Supplementary Material (ESI) for Chemical Communications

Supporting Information

Rational Reductive Fusion of Two Heterometallic Clusters: Formation of Highly Stable, Intensely Phosphorescent Au-Ag Aggregate and Application in Two-Photon Imaging in Human Mesenchymal Stem Cells

Igor O. Koshevoy,[*a] *Yi-Chih Lin,*[b] *Yu-Chun Chen,*[b] *Antti J. Karttunen,*[a] *Matti Haukka,*[a] *Pi-Tai Chou,*[*b] *Sergey P. Tunik,*[c] *and Tapani A. Pakkanen*[*a]

[a] Department of Chemistry, University of Joensuu, 80101, Joensuu, Finland;

[b] Department of Chemistry, National Taiwan University, Taipei 106, Taiwan;

[c] Department of Chemistry, St.-Petersburg State University, Universitetskii pr. 26, 198504, St.-Petersburg

E-mail: igor.koshevoy@joensuu.fi; tapani.pakkanen@joensuu.fi; chop@ntu.edu.tw

Experimental

General comments

Au(tht)Cl (tht = tetrahydrothiophene),[1] $(AuC_2Ph)_n$,[2] 1,4-PPh_2-C_6H_4-PPh_2 (dppb)[3] were synthesized according to published procedures. Other reagents and solvents were used as received. Solution ^1H, ^{13}C and ^{31}P NMR spectra were recorded on Bruker Avance 400 and Bruker DPX 300 spectrometers. Mass spectrum was determined on a Bruker APEX-Qe ESI FT-ICR instrument, in the ESI^+ mode. Microanalysis was carried out in the analytical laboratory of the University of Joensuu.

$[Au_{14}Ag_4(C_2Ph)_{12}(PPh_2C_6H_4PPh_2)_6][PF_6]_4$ (1)

$(AuC_2Ph)_n$ (50.0 mg, 0.168 mmol) was suspended in CH_2Cl_2 (10 cm^3) and dppb (37.5 mg, 0.84 mmol) was added. The reaction mixture was stirred for 15 min. to give transparent colourless solution, to which a solution of $AgPF_6$ (14.2 mg, 0.056 mmol) in acetone (3 cm^3) was added. The resulting yellow-greenish solution was stirred in the absence of light for 15 min. and then the solvents were removed on a rotary evaporator. The yellow-greenish solid was dissolved in acetone (10 cm^3) (*solution 1*) and placed under CO atmosphere under stirring. In 10 minutes *solution 2* was added followed by the solution of K_2CO_3 (2 mg, 0.014 mmol) in water (1 cm^3). The reaction mixture immediately darkened and was stirred under CO atmosphere for 4 h in the absence of light. The solvents were removed under vacuum and the crude **1** was extracted with CH_2Cl_2/Et_2O (4:3 v/v) mixture (4×7 cm^3). Repetitious extraction-recrystallization by gas-phase diffusion of diethyl ether into the CH_2Cl_2/NCMe/MeOH solution of **1** at room temperature gave bright-orange

crystalline material (73 mg, 68%). Single crystals suitable for X-ray diffraction study were grown by gas-phase diffusion of diethyl ether into the NCMe/MeOH solution of **1** at +5 °C.

Solution 2. Au(tht)Cl (9 mg, 0.028 mmol) was dissolved in CH_2Cl_2 (5 cm^3), dppb (6.3 mg, 0.014 mmol) was added and the reaction mixture was stirred for 15 min. Then a solution of $AgPF_6$ (7.2 mg, 0.028 mmol) in acetone (3 cm^3) was added causing immediate precipitation of AgCl. The resulting suspension was stirred for additional 15 min. then filtered and evaporated. The colourless solid was dissolved in acetone (5 cm^3) and added in one portion so the *solution 1*.

ES MS (*m*/*z*): $[Au_{14}Ag_4(C_2Ph)_{12}(PPh_2C_6H_4PPh_2)_6]^{4+}$ 1770.36 (calcd 1770.34).

For NMR numbering see Chart S1 below (**NB** for details).

$^{31}P\{^1H\}$ NMR (acetone-d_6, δ, 298 K): 50.7 (s, **^{3}P**, 4P), AB system of **^{1}P** and **^{2}P** (8P), δ **^{1}P** 44.4 and δ **^{2}P** 42.1, *J*(P-P) 300 Hz (simulated values), -144.8 (sept, 4P, PF_6). ^{1}H NMR (acetone-d_6, δ, 263 K): **three groups of Ph signals corresponding to inequivalent (C_2-C_6H_5) moieties: I** 6.175 (dd, H-meta, 8H, *J*(H-H) 7.1, 7.7 Hz), 6.905 (t, H-para, 4H, *J*(H-H) 7.7 Hz), 7.083 (d, H-orto, 8H, *J*(H-H) 7.1 Hz); **II** 6.403 and 6.480 (AB system H-orto and H-meta 16H, *J*(H-H) ca 7.5 Hz), 6.883 (d, H-para, 4H, *J*(H-H) 7.7 Hz); **III** 6.490 (d, H-orto, 8H, *J*(H-H) 7.5 Hz), 6.752 (dd, H- meta, 8H, *J*(H-H) 7.5, 7.8 Hz), 7.056 (t, H-para, 4H, *J*(H-H) 7.8 Hz); **six groups of Ph signals of the PPh_2 fragments: IV** 6.538 and 6.660 (ABX system H-orto and H-meta 16H, *J*(H-H) ca 7.5 Hz), 6.883 (d, H-para, 4H, *J*(H-H) 7.7 Hz); **V** 7.990 (d, H-orto, 8H, *J*(H-H) 7.6 Hz, , *J*(P-H) 12 Hz), 7.645 (t, H-para, 4H, *J*(H-H) 7.6 Hz), 7.422 (dd, H-meta, 8H, *J*(H-H) 7.5, 7.6 Hz) ; **VI** 8.303 (dd, H-orto, 8H, *J*(H-H) 7.0 Hz, , *J*(P-H) 12.5 Hz), 7.887 (t, H-para, 4H, *J*(H-H) 7.5 Hz), 7.730 (dd, H-meta, 8H, *J*(H-H) 7.0, 7.6 Hz); **VII** 7.020 and 7.096 (AB system H-orto and H-para 12H, *J*(H-H) ca 7.5 Hz), 7.410 (d, H-meta, 8H, *J*(H-H) 7.0 Hz); **VIII** 8.118 (dd, H-orto, 8H, *J*(H-H) 8.0 Hz, , *J*(P-H) 11.7 Hz), 7.722 and 7.625 (AB system H-meta and H-para 12H, *J*(H-H) ca 7.7 Hz); **IX** 7.990 (dd, H-orto, 8H, *J*(H-H) 7.6 Hz, *J*(P-H) 10 Hz), 7.645 (t, H-para, 4H, *J*(H-H) 7.6 Hz), 7.422 (dd, H-meta, 8H, *J*(H-H) ca. 7.6 Hz); **C_6H_4 spacers**: "***1***" 7.727 terminal (**^{1}P**-C_6H_4-**^{1}P**) diphosphine ligand, A_2X_2 system of 8H, *J*(P-H) ca. 11 Hz, "***2***" 8.039 and 7.868 16H two multiplets of ABXY system (**^{2}P**-C_6H_4-**^{3}P**).

Anal. Calc. for $C_{276}H_{204}Ag_4Au_{14}F_{24}P_{16}$: C, 43.27; H, 2.68. Found: C, 43.27; H, 3.04.

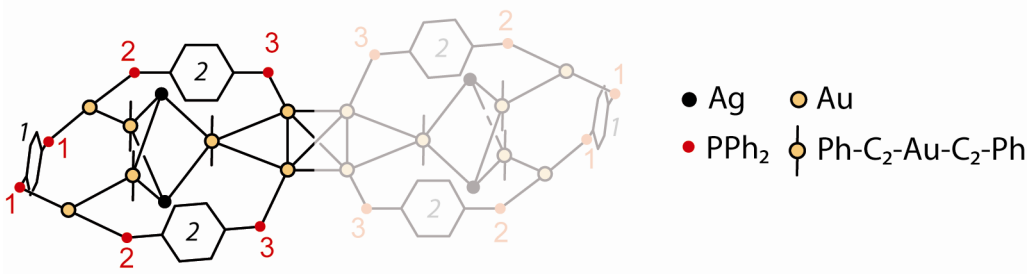

Chart S1.

NB. The molecule belongs to D_2 symmetry point group with two mutually perpendicular two-fold axis through the center of the molecule, which lies inside central tetrahedron of gold atoms. In accord with the D_2 symmetry the ^{31}P NMR spectrum of **1** (Figure S2) display three signals, one of which corresponds to the **^{3}P** nuclei appears as a singlet at 50.7 ppm whereas two others (**^{1}P** and **^{2}P**) coupled through the Au ions give AB system with the central components at 43.5 and 42.7 ppm and satelites at 46.0 and 40.2 ppm that corresponds to the chemical shifts of the nuclei 44.4 and 42.1 ppm with the J(P-P) coupling constant 300 Hz. The later values were obtained by AB-system simulation. The ^{1}H NMR spectrum revealed a dynamic process in solution at room temperature, but recording the spectra at 263 K made possible a complete assignment of the signals oserved. As expected for the molecule shown in Figure 1, the signals of –C_2-Ph fragments of six dialkynyl-gold "rods" appear as three groups of phenyl protons in the high field part of the proton spectrum between 7.1 and 6.0 ppm. Crosspeaks observed inside each set (ortho-meta-para) of the phenyl signals allows for easy grouping whereas the absence of phosphorus to proton coupling clearly point to their alkynyl ligand origin. In the low-field part of the spectrum, 7.0-8.4 ppm one can observe six groups of phenyl signals (twelve PPh_2 fragments) and three signals corresponding the protons of phenylene spacers, one of which (at 7.73 ppm) is not coupled to the other protons (-C_6H_4- of the terminal, **^{1}P**(-C_6H_4-)**^{1}P**, ligand) and two others (X**AB**Y system) originate from the spacer of **^{2}P**(-C_6H_4-)**^{3}P** diphosphine ligands. Relative intensities of all these signals, combinations of their crosspeaks and coupling patterns fits completely molecular structure found in the solid state. The VT spectra of **1** (Figure S3) may be interpreted as a dynamics related to the twist (skewing) of the whole molecule about "long" C_2 axis with only spacer of the **^{2}P**(-C_6H_4-)**^{3}P** diphosphine ligand (signals at ca. 8.05 and 7.8 ppm) kept rigid together with a set of signals corresponding to a certain group of phenyl substituents at alkynyl ligands, very probably those closest to the rigid phenylene spacer.

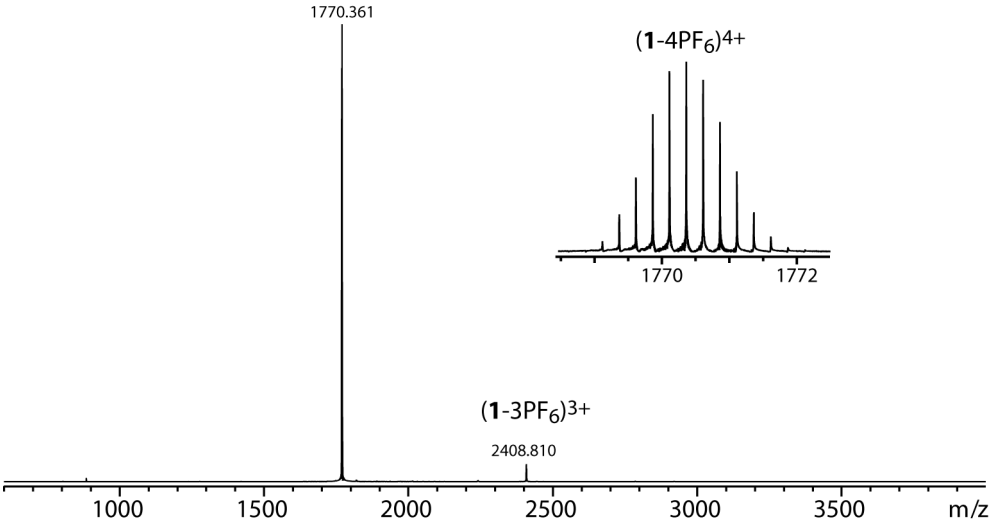

Figure S1. ESI-MS spectrum of the $[Au_{14}Ag_4(C_2Ph)_{12}(PPh_2C_6H_4PPh_2)_6]^{4+}$ tetracation (**1**-4PF_6).

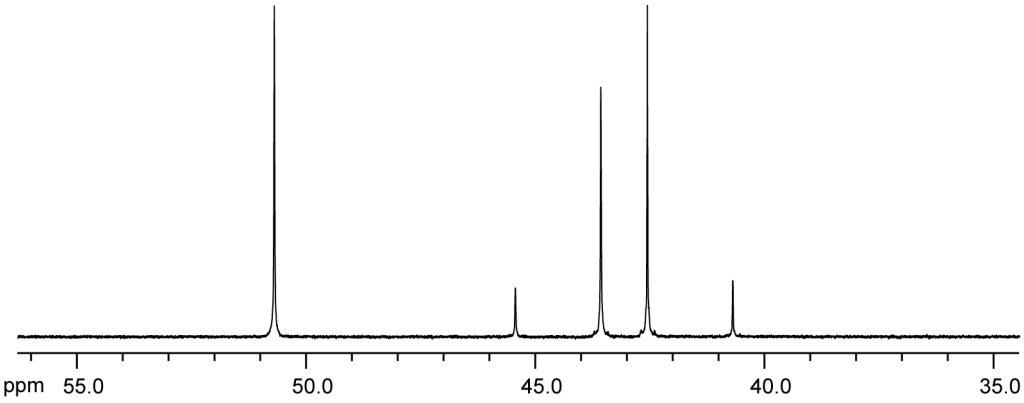

Figure S2. $^{31}P\{^{1}H\}$ NMR spectrum of **1**, acetone-d_6, 162 MHz, 298 K.

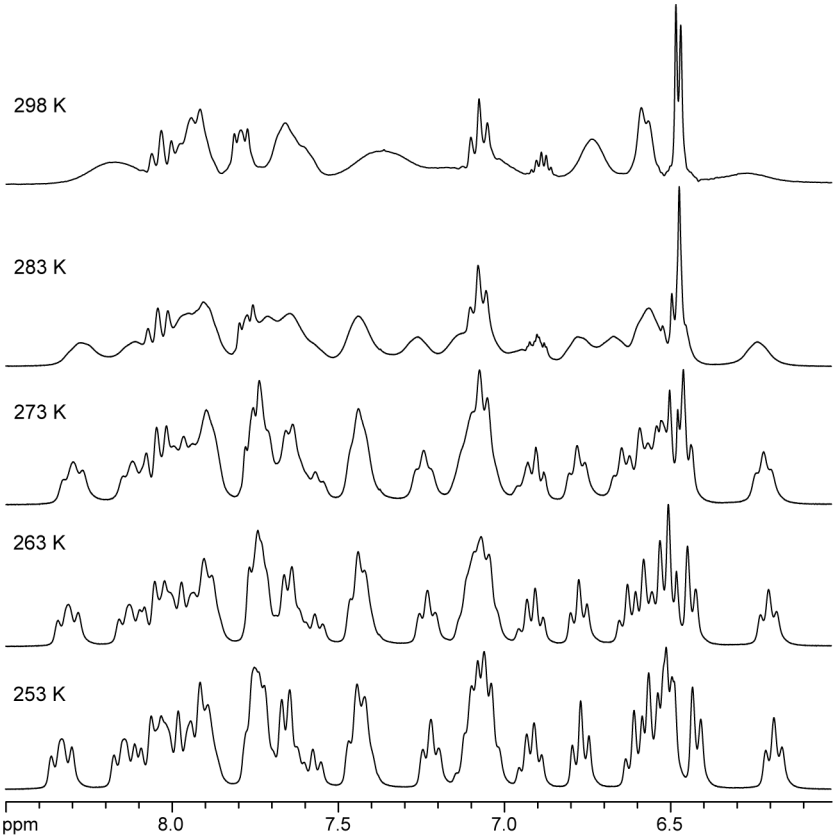

Figure S3. VT ^{1}H NMR spectra of **1**, acetone-d_6, 300 MHz.

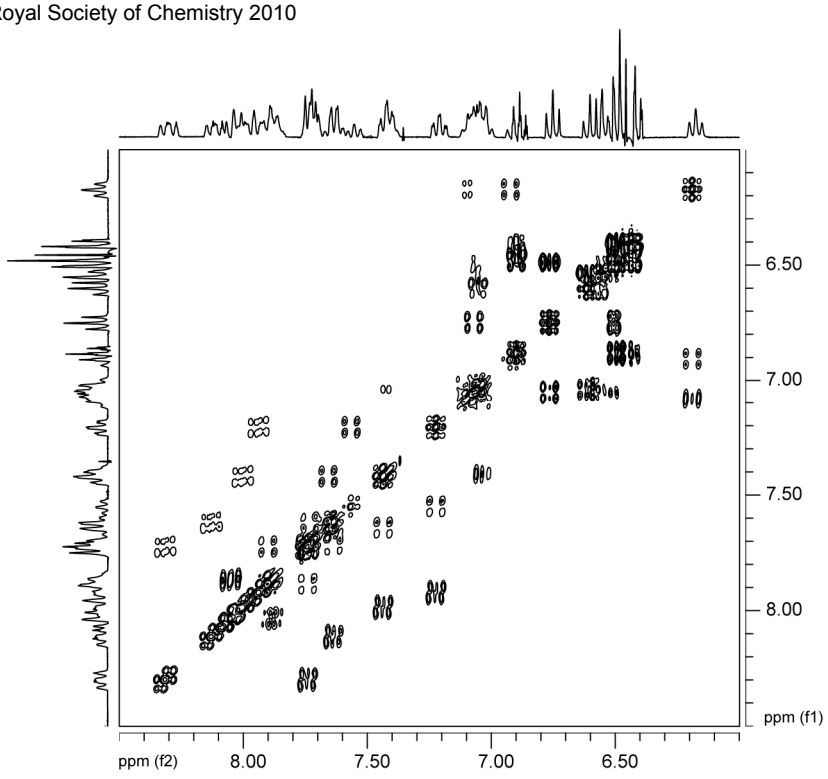

Figure S4. ^{1}H-^{1}H COSY NMR spectrum of **1**, acetone-d_6, 300 MHz, 263 K.

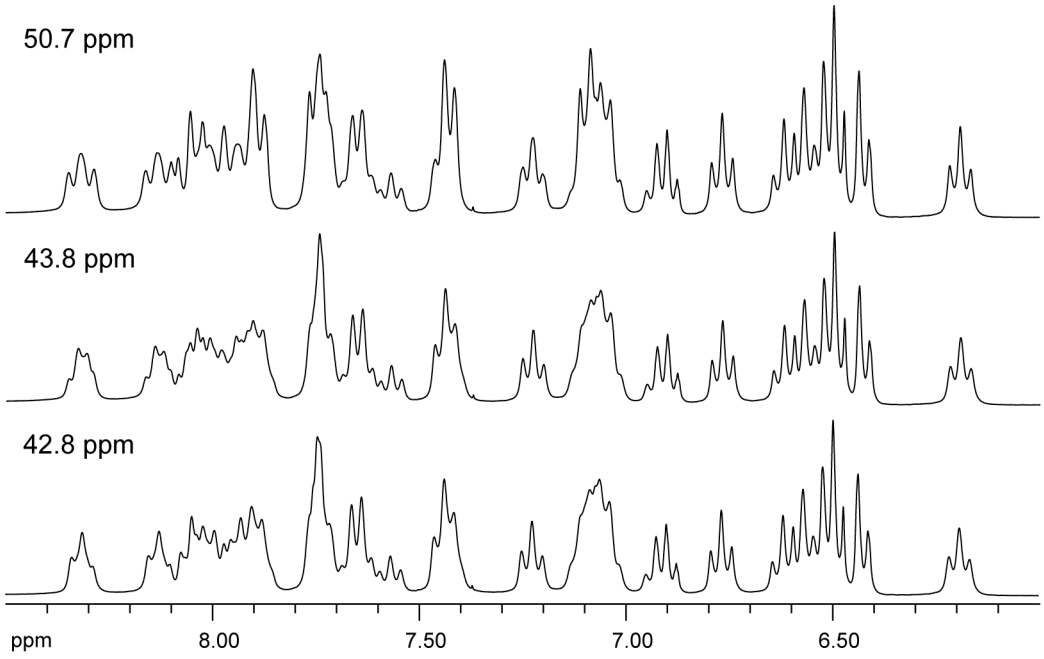

Figure S5. Selective ^{1}H{^{31}P}decoupled NMR spectra of **1**, acetone-d_6, 300 MHz, 263 K, PVC 46 dB.

X-ray Structure Determinations

The crystal of **1** was immersed in cryo-oil, mounted in a Nylon loop, and measured at a temperature of 100 K. The X-ray diffraction data was collected on a Nonius KappaCCD diffractometer using Mo Kα radiation (λ = 0.710 73 Å). The *Denzo-Scalepack*[4] program package was used for cell refinement and data reduction. The structure was solved by direct methods using the *SHELXS-97*[5] programs with the *WinGX*[6] graphical user interface. A semi-empirical absorption

correction (*SADABS*)[7] was applied to data. Structural refinement was carried out using *SHELXH-97*.[5] One of the acetonitrile solvent molecules and two PF_6 anions were disordered over two sites with occupancy ratio 0.48/0.52, 0.37/0.63, and 0.51/0.49 respectively. The solvent model used did not cover all solvent molecules. Some of the solvent molecules could not be located. The contribution of the missing solvent to the calculated structure factors was taken into account by using a SQUEEZE routine of PLATON.[8] Several geometric and displacement restraints were applied to solvent of crystallization, disordered PF_6 anions and to aromatic rings of some phenylacetylide ligands. Some of the phenylacetylide rings were slightly disordered but no disorder model was used in the final refinement. Therefore, the max/min U_{eq} ratio in these groups remained quite large. Hydrogen atoms were positioned geometrically and constrained to ride on their parent atoms, with C-H = 0.95-0.99 Å and U_{iso} = 1.2-1.5 U_{eq} (parent atom). The crystallographic details are summarized in Table S1.

Table S1. Crystal data and structure refinement for **1**.

Identification code	**1**	
Empirical formula	$C_{296}H_{241}Ag_4Au_{14}F_{24}N_6O_2P_{16}$	
Formula weight	8054.48	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 17.4680(2) Å	α= 70.1969(5)°.
	b = 27.4904(3) Å	β= 87.4219(5)°.
	c = 32.2603(3) Å	γ = 78.3190(4)°.
Volume	14268.8(3) $Å^3$	
Z	2	
Density (calculated)	1.875 Mg/m^3	
Absorption coefficient	7.591 mm^{-1}	
F(000)	7650	
Crystal size	0.20 x 0.17 x 0.07 mm^3	
Theta range for data collection	1.92 to 27.00°.	
Index ranges	-22<=h<=22, -35<=k<=35, -40<=l<=41	
Reflections collected	208382	
Independent reflections	61984 [R(int) = 0.0452]	
Completeness to theta = 27.00°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6110 and 0.3135	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	61984 / 535 / 3246	
Goodness-of-fit on F^2	1.059	
Final R indices [I>2sigma(I)]	R1 = 0.0444, wR2 = 0.0992	
R indices (all data)	R1 = 0.0736, wR2 = 0.1076	
Largest diff. peak and hole	2.463 and -2.242 $e.Å^{-3}$	

Photophyical results

Open-aperture Z-scan method

The open aperture Z-scan experiments were conducted by using essentially the same experimental setup and procedure as previously described.[9] In brief, a mode-locked Ti:sapphire

laser (Tsunami, Spectra Physics) produced Gaussian pulse trains (80 MHz) that was coupled to a regenerative amplifier, generating a ~200 fs, 1 mJ pulse (780-820 nm, 1 kHz, Spitfire Pro, Spectra Physics). The pulse energy, after suitable attenuation, was then reduced to 2.48 μJ. After passing through an f = 30 cm lens, the laser beam was focused and passed through a 1.00 mm cell filled with the sample solution, compound **1** in dichloromethane (1.60×10^{-3} M), and the beam radius at the focal position is 5.09×10^{-3} cm. When the sample cell changed its position along the beam direction (z-axis), the transmitted laser beam from the sample cell was detected by a photodiode (PD-10, Ophir). Accordingly, in theory, the two-photon absorption induced decrease of transmittance, *T(z)*, can be expressed as equations (1) and (2) and two-photon absorption coefficient (β) is extracted by fitting Z-scan curves to relationship (1) and (2).

$$T(z) = \sum_{n=0}^{\infty} \frac{(-q)^n}{(n+1)^{3/2}} \qquad (1)$$

$$q = \frac{\beta I_0 L}{1 + \frac{z^2}{z_0^2}} \qquad (2)$$

where n is an integer number from 0 to ∞ and has been truncated at n = 1000, L is the sample length, I_0 is the input intensity, z is the sample position with respect to the focal plane, and z_0 is the diffraction length of the incident beam (Rayleigh range).[9] After obtaining the two-photon absorption coefficient (β), two-photon absorption cross-section (σ_2) can be deduced by using equation (3)

$$\beta = \frac{\sigma_2 N_A d \times 10^{-3}}{h\nu} \qquad (3)$$

where N_A is the Avogadro constant, d is the concentration, h is the Planck constant, and υ is the frequency of the incident beam. As for the open aperture Z-scan experiments, we have measured TPA cross-sections of a well known TPA dye, coumarin 480, to ensure that the TPA cross-section values were not over-estimated. The resulting value of 165±10 GM (five replicas) is consistent with the reported data of 168.2 GM within 5% uncertainty.

Compound 1 embedded in silica nanoparticles

Silica nanoparticles were prepared from reverse micelles using a previously reported procedure.[10] The prepared compound **1** was then embedded during the growth of SiO_2. Briefly, various amounts of tetraethyl orthosilicate (TEOS, 20~50 μL) and compound **1** (1~3 mg) were added to a heterogenous solution containing cyclohexane (8 mL), hexanol (1.6 mL), triton X-100 (2 mL), and water (340 μL). After 6 h of stirring, NH_4OH (100 μL) was then added to initiate the

hydrolysis of TEOS. The reaction was allowed to continue for another 24 h with vigorous stirring at room temperature. The resulting colloids were then washed several times by ethanol and deionized water to remove unreacted material. After 72 h of dialysis, the final product was ready for use.

***In-vitro* biocompatibility test**

Human mesenchymal stem cells were cultured with Dulbecco's modified Eagle's medium DMEM (Sigma) supplemented with 10 % fetal bovine serum (High clone) and 1% penicillin/streptomycin (Sigma), and incubated in moist atmosphere of 5% CO_2/ 95% air at 37°C. Cells were passaged through trypsinization and nucleated cells were centrifuged at 100 g for harvesting. For cytotoxcity test, cells were seeded in a 24 well plate at 5×10^3 cell/well density in 0.5 mL culturing medium 24 hours prior to particles feeding. Different amount of compound **1** were given to each well to reach the final concentration of 0, 0.088, 0.177, 0.353, 0.706, and 1.412 nM. After 24 hours of incubation, each well was washed with Phosphate buffer saline (PBS: 137 mM NaCl, 2.68 mM KCl, 10 mM Na_2HPO_4, 1.76 mM KH_2PO_4, pH 7.4) three times, and replenished with 500 uL culturing medium with 10 % of MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) agent. After 1 hour of incubation and medium removal, the newly formed purple MTT-formazan was dissolved in 200 L dimethyl sulfoxide (Sigma) and the absorbance was measured at 570 nm by a spectrophotometer (Tecan Infinite F200). Total of 4 trails were performed for the assurance of reproducibility. For confocol microscopic study, hMSCs were seeded on 0.17mm cover slides at 5×10^4 cell/well density in 2 mL of culturing medium 24 hours prior to particles feeding. After 24 hours incubation with 0.706 nM of compound **1**, cells were washed three times with PBS and then fixed in a 4% paraformaldehyde solution in PBS at room temperature for 20 minutes. The cells were then washed three times with PBS and incubated with 0.5 % Triton X-100 (Sigma-Aldrich) plus 1 % bovine serum albumin (BSA; Sigma-Aldrich) in PBS at room temperature for 5 min. 4',6-diamidino-2-phenylindole (DAPI; Molecular Probes) and Rhodamine Phalloidin (Invitrogen) were used for nucleus and cytoskeleton staining, respectively. Cell samples were examined by a Zeiss LSM 710 Inverted Confocal Microscope equiped with HeNe laser for one-photon excitation at 458nm and Ti:Sapphire (Mai Tai DeepSee, Newport) for two-photon excitation at 760 nm. C-Apochromate 40X/1.20 W Korr M27 was used as the objective lens. Image aqusition and processing were achieved with Zen software.

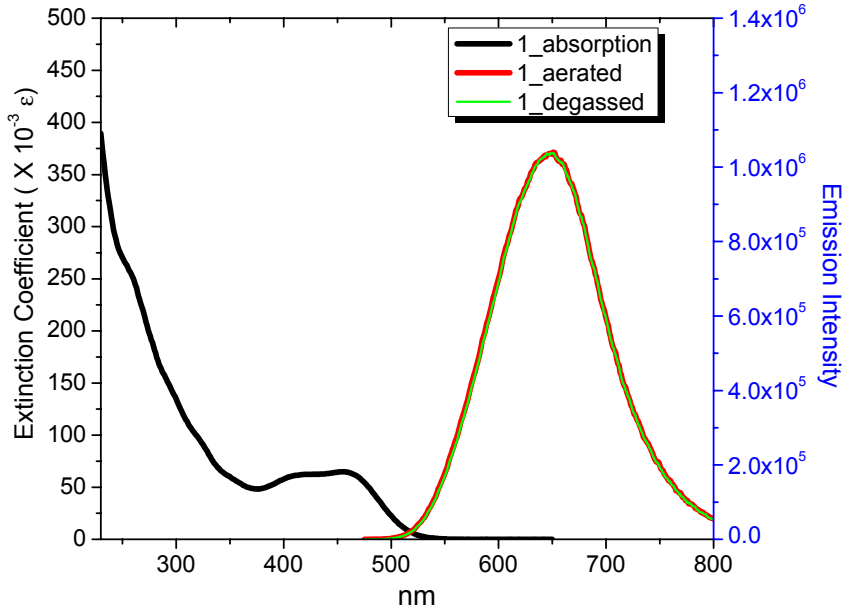

Figure S6. UV/VIS absorption and emission spectra of **1** in CH_2Cl_2 at room temperature, λ_{ex} = 450 nm.

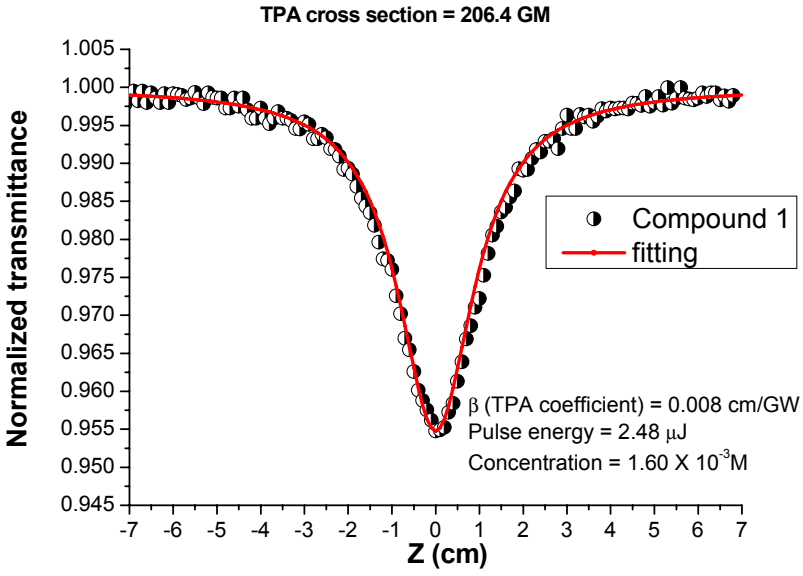

Figure S7. Z-scan experimental data of compound **1** in dichloromethane (circles) in a 1-mm cell. Solid lines are the best fit for the data points by equations (1) and (2).

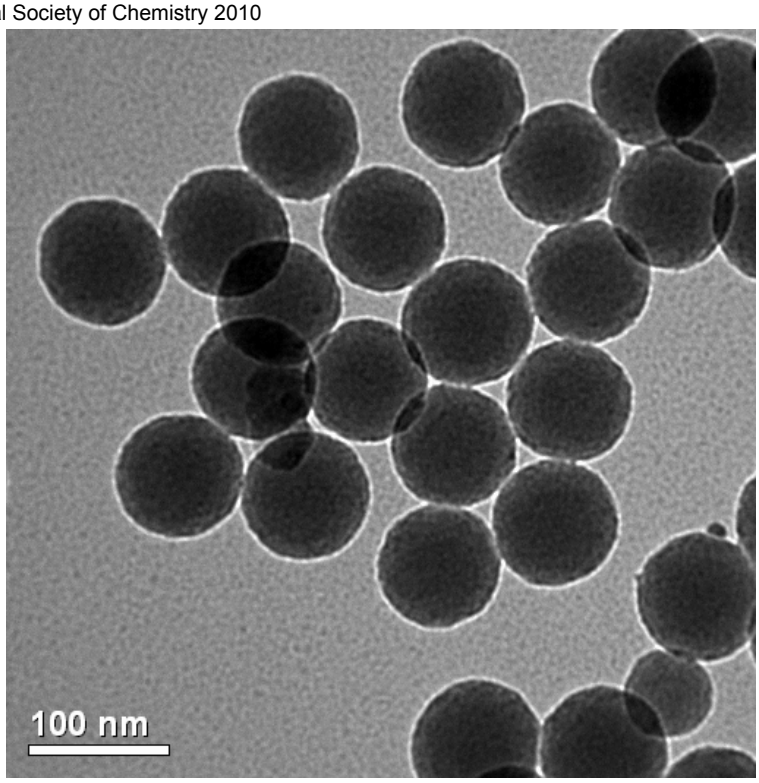

Figure S8. TEM of compound **1** embedded in SiO_2 with an average size of 84 ± 10 nm.

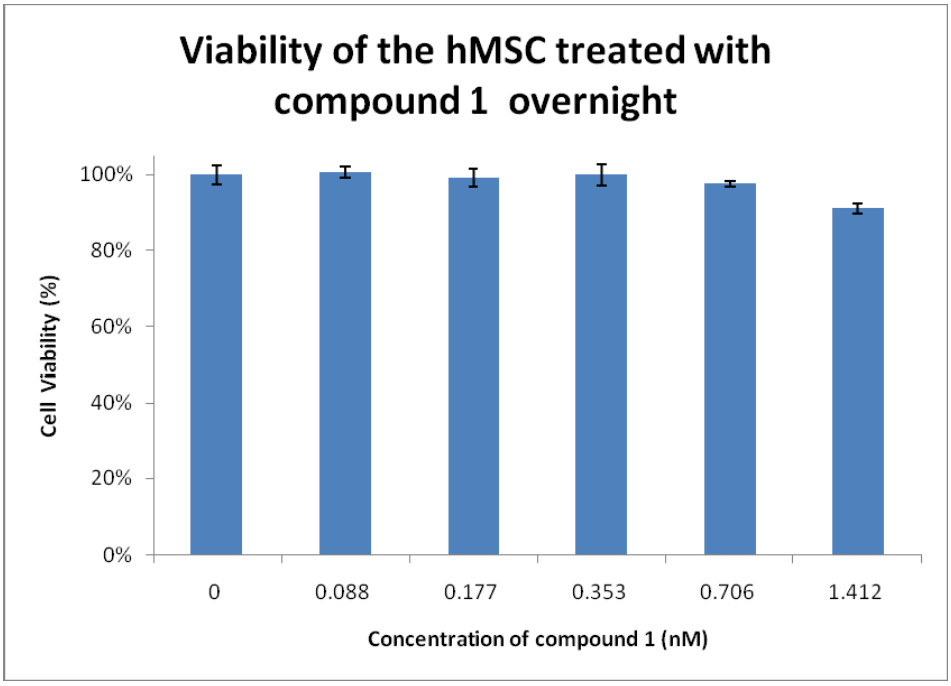

Figure S9. MTT assay for the viability of human mesenchymal stem cells (hMSCs) treated with various concentrations of silica-encapsulated compound **1** overnight. Error bars represent the standard deviations of 4 trails.

Computational details

The complex **1** was fully optimized without any symmetry constraints using the BP86 density functional method.[11] The silver and gold atoms were both described with a triple-valence-

zeta quality basis set with polarization functions (def2-TZVP),[12] employing 28-electron and 60-electron relativistic effective core potentials for Ag and Au, respectively.[13] A split-valence basis set with polarization functions on non-hydrogen atoms was used for all the other atoms (def2-SV(P)).[14] The multipole-accelerated resolution-of-the-identity technique was used to speed up the calculations.[15] The lowest triplet state of the complex **1** was studied using spin-unrestricted formalism. Population analyses were performed using the Natural Population Analysis scheme.[16] All electronic structure calculations were carried out with TURBOMOLE version 5.10,[17] with the exception of the calculation of the Nucleus-independent Chemical Shift (NICS) values,[18] which were obtained with Gaussian03.[19]

Computational results

The electronic properties and structural characteristics of the supramolecular Au(I)-Ag(I) complex **1** were investigated by means of density functional calculations. The experimentally observed structural motif of the complex **1** remained intact during a full geometry optimization, and comparison between the X-ray structure and the DFT optimized geometry shows them to be in fairly good agreement. The largest differences are found for the metal–metal distances, which are slightly overestimated by the BP86 density functional method. For example, the experimental and theoretical Au–Ag bond distances within the $[Au_3Ag_2(C_2Ph)_6]^-$ fragments are 2.85–3.05 Å and 2.91–3.11 Å, respectively, while the experimental and theoretical Au–Au bond distances within the same fragments are 2.84–2.92 Å and 2.95–3.00 Å. The theoretical Au–Au bond contacts within the $[Au_4]^{2+}$ tetrahedron (2.76–2.90 Å) are also somewhat overestimated in comparison to experiment (2.71–2.76 Å), but the agreement is still reasonable. The overestimation of the bond distances within $[Au_4]^{2+}$ at the BP86 level of theory is likely to be due to the underestimation of correlation contributions, which have been shown to play an important role for $[Au_4]^{2+}$.[20] The computational results were also verified with respect to a structural model, where the bond distances within the $[Au_4]^{2+}$ tetrahedron were fixed during the optimization.

The stability of the $[Au_4]^{2+}$ building block can be partially attributed to spherical aromaticity, which is known to stabilize cage-shaped clusters with a suitable electron count.[21] In $[Au_4]^{2+}$, two Au 6*s*-electrons are delocalized within the cluster, fulfilling the $2(N+1)^2$ criterion of spherical aromaticity for N = 0. The degree of aromaticity in cage-like molecules can be probed by calculating the Nucleus-Independent Chemical Shift (NICS) at the center of the cage.[18] The NICS value calculated for a naked $[Au_4]^{2+}$ cluster at the BP86/def2-TZVP level of theory is –31.1 ppm, which is very reasonable in comparison to the value of –45.4 ppm calculated for the larger, also spherically aromatic C_{2v}-symmetric Au_{18} cluster (N = 2).[22] Calculating the NICS for the $[Au_4]^{2+}$ cluster within the complex **1** results in a value of –21.6 ppm, which suggests that the interaction

with the rest of the complex does not decrease the aromatic character of the $[Au_4]^{2+}$ cluster significantly. Natural population analysis (NPA) of **1** also illustrates the special characteristics of the $[Au_4]^{2+}$ cluster. While the partial charges of the Au(I) atoms within the heterometallic $[Au_3Ag_2(C_2Ph)_6]^-$ fragments and the "belt" fragments are $+0.46e^-$ and $+0.25e^-$, the gold atoms within the $[Au_4]^{2+}$ tetrahedron show noticeably smaller partial charge of $+0.15e^-$. The two Au(I) atoms directly connected to the $[Au_4]^{2+}$ cluster show the highest partial charge of all gold atoms, 0.49 e^-. As can be expected from the structural characteristics of **1**, all Ag(I) atoms possess considerable positive partial charges of $+0.76e^-$.

The frontier orbital characteristics of the complex **1** at the DFT optimized geometry are illustrated in Figure S10. The main contributions to the highest occupied molecular orbitals (HOMOs) come from the alkynyl ligand π(C≡CPh) orbitals and metal d orbitals within the heterometallic $[Au_3Ag_2(C_2Ph)_6]^-$ fragments, while the $[Au_4]^{2+}$ cluster does not participate in the HOMOs. In contrast, the central $[Au_4]^{2+}$ tetrahedron contributes significantly to the lowest unoccupied molecular orbital (LUMO), which is mainly composed of orbitals of the $[Au_4]^{2+}$ cluster together with contributions from the two neighboring $[Au(C_2Ph)_2]^-$ rods. The HOMO-LUMO gap of **1** is 1.5 eV and there is a quite large energy gap of 0.55 eV between the LUMO and LUMO + 1, which is composed of metal sp orbitals and alkynyl ligand π*(C≡CPh) orbitals of the heterometallic $[Au_3Ag_2(C_2Ph)_6]^-$ fragments (not shown here). Inspection of the frontier orbitals of **1** at the relaxed geometry of the lowest energy triplet state T_1 shows that the highest singly occupied orbital (HSOMO), which is occupied by the excited electron, is centered on the $[Au_4]^{2+}$ tetrahedron very similarly to the LUMO. The structural differences between the S_0 and T_1 states of **1** are generally small, the most noticeable change in the T_1 state being the decrease in the two Au–Au bond lengths of the $[Au_4]^{2+}$ fragment along the P–Au–Au–P chains from 2.76 to 2.69 Å, together with corresponding small increase in other Au–Au distances within the tetrahedron. Overall, the frontier orbital characteristics of the S_0 and T_1 states suggest the observed phosphorescence to originate from a $\{[Au_4]^{2+} \rightarrow [Au_3Ag_2(C_2Ph)_6]^-\}$ triplet emission within the heterometallic core of **1**.

Comparing the frontier orbital characteristics of **1** to its overall structural properties suggests that the observed oxygen-quenching-free phosphorescence can be explained by sterical factors. The heterometallic core and especially the central $[Au_4]^{2+}$ cluster of the complex **1** are very well protected by bulky ligands (Figure S11). Hence, the protected nature of the central chromophore is likely to be a significant contributing factor to the observed high efficiency of the phosphorescence, as the bulky ligands prohibit the O_2 collisional quenching of the triplet state.

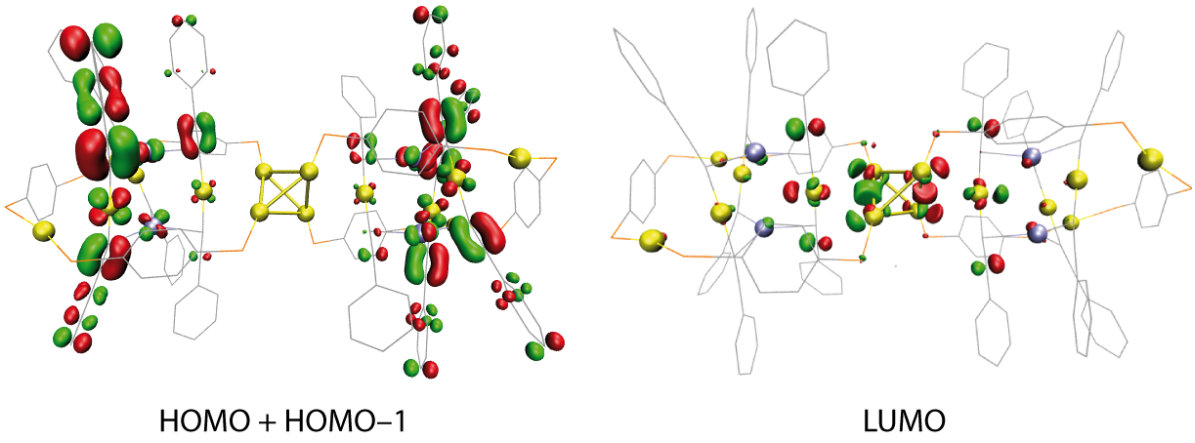

Figure S10. Frontier molecular orbital isodensity plots for the $Au_{14}Ag_4$ complex (isodensity value 0.04 a.u.). Hydrogen atoms and diphosphine-based phenyl rings omitted for clarity.

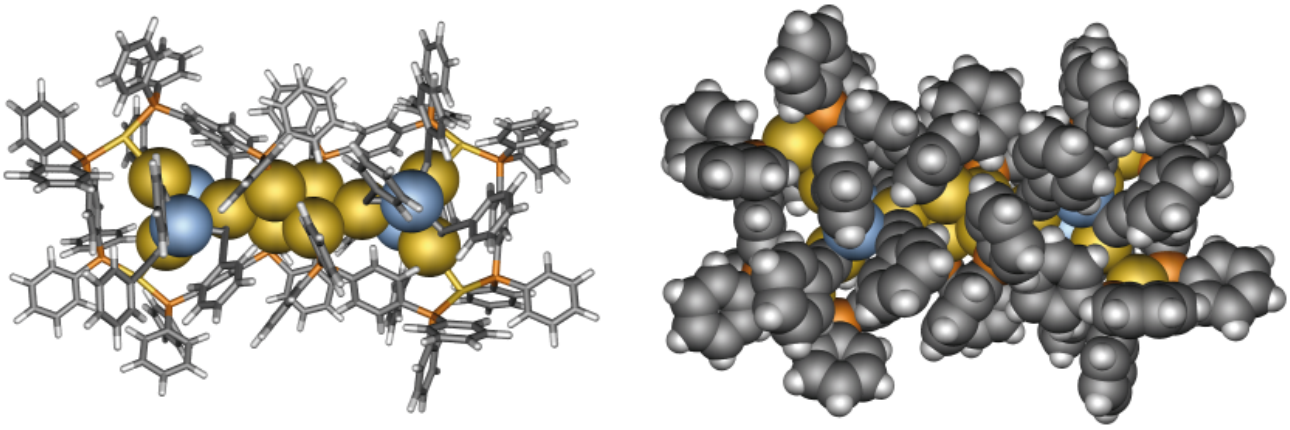

Figure S11. Two representations of the complex **1** at the DFT-optimized geometry. Left: The heterometallic core of the complex. Right: A space-filling model illustrating how the core is protected by bulky ligands.

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Additional computational data

Optimized cartesian coordinates of the studied systems in atomic units (BP86 level of theory).

$[Au_{14}Ag_4(C_2Ph)_{12}(PPh_2C_6H_4PPh_2)_6]^{4+}$ (1)

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9.51626008746001	4.68124164976020	3.77421599399215	c
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8.47932230132553	7.70873879672696	15.50576393707991	c
2.06085626863087	-11.55578504746344	-10.13920018634644	c
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11.62011483797845	-1.05098666816050	-9.36370186509630	c
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