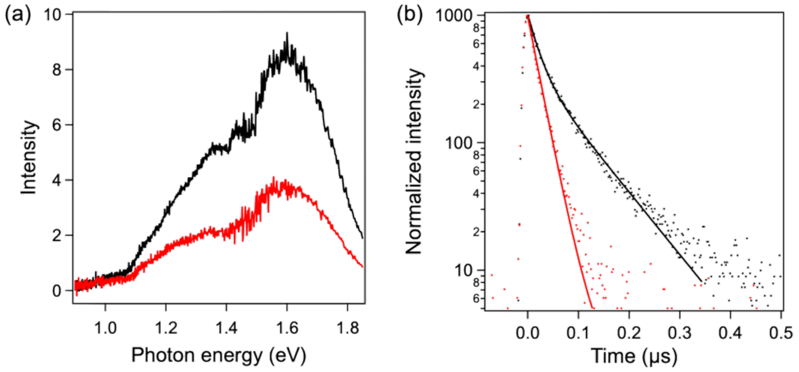

Fig S4. (a) PL spectra and (b) PL decay lifetime plots of toluene solution of $[Au_{23}(ScHex)_{16}]^-$ bubbled with Ar (black) and O_2 (red). The excited energy for (a) was 1.91 eV. The same solution was used in each measurement.

Table S3. Photophysical parameters of $[Au_{23}(SCy)_{16}]^-$ obtained by the curve fitting analysis on Fig. S4b.

Sample	$\frac{A_1}{A_1+A_2}$ (%)	τ_1 (ns)	$\frac{A_2}{A_1+A_2}$ (%)	τ_2 (ns)
Ar-bubbled $[Au_{23}(SCy)_{16}]^-$	61	21	39	89
O_2-bubbled $[Au_{23}(SCy)_{16}]^-$	99	21^a	1	89^a

^{a}The values of τ_1 and τ_2 were fixed to 21 and 89 ns, respectively.

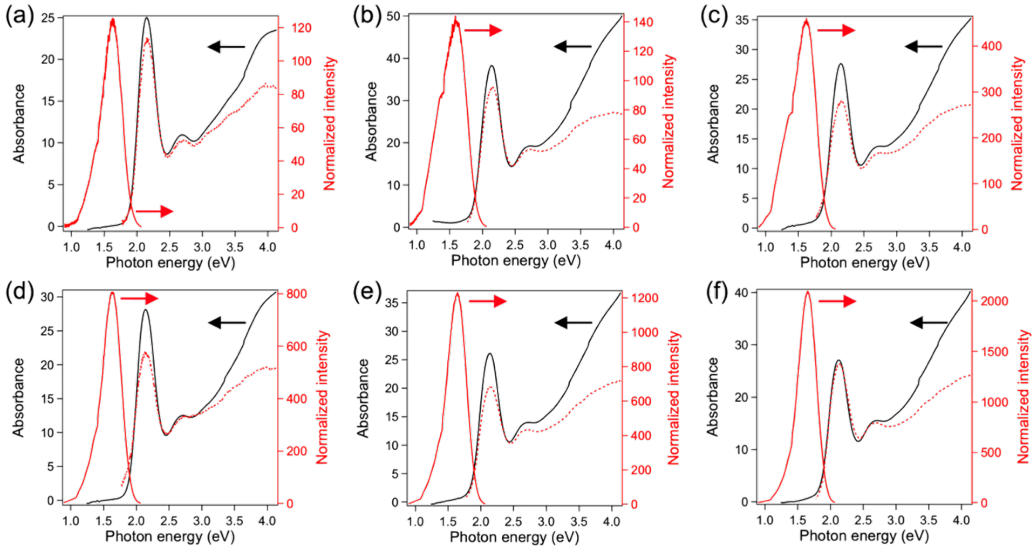

Fig. S5. Optical absorption (black), emission (red solid) and excitation spectra (red dashed) of $[Au_{23}(SCy)_{16-x}(SD2)_x]^-$ with x = (a) 0, (b) 3.0, (c) 7.7, (d) 9.4, (e) 10.0, and (f) 11.9. The excitation spectra are shown with arbitrary normalization.

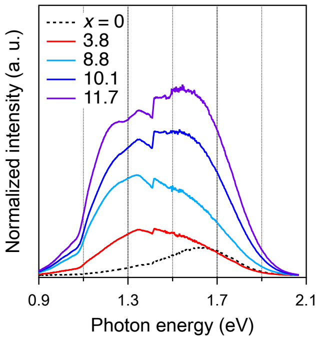

Fig. S6. PL spectra of $[Au_{23}(SCy)_{16-x}(SD1)_x]^-$ in Ar-bubbled toluene. The spectra are normalized by the absorbance at the excitation energy (2.16 eV).

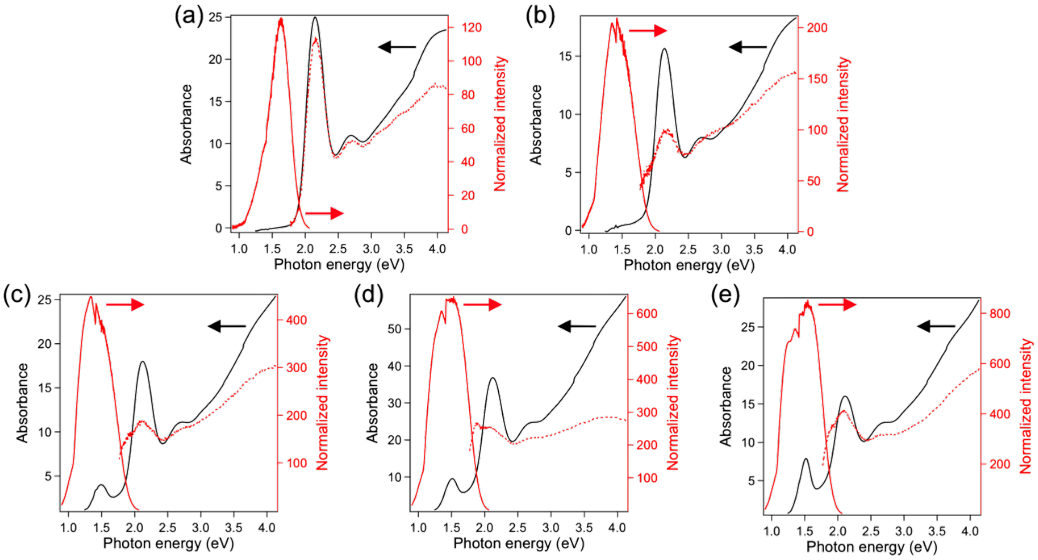

Fig. S7. Optical absorption (black), emission (red solid) and excitation spectra (red dashed) of $[Au_{23}(SCy)_{16-x}(SD1)_x]^-$ with x = (a) 0, (b) 3.8, (c) 8.8, (d) 10.1, and (e) 11.7. The excitation spectra are shown with arbitrary normalization.

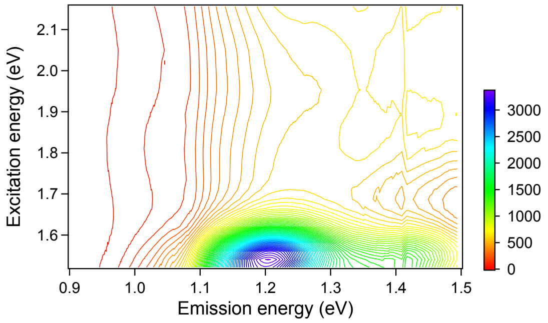

Fig. S8. PL contour map of the sample containing $[Au_{23}(SCy)_{4.3}(SD1)_{11.7}]^-$ in Ar-bubbled toluene.

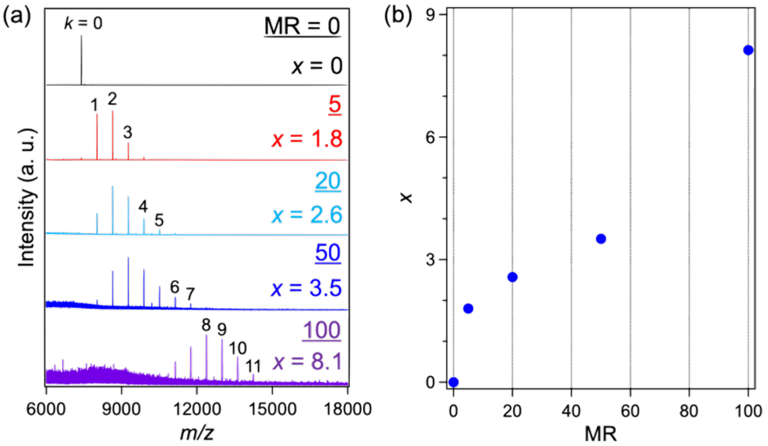

Fig. S9. (a) ESI mass spectra of $[Au_{25}(SEtPh)_{18-k}(SD2)_k]^-$ as a function of the MR of D2SH with respect to $[Au_{25}(SEtPh)_{18}]^-$. (b) Plots of the x values as a function of the MR of D2SH.

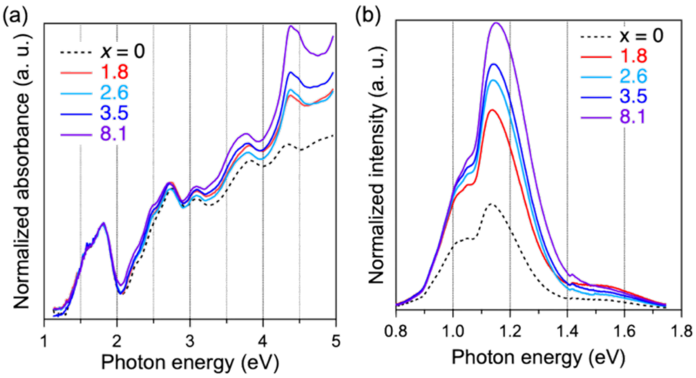

Fig. S10. (a) UV-vis absorption and (b) PL spectra of $[Au_{25}(SEtPh)_{18-x}(SD2)_x]^-$. PL was measured in Ar-bubbled toluene at the excitation energy of 1.81 eV. The spectra in (a) and (b) are normalized by the absorbance at 1.81 eV.

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