In our search of the Cambridge Structural Database (CSD) using the Cambridge Crystallographic Data Centre (CCDC) software, we found 166 matches for Ag_4 clusters with Ag–Ag interactions (**Figure S1**). Some of these structures were duplicates, which we eliminated, resulting in a total of 157 unique structures. In this work, we classified these clusters according to the scheme presented in **Figure S2** to calculate the average Ag–Ag distances ($d_{Ag–Ag}$). All entries are summarized in **Table S1** together with its emission performances.

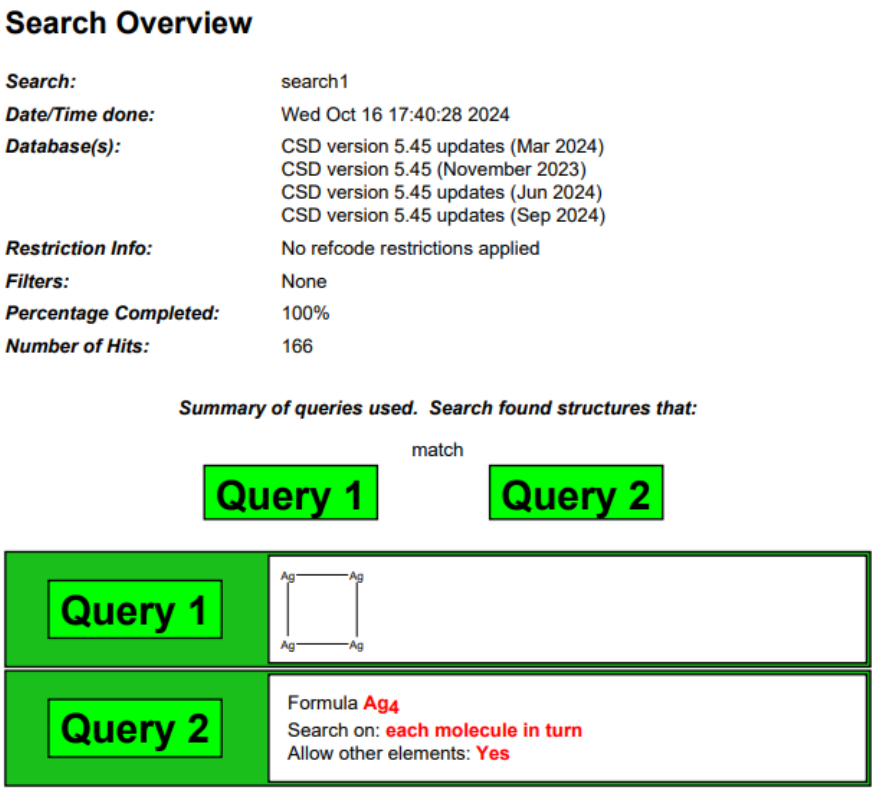


Figure S1. Results of the search for Ag_4 clusters with Ag-Ag interactions in the Cambridge Structural Database (CSD).

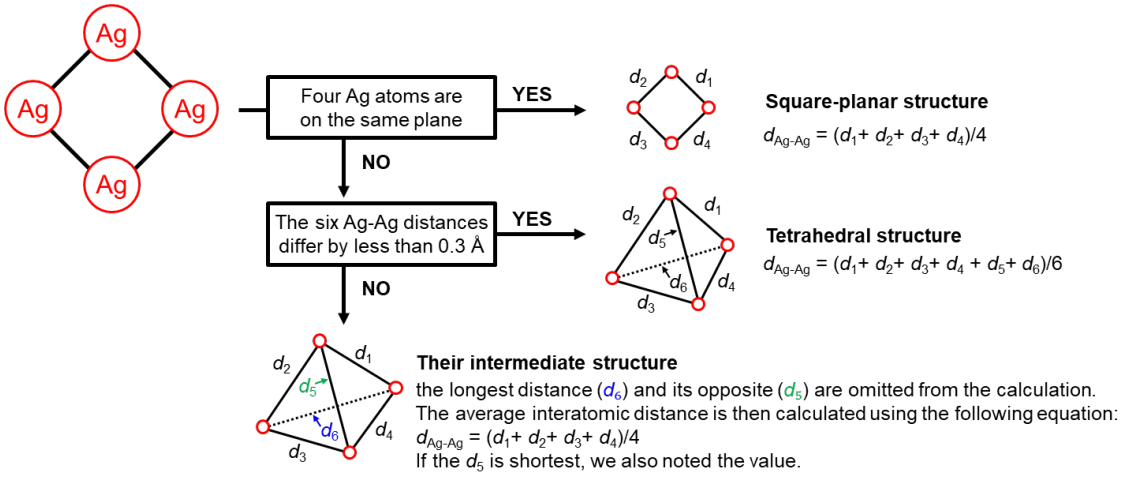


Figure S2. Schematic classification of Ag_4 clusters used for the calculation of average Ag–Ag distances ($d_{Ag–Ag}$).

Table S1. The summary of Ag–Ag distances for the clusters is presented in ascending order. When two or more molecules were present in a single CIF, the structure with the smallest $d_{Ag–Ag}$ was selected. Following Figure S2, if an intermediate structure exhibits the smallest d_5 value, this is explicitly noted. The Ag–Ag distances are reported to three decimal places.

CCDC Identifier	$d_{Ag–Ag}$ / Å (average)	Ag–Ag distances / Å	shortest Ag–Ag distance / Å (d_5 for intermediate structure)	Emission performances (λ_{MAX} / τ / Φ_{PL}, if available)
HEBLIK	2.597	2.102 / 3.092 / 2.102 / 3.092		
This work (Cluster **1**)	2.695	2.695 / 2.695 / 2.695 / 2.695		690 nm / 102 μs / 0.63 @77 K (glassy methyl-cyclohexane)
This work (Cluster **2**)	2.704	2.704 / 2.704 / 2.704 / 2.704		700 nm / 58 μs / 0.50 @77 K (glassy methyl-cyclohexane)
PENNEE	2.729	2.739 / 2.718 / 2.739 / 2.718		
NOWMER	2.739	2.733 / 2.748 / 2.744 / 2.731		
AGMFFE	2.740	2.740 / 2.740 / 2.740 / 2.740		
LEWLUU	2.740	2.754 / 2.726 / 2.754 / 2.726		
CAGBIV10	2.744	2.733 / 2.755 / 2.733 / 2.755		
BUKNUT	2.755	2.779 / 2.731 / 2.779 / 2.731		
KOMBIY	2.761	2.751 / 2.755 / 2.758 / 2.778		
HISTEI	2.763	2.762 / 2.765 / 2.774 / 2.751		
QIVHUB	2.772	2.781 / 2.762 / 2.781 / 2.762		
NEPKAU	2.788	2.768 / 2.808 / 2.768 / 2.808		
HIHTEY	2.790	2.790 / 2.791 / 2.790 / 2.791		475.9 nm @RT (solid)
KEYXUI	2.790	2.785 / 2.817 / 2.795 / 2.763		
HIHTOI	2.802	2.784 / 2.820 / 2.784 / 2.820		486.7 nm @RT (solid)
RAFSIA	2.809	2.813 / 2.782 / 2.833 / 2.807		
KENZUY	2.816	2.800 / 2.831 / 2.800 / 2.831		
TADHAH	2.821	2.807 / 2.807 / 2.834 / 2.834		
UMALOK	2.827	2.809 / 2.809 / 2.818 / 2.828 / 2.828 / 2.869		
UMALEA	2.845	2.792 / 2.792 / 2.854 / 2.854 / 2.890 / 2.890		
UJATEE	2.851	2.851 / 2.851 / 2.851 / 2.851		
KOMBIY	2.852	2.840 / 2.865 / 2.866 / 2.837		
FIQDUI	2.859	2.850 / 2.882 / 2.849 / 2.854		407nm / 0.1843 @ambient (CH_2Cl_2)
UMIFEB	2.861	2.861 / 2.861 / 2.861 / 2.861		
IBUGOE	2.869	2.829 / 2.909 / 2.909 / 2.829		
SUJTEX	2.871	2.841 / 2.900 / 2.841 / 2.900		
WAFVAE	2.871	2.852 / 2.852 / 2.874 / 2.874 / 2.879 / 2.897		
XALWUD	2.876	2.842 / 2.940 / 2.865 / 2.856		
HEXYAO	2.876	2.748 / 2.799 / 2.805 / 3.150		
VAMGIZ	2.880	2.821 / 2.880 / 2.935 / 2.882		

POJVUG	2.888	2.896 / 2.875 / 2.883 / 2.896		
TIMBAT	2.889	2.784 / 2.794 / 2.932 / 2.932 / 2.945 / 2.945		
VUVTOW	2.892	2.837 / 2.946 / 2.837 / 2.946		
COZPIT	2.893	2.846 / 2.941 / 2.846 / 2.941		433 nm in @RT (CH_2Cl_2)
IGAGAB	2.898	2.745 / 2.813 / 2.874 / 2.943 / 2.992 / 3.020		
UMALUQ	2.898	2.741 / 2.741 / 3.055 / 3.055		
JAVZEO	2.901	2.894 / 2.909 / 2.894 / 2.909		
JAVZAK	2.903	2.899 / 2.906 / 2.899 / 2.906		
LIBMAN	2.909	2.928 / 2.890 / 2.928 / 2.890		
WIXFAN	2.911	2.871 / 2.950 / 2.950 / 2.871		538 nm / 35.9 μs @77 K (2MeTHF) ~485 nm / 4.6, 37μs (biexponential fit) and 619 nm / 50 μs @16-20 K (solid)
WIXFER	2.920	2.889 / 2.952 / 2.952 / 2.889		572 nm / 35.7 μs @77 K (2MeTHF) 613 nm / 3.9, 21 μs (biexponential fit) @16-20 K (solid)
FAYHOC01	2.922	2.874 / 2.969 / 2.874 / 2.969		
FALJUY	2.923	2.809 / 3.036 / 2.809 / 3.036		
GENKAP	2.932	3.021 / 2.839 / 2.922 / 2.947		527 nm @RT (solid)
VAMGAR02	2.933	2.924 / 2.989 / 2.794 / 3.026		
MUCXIR	2.934	2.837 / 2.981 / 2.937 / 2.981		422 nm / 7.52 μs @298 K (solid) 442 nm @77 K (solid) 418 nm / 0.31 μs / 0.025 @298 K(CH_2Cl_2) 426 nm @77 K (MeOH/EtOH(4:1))
JEPBUE	2.935	2.935 / 2.935 / 2.935 / 2.935		
PEWZAS	2.938	2.938 / 2.938 / 2.938 / 2.938		
SALMAT01	2.945	2.869 / 3.021 / 2.869 / 3.021		
YASKUZ	2.950	3.127 / 2.772 / 3.127 / 2.772		
CAQJAG	2.951	3.004 / 2.898 / 3.004 / 2.898		
HEXYIW	2.952	2.903 / 2.897 / 2.908 / 3.098	2.889	
DAHCUK	2.953	2.936 / 2.970 / 2.936 / 2.970		
BOKPOH	2.954	2.887 / 2.990 / 3.028 / 2.912		
OHILUP	2.954	2.959 / 2.917 / 2.981 / 2.958		
RULMIX	2.954	2.887 / 2.990 / 3.028 / 2.912		
JOLJIH	2.954	2.912 / 2.912 / 2.912 / 2.912 / 3.038 / 3.038		Emission for its nanoparticle is reported
COZPEP	2.955	2.906 / 3.004 / 2.906 / 3.004		
VAMGAR	2.957	2.949 / 3.006 / 2.812 / 3.059		
QAFFUY	2.958	2.937 / 2.978 / 2.937 / 2.978		499 nm @RT (CH_2Cl_2)
NIXKAK	2.960	2.960 / 2.960 / 2.960 / 2.960 / 2.960 / 2.960		Emissive (details partly available in SI)
HACBEV	2.962	2.994 / 2.941 / 2.968 / 2.945		476 nm / 380 μs @77 K (solid) 468 nm / 109 μs @77 K (glass*)

				*ethanol−methanol−dichloromethane (4:1:0.1, v/v)
WEFJOG	2.963	2.916 / 3.010 / 2.916 / 3.010		
TILZOE	2.965	2.710 / 2.876 / 3.133 / 3.142		
MUCYEO	2.967	2.945 / 2.989 / 2.945 / 2.989		515 nm / 0.50 μs @298 K (solid) 544 nm @77 K (solid) 510 nm @298 K (CH_2Cl_2) 542 nm @77 K (MeOH/EtOH(4:1))
AVEXAB	2.969	2.997 / 2.941 / 2.997 / 2.941		
MUCXOX	2.969	2.867 / 3.071 / 2.867 / 3.071		479 nm / 0.93 μs @298 K (solid) 478 nm @77 K (solid) 426 nm @77 K (butyronitrile)
PIFYUZ	2.970	2.839 / 2.902 / 3.182 / 2.958	2.857	
TEMPEJ	2.971	2.945 / 2.996 / 2.945 / 2.996		
LEJCIP	2.975	2.945 / 3.005 / 2.945 / 3.005		
OHILEZ	2.976	2.974 / 2.977 / 2.974 / 2.977		
HOPRIR	2.977	2.960 / 2.972 / 2.976 / 2.999		
AGUXAE	2.982	2.911 / 3.052 / 2.911 / 3.052		
MUCXUD	2.983	3.053 / 2.913 / 3.053 / 2.913		496 nm / 0.88 μs @298 K (solid) 471 nm @77 K (solid) 435 nm / 0.22 μs / 0.00513 @298 K (CH_2Cl_2) 401–496nm @77 K (butyronitrile)
HACBIZ	2.985	2.922 / 3.020 / 2.998 / 3.000		465 nm / 503 μs @77 K (solid) 473 nm / 118 μs @77 K (glass*) *ethanol−methanol−dichloromethane (4:1:0.1, v/v)
ZUJDEN	2.985	3.083 / 2.988 / 2.922 / 2.948		
BEYLAV	2.986	2.942 / 3.016 / 3.005 / 2.980		
HACBAR	2.986	2.962 / 3.009 / 2.962 / 3.009		485 nm / 258 μs @298 K (solid) 483 nm / 495 μs @77 K (solid) 472 nm / 107 μs @77 K (glass*) *ethanol−methanol−dichloromethane (4:1:0.1, v/v)
TOVNEA	2.987	2.964 / 3.009 / 2.964 / 3.009		
HEXYOC	2.992	2.894 / 2.913 / 2.929 / 3.060 / 3.062 / 3.096		
LEJNIB	2.993	3.017 / 2.969 / 3.017 / 2.969		
ZOHVOL01	2.993	2.998 / 2.987 / 2.998 / 2.987		
QASSAF	2.995	2.927 / 3.057 / 2.909 / 3.086		
UGOKOR	2.997	3.054 / 3.011 / 2.909 / 3.012		
NUKQUH	3.003	3.010 / 3.214 / 2.939 / 2.850	2.826	
TODDUO	3.007	2.870 / 3.144 / 2.870 / 3.144		
QAFGAF	3.012	2.999 / 3.024 / 2.999 / 3.024		Detail not specified
OKIKID	3.014	3.072 / 2.956 / 3.072 / 2.956		

GENJUI	3.014	2.983 / 2.947 / 3.092 / 3.032		508 nm @RT (solid)
HEXYES	3.015	2.893 / 2.901 / 2.973 / 3.053 / 3.069 / 3.203		
JEPBOY	3.023	3.050 / 2.996 / 3.050 / 2.996		
ZINVOL	3.028	3.020 / 3.020 / 3.032 / 3.032 / 3.032 / 3.032		502 nm @RT (solid)
PUSQOK	3.030	2.859 / 2.912 / 3.288 / 3.062	2.830	
LAXJEB	3.031	2.962 / 3.070 / 3.016 / 3.075		
XEKREL	3.033	2.969 / 3.095 / 3.016 / 3.051		
FAPJAJ	3.034	2.943 / 3.124 / 2.943 / 3.124		
KEWQOV	3.034	2.850 / 3.177 / 2.841 / 3.268		
UJIWAO	3.036	3.009 / 3.009 / 3.009 / 3.063 / 3.063 / 3.063		
AGUXEI	3.037	3.149 / 2.925 / 3.149 / 2.925		
XEGSEI	3.037	3.127 / 3.205 / 2.904 / 2.910		
OWEPIR	3.044	2.866 / 3.222 / 2.866 / 3.222		
COHSEY	3.048	3.028 / 3.028 / 3.028 / 3.028 / 3.088 / 3.088		
ZIRNIX	3.048	2.944 / 3.088 / 2.944 / 3.216		
NIXKEO	3.048	2.977 / 2.977 / 2.977 / 3.118 / 3.118 / 3.118		608 nm / 34.77 μs / 0.0702 @ambient (solid) 615 nm / 2.03 μs / 0.0105 @ambient (CH_2Cl_2) ? nm / 78.68 μs / 0.1400 @ambient (polymer film)
KEBLUY	3.051	2.991 / 3.006 / 3.017 / 3.022 / 3.074 / 3.193		
MUCYAK	3.055	2.928 / 2.951 / 2.997 / 3.046 / 3.199 / 3.207		489 nm / 0.30 μs @298 K (solid) 489 nm @77 K (solid) 464 nm / 0.29 μs / 0.033 @298 K (CH_2Cl_2) 442 nm @77 K (MeOH/EtOH(4:1))
UFIVEM	3.056	3.122 / 2.989 / 3.122 / 2.989		
BONHOC	3.060	2.965 / 2.972 / 3.059 / 3.113 / 3.118 / 3.134		
PUPXUT	3.062	2.819 / 3.305 / 2.819 / 3.305		
OWEPOX	3.065	2.909 / 3.222 / 2.909 / 3.222		
QECGUA	3.065	2.958 / 2.988 / 3.078 / 3.085 / 3.132 / 3.151		
RECRAW	3.065	3.058 / 3.058 / 3.072 / 3.072		
FADMEE	3.070	2.963 / 3.224 / 3.116 / 2.976	2.860	Emissive in solid state (details not specified)
TIDHET	3.073	3.121 / 3.024 / 3.121 / 3.024		
AGUWOR	3.077	3.109 / 3.045 / 3.109 / 3.045		
FOLBOY	3.077	3.074 / 3.060 / 3.074 / 3.100		
PUSSOM	3.077	2.780 / 2.908 / 3.518 / 3.100		
SEJNED	3.083	3.083 / 3.083 / 3.083 / 3.083		562 nm / 17.7 μs @77 K (2MeTHF) 669 nm / 19.2 μs @77 K (solid)
UJIVUH	3.085	3.055 / 3.055 / 3.055 / 3.115 / 3.115 / 3.115		
VUHSAT	3.090	3.172 / 3.046 / 2.958 / 3.183	2.842	
ZELBEB01	3.095	3.080 / 3.080 / 3.094 / 3.099 / 3.099 / 3.118		
JOLHIB	3.098	3.083 / 3.112 / 3.083 / 3.112		

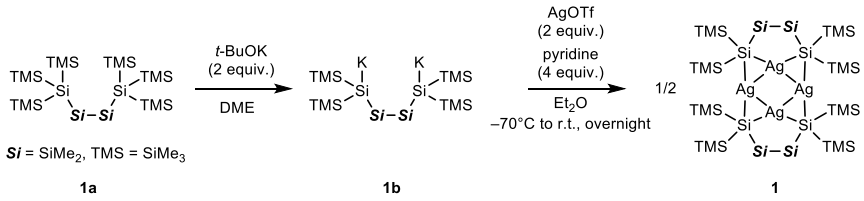
TOJSAM	3.099	3.038 / 3.160 / 3.038 / 3.160		516 nm / 1.0±0.1 μs @298 K (solid) 536 nm @77K (solid) 628 nm / 1.2±0.1 μs @298 K (acetone) 628 nm / 1.5±0.2 μs @298 K (MeCN)
ZELBAX	3.099	3.088 / 3.088 / 3.105 / 3.105 / 3.105 / 3.105		
IZECUM	3.103	2.885 / 3.320 / 2.885 / 3.320		464 nm @RT (solid)
KEBLIM	3.103	2.885 / 3.320 / 2.885 / 3.320		
ZELBEB	3.107	3.096 / 3.096 / 3.101 / 3.112 / 3.112 / 3.127		
ZELBIF01	3.108	3.088 / 3.088 / 3.091 / 3.123 / 3.123 / 3.132		
WOHVOI	3.115	3.065 / 3.102 / 3.127 / 3.164		
SEJNAZ	3.116	3.116 / 3.116 / 3.116 / 3.116		592 nm / 20.5 μs @77 K (2MeTHF) 682 nm / 20.4 μs @77 K (solid)
ZELBIF	3.119	3.092 / 3.102 / 3.102 / 3.138 / 3.138 / 3.144		
RENDOG	3.122	3.030 / 3.214 / 3.030 / 3.214		
NEYWIZ	3.127	3.186 / 3.020 / 3.179 / 3.124	2.819	
KIHCAF	3.134	3.013 / 3.049 / 3.111 / 3.189 / 3.213 / 3.232		
PIFXOS	3.134	3.051 / 3.188 / 3.017 / 3.281	2.874	
DAHCUK	3.135	3.129 / 3.145 / 3.161 / 3.104		
TOJSEQ	3.139	3.055 / 3.222 / 3.055 / 3.222		527 nm/ 0.9±0.1 μs @298 K (solid) 552 nm @77 K (solid) 570 nm / 1.3±0.1 μs @298 K (acetone) 572 nm / 3.4±0.3 μs @298 K (MeCN)
ZIWNAX	3.140	3.227 / 3.053 / 3.227 / 3.053		
PEQDIZ	3.143	3.256 / 3.030 / 3.256 / 3.030		537 nm / 3.47 μs @298 K (solid) 540 nm / 11.2 μs @77 K (solid) 570 nm / 0.39 @298 K (CH_2Cl_2) 557 nm / 0.019 @298 K (THF)
SAKTED	3.144	3.068 / 3.220 / 3.068 / 3.220		
IDIXOI	3.145	3.058 / 3.086 / 3.103 / 3.134 / 3.137 / 3.354		
YEMWUI	3.149	3.334 / 3.036 / 3.175 / 3.050		
YILHEK	3.150	3.062 / 3.086 / 3.143 / 3.162 / 3.183 / 3.263		
QUKCIJ	3.154	3.154 / 3.154 / 3.154 / 3.154		
PEQDUL	3.181	3.183 / 3.179 / 3.183 / 3.179		
SEPMIJ	3.200	3.220 / 3.214 / 3.171 / 3.193		
DUYKAJ	3.203	3.124 / 3.281 / 3.124 / 3.281		
TOJSIU	3.214	3.071 / 3.357 / 3.071 / 3.357		574 nm / 3.1±0.2 μs @298 K (solid) 588 nm @77 K (solid) 615 nm / 1.4±0.1 μs @298 K (acetone) 626 nm / 3.3±0.3 μs @298 K (MeCN)
PECKOY	3.217	3.259 / 3.174 / 3.259 / 3.174		

NIVHEG	3.228	3.223 / 3.232 / 3.223 / 3.232	
GIGJUC	3.252	3.208 / 3.295 / 3.208 / 3.295	425 nm (in solid state)
PEQDOF	3.262	3.266 / 3.258 / 3.266 / 3.258	660 nm / 0.15 μs @298 K (solid) 707 nm / 10.1 μs @77 K (solid)
XOKQIY	3.296	3.126 / 3.328 / 3.354 / 3.375	
COHSUO	3.306	3.306 / 3.306 / 3.306 / 3.306	
ZUQGUN	3.367	3.426 / 3.306 / 3.426 / 3.310	
KIFQOF	3.384	3.302 / 3.186 / 3.451 / 3.595	
VASCIC	3.457	3.408 / 3.429 / 3.506 / 3.483	
FILNUJ	N.A.	Structure not available	

General for the synthesis and characterization of the Ag_4 clusters **1** and **2**.

All reactions were carried out under a dry nitrogen atmosphere using either Schlenk-line or glove-box techniques. All solvents used for the reaction were treated with oven-dried molecular sieves before use. ^{1}H and proton-decoupled ^{13}C ($^{13}C\{^{1}H\}$) and ^{29}Si ($^{29}Si\{^{1}H\}$) NMR spectra were recorded using a JEOL ECP 600 (600 MHz for ^{1}H, 151 MHz for $^{13}C\{^{1}H\}$, and 119 MHz for $^{29}Si\{^{1}H\}$). Chemical shifts (δ) are reported in ppm, using the residual protons in the deuterated solvents as internal standards for the ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra, as well as tetramethylsilane for ^{29}Si NMR. Elemental analyses (C, H) were carried out on a Thermo Scientific FLASH 2000 Organic Elemental Analyzer. X-ray crystallography on single crystals of **1** and **2** was performed using a Rigaku Saturn CCD area detector with graphite-monochromated Mo-Kα radiation (λ = 0.71075 Å). The data were collected at 113 K using the ω scan mode in the θ range of $1.784 \leq \theta \leq 31.180$ deg (**1**) or $1.520 \leq \theta \leq 31.137$ deg (**2**). The data obtained were processed using Crystal-Clear (Rigaku) and were corrected for Lorentz and polarization effects. The structures were solved by direct methods[1], and expanded using Fourier techniques. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 14,970 observed reflections and 378 variable parameters for **1**, or 15219 observed reflections and 378 variable parameters for **2**. Neutral atom scattering factors were taken from the International Tables for Crystallography (IT), Vol. C, Table 6.1.1.4[2]. Anomalous dispersion effects were included in Fcalc[3]; the values for Δf′ and Δf″ were those of Creagh and McAuley[4]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[5]. All calculations were performed using the CrystalStructure[6] crystallographic software package, except for the refinement, which was performed using SHELXL Version 2017/1[7]. ORTEP illustrations with thermal displacement ellipsoids at 50% probability are also shown, where the H atoms are omitted for clarity (**Figures S9-S10**).

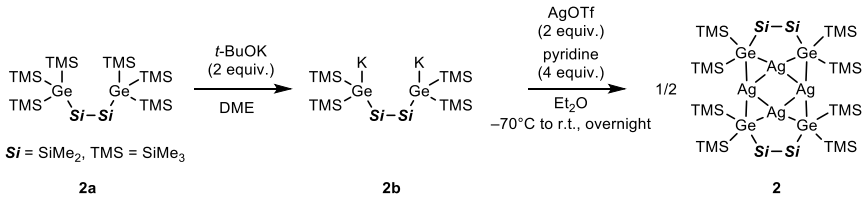
Synthesis of the Ag_4 cluster 1:



We prepared the silyl dianion **1b** using a slightly modified version of the reference method.[8] In a 50 mL Schlenk flask, 1,1,1,4,4,4-hexakis(trimethylsilyl)tetramethyltetrasilane (612 mg, 1.00 mmol) (**1a**) was prepared, to which a solution of *t*-BuOK (231 mg, 2.06 mmol) in 10 mL of 1,2-dimethoxyethane (DME) was added, and the mixture was stirred at room temperature for 21 hours. After removing the solvent, the residue was dissolved in 10 mL of diethyl ether to prepare the silyl dianion (**1b**) solution. In a separate 50 mL Schlenk flask, AgOTf (516 mg, 2.01 mmol) was dispersed in 10 mL of diethyl ether, followed by the addition of pyridine (325 μL, 4.03 mmol), and stirred at room temperature for 10 minutes. The suspension was then cooled to –78 °C, and the **1b** solution was added dropwise. The reaction mixture was stirred at –78 °C for 16.5 hours, after which insoluble materials were removed by centrifugation. The solvent was removed from the supernatant, and the crude product was purified by passing through silica gel using pentane as the eluent. After concentration of the solution and recrystallization at –78 °C, Ag_4 cluster **1** was obtained as orange crystals (348 mg, 52%). ^{1}H NMR (600 MHz, r.t., C_6D_6): δ = 0.54 (s, 24H,

$SiMe_2$), 0.52 (s, 72H, $SiMe_3$). ^{13}C NMR (151 MHz, r.t., C_6D_6): 6.70 ($SiMe_3$), 1.28 ($SiMe_2$). ^{29}Si NMR (119 MHz, r.t., C_6D_6): −2.25 (Si(*Si*Me_3)), −33.53 (*Si*Me_2), −146.60 (*Si*($SiMe_3$)). Anal. Calcd. for $C_{32}H_{96}Ag_4Si_{16}$: C, 28.22; H, 7.11. Found: C, 27.82; H, 7.29.

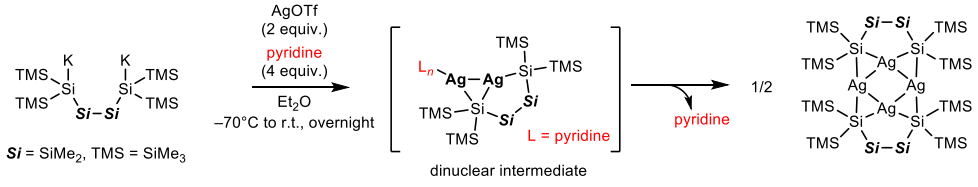
Synthesis of the Ag_4 cluster 2:



We prepared the silyl dianion **1b** using a slightly modified version of the reference method.[9] In a 50 mL Schlenk flask, 1,2-bis[tris(trimethylsilyl)germyl]tetramethyldisilane (701 mg, 1.00 mmol) (**2a**) was prepared, to which a solution of *t*-BuOK (227 mg, 2.02 mmol) in 10 mL of DME was added, and the mixture was stirred at room temperature for 21 hours. After removing the solvent, the residue was dissolved in 10 mL of diethyl ether to prepare the germyl dianion (**2b**) solution. In a separate 50 mL Schlenk flask, AgOTf (515 mg, 2.00 mmol) was dispersed in 10 mL of diethyl ether, followed by the addition of pyridine (325 μL, 4.03 mmol), and stirred at room temperature for 10 minutes. The suspension was then cooled to –78 °C, and the germyl dianion solution was added dropwise. The reaction mixture was stirred at –78 °C for 16.5 hours, after which insoluble materials were removed by centrifugation. The solvent was removed from the supernatant, and the crude product was purified by passing through silica gel using pentane as the eluent. After concentration of the solution and recrystallization at –78 °C, Ag_4 cluster **2** was obtained as orange crystals (274 mg, 36%). ^1H NMR (600 MHz, r.t., C_6D_6): δ = 0.59 (s, 24H, $SiMe_2$), 0.55 (s, 72H, $SiMe_3$). ^{13}C NMR (151 MHz, r.t., C_6D_6): 7.19 ($SiMe_3$), 1.90 ($SiMe_2$). ^{29}Si NMR (119 MHz, r.t., C_6D_6): 3.01 ($SiMe_3$), −22.95 ($SiMe_2$). Anal. Calcd. for $C_{32}H_{96}Ag_4Ge_4Si_{12}$: C, 24.96; H, 6.28. Found: C, 24.98; H, 6.37.

Probable role of pyridine as an additive:

Piers and co-workers have reported Ag_2 complexes with DMAP or bipyridine ligands,[10] and their structures correspond to half of our tetranuclear cluster. Based on this observation, pyridine likely plays a role in stabilizing a dinuclear intermediate, similar to their Ag_2 complexes, as shown in the scheme below. Although we did not directly isolate such a dinuclear intermediate in our synthesis, computational studies by Tsipis and co-workers have shown that in the absence of an auxiliary ligand, the tetranuclear cluster is thermodynamically more stable than the dinuclear species.[11] Thus, we suggest that pyridine, being a relatively labile auxiliary ligand, temporarily stabilizes the dinuclear intermediate but subsequently dissociates, enabling the selective formation of the tetranuclear cluster.



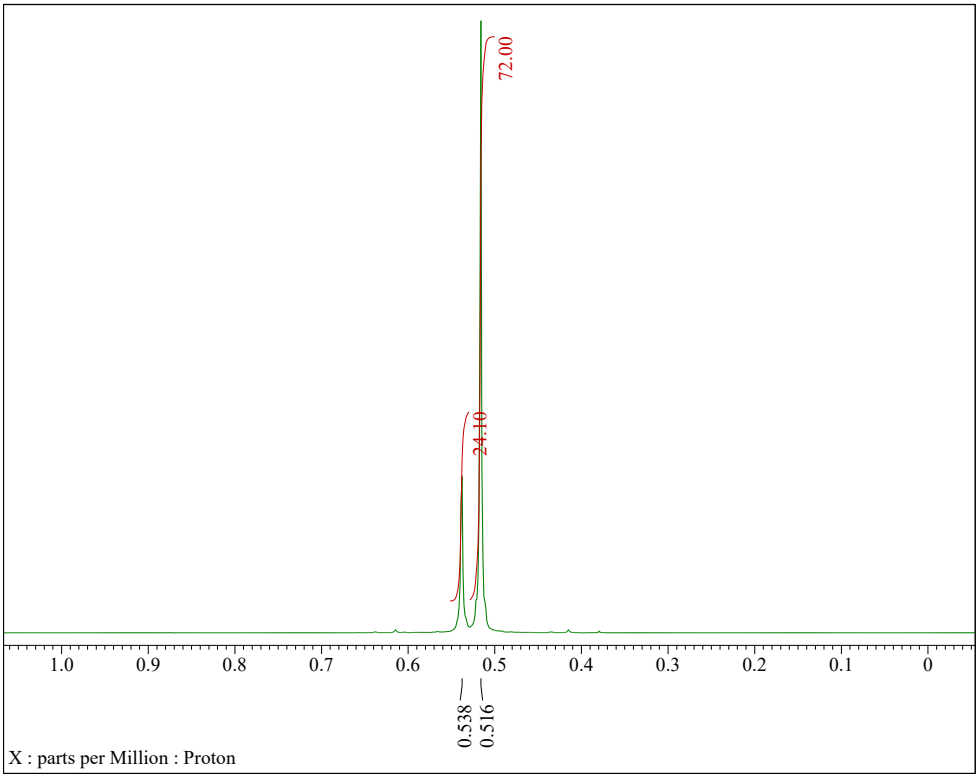


Figure S3. ^{1}H NMR spectra of the Ag_4 cluster **1**.

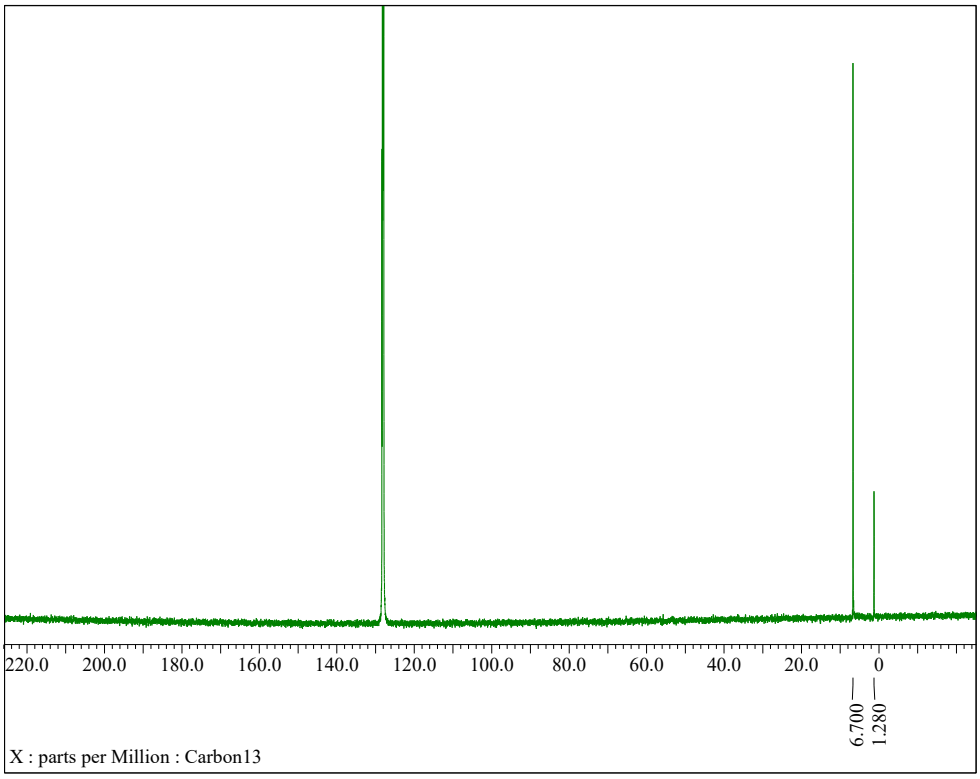


Figure S4. ^{13}C NMR of the Ag_4 cluster **1**.

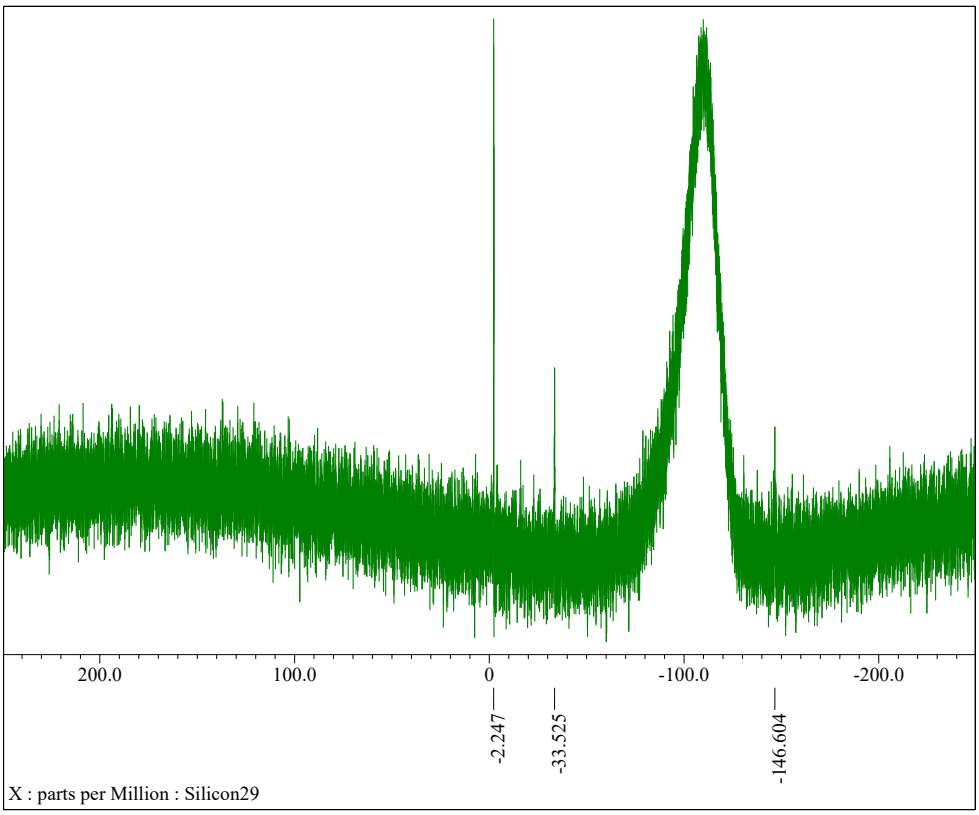


Figure S5. ^{29}Si NMR of the Ag_4 cluster **1**

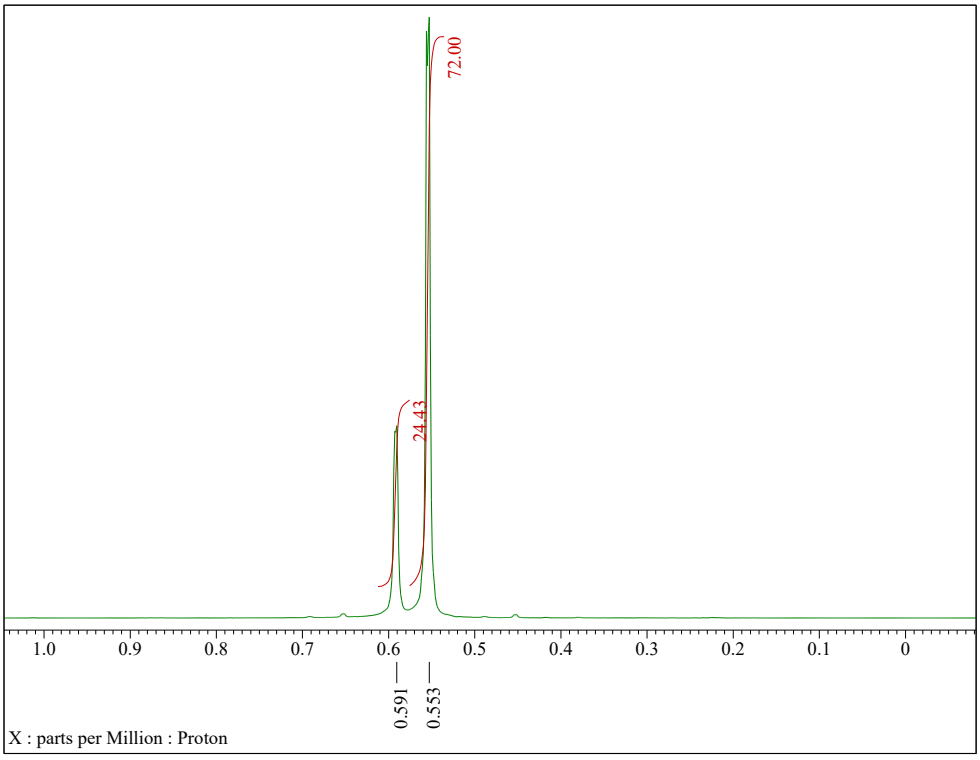


Figure S6. ^{1}H NMR spectra of the Ag_4 cluster **2**.

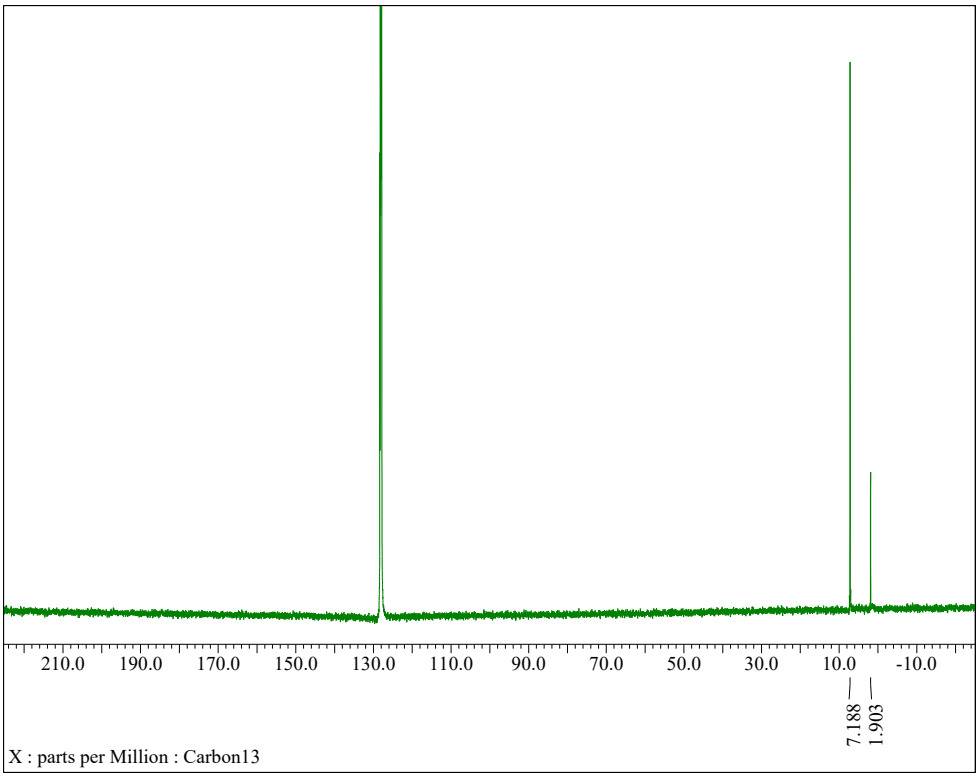


Figure S7. ^{13}C NMR of the Ag_4 cluster **2**.

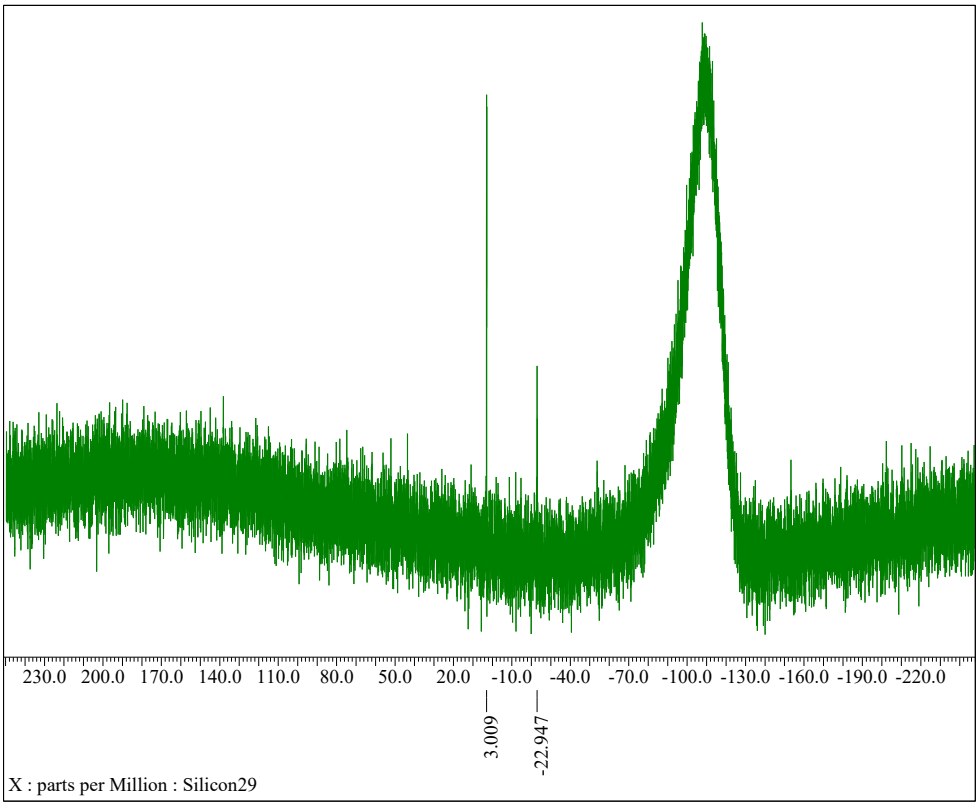


Figure S8. ^{29}Si NMR of the Ag_4 cluster **2**.

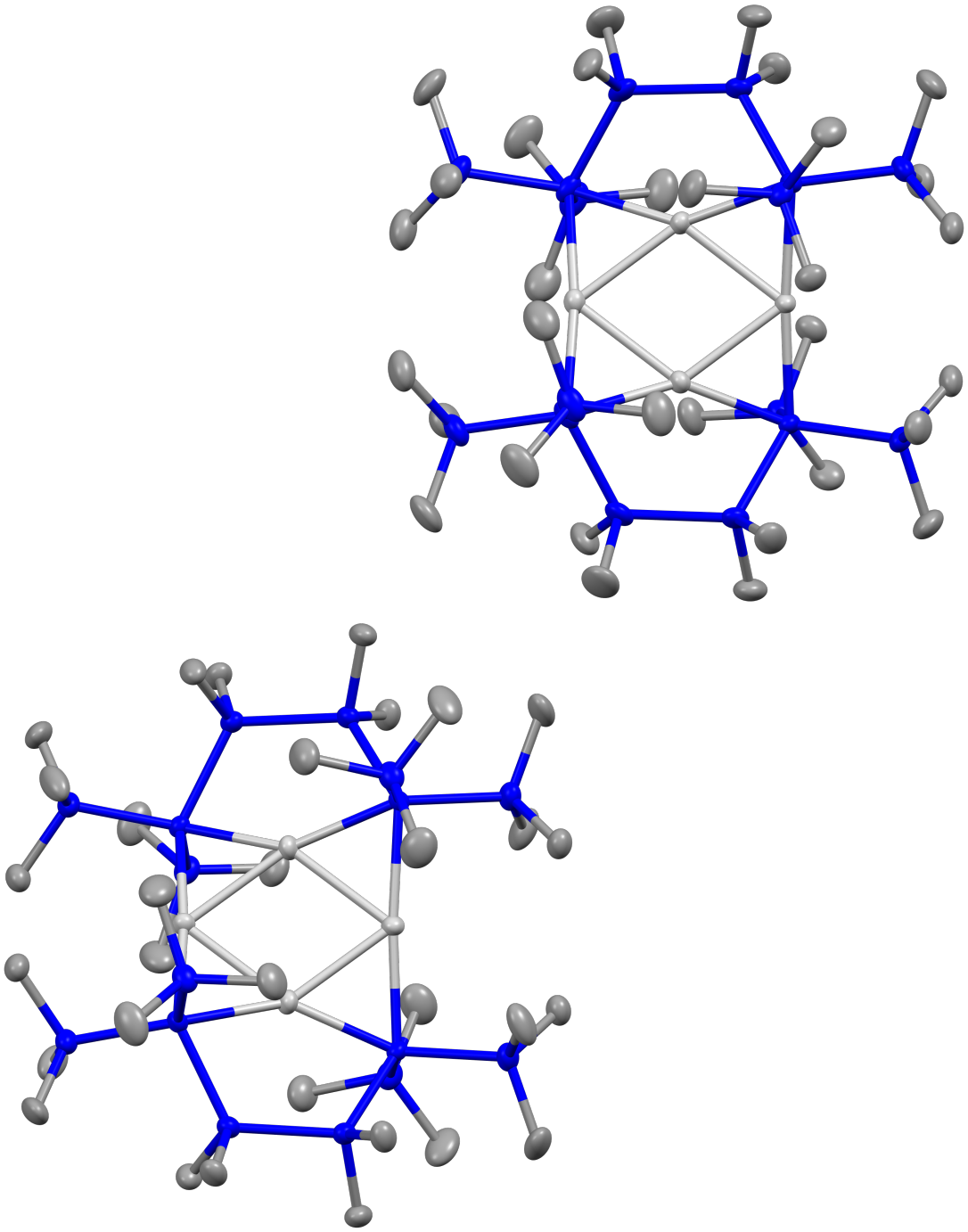


Figure S9. ORTEP drawing of the Ag_4 cluster **1** with 50% probability of thermal ellipsoids. H atoms are omitted for clarity.

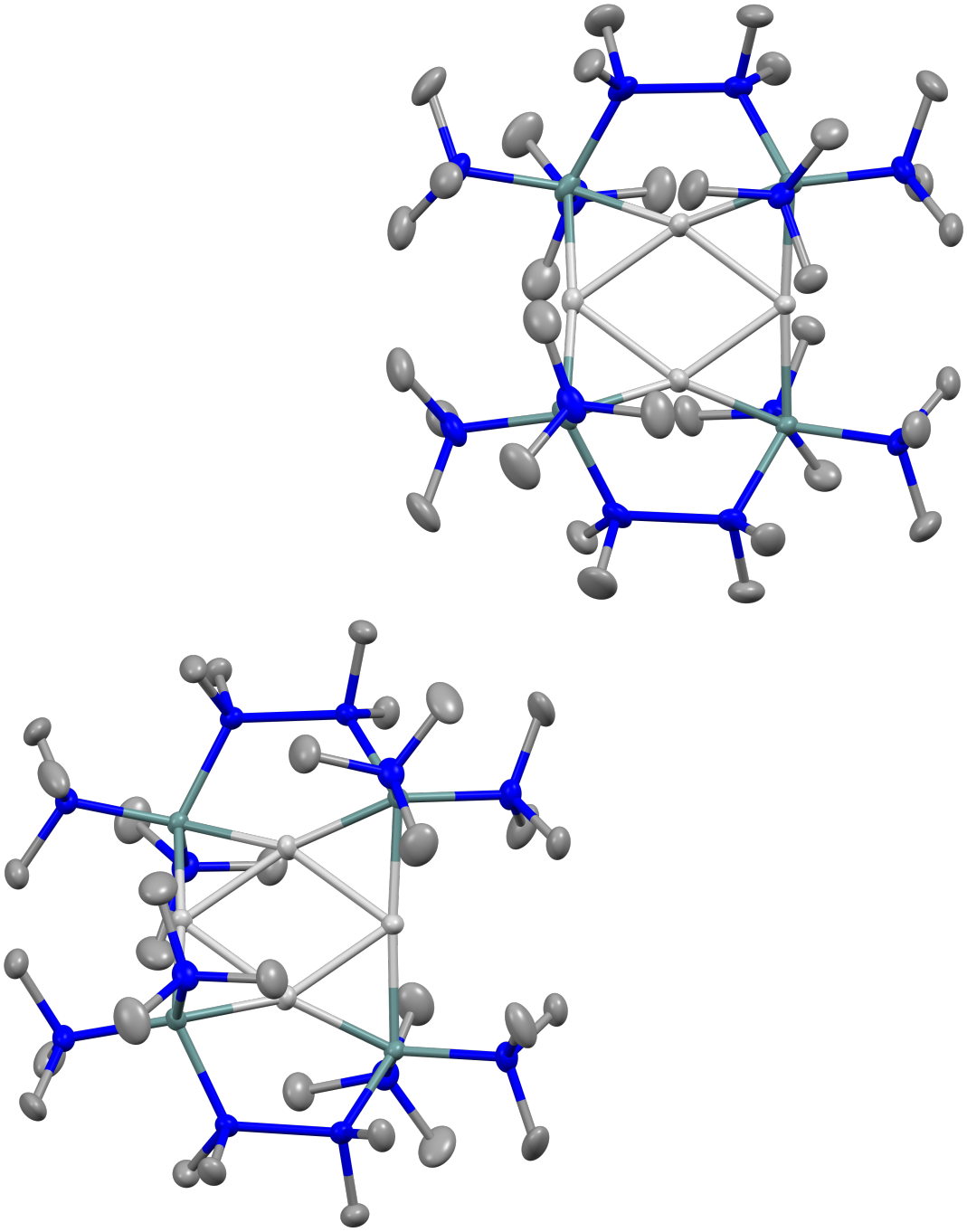


Figure S10. ORTEP drawing of the Ag_4 cluster **2** with 50% probability of thermal ellipsoids. H atoms are omitted for clarity.

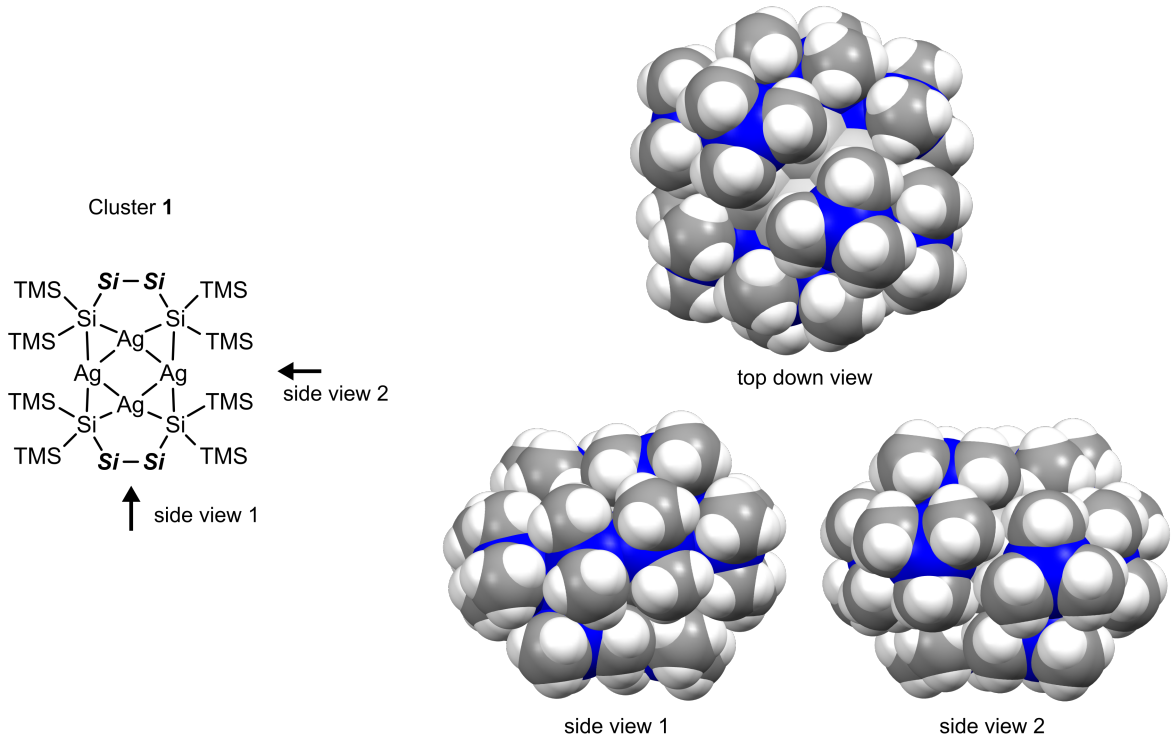


Figure S11. Space-filling model of the Ag_4 cluster **1**.

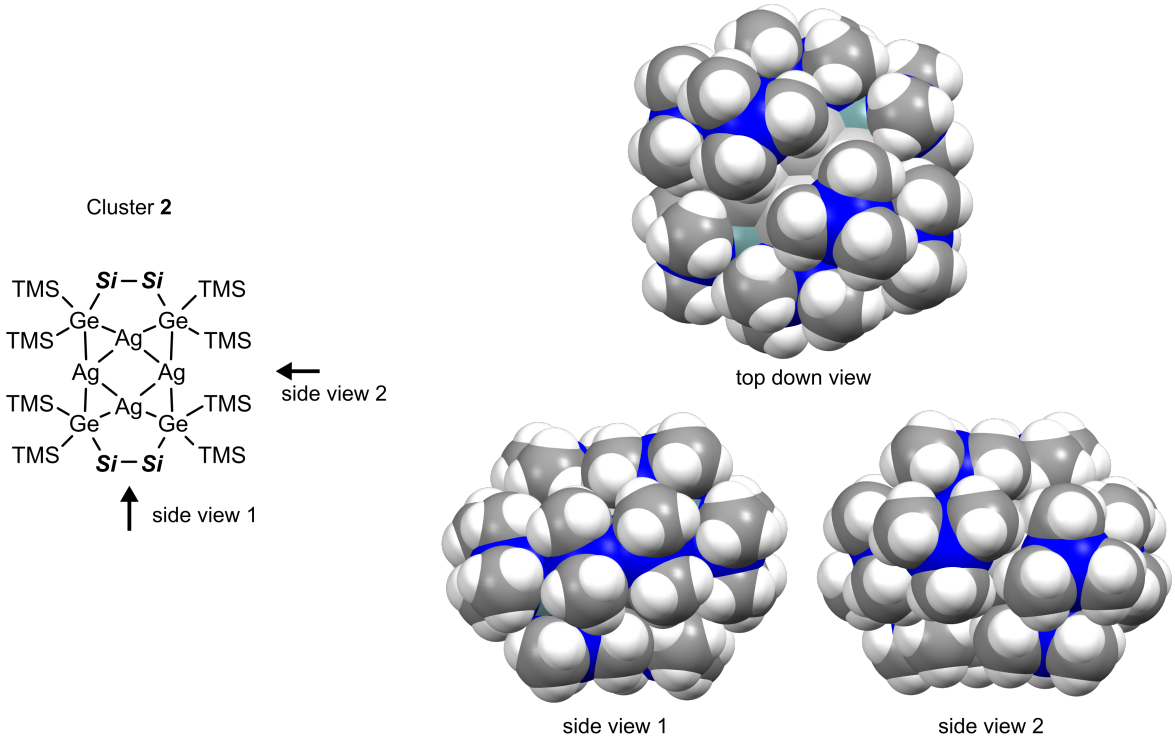


Figure S12. Space-filling model of the Ag_4 cluster **2**.

General procedure for theoretical calculations

Structure optimization, natural atomic orbital (NAO) analysis, and exited state calculation for the Ag_4 clusters **1** and **2** were performed using density functional theory (DFT) with Gaussian 16, Revision C.01. The Cartesian coordinates for the ground-state (S_0) optimized geometries are summarized in **Tables S2–S3**. The results of the NAO analysis, conducted on the optimized structures, are shown in **Tables S4–S7**, with numbering consistent with **Tables S2–S3**. Rydberg NAOs/shells or contributions ≤ 0.10 % were excluded. NAO-based analyses are known to provide less reliable results when Rydberg orbital contributions are significant. Therefore, atom contribution for the LUMO were also analyzed by Hirshfeld method using Multiwfn[12]. The atomic contributions were calculated to be Ag 47.2% and Si 17.5% (cluster **1**), and Ag 48.5% and Ge 17.0% (cluster **2**). These values are in good agreement with the results obtained from NAO analysis: Ag 50.1%, Si 18.6% (cluster **1**), and Ag 50.4%, Ge 19.9% (cluster **2**) as shown in **Figure 2** in the main text. This consistency can be attributed to the fact that the contributions of Rydberg orbitals to the LUMO for both Ag and Si (or Ge) were less than 10% in each case, allowing the NAO method to provide reliable results.

Excited state calculations were carried out using time-dependent DFT on the optimized structures, and these results are summarized in **Tables S8–S9**. Additionally, structure optimization for the lowest triplet state (T_1) was performed using DFT to investigate the origin of the lower energy phosphorescence of the cluster **2** compared to the cluster **1** (**Table S10–S11**). As shown in **Table S12**, the phosphorescence energies at the T_1-optimized structures ($E_{T_1-S_0}^{@T_1-opt}$) are 1.68 eV and 1.51 eV for the cluster **1** and **2**, respectively, indicating a red-shifted emission for cluster **2** consistent with the observed trend, although the absolute energies slightly deviate from the λ_{MAX}. Unless otherwise specified, the default settings were used throughout the study. The distance dependence of the LUMO energy change for the square-planar Ag_4 clusters is shown in **Figure S14**. To well describe the atomic orbital energy level, here we used long-range corrected functional, ωB97X, and sufficiently large basis set, cc-PVQZ. Here we used ORCA 5.0.3[13]. The σ-type LUMO that appears at the center of the Ag_4 cluster is shown in **Figure S14(a)**, and its energy level is indicated by a blue horizontal bar. The relative LUMO energy is plotted in **Figure S14(b)**, with the LUMO of the $d_{Ag\text{-}Ag}$ of 4.24 Å—corresponding to a 3.00 Å distance between the center of the Ag_4(IV) cluster and each Ag atom—set as the zero reference.

DFT and TD-DFT Calculations for Cu_4 and Au_4 clusters are performed at the same level of theory as that for cluster 1. The hybrid functional PBE0 with Grimme's D3BJ dispersion corrections was employed. The def2-TZVP basis set was applied to H, C, and Si atoms, while the SDD basis set was used for Cu and Au atoms. S_0- and T_1-optimized structures are summarized in **Tables S13-16**. The calculated phosphorescence energies at the T_1-optimized structures ($E_{T_1-S_0}^{@T_1-opt}$) are provided in **Table S10**.

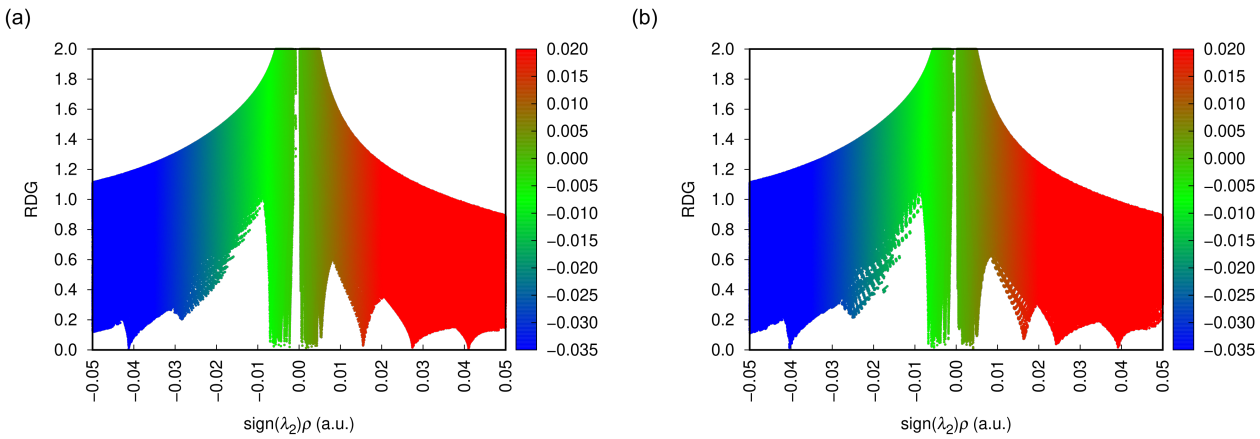


Figure S13. RDG scatter plots for clusters (a) **1** and (b) **2**, shown as functions of the electron density (ρ) and the sign of its second-largest Hessian matrix (λ_2).

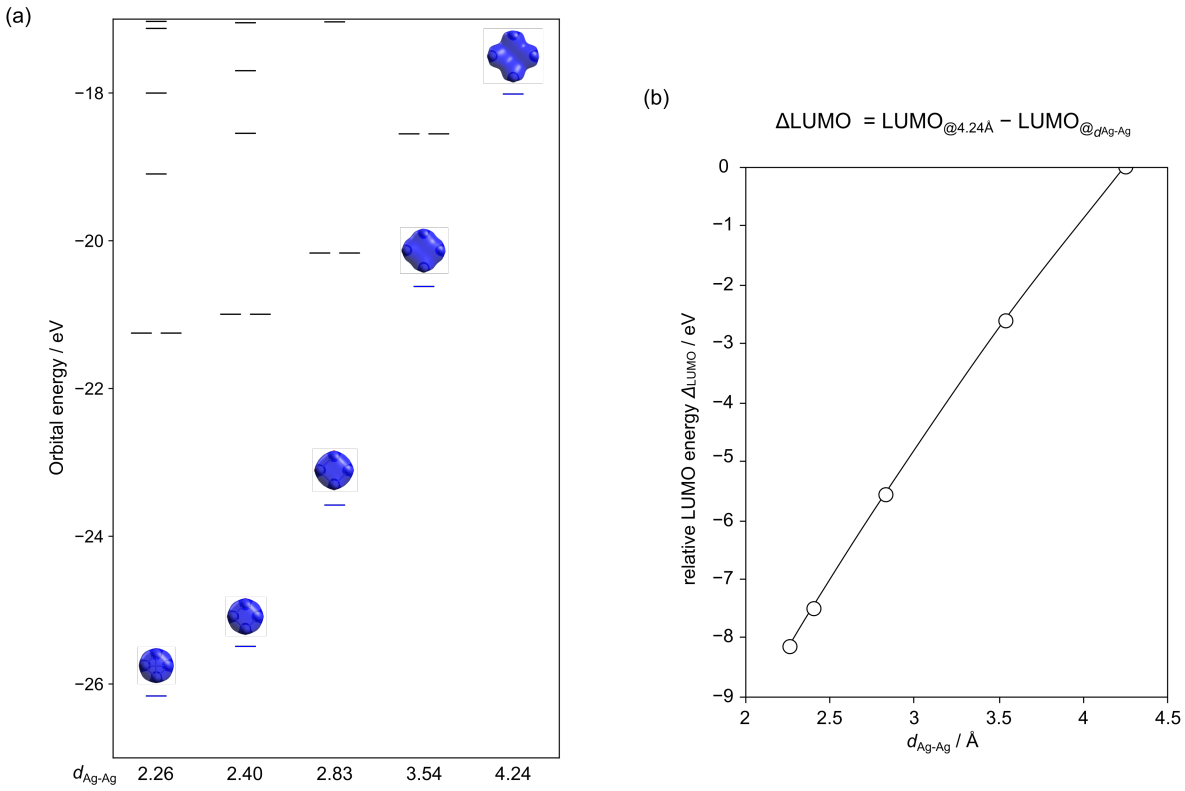


Figure S14. Distance dependence of the LUMO energy changes for the square planar Ag_4(IV) cluster.

Explanation for the larger *f* of the HOMO→LUMO transition compared to the HOMO−1→LUMO transition

Here, we first explain this analysis using cluster **1** as a representative case. Given the D_2 symmetry of the cluster structure, with the Cartesian axes defined as shown in **Figure S15**, the HOMO, HOMO−1, and LUMO correspond to the irreducible representations (irrep) b_3, b_1, and a, respectively in the D_2 point group. Accordingly, the electronic transition dipole moments (μ) of $\langle\Psi_{HOMO}|-e\boldsymbol{r}|\Psi_{LUMO}\rangle$ and $\langle\Psi_{HOMO-1}|-e\boldsymbol{r}|\Psi_{LUMO}\rangle$ are governed by different selection rules along the x, y, and z axes. While $\langle\Psi_{HOMO}|-e\boldsymbol{r}|\Psi_{LUMO}\rangle$ provides a totally symmetric irrep a, making it an allowed transition through the x component (irrep b_3), $\langle\Psi_{HOMO-1}|-e\boldsymbol{r}|\Psi_{LUMO}\rangle$ is allowed through the z component (irrep b_1). Since the μ value depends on $-e\boldsymbol{r}$ term, MO distribution plays a crucial role. The MOs are widely delocalized along the x and y axes but not along the z axis. Consequently, $\langle\Psi_{HOMO}|-e\boldsymbol{r}|\Psi_{LUMO}\rangle$ (allowed through x) has a larger value compared to $\langle\Psi_{HOMO-1}|-e\boldsymbol{r}|\Psi_{LUMO}\rangle$ (allowed through z). This interpretation is supported by the TD-DFT calculation results, which yield μ=1.0117 along the x-axis for the HOMO→LUMO transition and μ=−0.3512 along the z-axis for HOMO−1→LUMO transition. Since the oscillator strength (f) is proportional to the product of the transition energy (E) and the square of the transition dipole moment (S), where $S=\mu^2$, the calculated values are $S_{HOMO\rightarrow LUMO}$=1.02 (E=2.78 eV) and $S_{HOMO-1\rightarrow LUMO}$=0.12 ($E$=2.99 eV), resulting in $f_{HOMO\rightarrow LUMO}$=0.0698 and $f_{HOMO-1\rightarrow LUMO}$=0.0090.

The same symmetry-based considerations, supported by TD-DFT calculation results for cluster **2**, confirm that the discussion presented for cluster **1** also holds for cluster **2**.

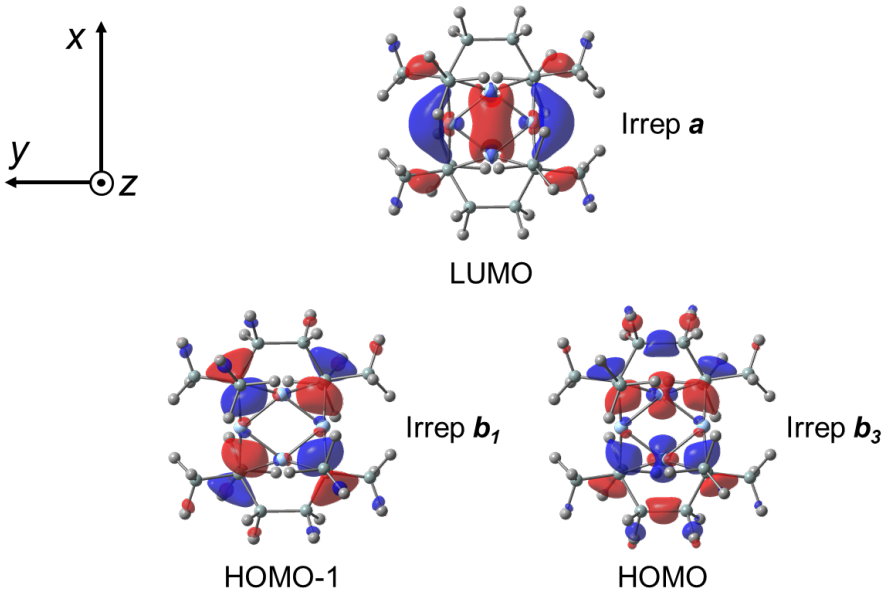


Figure S15. HOMO−1, HOMO, and LUMO (isosurface value = 0.03) of cluster **1**, along with their irreducible representations (irreps) in the D_2 point group. The Cartesian axis definitions are shown in the top left.

Table S2. Cartesian coordinates of the ground-state optimized geometry for the cluster **1**.

1(Ag)	3.34719135	21.0058546	25.2904644
2(Ag)	5.03544454	21.0062996	27.4405896
3(Si)	5.74859491	21.8483203	25.151722
4(Si)	6.04762567	21.2097081	22.9110854
5(Si)	7.72237977	21.1069554	26.2500698
6(Si)	5.55360275	24.1771531	25.2915715
7(C)	5.74791696	19.3699792	22.6782268
8(H)	4.75652608	19.0772577	23.0288773
9(H)	5.82996086	19.098093	21.6213883
10(H)	6.47712613	18.7809075	23.2377554
11(C)	7.78803751	21.617962	22.3200818
12(H)	8.01008485	22.6785591	22.4585269
13(H)	8.54984115	21.0428777	22.8494549
14(H)	7.87837974	21.3909751	21.2528866
15(C)	4.87050352	22.1895933	21.8182829
16(H)	3.82693328	22.0565711	22.1055768
17(H)	5.09694153	23.2574624	21.868458
18(H)	4.97480306	21.8742126	20.7753712
19(C)	5.7144347	24.7125596	27.0866533
20(H)	6.72291373	24.5295216	27.4631772
21(H)	5.50191055	25.7802187	27.1962791
22(H)	5.01320713	24.162691	27.7200472
23(C)	3.85609429	24.6970188	24.6689269
24(H)	3.7288029	24.4535242	23.6117807
25(H)	3.0608575	24.194702	25.2252076
26(H)	3.7170695	25.7765366	24.7835923
27(C)	6.85456801	25.0713237	24.2667613
28(H)	7.86555631	24.8007051	24.5787006
29(H)	6.7553506	24.8266148	23.2062485
30(H)	6.74559145	26.155374	24.3706146
31(C)	8.1741385	19.4068019	25.5622104
32(H)	7.34264345	18.7069202	25.6602169
33(H)	8.43347082	19.4732779	24.5035982
34(H)	9.0348942	18.993097	26.0938189
35(C)	9.14189149	22.3003715	25.8754799
36(H)	8.93225703	23.2952172	26.2731619
37(H)	10.073795	21.9453098	26.3256103
38(H)	9.29383701	22.3916021	24.7976453
39(Si)	5.74904373	20.1641994	29.7292804
40(Si)	6.04752398	20.8017139	31.9702496
41(Si)	7.72234388	20.9072349	28.6312853
42(Si)	5.55559642	17.8352842	29.5885946
43(C)	5.74703014	22.6411572	32.2042926
44(H)	4.7555436	22.9337311	31.8538136
45(H)	5.82894675	22.9123734	33.2613133
46(H)	6.4760166	23.2308933	31.64517
47(C)	7.78809596	20.3939601	32.561157
48(H)	8.01096257	19.3336844	32.4215572
49(H)	8.54954649	20.9702132	32.0325383
50(H)	7.87810014	20.6198499	33.6286123
51(C)	4.87067772	19.8205418	33.0622139
52(H)	3.82709212	19.9531406	32.77475
53(H)	5.09772739	18.7528321	33.0114235
54(H)	4.97455478	20.1353264	34.1053476
55(C)	5.71904885	17.3001284	27.7936645
56(H)	6.7279806	17.4836036	27.4185688

57(H)	5.50715885	16.2323756	27.683718
58(H)	5.01849008	17.8496847	27.1592625
59(C)	3.85766157	17.3142836	30.2091369
60(H)	3.72890316	17.5576377	31.2661417
61(H)	3.06281454	17.8161581	29.6518988
62(H)	3.71943625	16.2346881	30.0942375
63(C)	6.85601058	16.941794	30.6147008
64(H)	7.86713427	17.2133703	30.3040167
65(H)	6.75536076	17.1860517	31.6751791
66(H)	6.74805851	15.8576908	30.5103373
67(C)	8.17278762	22.6076798	29.3192854
68(H)	7.34087462	23.307056	29.2211655
69(H)	8.43197045	22.5413079	30.3779453
70(H)	9.03337808	23.0219541	28.7878568
71(C)	9.14275093	19.7149175	29.0060017
72(H)	8.93392887	18.7198615	28.6084198
73(H)	10.0743894	20.07067	28.5558724
74(H)	9.29473451	19.6239017	30.0838476
75(Ag)	3.34731373	21.0058558	29.5907847
76(Ag)	1.65905959	21.0063004	27.4406575
77(Si)	0.94590287	21.8483069	29.7295316
78(Si)	0.64686293	21.2096802	31.9701645
79(Si)	-1.0278773	21.1069385	28.6311768
80(Si)	1.14087586	24.1771429	29.5896902
81(C)	0.9467325	19.3699799	32.2030422
82(H)	1.93816699	19.0773535	31.8524348
83(H)	0.86467061	19.0980891	33.2598781
84(H)	0.21760471	18.7808354	31.6434847
85(C)	-1.0936044	21.6177832	32.5611083
86(H)	-1.3157414	22.6783596	32.4226496
87(H)	-1.8553389	21.042628	32.0317128
88(H)	-1.1839621	21.390794	33.6283017
89(C)	1.82386084	22.1896719	33.0630036
90(H)	2.86745181	22.0567328	32.7757498
91(H)	1.59733716	23.2575223	33.0128141
92(H)	1.71954821	21.8742882	34.1059131
93(C)	0.98007934	24.7125548	27.7946069
94(H)	-0.028389	24.5295077	27.4180593
95(H)	1.19259373	25.780217	27.6849917
96(H)	1.68132763	24.1626975	27.1612259
97(C)	2.83836542	24.6970222	30.2123745
98(H)	2.96563179	24.4535327	31.2695249
99(H)	3.63361844	24.1947066	29.6561161
100(H)	2.97738842	25.7765401	30.0977082
101(C)	-0.1601212	25.0712989	30.6144726
102(H)	-1.1710994	24.8006684	30.3025105
103(H)	-0.0609247	24.826591	31.6749875
104(H)	-0.0511552	26.1553505	30.5106215
105(C)	-1.4796372	19.4067836	29.3190312
106(H)	-0.6481426	18.7069013	29.2210236
107(H)	-1.7389704	19.4732583	30.3776432
108(H)	-2.3403928	18.9930802	28.7874213
109(C)	-2.4473915	22.3003526	29.0057646
110(H)	-2.2377553	23.2951991	28.6080856
111(H)	-3.3792933	21.9452922	28.5556295
112(H)	-2.5993417	22.3915816	30.0835987
113(Si)	0.94546415	20.1641963	25.1519681

114(Si)	0.64700366	20.8017084	22.9109947
115(Si)	-1.0278385	20.907224	26.2499611
116(Si)	1.1389173	17.8352823	25.2926555
117(C)	0.94783021	22.6410899	22.6768899
118(H)	1.93938395	22.9334894	23.0273264
119(H)	0.86592753	22.912292	21.6198645
120(H)	0.21897208	23.230976	23.2360205
121(C)	-1.0936687	20.3942588	22.320174
122(H)	-1.3167268	19.3340293	22.4598185
123(H)	-1.8549885	20.9706715	22.848808
124(H)	-1.183678	20.6201309	21.2527154
125(C)	1.82362579	19.8202932	21.8190074
126(H)	2.86724713	19.9527061	22.1064275
127(H)	1.59638069	18.7526267	21.8698347
128(H)	1.71976704	20.1350692	20.7758693
129(C)	0.97551066	17.3001343	27.0875925
130(H)	-0.0334122	17.4836098	27.4627123
131(H)	1.18740609	16.2323828	27.1975405
132(H)	1.67608398	17.8496964	27.7219738
133(C)	2.83683647	17.3142813	24.6720706
134(H)	2.96556685	17.5576326	23.6150618
135(H)	3.63169898	17.8161561	25.229286
136(H)	2.97506361	16.2346857	24.7869687
137(C)	-0.1615191	16.9417845	24.2665845
138(H)	-1.1726369	17.2133608	24.5772882
139(H)	-0.0608918	17.1860345	23.2061023
140(H)	-0.053562	15.8576824	24.3709536
141(C)	-1.4782851	22.6076672	25.561961
142(H)	-0.6463713	23.307043	25.6600748
143(H)	-1.7374735	22.541292	24.5033023
144(H)	-2.3388731	23.0219427	26.0933926
145(C)	-2.4482423	19.7149037	25.8752405
146(H)	-2.2394188	18.7198476	26.2728215
147(H)	-3.3798822	20.070654	26.3253686
148(H)	-2.600224	19.6238885	24.7973943

Table S3. Cartesian coordinates of the ground-state optimized geometry for the cluster **2**.

1(Ag)	0.00029772	-2.1789245	4.8419E-05
2(Ag)	1.65915603	0.00023201	4.4291E-05
3(Si)	2.72711625	-4.5840033	-0.1937916
4(Si)	4.43725792	-1.1862226	-0.0873179
5(Si)	2.23448722	-2.1606158	-3.2373777
6(C)	2.39982708	-4.7864621	1.64359075
7(H)	1.40120253	-4.4365502	1.91231194
8(H)	2.48425094	-5.8371647	1.93790145
9(H)	3.1154189	-4.2097587	2.23302447
10(C)	4.47166462	-5.1761055	-0.5751528
11(H)	4.70299579	-5.0505399	-1.6355341
12(H)	5.22386274	-4.6323093	-0.0005683
13(H)	4.56730347	-6.2392728	-0.3319362
14(C)	1.55164985	-5.6704092	-1.1801654
15(H)	0.50956277	-5.375521	-1.0499606
16(H)	1.78254489	-5.617822	-2.247039
17(H)	1.64751262	-6.7149913	-0.8675436
18(C)	2.38492612	-0.3639487	-3.7658672
19(H)	3.3923023	0.01601762	-3.5832095
20(H)	2.16933358	-0.2504691	-4.8325922
21(H)	1.6822585	0.26303418	-3.210546
22(C)	0.53647284	-2.7932506	-3.7383567
23(H)	0.41408406	-3.8479707	-3.4815942
24(H)	-0.2540978	-2.2330561	-3.2328089
25(H)	0.38616314	-2.6902335	-4.817566
26(C)	3.54306029	-3.1800841	-4.1244913
27(H)	4.55016636	-2.8574557	-3.8509583
28(H)	3.45207074	-4.2394658	-3.8713663
29(H)	3.43839446	-3.0852179	-5.20982
30(C)	4.85121676	-1.8694192	1.6236129
31(H)	4.00860139	-1.7554015	2.3078286
32(H)	5.09742062	-2.9320445	1.56848126
33(H)	5.71179605	-1.3467181	2.04948218
34(C)	5.87107512	-1.5868379	-1.2552064
35(H)	5.67608439	-1.2005054	-2.2577793
36(H)	6.80272634	-1.139587	-0.8955014
37(H)	6.01602736	-2.6669651	-1.3319573
38(Si)	2.72591169	4.58473823	0.19377302
39(Si)	4.4369424	1.18742324	0.08743025
40(Si)	2.23390321	2.16129945	3.23744763
41(C)	2.39853988	4.78703194	-1.6436154
42(H)	1.39999696	4.43685801	-1.9123075
43(H)	2.48269505	5.83774301	-1.9379727
44(H)	3.11426838	4.21048344	-2.2330345
45(C)	4.47031817	5.17729488	0.57507891
46(H)	4.70169925	5.05184538	1.63546293
47(H)	5.22264443	4.63365887	0.00051056
48(H)	4.5656857	6.24047345	0.3318043
49(C)	1.55019157	5.6709046	1.18010373
50(H)	0.50817529	5.375769	1.04990497
51(H)	1.78109572	5.61841863	2.24698049
52(H)	1.64580965	6.71549554	0.86743646
53(C)	2.38477162	0.36467565	3.76596206
54(H)	3.39224016	-0.0150554	3.58331932
55(H)	2.16919176	0.25115569	4.83268516
56(H)	1.68225824	-0.2624775	3.21063879

57(C)	0.53574076	2.79353552	3.73842054
58(H)	0.41310663	3.84822516	3.48165383
59(H)	-0.2546979	2.23315469	3.23287333
60(H)	0.38545391	2.69048923	4.81763024
61(C)	3.54222888	3.18110407	4.12453988
62(H)	4.54941463	2.85871472	3.85101804
63(H)	3.45098269	4.24045761	3.87138973
64(H)	3.43758218	3.08623758	5.20987033
65(C)	4.85072152	1.87072204	-1.6235038
66(H)	4.00812757	1.75648905	-2.3077087
67(H)	5.09665306	2.93341013	-1.5683775
68(H)	5.7114314	1.34824139	-2.0493796
69(C)	5.87064548	1.58843139	1.2553229
70(H)	5.67574736	1.20205427	2.25789684
71(H)	6.80242069	1.14142894	0.89563055
72(H)	6.01530469	2.66859844	1.33206595
73(Ag)	-0.0002966	2.1789369	5.3166E-05
74(Ag)	-1.6591553	-0.0002238	5.1126E-05
75(Si)	-2.7271374	4.58400282	-0.1937846
76(Si)	-4.4372567	1.18621955	-0.0873534
77(Si)	-2.2344423	2.16062958	-3.2373812
78(C)	-2.3998931	4.78644431	1.64360766
79(H)	-1.4012736	4.43653493	1.91234975
80(H)	-2.4843306	5.83714318	1.93792789
81(H)	-3.1154958	4.20972984	2.23301763
82(C)	-4.4716818	5.17609647	-0.5751759
83(H)	-4.7029896	5.05053968	-1.6355633
84(H)	-5.2238878	4.63228839	-0.0006126
85(H)	-4.5673339	6.23926054	-0.3319505
86(C)	-1.5516565	5.67042773	-1.1801195
87(H)	-0.5095704	5.37554858	-1.0498889
88(H)	-1.7825231	5.61784796	-2.2469997
89(H)	-1.6475371	6.71500617	-0.8674908
90(C)	-2.3848655	0.36396279	-3.7658765
91(H)	-3.3922454	-0.016005	-3.5832428
92(H)	-2.1692476	0.25048419	-4.8325966
93(H)	-1.68221	-0.2630194	-3.210539
94(C)	-0.5364221	2.79327145	-3.7383317
95(H)	-0.4140408	3.84799125	-3.4815648
96(H)	0.25414227	2.23307864	-3.2327722
97(H)	-0.3860947	2.69025726	-4.8175389
98(C)	-3.5430054	3.18009448	-4.1245135
99(H)	-4.5501143	2.85745993	-3.8509978
100(H)	-3.4520256	4.23947574	-3.8713836
101(H)	-3.4383215	3.08523227	-5.2098408
102(C)	-4.8512263	1.86941202	1.62357654
103(H)	-4.0086151	1.75539145	2.30779717
104(H)	-5.0974274	2.93203809	1.56844533
105(H)	-5.7118093	1.34671189	2.04943955
106(C)	-5.8710652	1.58683921	-1.2552508
107(H)	-5.6760659	1.20051297	-2.2578245
108(H)	-6.8027185	1.13958464	-0.8955558
109(H)	-6.0160186	2.66696674	-1.3319966
110(Si)	-2.7258887	-4.5847403	0.1937654
111(Si)	-4.4369399	-1.1874267	0.08739109
112(Si)	-2.2339446	-2.1612966	3.23743656
113(C)	-2.3984727	-4.7870463	-1.6436138

114(H)	-1.3999251	-4.4368684	-1.9122846
115(H)	-2.4826136	-5.8377604	-1.9379642
116(H)	-3.114191	-4.210508	-2.2330548
117(C)	-4.4702993	-5.1773055	0.57504002
118(H)	-4.7017033	-5.0518504	1.6354184
119(H)	-5.2226175	-4.6336787	0.00045262
120(H)	-4.5656548	-6.2404864	0.33177086
121(C)	-1.5501831	-5.670891	1.18013138
122(H)	-0.5081657	-5.3757473	1.0499576
123(H)	-1.7811142	-5.6183996	2.24700203
124(H)	-1.6457851	-6.7154848	0.86746893
125(C)	-2.3848285	-0.364674	3.76595024
126(H)	-3.3922929	0.01505686	3.58328342
127(H)	-2.1692752	-0.2511563	4.83267895
128(H)	-1.6823018	0.26248093	3.21064598
129(C)	-0.5357878	-2.7935265	3.73843623
130(H)	-0.4131452	-3.8482154	3.48167009
131(H)	0.25465685	-2.2331415	3.23290305
132(H)	-0.3855191	-2.6904812	4.81764858
133(C)	-3.5422801	-3.1811074	4.12450721
134(H)	-4.5494631	-2.8587237	3.85096889
135(H)	-3.4510238	-4.2404606	3.87135932
136(H)	-3.4376513	-3.0862395	5.20983928
137(C)	-4.8507093	-1.8707241	-1.6235459
138(H)	-4.0081115	-1.7564916	-2.307746
139(H)	-5.0966433	-2.9334116	-1.5684225
140(H)	-5.7114157	-1.3482411	-2.0494257
141(C)	-5.8706516	-1.5884333	1.25527391
142(H)	-5.6757616	-1.2020537	2.25784849
143(H)	-6.8024244	-1.1414323	0.89557334
144(H)	-6.0153108	-2.6686002	1.33201816
145(Ge)	2.44322864	2.31112529	0.86992151
146(Ge)	2.44384614	-2.3104407	-0.8698547
147(Ge)	-2.4432304	-2.3111227	0.86990755
148(Ge)	-2.4438407	2.31044695	-0.8698606

Table S4. Condensed NAO terms to electron shells for the HOMO-1, HOMO, and LUMO of the cluster **1**.

HOMO−1		(%)	HOMO		(%)	LUMO		(%)
1(Ag)	(4p Cor)	0.173	1(Ag)	(4p Cor)	0.122	1(Ag)	(5s Val)	4.61
1(Ag)	(4d Val)	0.209	1(Ag)	(5p Val)	0.173	1(Ag)	(5p Val)	2.008
2(Ag)	(5p Val)	0.705	1(Ag)	(4d Val)	0.271	1(Ag)	(4d Val)	0.685
3(Si)	(3s Val)	0.666	2(Ag)	(4s Cor)	0.292	2(Ag)	(5s Val)	12.412
3(Si)	(3p Val)	18.15	2(Ag)	(5s Val)	4.036	2(Ag)	(5p Val)	3.112
4(Si)	(3p Val)	0.424	2(Ag)	(4d Val)	4.181	2(Ag)	(4d Val)	0.231
5(Si)	(3p Val)	0.636	3(Si)	(3s Val)	0.281	3(Si)	(3s Val)	0.49
6(Si)	(3p Val)	0.513	3(Si)	(3p Val)	12.551	3(Si)	(3p Val)	3.713
11(C)	(2s Val)	0.14	4(Si)	(3p Val)	0.466	4(Si)	(3s Val)	0.674
11(C)	(2p Val)	0.793	5(Si)	(3s Val)	0.924	4(Si)	(3p Val)	2.442
14(H)	(1s Val)	0.143	5(Si)	(3p Val)	1.505	5(Si)	(3s Val)	0.283
27(C)	(2s Val)	0.129	6(Si)	(3p Val)	0.223	5(Si)	(3p Val)	1.362
27(C)	(2p Val)	0.765	11(C)	(2s Val)	0.102	7(C)	(2s Val)	0.144
30(H)	(1s Val)	0.138	11(C)	(2p Val)	0.479	11(C)	(2s Val)	0.28
35(C)	(2s Val)	0.132	14(H)	(1s Val)	0.112	11(C)	(2p Val)	0.581
35(C)	(2p Val)	0.728	27(C)	(2p Val)	0.374	14(H)	(1s Val)	0.206
37(H)	(1s Val)	0.138	31(C)	(2p Val)	0.407	15(C)	(2s Val)	0.104
39(Si)	(3s Val)	0.666	35(C)	(2s Val)	0.271	15(C)	(2p Val)	0.132
39(Si)	(3p Val)	18.157	35(C)	(2p Val)	1.603	39(Si)	(3s Val)	0.489
40(Si)	(3p Val)	0.424	39(Si)	(3s Val)	0.281	39(Si)	(3p Val)	3.713
41(Si)	(3p Val)	0.636	39(Si)	(3p Val)	12.546	40(Si)	(3s Val)	0.674
42(Si)	(3p Val)	0.513	40(Si)	(3p Val)	0.465	40(Si)	(3p Val)	2.44
47(C)	(2s Val)	0.14	41(Si)	(3s Val)	0.924	41(Si)	(3s Val)	0.283
47(C)	(2p Val)	0.794	41(Si)	(3p Val)	1.507	41(Si)	(3p Val)	1.36
50(H)	(1s Val)	0.143	42(Si)	(3p Val)	0.223	43(C)	(2s Val)	0.144
63(C)	(2s Val)	0.129	47(C)	(2s Val)	0.102	47(C)	(2s Val)	0.28
63(C)	(2p Val)	0.765	47(C)	(2p Val)	0.479	47(C)	(2p Val)	0.581
66(H)	(1s Val)	0.138	50(H)	(1s Val)	0.112	50(H)	(1s Val)	0.206
71(C)	(2s Val)	0.132	63(C)	(2p Val)	0.373	51(C)	(2s Val)	0.104
71(C)	(2p Val)	0.729	67(C)	(2p Val)	0.406	51(C)	(2p Val)	0.133
73(H)	(1s Val)	0.138	71(C)	(2s Val)	0.271	75(Ag)	(5s Val)	4.61
75(Ag)	(4p Cor)	0.173	71(C)	(2p Val)	1.605	75(Ag)	(5p Val)	2.008
75(Ag)	(4d Val)	0.209	75(Ag)	(4p Cor)	0.122	75(Ag)	(4d Val)	0.685
76(Ag)	(5p Val)	0.705	75(Ag)	(5p Val)	0.173	76(Ag)	(5s Val)	12.412
77(Si)	(3s Val)	0.666	75(Ag)	(4d Val)	0.271	76(Ag)	(5p Val)	3.112
77(Si)	(3p Val)	18.15	76(Ag)	(4s Cor)	0.292	76(Ag)	(4d Val)	0.231
78(Si)	(3p Val)	0.424	76(Ag)	(5s Val)	4.036	77(Si)	(3s Val)	0.49
79(Si)	(3p Val)	0.636	76(Ag)	(4d Val)	4.181	77(Si)	(3p Val)	3.713
80(Si)	(3p Val)	0.513	77(Si)	(3s Val)	0.281	78(Si)	(3s Val)	0.674
85(C)	(2s Val)	0.14	77(Si)	(3p Val)	12.551	78(Si)	(3p Val)	2.442
85(C)	(2p Val)	0.793	78(Si)	(3p Val)	0.466	79(Si)	(3s Val)	0.283
88(H)	(1s Val)	0.143	79(Si)	(3s Val)	0.924	79(Si)	(3p Val)	1.362
101(C)	(2s Val)	0.129	79(Si)	(3p Val)	1.505	81(C)	(2s Val)	0.144
101(C)	(2p Val)	0.765	80(Si)	(3p Val)	0.223	85(C)	(2s Val)	0.28
104(H)	(1s Val)	0.138	85(C)	(2s Val)	0.102	85(C)	(2p Val)	0.581
109(C)	(2s Val)	0.132	85(C)	(2p Val)	0.479	88(H)	(1s Val)	0.206
109(C)	(2p Val)	0.728	88(H)	(1s Val)	0.112	89(C)	(2s Val)	0.104
111(H)	(1s Val)	0.138	101(C)	(2p Val)	0.373	89(C)	(2p Val)	0.132
113(Si)	(3s Val)	0.666	105(C)	(2p Val)	0.407	113(Si)	(3s Val)	0.489
113(Si)	(3p Val)	18.15	109(C)	(2s Val)	0.271	113(Si)	(3p Val)	3.713
114(Si)	(3p Val)	0.424	109(C)	(2p Val)	1.603	114(Si)	(3s Val)	0.674
115(Si)	(3p Val)	0.636	113(Si)	(3s Val)	0.281	114(Si)	(3p Val)	2.442
116(Si)	(3p Val)	0.513	113(Si)	(3p Val)	12.552	115(Si)	(3s Val)	0.283
121(C)	(2s Val)	0.14	114(Si)	(3p Val)	0.465	115(Si)	(3p Val)	1.361

121(C)	(2p Val)	0.794	115(Si)	(3s Val)	0.924	117(C)	(2s Val)	0.144
124(H)	(1s Val)	0.143	115(Si)	(3p Val)	1.507	121(C)	(2s Val)	0.28
137(C)	(2s Val)	0.129	116(Si)	(3p Val)	0.223	121(C)	(2p Val)	0.581
137(C)	(2p Val)	0.765	121(C)	(2s Val)	0.102	124(H)	(1s Val)	0.206
140(H)	(1s Val)	0.138	121(C)	(2p Val)	0.479	125(C)	(2s Val)	0.104
145(C)	(2s Val)	0.132	124(H)	(1s Val)	0.112	125(C)	(2p Val)	0.133
145(C)	(2p Val)	0.729	137(C)	(2p Val)	0.373			
147(H)	(1s Val)	0.138	141(C)	(2p Val)	0.406			

Table S5. Condensed NAO terms to electron shells for the HOMO-1, HOMO, and LUMO of the cluster **2**.

HOMO−1			HOMO			LUMO		
	(%)			(%)			(%)	
1(Ag)	(4p Cor)	0.178	1(Ag)	(4p Cor)	0.136	1(Ag)	(5s Val)	3.968
1(Ag)	(4d Val)	0.312	1(Ag)	(5p Val)	0.197	1(Ag)	(5p Val)	2.056
2(Ag)	(4p Cor)	0.106	1(Ag)	(4d Val)	0.216	1(Ag)	(4d Val)	0.705
2(Ag)	(5p Val)	0.55	2(Ag)	(4s Cor)	0.317	2(Ag)	(5s Val)	12.845
2(Ag)	(4d Val)	0.116	2(Ag)	(5s Val)	4.381	2(Ag)	(5p Val)	2.989
3(Si)	(3p Val)	0.548	2(Ag)	(4d Val)	3.987	2(Ag)	(4d Val)	0.334
4(Si)	(3p Val)	0.496	3(Si)	(3p Val)	0.33	3(Si)	(3s Val)	0.59
5(Si)	(3p Val)	0.582	4(Si)	(3s Val)	0.882	3(Si)	(3p Val)	2.315
10(C)	(2s Val)	0.138	4(Si)	(3p Val)	0.993	4(Si)	(3s Val)	0.159
10(C)	(2p Val)	0.747	5(Si)	(3p Val)	0.254	4(Si)	(3p Val)	1.227
13(H)	(1s Val)	0.155	10(C)	(2p Val)	0.455	6(C)	(2s Val)	0.141
26(C)	(2s Val)	0.128	13(H)	(1s Val)	0.105	10(C)	(2s Val)	0.274
26(C)	(2p Val)	0.724	26(C)	(2p Val)	0.376	10(C)	(2p Val)	0.528
29(H)	(1s Val)	0.15	30(C)	(2p Val)	0.338	13(H)	(1s Val)	0.217
34(C)	(2s Val)	0.117	34(C)	(2s Val)	0.261	14(C)	(2p Val)	0.134
34(C)	(2p Val)	0.605	34(C)	(2p Val)	1.479	38(Si)	(3s Val)	0.59
36(H)	(1s Val)	0.123	36(H)	(1s Val)	0.125	38(Si)	(3p Val)	2.315
38(Si)	(3p Val)	0.548	38(Si)	(3p Val)	0.33	39(Si)	(3s Val)	0.159
39(Si)	(3p Val)	0.496	39(Si)	(3s Val)	0.882	39(Si)	(3p Val)	1.227
40(Si)	(3p Val)	0.582	39(Si)	(3p Val)	0.992	41(C)	(2s Val)	0.141
45(C)	(2s Val)	0.138	40(Si)	(3p Val)	0.255	45(C)	(2s Val)	0.274
45(C)	(2p Val)	0.747	45(C)	(2p Val)	0.455	45(C)	(2p Val)	0.528
48(H)	(1s Val)	0.155	48(H)	(1s Val)	0.105	48(H)	(1s Val)	0.217
61(C)	(2s Val)	0.128	61(C)	(2p Val)	0.376	49(C)	(2p Val)	0.134
61(C)	(2p Val)	0.725	65(C)	(2p Val)	0.338	73(Ag)	(5s Val)	3.968
64(H)	(1s Val)	0.15	69(C)	(2s Val)	0.261	73(Ag)	(5p Val)	2.056
69(C)	(2s Val)	0.117	69(C)	(2p Val)	1.478	73(Ag)	(4d Val)	0.705
69(C)	(2p Val)	0.605	71(H)	(1s Val)	0.125	74(Ag)	(5s Val)	12.845
71(H)	(1s Val)	0.123	73(Ag)	(4p Cor)	0.136	74(Ag)	(5p Val)	2.989
73(Ag)	(4p Cor)	0.178	73(Ag)	(5p Val)	0.197	74(Ag)	(4d Val)	0.334
73(Ag)	(4d Val)	0.312	73(Ag)	(4d Val)	0.216	75(Si)	(3s Val)	0.59
74(Ag)	(4p Cor)	0.106	74(Ag)	(4s Cor)	0.317	75(Si)	(3p Val)	2.313
74(Ag)	(5p Val)	0.55	74(Ag)	(5s Val)	4.381	76(Si)	(3s Val)	0.159
74(Ag)	(4d Val)	0.116	74(Ag)	(4d Val)	3.987	76(Si)	(3p Val)	1.227
75(Si)	(3p Val)	0.548	75(Si)	(3p Val)	0.33	78(C)	(2s Val)	0.141
76(Si)	(3p Val)	0.496	76(Si)	(3s Val)	0.882	82(C)	(2s Val)	0.274
77(Si)	(3p Val)	0.582	76(Si)	(3p Val)	0.993	82(C)	(2p Val)	0.528
82(C)	(2s Val)	0.138	77(Si)	(3p Val)	0.255	85(H)	(1s Val)	0.217
82(C)	(2p Val)	0.747	82(C)	(2p Val)	0.455	86(C)	(2p Val)	0.134
85(H)	(1s Val)	0.155	85(H)	(1s Val)	0.105	110(Si)	(3s Val)	0.59
98(C)	(2s Val)	0.128	98(C)	(2p Val)	0.376	110(Si)	(3p Val)	2.315
98(C)	(2p Val)	0.724	102(C)	(2p Val)	0.338	111(Si)	(3s Val)	0.159
101(H)	(1s Val)	0.15	106(C)	(2s Val)	0.261	111(Si)	(3p Val)	1.227
106(C)	(2s Val)	0.117	106(C)	(2p Val)	1.479	113(C)	(2s Val)	0.141

106(C)	(2p Val)	0.605	108(H)	(1s Val)	0.125	117(C)	(2s Val)	0.274
108(H)	(1s Val)	0.123	110(Si)	(3p Val)	0.33	117(C)	(2p Val)	0.528
110(Si)	(3p Val)	0.548	111(Si)	(3s Val)	0.882	120(H)	(1s Val)	0.217
111(Si)	(3p Val)	0.496	111(Si)	(3p Val)	0.992	121(C)	(2p Val)	0.134
112(Si)	(3p Val)	0.582	112(Si)	(3p Val)	0.254	145(Ge)	(4s Val)	0.572
117(C)	(2s Val)	0.138	117(C)	(2p Val)	0.455	145(Ge)	(4p Val)	4.101
117(C)	(2p Val)	0.747	120(H)	(1s Val)	0.105	146(Ge)	(4s Val)	0.572
120(H)	(1s Val)	0.155	133(C)	(2p Val)	0.376	146(Ge)	(4p Val)	4.101
133(C)	(2s Val)	0.128	137(C)	(2p Val)	0.338	147(Ge)	(4s Val)	0.572
133(C)	(2p Val)	0.725	141(C)	(2s Val)	0.261	147(Ge)	(4p Val)	4.101
136(H)	(1s Val)	0.15	141(C)	(2p Val)	1.478	148(Ge)	(4s Val)	0.572
141(C)	(2s Val)	0.117	143(H)	(1s Val)	0.125	148(Ge)	(4p Val)	4.101
141(C)	(2p Val)	0.605	145(Ge)	(4s Val)	0.215			
143(H)	(1s Val)	0.123	145(Ge)	(4p Val)	13.462			
145(Ge)	(4s Val)	0.598	146(Ge)	(4s Val)	0.215			
145(Ge)	(4p Val)	18.375	146(Ge)	(4p Val)	13.459			
146(Ge)	(4s Val)	0.598	147(Ge)	(4s Val)	0.215			
146(Ge)	(4p Val)	18.375	147(Ge)	(4p Val)	13.462			
147(Ge)	(4s Val)	0.598	148(Ge)	(4s Val)	0.215			
147(Ge)	(4p Val)	18.375	148(Ge)	(4p Val)	13.459			
148(Ge)	(4s Val)	0.598						
148(Ge)	(4p Val)	18.375						

Table S6. Condensed NAO terms to atomic contributions for the HOMO-1, HOMO, and LUMO of the cluster **1**.

HOMO	(%)	HOMO−1	(%)	LUMO	(%)
1(Ag)	0.417	1(Ag)	0.586	1(Ag)	8.066
2(Ag)	0.872	2(Ag)	8.609	2(Ag)	17.004
3(Si)	19.051	3(Si)	12.958	3(Si)	4.656
4(Si)	0.503	4(Si)	0.553	4(Si)	3.349
5(Si)	0.705	5(Si)	2.533	5(Si)	1.982
6(Si)	0.625	6(Si)	0.29	6(Si)	0.128
11(C)	0.966	11(C)	0.603	7(C)	0.267
14(H)	0.144	14(H)	0.113	11(C)	0.957
27(C)	0.925	27(C)	0.461	14(H)	0.214
30(H)	0.139	31(C)	0.448	15(C)	0.262
35(C)	0.891	35(C)	1.929	19(C)	0.114
37(H)	0.139	39(Si)	12.953	39(Si)	4.654
39(Si)	19.059	40(Si)	0.552	40(Si)	3.347
40(Si)	0.503	41(Si)	2.534	41(Si)	1.98
41(Si)	0.705	42(Si)	0.291	42(Si)	0.128
42(Si)	0.625	47(C)	0.604	43(C)	0.266
47(C)	0.967	50(H)	0.113	47(C)	0.957
50(H)	0.144	63(C)	0.46	50(H)	0.214
63(C)	0.926	67(C)	0.448	51(C)	0.263
66(H)	0.139	71(C)	1.931	55(C)	0.114
71(C)	0.891	75(Ag)	0.586	75(Ag)	8.066
73(H)	0.139	76(Ag)	8.609	76(Ag)	17.004
75(Ag)	0.417	77(Si)	12.958	77(Si)	4.656
76(Ag)	0.872	78(Si)	0.553	78(Si)	3.349
77(Si)	19.051	79(Si)	2.533	79(Si)	1.982
78(Si)	0.503	80(Si)	0.29	80(Si)	0.128
79(Si)	0.705	85(C)	0.603	81(C)	0.267
80(Si)	0.625	88(H)	0.113	85(C)	0.957
85(C)	0.966	101(C)	0.46	88(H)	0.214
88(H)	0.144	105(C)	0.448	89(C)	0.262

101(C)	0.925	109(C)	1.929	93(C)	0.114
104(H)	0.139	113(Si)	12.959	113(Si)	4.654
109(C)	0.891	114(Si)	0.552	114(Si)	3.349
111(H)	0.139	115(Si)	2.534	115(Si)	1.981
113(Si)	19.052	116(Si)	0.291	116(Si)	0.128
114(Si)	0.503	121(C)	0.604	117(C)	0.266
115(Si)	0.705	124(H)	0.113	121(C)	0.957
116(Si)	0.625	137(C)	0.46	124(H)	0.214
121(C)	0.967	141(C)	0.448	125(C)	0.263
124(H)	0.144	145(C)	1.931	129(C)	0.114
137(C)	0.926				
140(H)	0.139				
145(C)	0.891				
147(H)	0.139				

Table S7. Condensed NAO terms to atomic contributions for the HOMO-1, HOMO, and LUMO of the cluster **2**.

HOMO	(%)	HOMO−1	(%)	LUMO	(%)
1(Ag)	0.52	1(Ag)	0.575	1(Ag)	7.53
2(Ag)	0.793	2(Ag)	8.818	2(Ag)	17.674
3(Si)	0.649	3(Si)	0.399	3(Si)	3.137
4(Si)	0.555	4(Si)	1.975	4(Si)	1.78
5(Si)	0.709	5(Si)	0.332	5(Si)	0.123
10(C)	0.922	10(C)	0.576	6(C)	0.259
13(H)	0.157	13(H)	0.106	10(C)	0.898
26(C)	0.887	26(C)	0.466	13(H)	0.226
29(H)	0.151	30(C)	0.368	14(C)	0.254
34(C)	0.753	34(C)	1.796	18(C)	0.115
36(H)	0.124	36(H)	0.127	34(C)	0.154
38(Si)	0.649	38(Si)	0.399	38(Si)	3.137
39(Si)	0.555	39(Si)	1.974	39(Si)	1.78
40(Si)	0.709	40(Si)	0.333	40(Si)	0.123
45(C)	0.922	45(C)	0.576	41(C)	0.259
48(H)	0.157	48(H)	0.106	45(C)	0.898
61(C)	0.888	61(C)	0.465	48(H)	0.226
64(H)	0.151	65(C)	0.368	49(C)	0.254
69(C)	0.753	69(C)	1.795	53(C)	0.115
71(H)	0.124	71(H)	0.127	69(C)	0.154
73(Ag)	0.52	73(Ag)	0.575	73(Ag)	7.53
74(Ag)	0.793	74(Ag)	8.818	74(Ag)	17.674
75(Si)	0.649	75(Si)	0.399	75(Si)	3.136
76(Si)	0.555	76(Si)	1.975	76(Si)	1.78
77(Si)	0.709	77(Si)	0.333	77(Si)	0.123
82(C)	0.922	82(C)	0.576	78(C)	0.259
85(H)	0.157	85(H)	0.106	82(C)	0.898
98(C)	0.887	98(C)	0.466	85(H)	0.226
101(H)	0.151	102(C)	0.368	86(C)	0.254
106(C)	0.753	106(C)	1.796	90(C)	0.115
108(H)	0.124	108(H)	0.127	106(C)	0.154
110(Si)	0.649	110(Si)	0.399	110(Si)	3.137
111(Si)	0.555	111(Si)	1.974	111(Si)	1.78
112(Si)	0.709	112(Si)	0.332	112(Si)	0.123
117(C)	0.922	117(C)	0.576	113(C)	0.259
120(H)	0.157	120(H)	0.106	117(C)	0.898
133(C)	0.888	133(C)	0.465	120(H)	0.226
136(H)	0.151	137(C)	0.368	121(C)	0.254

141(C)	0.753	141(C)	1.795	125(C)	0.115
143(H)	0.124	143(H)	0.127	141(C)	0.154
145(Ge)	19.206	145(Ge)	13.808	145(Ge)	4.977
146(Ge)	19.206	146(Ge)	13.805	146(Ge)	4.978
147(Ge)	19.206	147(Ge)	13.808	147(Ge)	4.977
148(Ge)	19.206	148(Ge)	13.805	148(Ge)	4.978

Table S8. The 20 low-energy excited states of the cluster **1**, with 10 singlet and 10 triplet states, were calculated. H and L denote HOMO and LUMO, respectively.

Excited state		composition		Energy / eV	Wavelength / nm	oscillator strength
1	Triplet	H -> L	96.8%	2.4890	498.13	0
2	Triplet	H−1 -> L	95.7%	2.6557	466.87	0
3	Singlet	H -> L	97.9%	2.7836	445.41	0.0698
4	Singlet	H−1 -> L	97.7%	2.9913	414.48	0.009
5	Triplet	H -> L+1	95.8%	2.9915	414.45	0
6	Triplet	H−2 -> L	91.1%	3.1543	393.07	0
		H−9 -> L	3.0%			
		H−1 -> L+5	2.3%			
7	Triplet	H−1 -> L+1	93.5%	3.2034	387.04	0
		H -> L+5	2.0%			
8	Singlet	H -> L+1	98.8%	3.2248	384.47	0.0006
9	Singlet	H−1 -> L+1	98.0%	3.4099	363.60	0
10	Triplet	H−5 -> L	94.3%	3.4491	359.46	0
11	Triplet	H−3 -> L	93.5%	3.4541	358.95	0
12	Triplet	H−4 -> L	92.6%	3.5245	351.78	0
13	Triplet	H -> L+2	77.9%	3.5721	347.09	0
		H−1 -> L+3	15.2%			
14	Singlet	H−5 -> L	96.9%	3.6145	343.02	0
15	Singlet	H−3 -> L	94.3%	3.6291	341.64	0.0142
		H -> L+2	3.7%			
16	Singlet	H−2 -> L	91.7%	3.7101	334.18	0.1805
		H−7 -> L	2.3%			
17	Triplet	H−2 -> L+1	78.2%	3.7172	333.54	0
		H−1 -> L+4	9.5%			
		H−7 -> L+1	4.6%			
18	Singlet	H−4 -> L	97.1%	3.7504	330.59	0
19	Singlet	H−7 -> L	94.4%	3.8966	318.19	0.0367
20	Singlet	H−6 -> L	97.6%	3.8982	318.05	0

Table S9. The 20 low-energy excited states of the cluster **2**, with 10 singlet and 10 triplet states, were calculated. H and L denote HOMO and LUMO, respectively.

Excited state		composition		Energy / eV	Wavelength / nm	oscillator strength
1	Triplet	H -> L	97.6%	2.5616	484.00	0
2	Triplet	H−1 -> L	97.1%	2.6437	468.97	0
3	Singlet	H -> L	97.7%	2.8470	435.49	0.0862
4	Singlet	H−1 -> L	97.9%	2.9676	417.79	0.0119
5	Triplet	H -> L+1	96.1%	3.1125	398.34	0
6	Triplet	H−3 -> L	91.4%	3.2203	385.01	0
		H−6 -> L	3.5%			
7	Triplet	H−1 -> L+1	95.0%	3.2422	382.41	0
8	Singlet	H -> L+1	98.7%	3.3324	372.05	0.0004
9	Singlet	H−1 -> L+1	98.4%	3.4178	362.76	0
10	Triplet	H−4 -> L	95.5%	3.5023	354.01	0
11	Triplet	H−2 -> L	95.2%	3.5181	352.42	0
12	Triplet	H−5 -> L	92.4%	3.6207	342.43	0
		H−7 -> L	2.6%			
13	Triplet	H -> L+2	72.9%	3.6358	341.01	0
		H−1 -> L+3	19.8%			
14	Singlet	H−4 -> L	97.7%	3.6389	340.72	0
15	Singlet	H−2 -> L	95.5%	3.6760	337.28	0.023
		H -> L+2	2.6%			
16	Triplet	H−1 -> L+2	61.5%	3.6962	335.44	0
		H -> L+3	29.3%			

		H−1 -> L+9	2.3%			
17	Singlet	H−3 -> L	91.6%	3.7563	330.07	0.189
		H−6 -> L	2.6%			
18	Singlet	H−5 -> L	97.7%	3.8400	322.87	0
19	Singlet	H−6 -> L	95.1%	3.9111	317.01	0.0455
		H−3 -> L	2.0%			
20	Singlet	H−7 -> L	98.2%	3.9275	315.68	0

Table S10. Cartesian coordinates of the T_1-optimized geometry for the Ag cluster **1**.

1(Ag)	-2.31743057	-0.00009626	0.00005360
2(Ag)	0.00006008	-1.47753343	0.00001403
3(Si)	-2.48603070	-2.29640843	-0.89971160
4(Si)	-4.71688539	-2.76882232	-0.33899920
5(Si)	-1.20682742	-4.08739282	-0.10303061
6(Si)	-2.20456619	-1.98762151	-3.20208251
7(C)	-5.02731044	-2.49942888	1.49379818
8(H)	-4.74798915	-1.48665963	1.79108995
9(H)	-6.08703001	-2.64491398	1.72535684
10(H)	-4.44860927	-3.19359644	2.10612669
11(C)	-5.18526697	-4.54118251	-0.77746262
12(H)	-5.00304706	-4.74635495	-1.83503457
13(H)	-4.61559206	-5.26580793	-0.19139961
14(H)	-6.24802176	-4.71202523	-0.57750500
15(C)	-5.83002068	-1.61803339	-1.32476767
16(H)	-5.59201824	-0.57176308	-1.12383710
17(H)	-5.72582240	-1.78789473	-2.39905309
18(H)	-6.87823218	-1.78535706	-1.05823714
19(C)	-0.36911291	-2.01411910	-3.60737259
20(H)	0.05707084	-3.00456594	-3.43371680
21(H)	-0.19144837	-1.74818236	-4.65368428
22(H)	0.17288727	-1.29922517	-2.98209743
23(C)	-2.91683944	-0.32053697	-3.69801160
24(H)	-3.98911681	-0.27486008	-3.49482237
25(H)	-2.43876852	0.49022605	-3.14346955
26(H)	-2.76603597	-0.13655195	-4.76629435
27(C)	-3.07940720	-3.32759941	-4.19342517
28(H)	-2.71026020	-4.32239276	-3.93467947
29(H)	-4.15592228	-3.31185607	-4.00552821
30(H)	-2.92423686	-3.17548269	-5.26618249
31(C)	-1.87795026	-4.56815155	1.59445391
32(H)	-1.88349094	-3.71165527	2.27083679
33(H)	-2.90673040	-4.92245399	1.49545930
34(H)	-1.28941408	-5.36686205	2.05017299
35(C)	-1.42822135	-5.55079449	-1.28610452
36(H)	-1.08264222	-5.30079496	-2.29027241
37(H)	-0.87800115	-6.43058791	-0.94198577
38(H)	-2.48858338	-5.80691442	-1.34799838
39(Si)	2.48621554	-2.29624958	0.89971874
40(Si)	4.71710957	-2.76845331	0.33898788
41(Si)	1.20715565	-4.08729602	0.10295362
42(Si)	2.20471312	-1.98758402	3.20210403
43(C)	5.02751213	-2.49895816	-1.49379831
44(H)	4.74809706	-1.48620327	-1.79104937
45(H)	6.08724565	-2.64433479	-1.72536107
46(H)	4.44887695	-3.19315591	-2.10615559
47(C)	5.18563610	-4.54079187	0.77737956

48(H)	5.00343247	-4.74602261	1.83494284
49(H)	4.61602196	-5.26544061	0.19128595
50(H)	6.24840526	-4.71153715	0.57741552
51(C)	5.83014578	-1.61761030	1.32480554
52(H)	5.59205867	-0.57135288	1.12391320
53(H)	5.72595650	-1.78751902	2.39908449
54(H)	6.87837220	-1.78483785	1.05827349
55(C)	0.36924535	-2.01393050	3.60734041
56(H)	-0.05702817	-3.00432366	3.43360873
57(H)	0.19157679	-1.74804496	4.65366443
58(H)	-0.17267092	-1.29894453	2.98209709
59(C)	2.91715570	-0.32061503	3.69817479
60(H)	3.98944536	-0.27504830	3.49502495
61(H)	2.43919705	0.49024029	3.14367456
62(H)	2.76633813	-0.13668685	4.76646538
63(C)	3.07938714	-3.32772783	4.19336832
64(H)	2.71013898	-4.32246237	3.93454075
65(H)	4.15590800	-3.31208542	4.00549763
66(H)	2.92420728	-3.17567338	5.26613309
67(C)	1.87832255	-4.56792270	-1.59455070
68(H)	1.88378947	-3.71139556	-2.27089660
69(H)	2.90713281	-4.92214289	-1.49557154
70(H)	1.28985338	-5.36666324	-2.05030486
71(C)	1.42868455	-5.55072585	1.28596994
72(H)	1.08309511	-5.30079491	2.29015104
73(H)	0.87853286	-6.43055039	0.94182133
74(H)	2.48906844	-5.80676107	1.34784430
75(Ag)	2.31743420	0.00009205	0.00004227
76(Ag)	-0.00005959	1.47753008	0.00002238
77(Si)	2.48604174	2.29641175	-0.89970924
78(Si)	4.71689520	2.76882157	-0.33899274
79(Si)	1.20682817	4.08738168	-0.10301326
80(Si)	2.20457960	1.98762591	-3.20208127
81(C)	5.02730984	2.49946965	1.49381216
82(H)	4.74797425	1.48671201	1.79112749
83(H)	6.08703059	2.64494702	1.72537055
84(H)	4.44861534	3.19365912	2.10612187
85(C)	5.18528484	4.54116941	-0.77749485
86(H)	5.00307005	4.74631905	-1.83507196
87(H)	4.61561090	5.26580975	-0.19144956
88(H)	6.24803959	4.71201182	-0.57753682
89(C)	5.83002423	1.61800333	-1.32473463
90(H)	5.59201184	0.57173935	-1.12378459
91(H)	5.72583098	1.78784298	-2.39902403
92(H)	6.87823615	1.78532321	-1.05820358
93(C)	0.36911477	2.01386479	-3.60734231
94(H)	-0.05721100	3.00424486	-3.43365625
95(H)	0.19147400	1.74792779	-4.65365797
96(H)	-0.17277438	1.29887600	-2.98207801
97(C)	2.91709845	0.32066112	-3.69805730
98(H)	3.98938456	0.27514186	-3.49487807
99(H)	2.43915479	-0.49018724	-3.14353191
100(H)	2.76631420	0.13667985	-4.76634342
101(C)	3.07921125	3.32775656	-4.19340117
102(H)	2.70992130	4.32248919	-3.93462432
103(H)	4.15573143	3.31216593	-4.00552125
104(H)	2.92404647	3.17564423	-5.26615985

105(C)	1.87794856	4.56812739	1.59447612
106(H)	1.88348882	3.71162536	2.27085204
107(H)	2.90672876	4.92243115	1.49548819
108(H)	1.28941025	5.36683369	2.05019980
109(C)	1.42823745	5.55078539	-1.28608284
110(H)	1.08267132	5.30078729	-2.29025559
111(H)	0.87801164	6.43057685	-0.94196864
112(H)	2.48859983	5.80690733	-1.34796311
113(Si)	-2.48622263	2.29624374	0.89971451
114(Si)	-4.71710815	2.76845123	0.33895302
115(Si)	-1.20715775	4.08729253	0.10295656
116(Si)	-2.20475712	1.98760062	3.20210542
117(C)	-5.02747335	2.49899630	-1.49384543
118(H)	-4.74804523	1.48625060	-1.79111599
119(H)	-6.08720358	2.64437101	-1.72542493
120(H)	-4.44883120	3.19321317	-2.10617514
121(C)	-5.18565713	4.54077631	0.77737483
122(H)	-5.00347452	4.74598432	1.83494616
123(H)	-4.61603781	5.26544318	0.19130885
124(H)	-6.24842388	4.71151835	0.57739479
125(C)	-5.83016139	1.61758178	1.32472145
126(H)	-5.59206026	0.57132862	1.12381869
127(H)	-5.72600328	1.78747423	2.39900581
128(H)	-6.87838172	1.78480600	1.05816344
129(C)	-0.36931869	2.01442880	3.60742828
130(H)	0.05669800	3.00494082	3.43374306
131(H)	-0.19162499	1.74856169	4.65375284
132(H)	0.17281174	1.29960557	2.98218741
133(C)	-2.91675866	0.32041840	3.69809627
134(H)	-3.98902187	0.27454661	3.49487797
135(H)	-2.43853135	-0.49028915	3.14360898
136(H)	-2.76595480	0.13651206	4.76639255
137(C)	-3.07983949	3.32747581	4.19337348
138(H)	-2.71085420	4.32231938	3.93459294
139(H)	-4.15634790	3.31154429	4.00545495
140(H)	-2.92466532	3.17543105	5.26614059
141(C)	-1.87830434	4.56791418	-1.59455786
142(H)	-1.88377102	3.71138269	-2.27089799
143(H)	-2.90711324	4.92214190	-1.49559011
144(H)	-1.28982695	5.36664821	-2.05031241
145(C)	-1.42867579	5.55073675	1.28595641
146(H)	-1.08308697	5.30081385	2.29013943
147(H)	-0.87852052	6.43055574	0.94179954
148(H)	-2.48905862	5.80677737	1.34782892

Table S11. Cartesian coordinates of the T_1-optimized geometry for the Ag cluster **2**.

1(Ag)	-2.37157134	-0.00031458	-0.00021745
2(Ag)	-0.04018400	-1.45037941	-0.01785247
3(Si)	-4.71316680	-2.86955807	-0.13649896
4(Si)	-1.16689000	-4.20486661	0.04242739
5(Si)	-2.30299627	-2.33093214	-3.19172901
6(C)	-4.94591742	-2.44532275	1.67860136
7(H)	-4.69872894	-1.39706576	1.86211528
8(H)	-5.98348346	-2.61200313	1.98466506
9(H)	-4.30139818	-3.05160588	2.31828381
10(C)	-5.19981119	-4.66791990	-0.41455617

11(H)	-5.05851514	-4.95210662	-1.46013574
12(H)	-4.60476424	-5.34694991	0.20040990
13(H)	-6.25332269	-4.82320541	-0.16017130
14(C)	-5.86323232	-1.79272585	-1.16390568
15(H)	-5.61390448	-0.73516573	-1.05227866
16(H)	-5.79817559	-2.04323760	-2.22556150
17(H)	-6.90195583	-1.93188055	-0.84818720
18(C)	-0.48884375	-2.41501518	-3.68400072
19(H)	-0.05996716	-3.38837849	-3.43513710
20(H)	-0.36315705	-2.25596916	-4.75946482
21(H)	0.08809032	-1.64902567	-3.15895602
22(C)	-3.02267571	-0.70503953	-3.80230007
23(H)	-4.08013319	-0.62152331	-3.54039690
24(H)	-2.50205703	0.14345817	-3.35228556
25(H)	-2.93606371	-0.62143403	-4.89029851
26(C)	-3.22789851	-3.74356922	-4.02377066
27(H)	-2.84965101	-4.71455842	-3.69604114
28(H)	-4.29379684	-3.70417541	-3.78490966
29(H)	-3.12616506	-3.68824845	-5.11227745
30(C)	-1.77316549	-4.58723906	1.78926740
31(H)	-1.74707807	-3.69609448	2.41871925
32(H)	-2.80923959	-4.93224484	1.74856302
33(H)	-1.17658149	-5.36875386	2.26510990
34(C)	-1.41328448	-5.75069701	-1.02328372
35(H)	-1.07667601	-5.57781978	-2.04728497
36(H)	-0.87189787	-6.61365541	-0.62512257
37(H)	-2.47745301	-5.99822242	-1.05881328
38(Si)	4.86261247	-2.76177868	0.51955848
39(Si)	1.21973922	-4.14180877	0.18234106
40(Si)	2.12602847	-1.66092287	3.27794675
41(C)	5.18053082	-2.56285200	-1.31833784
42(H)	4.86336785	-1.57743030	-1.66416442
43(H)	6.24792990	-2.67523423	-1.53258010
44(H)	4.63700481	-3.30755114	-1.90286275
45(C)	5.34913054	-4.50471040	1.03820091
46(H)	5.14455198	-4.67791876	2.09733476
47(H)	4.80785904	-5.25825233	0.46159372
48(H)	6.41967030	-4.66099706	0.86994354
49(C)	5.91262441	-1.53257205	1.47376417
50(H)	5.65534509	-0.50711818	1.20183797
51(H)	5.77507557	-1.64226664	2.55210187
52(H)	6.97315906	-1.68669133	1.25190998
53(C)	0.27469333	-1.59625732	3.56346129
54(H)	-0.16927697	-2.59083364	3.48791592
55(H)	0.04735425	-1.19745141	4.55669836
56(H)	-0.20772871	-0.95239324	2.82232674
57(C)	2.86810083	0.03469479	3.58661899
58(H)	3.94987506	0.02807797	3.43699980
59(H)	2.43994219	0.77605273	2.90720692
60(H)	2.66763011	0.35933888	4.61242813
61(C)	2.91250129	-2.90271109	4.45182052
62(H)	2.50867563	-3.90582693	4.29674279
63(H)	3.99452889	-2.95076470	4.30603314
64(H)	2.72474950	-2.61826652	5.49202681
65(C)	1.94318685	-4.59611704	-1.49890071
66(H)	1.90347664	-3.75053025	-2.18791331
67(H)	2.98795937	-4.89692807	-1.39147690

68(H)	1.39658068	-5.42971053	-1.94652852
69(C)	1.59417046	-5.54384867	1.40494107
70(H)	1.24861857	-5.29039036	2.40878751
71(H)	1.09257899	-6.46550028	1.09554139
72(H)	2.66822782	-5.73498929	1.45395898
73(Ag)	2.29129847	0.00054201	-0.00002758
74(Ag)	-0.04069293	1.45050616	0.01874182
75(Si)	4.86176630	2.76303530	-0.52040320
76(Si)	1.21862193	4.14215847	-0.18167699
77(Si)	2.12450938	1.66166469	-3.27816353
78(C)	5.18012605	2.56362580	1.31736640
79(H)	4.86339742	1.57798515	1.66295876
80(H)	6.24753079	2.67633320	1.53141472
81(H)	4.63645350	3.30794225	1.90223972
82(C)	5.34789449	4.50622816	-1.03853675
83(H)	5.14298147	4.67983545	-2.09754004
84(H)	4.80669724	5.25946902	-0.46146566
85(H)	6.41846309	4.66258800	-0.87052940
86(C)	5.91179354	1.53432454	-1.47522866
87(H)	5.65450603	0.50872465	-1.20385654
88(H)	5.77425307	1.64460310	-2.55350838
89(H)	6.97232524	1.68832754	-1.25328161
90(C)	0.27308543	1.59524984	-3.56264302
91(H)	-0.17175924	2.58943098	-3.48705927
92(H)	0.04557147	1.19603251	-4.55567354
93(H)	-0.20834022	0.95109944	-2.82110897
94(C)	2.86797527	-0.03326748	-3.58724515
95(H)	3.94982174	-0.02568725	-3.43820343
96(H)	2.44084534	-0.77503042	-2.90762939
97(H)	2.66724572	-0.35805681	-4.61295784
98(C)	2.90916429	2.90421549	-4.45244286
99(H)	2.50435044	3.90691008	-4.29721454
100(H)	3.99120628	2.95341629	-4.30714982
101(H)	2.72123075	2.61954159	-5.49255356
102(C)	1.94203209	4.59557790	1.49981937
103(H)	1.90259814	3.74954087	2.18829668
104(H)	2.98671222	4.89675856	1.39253038
105(H)	1.39521882	5.42873102	1.94801619
106(C)	1.59267051	5.54507847	-1.40338687
107(H)	1.24722106	5.29215477	-2.40740258
108(H)	1.09080787	6.46638913	-1.09341446
109(H)	2.66667413	5.73655391	-1.45225833
110(Si)	-4.71411105	2.86833564	0.13594985
111(Si)	-1.16804164	4.20459625	-0.04178587
112(Si)	-2.30431060	2.32966283	3.19165381
113(C)	-4.94619504	2.44447284	-1.67932294
114(H)	-4.69857674	1.39634543	-1.86300871
115(H)	-5.98373122	2.61085364	-1.98564985
116(H)	-4.30170725	3.05113724	-2.31867585
117(C)	-5.20139956	4.66646553	0.41437350
118(H)	-5.06061244	4.95035045	1.46010473
119(H)	-4.60630071	5.34587578	-0.20012128
120(H)	-6.25485328	4.82152609	0.15961328
121(C)	-5.86408880	1.79084596	1.16275878
122(H)	-5.61448399	0.73339144	1.05076234
123(H)	-5.79926199	2.04096432	2.22452112
124(H)	-6.90279531	1.92986672	0.84692535

125(C)	-0.49027247	2.41429199	3.68424535
126(H)	-0.06156650	3.38773330	3.43540010
127(H)	-0.36476338	2.25534600	4.75974560
128(H)	0.08694356	1.64839302	3.15937170
129(C)	-3.02336483	0.70331079	3.80174209
130(H)	-4.08072509	0.61932704	3.53959599
131(H)	-2.50223687	-0.14485421	3.35168240
132(H)	-2.93694720	0.61953926	4.88974329
133(C)	-3.22990976	3.74172189	4.02390026
134(H)	-2.85196873	4.71293476	3.69647700
135(H)	-4.29574884	3.70198386	3.78483045
136(H)	-3.12835525	3.68617053	5.11241128
137(C)	-1.77423096	4.58763722	-1.78850926
138(H)	-1.74764348	3.69686370	-2.41846260
139(H)	-2.81046633	4.93215032	-1.74777860
140(H)	-1.17791796	5.36968405	-2.26381531
141(C)	-1.41479015	5.74994299	1.02454863
142(H)	-1.07817827	5.57674063	2.04849395
143(H)	-0.87358541	6.61318169	0.62674901
144(H)	-2.47901665	5.99721667	1.06014077
145(Ge)	2.56171259	-2.32709355	1.02323501
146(Ge)	-2.47677415	-2.39820839	-0.82180915
147(Ge)	-2.47777829	2.39744346	0.82171512
148(Ge)	2.56081451	2.32815093	-1.02368555

Table S12. Total energies of the Ag cluster **1**, **2** and Cu and Au clusters at their T_1-optimized structures.

Clusters	T_1 total energy@T_1-opt / Hartree	S_0 total energy@T_1-opt / Hartree	$E_{T_1-S_0}^{@T_1-opt}$ / Hartree
1	-6494.89019115	-6494.95201890	0.06182775
2	-13644.4138880	-13644.4694176	0.0555296
Cu	-6696.19745058	-6696.23436962	0.03691904
Au	-6450.06737961	-6450.10627215	0.03889254

Table S13. Cartesian coordinates of the S_0-optimized geometry for the Cu_4 cluster.

Cu	-1.61890084	0.00000000	0.00000000
Cu	-0.00000000	1.89321831	0.00000000
Si	-2.19559260	2.15782499	0.83305138
Si	-4.43441315	2.53605651	0.22331237
Si	-1.18878727	4.19882157	0.14878009
Si	-2.07178929	2.00847840	3.17000461
C	-4.71185727	2.32574828	-1.62149352
H	-4.31135754	1.38047592	-1.98787574
H	-5.78095854	2.35813054	-1.85276466
H	-4.22145215	3.12575951	-2.17914704
C	-4.96796870	4.27632202	0.70992118
H	-4.80598136	4.45383836	1.77528023
H	-4.44109435	5.05354317	0.15498594
H	-6.03850657	4.39082722	0.51027997
C	-5.55681176	1.38813886	1.20159837
H	-5.30086772	0.33721867	1.08032097
H	-5.50148337	1.62696298	2.26667636
H	-6.59549314	1.52335161	0.88376868
C	-0.27077410	2.12394124	3.69243410
H	0.12781180	3.12352386	3.50580171
H	-0.15113186	1.90590087	4.75774165
H	0.33580822	1.40975953	3.13132978

C	-2.76876211	0.35476052	3.73224287
H	-3.84777860	0.31291088	3.56785784
H	-2.31797684	-0.48077564	3.19395894
H	-2.58660177	0.20531358	4.80096365
C	-3.05458656	3.35101837	4.04992447
H	-2.72074570	4.35213623	3.77214151
H	-4.11945018	3.27432377	3.81711931
H	-2.94359542	3.24423360	5.13370378
C	-1.90219518	4.71555520	-1.52192802
H	-1.80464961	3.91241633	-2.25454079
H	-2.96082791	4.96701541	-1.44068202
H	-1.37714792	5.59375368	-1.90529872
C	-1.48436852	5.58215189	1.40158520
H	-1.03721203	5.33853154	2.36666553
H	-1.04202867	6.51856808	1.04926247
H	-2.55360781	5.74310613	1.55287012
Si	2.19559260	2.15782499	-0.83305138
Si	4.43441315	2.53605651	-0.22331237
Si	1.18878727	4.19882157	-0.14878009
Si	2.07178929	2.00847840	-3.17000461
C	4.71185727	2.32574828	1.62149352
H	4.31135754	1.38047592	1.98787574
H	5.78095854	2.35813054	1.85276466
H	4.22145215	3.12575951	2.17914704
C	4.96796870	4.27632202	-0.70992118
H	4.80598136	4.45383836	-1.77528023
H	4.44109435	5.05354317	-0.15498594
H	6.03850657	4.39082722	-0.51027997
C	5.55681176	1.38813886	-1.20159837
H	5.30086772	0.33721867	-1.08032097
H	5.50148337	1.62696298	-2.26667636
H	6.59549314	1.52335161	-0.88376868
C	0.27077410	2.12394124	-3.69243410
H	-0.12781180	3.12352386	-3.50580171
H	0.15113186	1.90590087	-4.75774165
H	-0.33580822	1.40975953	-3.13132978
C	2.76876211	0.35476052	-3.73224287
H	3.84777860	0.31291088	-3.56785784
H	2.31797684	-0.48077564	-3.19395894
H	2.58660177	0.20531358	-4.80096365
C	3.05458656	3.35101837	-4.04992447
H	2.72074570	4.35213623	-3.77214151
H	4.11945018	3.27432377	-3.81711931
H	2.94359542	3.24423360	-5.13370378
C	1.90219518	4.71555520	1.52192802
H	1.80464961	3.91241633	2.25454079
H	2.96082791	4.96701541	1.44068202
H	1.37714792	5.59375368	1.90529872
C	1.48436852	5.58215189	-1.40158520
H	1.03721203	5.33853154	-2.36666553
H	1.04202867	6.51856808	-1.04926247
H	2.55360781	5.74310613	-1.55287012
Cu	1.61890084	-0.00000000	0.00000000
Cu	-0.00000000	-1.89321831	0.00000000
Si	2.19559260	-2.15782499	0.83305138
Si	4.43441315	-2.53605651	0.22331237
Si	1.18878727	-4.19882157	0.14878009

Si	2.07178929	-2.00847840	3.17000461
C	4.71185727	-2.32574828	-1.62149352
H	4.31135754	-1.38047592	-1.98787574
H	5.78095854	-2.35813054	-1.85276466
H	4.22145215	-3.12575951	-2.17914704
C	4.96796870	-4.27632202	0.70992118
H	4.80598136	-4.45383836	1.77528023
H	4.44109435	-5.05354317	0.15498594
H	6.03850657	-4.39082722	0.51027997
C	5.55681176	-1.38813886	1.20159837
H	5.30086772	-0.33721867	1.08032097
H	5.50148337	-1.62696298	2.26667636
H	6.59549314	-1.52335161	0.88376868
C	0.27077410	-2.12394124	3.69243410
H	-0.12781180	-3.12352386	3.50580171
H	0.15113186	-1.90590087	4.75774165
H	-0.33580822	-1.40975953	3.13132978
C	2.76876211	-0.35476052	3.73224287
H	3.84777860	-0.31291088	3.56785784
H	2.31797684	0.48077564	3.19395894
H	2.58660177	-0.20531358	4.80096365
C	3.05458656	-3.35101837	4.04992447
H	2.72074570	-4.35213623	3.77214151
H	4.11945018	-3.27432377	3.81711931
H	2.94359542	-3.24423360	5.13370378
C	1.90219518	-4.71555520	-1.52192802
H	1.80464961	-3.91241633	-2.25454079
H	2.96082791	-4.96701541	-1.44068202
H	1.37714792	-5.59375368	-1.90529872
C	1.48436852	-5.58215189	1.40158520
H	1.03721203	-5.33853154	2.36666553
H	1.04202867	-6.51856808	1.04926247
H	2.55360781	-5.74310613	1.55287012
Si	-2.19559260	-2.15782499	-0.83305138
Si	-4.43441315	-2.53605651	-0.22331237
Si	-1.18878727	-4.19882157	-0.14878009
Si	-2.07178929	-2.00847840	-3.17000461
C	-4.71185727	-2.32574828	1.62149352
H	-4.31135754	-1.38047592	1.98787574
H	-5.78095854	-2.35813054	1.85276466
H	-4.22145215	-3.12575951	2.17914704
C	-4.96796870	-4.27632202	-0.70992118
H	-4.80598136	-4.45383836	-1.77528023
H	-4.44109435	-5.05354317	-0.15498594
H	-6.03850657	-4.39082722	-0.51027997
C	-5.55681176	-1.38813886	-1.20159837
H	-5.30086772	-0.33721867	-1.08032097
H	-5.50148337	-1.62696298	-2.26667636
H	-6.59549314	-1.52335161	-0.88376868
C	-0.27077410	-2.12394124	-3.69243410
H	0.12781180	-3.12352386	-3.50580171
H	-0.15113186	-1.90590087	-4.75774165
H	0.33580822	-1.40975953	-3.13132978
C	-2.76876211	-0.35476052	-3.73224287
H	-3.84777860	-0.31291088	-3.56785784
H	-2.31797684	0.48077564	-3.19395894
H	-2.58660177	-0.20531358	-4.80096365

C	-3.05458656	-3.35101837	-4.04992447
H	-2.72074570	-4.35213623	-3.77214151
H	-4.11945018	-3.27432377	-3.81711931
H	-2.94359542	-3.24423360	-5.13370378
C	-1.90219518	-4.71555520	1.52192802
H	-1.80464961	-3.91241633	2.25454079
H	-2.96082791	-4.96701541	1.44068202
H	-1.37714792	-5.59375368	1.90529872
C	-1.48436852	-5.58215189	-1.40158520
H	-1.03721203	-5.33853154	-2.36666553
H	-1.04202867	-6.51856808	-1.04926247
H	-2.55360781	-5.74310613	-1.55287012

Table S13. Cartesian coordinates of the S_0-optimized geometry for the Au_4 cluster.

Au	0.00000000	2.00235632	0.00000000
Au	1.89190194	-0.00000000	0.00000000
Si	2.33603843	2.31887812	0.84764718
Si	2.66074387	4.54236585	0.16320860
Si	4.33959047	1.19824359	0.11651406
Si	2.14097980	2.16634819	3.17889204
C	2.36796322	4.75494651	-1.67693889
H	1.38064397	4.39024790	-1.96356341
H	2.44204608	5.80960841	-1.95902167
H	3.10405269	4.19548783	-2.25737139
C	4.40511066	5.11098519	0.58562099
H	4.61172235	4.97546275	1.64985096
H	5.16981684	4.57308747	0.02306615
H	4.50830748	6.17669174	0.35694989
C	1.49751349	5.64016443	1.15122199
H	0.45520233	5.34397096	1.03593038
H	1.74281699	5.59409611	2.21527476
H	1.59400074	6.68222985	0.83065469
C	2.30838925	0.36665546	3.69282471
H	3.31733278	-0.00532844	3.50251108
H	2.09750921	0.24243231	4.75918906
H	1.60857588	-0.25782684	3.13188189
C	0.45206706	2.79078546	3.71678765
H	0.33749155	3.85493338	3.49894436
H	-0.34749553	2.25643604	3.19893271
H	0.31455232	2.65097300	4.79352232
C	3.45203062	3.19010293	4.05955169
H	4.46112207	2.87317241	3.78850720
H	3.35563048	4.25009599	3.81134721
H	3.34523517	3.09156791	5.14432282
C	4.81741343	1.89546528	-1.57034798
H	4.00065887	1.77826727	-2.28465978
H	5.05747782	2.95822587	-1.50529747
H	5.69399255	1.37509338	-1.96458247
C	5.71570654	1.55723775	1.36249033
H	5.47462937	1.13935194	2.34150817
H	6.65883354	1.11504135	1.02785014
H	5.85956057	2.63373698	1.47789067
Si	2.33603843	-2.31887812	-0.84764718
Si	2.66074387	-4.54236585	-0.16320860
Si	4.33959047	-1.19824359	-0.11651406
Si	2.14097980	-2.16634819	-3.17889204

C	2.36796322	-4.75494651	1.67693889
H	1.38064397	-4.39024790	1.96356341
H	2.44204608	-5.80960841	1.95902167
H	3.10405269	-4.19548783	2.25737139
C	4.40511066	-5.11098519	-0.58562099
H	4.61172235	-4.97546275	-1.64985096
H	5.16981684	-4.57308747	-0.02306615
H	4.50830748	-6.17669174	-0.35694989
C	1.49751349	-5.64016443	-1.15122199
H	0.45520233	-5.34397096	-1.03593038
H	1.74281699	-5.59409611	-2.21527476
H	1.59400074	-6.68222985	-0.83065469
C	2.30838925	-0.36665546	-3.69282471
H	3.31733278	0.00532844	-3.50251108
H	2.09750921	-0.24243231	-4.75918906
H	1.60857588	0.25782684	-3.13188189
C	0.45206706	-2.79078546	-3.71678765
H	0.33749155	-3.85493338	-3.49894436
H	-0.34749553	-2.25643604	-3.19893271
H	0.31455232	-2.65097300	-4.79352232
C	3.45203062	-3.19010293	-4.05955169
H	4.46112207	-2.87317241	-3.78850720
H	3.35563048	-4.25009599	-3.81134721
H	3.34523517	-3.09156791	-5.14432282
C	4.81741343	-1.89546528	1.57034798
H	4.00065887	-1.77826727	2.28465978
H	5.05747782	-2.95822587	1.50529747
H	5.69399255	-1.37509338	1.96458247
C	5.71570654	-1.55723775	-1.36249033
H	5.47462937	-1.13935194	-2.34150817
H	6.65883354	-1.11504135	-1.02785014
H	5.85956057	-2.63373698	-1.47789067
Au	-0.00000000	-2.00235632	0.00000000
Au	-1.89190194	0.00000000	0.00000000
Si	-2.33603843	-2.31887812	0.84764718
Si	-2.66074387	-4.54236585	0.16320860
Si	-4.33959047	-1.19824359	0.11651406
Si	-2.14097980	-2.16634819	3.17889204
C	-2.36796322	-4.75494651	-1.67693889
H	-1.38064397	-4.39024790	-1.96356341
H	-2.44204608	-5.80960841	-1.95902167
H	-3.10405269	-4.19548783	-2.25737139
C	-4.40511066	-5.11098519	0.58562099
H	-4.61172235	-4.97546275	1.64985096
H	-5.16981684	-4.57308747	0.02306615
H	-4.50830748	-6.17669174	0.35694989
C	-1.49751349	-5.64016443	1.15122199
H	-0.45520233	-5.34397096	1.03593038
H	-1.74281699	-5.59409611	2.21527476
H	-1.59400074	-6.68222985	0.83065469
C	-2.30838925	-0.36665546	3.69282471
H	-3.31733278	0.00532844	3.50251108
H	-2.09750921	-0.24243231	4.75918906
H	-1.60857588	0.25782684	3.13188189
C	-0.45206706	-2.79078546	3.71678765
H	-0.33749155	-3.85493338	3.49894436
H	0.34749553	-2.25643604	3.19893271

H	-0.31455232	-2.65097300	4.79352232
C	-3.45203062	-3.19010293	4.05955169
H	-4.46112207	-2.87317241	3.78850720
H	-3.35563048	-4.25009599	3.81134721
H	-3.34523517	-3.09156791	5.14432282
C	-4.81741343	-1.89546528	-1.57034798
H	-4.00065887	-1.77826727	-2.28465978
H	-5.05747782	-2.95822587	-1.50529747
H	-5.69399255	-1.37509338	-1.96458247
C	-5.71570654	-1.55723775	1.36249033
H	-5.47462937	-1.13935194	2.34150817
H	-6.65883354	-1.11504135	1.02785014
H	-5.85956057	-2.63373698	1.47789067
Si	-2.33603843	2.31887812	-0.84764718
Si	-2.66074387	4.54236585	-0.16320860
Si	-4.33959047	1.19824359	-0.11651406
Si	-2.14097980	2.16634819	-3.17889204
C	-2.36796322	4.75494651	1.67693889
H	-1.38064397	4.39024790	1.96356341
H	-2.44204608	5.80960841	1.95902167
H	-3.10405269	4.19548783	2.25737139
C	-4.40511066	5.11098519	-0.58562099
H	-4.61172235	4.97546275	-1.64985096
H	-5.16981684	4.57308747	-0.02306615
H	-4.50830748	6.17669174	-0.35694989
C	-1.49751349	5.64016443	-1.15122199
H	-0.45520233	5.34397096	-1.03593038
H	-1.74281699	5.59409611	-2.21527476
H	-1.59400074	6.68222985	-0.83065469
C	-2.30838925	0.36665546	-3.69282471
H	-3.31733278	-0.00532844	-3.50251108
H	-2.09750921	0.24243231	-4.75918906
H	-1.60857588	-0.25782684	-3.13188189
C	-0.45206706	2.79078546	-3.71678765
H	-0.33749155	3.85493338	-3.49894436
H	0.34749553	2.25643604	-3.19893271
H	-0.31455232	2.65097300	-4.79352232
C	-3.45203062	3.19010293	-4.05955169
H	-4.46112207	2.87317241	-3.78850720
H	-3.35563048	4.25009599	-3.81134721
H	-3.34523517	3.09156791	-5.14432282
C	-4.81741343	1.89546528	1.57034798
H	-4.00065887	1.77826727	2.28465978
H	-5.05747782	2.95822587	1.50529747
H	-5.69399255	1.37509338	1.96458247
C	-5.71570654	1.55723775	-1.36249033
H	-5.47462937	1.13935194	-2.34150817
H	-6.65883354	1.11504135	-1.02785014
H	-5.85956057	2.63373698	-1.47789067

Table S15. Cartesian coordinates of the T_1-optimized geometry for the Cu_4 cluster.

Cu	-1.31988290	0.00000000	0.00000000
Cu	-0.00000000	2.03339020	0.00000000
Si	-2.33390415	2.03342835	0.66516731
Si	-4.56786825	2.59320419	0.18973017
Si	-1.21602594	4.11229070	0.12395861

Si	-2.15359884	1.79948912	2.99920528
C	-4.96444924	2.47108460	-1.64067762
H	-4.75206372	1.47722034	-2.03428757
H	-6.02352519	2.68817058	-1.81090168
H	-4.37521729	3.18550952	-2.21950242
C	-5.00289118	4.33732150	0.75808594
H	-4.79443485	4.47372617	1.82112773
H	-4.46610757	5.10947068	0.20456589
H	-6.07431541	4.50308183	0.60317961
C	-5.67651621	1.43680655	1.17595285
H	-5.40974975	0.39022615	1.03503880
H	-5.60545194	1.66068447	2.24312679
H	-6.72120846	1.56430380	0.87562368
C	-0.34107558	1.91863101	3.48329199
H	0.04145276	2.92818364	3.31490665
H	-0.19327169	1.67459217	4.53949897
H	0.26150298	1.22932248	2.88843792
C	-2.83431264	0.12392286	3.51398704
H	-3.92425864	0.12271473	3.44052643
H	-2.45802167	-0.68229419	2.88232075
H	-2.56760121	-0.09939278	4.55145434
C	-3.11537065	3.09795621	3.96797258
H	-2.78223036	4.11220927	3.74261569
H	-4.18534547	3.03904040	3.75569341
H	-2.98010696	2.92799797	5.04110431
C	-1.89484115	4.75195110	-1.51483474
H	-1.77469803	4.00573519	-2.30251242
H	-2.95938004	4.97828728	-1.43135344
H	-1.37915673	5.66422919	-1.82382077
C	-1.49063793	5.39271099	1.48136541
H	-1.02337247	5.08026063	2.41619323
H	-1.05489767	6.35194445	1.18728320
H	-2.55631568	5.54077806	1.66318434
Si	2.33390415	2.03342835	-0.66516731
Si	4.56786825	2.59320419	-0.18973017
Si	1.21602594	4.11229070	-0.12395861
Si	2.15359884	1.79948912	-2.99920528
C	4.96444924	2.47108460	1.64067762
H	4.75206372	1.47722034	2.03428757
H	6.02352519	2.68817058	1.81090168
H	4.37521729	3.18550952	2.21950242
C	5.00289118	4.33732150	-0.75808594
H	4.79443485	4.47372617	-1.82112773
H	4.46610757	5.10947068	-0.20456589
H	6.07431541	4.50308183	-0.60317961
C	5.67651621	1.43680655	-1.17595285
H	5.40974975	0.39022615	-1.03503880
H	5.60545194	1.66068447	-2.24312679
H	6.72120846	1.56430380	-0.87562368
C	0.34107558	1.91863101	-3.48329199
H	-0.04145276	2.92818364	-3.31490665
H	0.19327169	1.67459217	-4.53949897
H	-0.26150298	1.22932248	-2.88843792
C	2.83431264	0.12392286	-3.51398704
H	3.92425864	0.12271473	-3.44052643
H	2.45802167	-0.68229419	-2.88232075
H	2.56760121	-0.09939278	-4.55145434

C	3.11537065	3.09795621	-3.96797258
H	2.78223036	4.11220927	-3.74261569
H	4.18534547	3.03904040	-3.75569341
H	2.98010696	2.92799797	-5.04110431
C	1.89484115	4.75195110	1.51483474
H	1.77469803	4.00573519	2.30251242
H	2.95938004	4.97828728	1.43135344
H	1.37915673	5.66422919	1.82382077
C	1.49063793	5.39271099	-1.48136541
H	1.02337247	5.08026063	-2.41619323
H	1.05489767	6.35194445	-1.18728320
H	2.55631568	5.54077806	-1.66318434
Cu	1.31988290	-0.00000000	0.00000000
Cu	-0.00000000	-2.03339020	0.00000000
Si	2.33390415	-2.03342835	0.66516731
Si	4.56786825	-2.59320419	0.18973017
Si	1.21602594	-4.11229070	0.12395861
Si	2.15359884	-1.79948912	2.99920528
C	4.96444924	-2.47108460	-1.64067762
H	4.75206372	-1.47722034	-2.03428757
H	6.02352519	-2.68817058	-1.81090168
H	4.37521729	-3.18550952	-2.21950242
C	5.00289118	-4.33732150	0.75808594
H	4.79443485	-4.47372617	1.82112773
H	4.46610757	-5.10947068	0.20456589
H	6.07431541	-4.50308183	0.60317961
C	5.67651621	-1.43680655	1.17595285
H	5.40974975	-0.39022615	1.03503880
H	5.60545194	-1.66068447	2.24312679
H	6.72120846	-1.56430380	0.87562368
C	0.34107558	-1.91863101	3.48329199
H	-0.04145276	-2.92818364	3.31490665
H	0.19327169	-1.67459217	4.53949897
H	-0.26150298	-1.22932248	2.88843792
C	2.83431264	-0.12392286	3.51398704
H	3.92425864	-0.12271473	3.44052643
H	2.45802167	0.68229419	2.88232075
H	2.56760121	0.09939278	4.55145434
C	3.11537065	-3.09795621	3.96797258
H	2.78223036	-4.11220927	3.74261569
H	4.18534547	-3.03904040	3.75569341
H	2.98010696	-2.92799797	5.04110431
C	1.89484115	-4.75195110	-1.51483474
H	1.77469803	-4.00573519	-2.30251242
H	2.95938004	-4.97828728	-1.43135344
H	1.37915673	-5.66422919	-1.82382077
C	1.49063793	-5.39271099	1.48136541
H	1.02337247	-5.08026063	2.41619323
H	1.05489767	-6.35194445	1.18728320
H	2.55631568	-5.54077806	1.66318434
Si	-2.33390415	-2.03342835	-0.66516731
Si	-4.56786825	-2.59320419	-0.18973017
Si	-1.21602594	-4.11229070	-0.12395861
Si	-2.15359884	-1.79948912	-2.99920528
C	-4.96444924	-2.47108460	1.64067762
H	-4.75206372	-1.47722034	2.03428757
H	-6.02352519	-2.68817058	1.81090168

H	-4.37521729	-3.18550952	2.21950242
C	-5.00289118	-4.33732150	-0.75808594
H	-4.79443485	-4.47372617	-1.82112773
H	-4.46610757	-5.10947068	-0.20456589
H	-6.07431541	-4.50308183	-0.60317961
C	-5.67651621	-1.43680655	-1.17595285
H	-5.40974975	-0.39022615	-1.03503880
H	-5.60545194	-1.66068447	-2.24312679
H	-6.72120846	-1.56430380	-0.87562368
C	-0.34107558	-1.91863101	-3.48329199
H	0.04145276	-2.92818364	-3.31490665
H	-0.19327169	-1.67459217	-4.53949897
H	0.26150298	-1.22932248	-2.88843792
C	-2.83431264	-0.12392286	-3.51398704
H	-3.92425864	-0.12271473	-3.44052643
H	-2.45802167	0.68229419	-2.88232075
H	-2.56760121	0.09939278	-4.55145434
C	-3.11537065	-3.09795621	-3.96797258
H	-2.78223036	-4.11220927	-3.74261569
H	-4.18534547	-3.03904040	-3.75569341
H	-2.98010696	-2.92799797	-5.04110431
C	-1.89484115	-4.75195110	1.51483474
H	-1.77469803	-4.00573519	2.30251242
H	-2.95938004	-4.97828728	1.43135344
H	-1.37915673	-5.66422919	1.82382077
C	-1.49063793	-5.39271099	-1.48136541
H	-1.02337247	-5.08026063	-2.41619323
H	-1.05489767	-6.35194445	-1.18728320
H	-2.55631568	-5.54077806	-1.66318434

Table S16. Cartesian coordinates of the T_1-optimized geometry for the Au_4 cluster.

Au	-1.77094710	0.00000000	0.00000000
Au	-0.00000000	2.07424650	0.00000000
Si	-2.46914207	2.21262120	0.76186614
Si	-4.68396025	2.72757291	0.18817908
Si	-1.23409021	4.25773698	0.12780005
Si	-2.25743299	1.96273611	3.09140918
C	-4.97507319	2.51606053	-1.65252301
H	-4.68515619	1.51536517	-1.97637615
H	-6.03182724	2.66463437	-1.89455244
H	-4.38964941	3.23228422	-2.23296658
C	-5.16302242	4.47640184	0.69861351
H	-4.99967818	4.62904875	1.76799587
H	-4.59704659	5.23816755	0.15914232
H	-6.22544066	4.64400924	0.49453374
C	-5.77953373	1.54434089	1.15623771
H	-5.46713654	0.50869977	1.01773523
H	-5.73834422	1.76831046	2.22504693
H	-6.82149945	1.63353503	0.83359905
C	-0.44002539	2.06448468	3.56474379
H	-0.02521161	3.05120690	3.34603950
H	-0.30276581	1.86952226	4.63273459
H	0.14078264	1.32702801	3.00564419
C	-2.91709767	0.27895047	3.60160552
H	-3.99126501	0.20915693	3.41671224
H	-2.42956935	-0.52055416	3.03991229

H	-2.74554904	0.10628258	4.66870507
C	-3.21996266	3.26898571	4.04792669
H	-2.87931037	4.27999827	3.81745062
H	-4.28763560	3.21425850	3.82126763
H	-3.10015979	3.10870950	5.12412395
C	-1.92546143	4.87814907	-1.50949514
H	-1.79169539	4.12437267	-2.28801169
H	-2.99293006	5.09152712	-1.42999947
H	-1.41835693	5.79266230	-1.82674505
C	-1.51993930	5.50725765	1.51090721
H	-1.05533000	5.17530857	2.44033238
H	-1.08645940	6.47431002	1.23981995
H	-2.58800112	5.64506244	1.69033400
Si	2.46914207	2.21262120	-0.76186614
Si	4.68396025	2.72757291	-0.18817908
Si	1.23409021	4.25773698	-0.12780005
Si	2.25743299	1.96273611	-3.09140918
C	4.97507319	2.51606053	1.65252301
H	4.68515619	1.51536517	1.97637615
H	6.03182724	2.66463437	1.89455244
H	4.38964941	3.23228422	2.23296658
C	5.16302242	4.47640184	-0.69861351
H	4.99967818	4.62904875	-1.76799587
H	4.59704659	5.23816755	-0.15914232
H	6.22544066	4.64400924	-0.49453374
C	5.77953373	1.54434089	-1.15623771
H	5.46713654	0.50869977	-1.01773523
H	5.73834422	1.76831046	-2.22504693
H	6.82149945	1.63353503	-0.83359905
C	0.44002539	2.06448468	-3.56474379
H	0.02521161	3.05120690	-3.34603950
H	0.30276581	1.86952226	-4.63273459
H	-0.14078264	1.32702801	-3.00564419
C	2.91709767	0.27895047	-3.60160552
H	3.99126501	0.20915693	-3.41671224
H	2.42956935	-0.52055416	-3.03991229
H	2.74554904	0.10628258	-4.66870507
C	3.21996266	3.26898571	-4.04792669
H	2.87931037	4.27999827	-3.81745062
H	4.28763560	3.21425850	-3.82126763
H	3.10015979	3.10870950	-5.12412395
C	1.92546143	4.87814907	1.50949514
H	1.79169539	4.12437267	2.28801169
H	2.99293006	5.09152712	1.42999947
H	1.41835693	5.79266230	1.82674505
C	1.51993930	5.50725765	-1.51090721
H	1.05533000	5.17530857	-2.44033238
H	1.08645940	6.47431002	-1.23981995
H	2.58800112	5.64506244	-1.69033400
Au	1.77094710	-0.00000000	0.00000000
Au	-0.00000000	-2.07424650	0.00000000
Si	2.46914207	-2.21262120	0.76186614
Si	4.68396025	-2.72757291	0.18817908
Si	1.23409021	-4.25773698	0.12780005
Si	2.25743299	-1.96273611	3.09140918
C	4.97507319	-2.51606053	-1.65252301
H	4.68515619	-1.51536517	-1.97637615

H	6.03182724	-2.66463437	-1.89455244
H	4.38964941	-3.23228422	-2.23296658
C	5.16302242	-4.47640184	0.69861351
H	4.99967818	-4.62904875	1.76799587
H	4.59704659	-5.23816755	0.15914232
H	6.22544066	-4.64400924	0.49453374
C	5.77953373	-1.54434089	1.15623771
H	5.46713654	-0.50869977	1.01773523
H	5.73834422	-1.76831046	2.22504693
H	6.82149945	-1.63353503	0.83359905
C	0.44002539	-2.06448468	3.56474379
H	0.02521161	-3.05120690	3.34603950
H	0.30276581	-1.86952226	4.63273459
H	-0.14078264	-1.32702801	3.00564419
C	2.91709767	-0.27895047	3.60160552
H	3.99126501	-0.20915693	3.41671224
H	2.42956935	0.52055416	3.03991229
H	2.74554904	-0.10628258	4.66870507
C	3.21996266	-3.26898571	4.04792669
H	2.87931037	-4.27999827	3.81745062
H	4.28763560	-3.21425850	3.82126763
H	3.10015979	-3.10870950	5.12412395
C	1.92546143	-4.87814907	-1.50949514
H	1.79169539	-4.12437267	-2.28801169
H	2.99293006	-5.09152712	-1.42999947
H	1.41835693	-5.79266230	-1.82674505
C	1.51993930	-5.50725765	1.51090721
H	1.05533000	-5.17530857	2.44033238
H	1.08645940	-6.47431002	1.23981995
H	2.58800112	-5.64506244	1.69033400
Si	-2.46914207	-2.21262120	-0.76186614
Si	-4.68396025	-2.72757291	-0.18817908
Si	-1.23409021	-4.25773698	-0.12780005
Si	-2.25743299	-1.96273611	-3.09140918
C	-4.97507319	-2.51606053	1.65252301
H	-4.68515619	-1.51536517	1.97637615
H	-6.03182724	-2.66463437	1.89455244
H	-4.38964941	-3.23228422	2.23296658
C	-5.16302242	-4.47640184	-0.69861351
H	-4.99967818	-4.62904875	-1.76799587
H	-4.59704659	-5.23816755	-0.15914232
H	-6.22544066	-4.64400924	-0.49453374
C	-5.77953373	-1.54434089	-1.15623771
H	-5.46713654	-0.50869977	-1.01773523
H	-5.73834422	-1.76831046	-2.22504693
H	-6.82149945	-1.63353503	-0.83359905
C	-0.44002539	-2.06448468	-3.56474379
H	-0.02521161	-3.05120690	-3.34603950
H	-0.30276581	-1.86952226	-4.63273459
H	0.14078264	-1.32702801	-3.00564419
C	-2.91709767	-0.27895047	-3.60160552
H	-3.99126501	-0.20915693	-3.41671224
H	-2.42956935	0.52055416	-3.03991229
H	-2.74554904	-0.10628258	-4.66870507
C	-3.21996266	-3.26898571	-4.04792669
H	-2.87931037	-4.27999827	-3.81745062
H	-4.28763560	-3.21425850	-3.82126763

H	-3.10015979	-3.10870950	-5.12412395
C	-1.92546143	-4.87814907	1.50949514
H	-1.79169539	-4.12437267	2.28801169
H	-2.99293006	-5.09152712	1.42999947
H	-1.41835693	-5.79266230	1.82674505
C	-1.51993930	-5.50725765	-1.51090721
H	-1.05533000	-5.17530857	-2.44033238
H	-1.08645940	-6.47431002	-1.23981995
H	-2.58800112	-5.64506244	-1.69033400

General procedure for the photophysical measurements

Crystal-grade samples of **1** and **2** were used to prepare the solutions. Since these clusters are air- and moisture-sensitive, methylcyclohexane (dehydrated -Super- grade, KANTO KAGAKU, Japan) was pretreated with oven-dried molecular sieves before use, and all sample preparations were conducted in a dry-N_2 filled glovebox. The concentrations of **1** and **2** in methylcyclohexane were 1.8×10^{-4} M. UV-vis absorption spectra were recorded using a UV-vis spectrophotometer (UV-2600i, Shimadzu, Japan). PL spectra and the PL quantum yield (PLQY, Φ_{PL}) at liquid-N_2 temperature was measured using an absolute PLQY spectrometer (Quantaurus-QY C11347-01, Hamamatsu Photonics, Japan). Transient PL decay measurements were conducted using a photoluminescence lifetime measurement system (Quantaurus-Tau C11367-01, Hamamatsu Photonics, Japan) with a xenon flash lamp unit (C11567-02, Hamamatsu Photonics, Japan) with the excitation wavelength of 445 nm using a bandpass filter (20-25 nm band width) together with C11367-01 as shown in **Figure S17**. The phosphorescence lifetime was determined by the single exponential fitting of the decay curve using the equipped software. For the determination of the rate constant, we reasonably considered that radiative and non-radiative decay occur only from triplet states via immediate intersystem crossing after photo excitation because there observed no fast lifetime component of fluorescence.

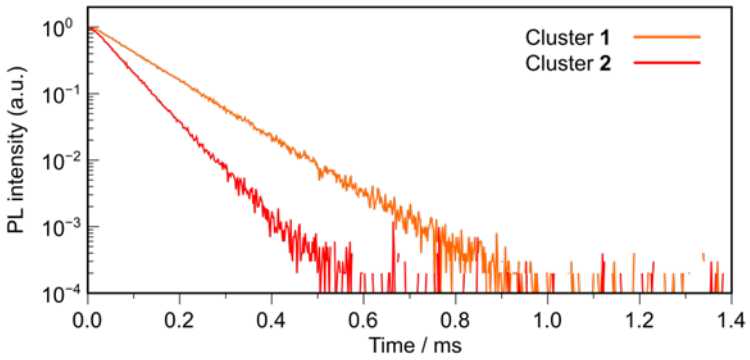


Figure S17. PL decay curves of clusters **1** and **2**.

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