Photochemistry

Strongly Luminous Tetranuclear Gold(I) Complexes Supported by Tetraphosphine Ligands, meso- or rac-Bis[(diphenylphosphinomethyl)phenylphosphino]methane

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Abstract: A series of tetragold(I) complexes supported by tetraphosphine ligands, meso- and rac-bis[(diphenylphosphinomethyl)phenylphosphino]methane (meso- and racdpmppm) were synthesized and characterized to show that the tetranuclear Au¹ alignment varies depending on syn- and anti-arrangements of the two dpmppm ligands with respect to the metal chain. The structures of syn-[Au₄(mesodpmppm)₂X]X'₃ (X = Cl; X' = Cl (4a), PF₆ (4b), BF₄ (4c)) and syn-[Au₄(meso-dpmppm)₂]X₄ (X = PF₆ (**4 d**), BF₄ (**4 e**), TfO (**4 f**); TfO = triflate) involved a bent tetragold(I) core with a counter anion X incorporated into the bent pocket. Complexes anti- $[Au_4(meso-dpmppm)_2]X_4$ (X = PF₆ (5d), BF₄ (5e), TfO (5f)) contain a linearly ordered Au₄ string and complexes syn- $[Au_4(rac-dpmppm)_2X_2]X'_2$ (X = Cl, X' = Cl (6a), PF₆ (6b), BF₄ (6c)) and syn-[Au₄(rac-dpmppm)₂]X₄ (X = PF₆ (6d), BF₄ (6e), TfO (6 f)) consist of a zigzag tetragold(I) chain supported by the two syn-arranged rac-dpmppm ligands. Complexes 4d-f, 5d-f, and 6d-f with non-coordinative large anions are

Introduction

Gold nanoclusters and nanoparticles have attracted extensive attention because they can be used for various chemical and biochemical sensing systems, optical and electronic devices, and catalytic reactions.^[1-4] In their syntheses by means of "bottom-up" approaches, small-size multinuclear gold complexes are recognized as very important building blocks for the construction of larger nanoclusters. In particular, multinu-

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strongly luminescent in the solid state ($\lambda_{max} = 475 - 515$ nm, $\Phi\!=\!$ 0.67–0.85) and in acetonitrile ($\lambda_{\max}\!=\!$ 491–520 nm, $\Phi\!=\!$ 0.33-0.97); the emission was assigned to phosphorescence from ${}^{3}[d_{\alpha^{*}\alpha^{*}\sigma^{*}}p_{\alpha\alpha\alpha}]$ excited state of the Au₄ centers on the basis of DFT calculations as well as the long lifetime (a few μs). The emission energy is predominantly determined by the HOMO and LUMO characters of the Au₄ centers, which depend on the bent (4), linear (5), and zigzag (6) alignments. The strong emissions in acetonitrile were quenched by chloride anions through simultaneous dynamic and static quenching processes, in which static binding of chloride ions to the Au₄ excited species should be the most effective. The present study demonstrates that the structures of linear tetranuclear gold(I) chains can be modified by utilizing the stereoisomeric tetraphosphines, meso- and rac-dpmppm, which may lead to fine tuning of the strongly luminescent properties intrinsic to the Au¹₄ cluster centers.

clear gold(I) complexes are of rapidly increasing interest due to intriguing photophysical properties, in which aurophilic interactions have crucial effects on the steric and electronic structures of multinuclear gold centers. Linearly assembled crystal structures with Au-Au separations of 2.7-3.3 Å are often established by the presence of the weak aurophilic attractions, which are known to arise from dispersion effects with some virtual charge transfer contribution between d¹⁰ closed-shells and are considerably strengthened by relativistic effects.^[1a,b,2] In addition, to create molecular-based linear gold(I) chains by controlling the aurophilic interactions, judicious choice of bridging ligands is very important and, among them, single methylene-bridged di- and tridentate phosphines, such as dppm (bis(diphenylphosphino)methane) and dpmp (bis(diphenylphosphinomethyl)phenylphosphine), have been known very effective to stabilize photochemical and catalytic active multimetallic centers.^[5,6] Fackler, Jr. and Che independently reported that $[Au_2(dppm)_2]X_2$ (X = BF₄, ClO₄ etc.)^[5b,c] is strongly phosphorescent, for example with BF₄, at λ_{max} = 593 nm (τ = 21 µs) with a high quantum yield $\Phi\!=\!0.31$ in acetonitrile.^[5b] While the emission was originally assigned to arise from a triplet state of 3 [5d_{a*}6p_a] in which both the antibonding 5d_{a*} and bonding 6p_a

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orbitals of Au₂ centers are singly occupied, it was thereafter reconsidered to come from an adduct of the excited states with solvent, a so-called exciplex, and the intrinsic metal-centered emission from the 3 [5d $_{\sigma*}6p_{\sigma}$] excited state of digold(I) center was found in a higher energy region around $\lambda_{max} = 360-$ 368 nm for $[Au_2(dcpm)_2]X_2$ (X = CIO₄, PF₆, TfO, Au(CN)₂) by using a transparent diphosphine, bis(dicyclohexylphosphino)methane (dcpm).^[7a] Although metal-centered intense emissions have not been observed in trigold(I) complexes with a dpmp bridging ligand,^[6] bis(dicyclohexylphosphinomethyl)cyclohexylphosphine (dcmp) was recently synthesized and a series [Au₃- $(dcmp)_2 X_3 (X = ClO_4, TfO, PF_6)$ complexes exhibited very strong high-energy emission from the $^3[5d_{\sigma^*\sigma^*}\!6p_{\sigma\sigma}]$ excited state at $\lambda_{max} =$ 442–452 nm with quantum yields of 0.52–0.80.^[7b] On the basis of these observations, red-shifted energy for the goldcentered emission band is of particular interest if the Au^I chain can be extended linearly, and hence, single methylene-bridged polydentate phosphine ligands are good candidates for exploring the metal-metal concerted photochemical properties of extended Au¹ chains. However, progress along this line have not been made in the last decade owing to their difficult synthesis, whereas multinuclear complexes supported by tetradentate phosphine ligands with ethylene and longer methylene chains have been prepared and exhibited interesting synergistic effects by multinuclear metal centers.[3b,8,9]

Recently, we have expanded our studies with the linear triphosphine dpmp^[6f, 10] to those utilizing a methylene-linked linear tetraphosphine, bis[(diphenylphosphinomethyl)phenylphosphino]methane (dpmppm).^[11] This ligand has two stereo-isomers, *meso-* and *rac-*forms, with respect to the chiral centers of the two inner P atoms, and when two dpmppm ligands support four gold(I) ions, four topologically different structures of the Au₄ chain can be established as depicted in Figure 1. Ideally in the *syn-*arrangement, the two dpmppm's are enantio-



Figure 1. The ideal structures of $[Au_4(\mu-dpmppm)_2]^{4+}$ showing the arrangements of two dpmppm ligands with respect to the tetragold chains abbreviated as a) top: *syn-(meso-*dpmppm)₂ with *C*_{2v} symmetry; bottom: *anti-(meso-*dpmppm)₂ with *C*_{2h} symmetry; and b) top: *syn-(rac-*dpmppm)₂ with *C*_{2h} symmetry; bottom: *anti-(rac-*dpmppm)₂ with *D*₂ symmetry.

meric to each other with respect to the mirror plane composed of four Au atoms; as a result, a bent Au₄ chain is constructed with the *meso*-isomer (abbreviated as *syn-(meso*dpmppm)₂ with C_{2v} symmetry; Figure 1 a top) and a zigzag Au₄ chain with the *rac*-form (*syn-(rac-*dpmppm)₂ with C_{2h} symmetry; Figure 1 b top). In the *anti* arrangement, the two dpmppm's are related with C_2 symmetry and both *meso-* and *rac-*isomers are able to support the linear Au₄ chain of the C_2 axis (*anti-(meso-*dpmppm)₂ with C_{2h} symmetry—Figure 1 a bottom—and *anti-(rac-*dpmppm)₂ with D_2 symmetry—Figure 1 b bottom). Consequently, the structures of Au₄ chains could be varied depending on the arrangement of two dpmppm ligands and their configurational structures.

In the present study, we have been successful in synthesizing a new single methylene-bridged tetraphosphine ligand, bis[(diphenylphosphinomethyl)phenylphosphino]methane (dpmppm), meso- and rac-isomers being isolated as pure forms. Since tetragold(I) ions aggregated by two dpmppm ligands, $[Au_4(\mu-dpmppm)_2]^{4+}$ would provide a useful platform to study structure-related multinuclear effects on their photophysical properties, we have prepared a series of their isomers, $syn-[Au_4(meso-dpmppm)_2]X_4$ (4), $anti-[Au_4(meso-dpmppm)_2]X_4$ (5), and $syn-[Au_4(rac-dpmppm)_2]X_4$ (6), which were characterized to contain a flexibly bent, entirely linear, and zigzag Au₄ chains, respectively. The Au₄ molecular units with large counterions, $[Au_4(\mu-dpmppm)_2]X_4$ (X = PF₆, BF₄, TfO), are strongly luminous in the solid state ($\Phi = 0.67-0.85$) from their $^3[5d_{\sigma^*\sigma^*} 6p_{\sigma\sigma\sigma}]$ excited states and the emission energy changed systematically depending on the tetragold(I) structures from the zigzag **6** ($\lambda_{em} = 485-494$ nm) to the bent **4** ($\lambda_{em} = 475-494$ nm) 508 nm) and the linear **5** (λ_{em} = 513–515 nm). The phosphorescence of 4-6 was interestingly quenched by introducing chloride anions with remarkable efficiency. The present results could be quite important to understand multinuclear d¹⁰ closed-shell concerted photochemical properties. Some of the data, including the crystal structures of 4b, 4d, and 4g, have already been communicated.^[11a]

Results and Discussion

Preparations of *meso-* and *rac-*dpmppm and [Au₄Cl₄(*meso-* or *rac-*dpmppm)] (2 or 3)

Bis[(diphenylphosphinomethyl)phenylphosphino]methane (*meso*-dpmppm) was prepared as shown in Scheme 1. Bis(phenylphosphino)methane^[8a, 12] was treated with *n*BuLi and then with Me₃SiCH₂Cl to afford bis[(trimethylsilylmethyl)phenylphosphino]methane (tmsmppm), in which the ratio of *meso*- and *rac*-isomers was about 4:1 determined by ³¹P{¹H} NMR spectroscopy. Addition of Ph₂PCl to tmsmppm, followed by heating at 95 °C for 1 h, yielded *meso*-isomer-rich dpmppm, which was precipitated from acetone and washed with methanol to give *meso*-dpmppm as pure white powder in 50% yield versus tmsmppm. The ³¹P{¹H} NMR spectrum showed two resonances in AA'BB' spin system of the P nuclei, which were simulated with the parameters $\delta = -23.0$ (P_{out}) and -34.7 ppm (P_{in}) for the outer and inner P atoms, and ²J_{PmPout} = 117.1, ²J_{PmPut} = 92.1,

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Scheme 1. Preparations of meso- and rac-dpmppm.

 ${}^{4}J_{P_{out}P_{int}} = 3.9$, and ${}^{6}J_{P_{out}P_{out}} = 0.1$ Hz (see Figure S1 a in the Supporting Information).

When solid meso-dpmppm was heated under argon atmosphere at 165 °C for 1 h, the chiral centers of the P atoms were readily epimerized through pyramidal inversion mechanisms^[13] to result in an equilibrium mixture of meso- and rac-dpmppm in an approximate 1:1 ratio. The isomerization of mesodpmppm occurred even in a [D₈]toluene solution at 100°C, obeying first-order kinetics, with the analyzed values of $k_1 =$ $1.54 \times 10^{-2} \text{ s}^{-1}$, $k_{-1} = 1.80 \times 10^{-2} \text{ s}^{-1}$, and $K = k_1/k_{-1} = 0.85$ (Figure S2 in the Supporting Information). The oily mixture of meso- and rac-dpmppm was further reacted with about three equivalents of [PdCl₂(cod)] in dichloromethane, immediately forming a pale yellow precipitate of $[Pd_2Cl_4(rac-dpmppm)]$ (1) in 43% yield with respect to the starting material mesodpmppm. Complex 1 was recrystallized from N,N-dimethyl formamide (DMF) and characterized by X-ray crystallography (Figure S3 in the Supporting Information); the X-ray analysis indicates that it contains two *cis*-Pd^{II}Cl₂ units bridged by a *rac*dpmppm ligand with pseudo- C_2 symmetry. The two palladium atoms are spanned at an average distance of 4.430 Å with triple bridges of the $P_{in}P_{in}$ and two $P_{out}P_{in}$ pairs. The $^{31}P\{^{1}H\}$ spectrum in [D₇]DMF consisted of two resonances at $\delta = 19.4$ (Pout) and 17.7 ppm (Pin) with the simulated coupling constants of ${}^{2}J_{P_{in}P_{out}} = 45.7$, ${}^{2}J_{P_{in}P_{in'}} = 38.6$, ${}^{4}J_{P_{out}P_{in'}} = 0.3$, and ${}^{6}J_{P_{out}P_{out'}} = 0.1 \text{ Hz}$ (Figure S1c in the Supporting Information), which are in agreement with the crystal structure. Since the mother liquor predominantly contained dipalladium complex with mesodpmppm, [Pd₂Cl₄(meso-dpmppm)] (the detailed structure is not identified), the low solubility of 1 in CH₂Cl₂ should be responsible for its successful isolation. Treatment of 1 with excess of NaCN in a biphasic system with dichloromethane and water^[14] lead to the quantitative isolation of *rac*-dpmppm as pure oil; it was characterized by ³¹P{¹H} NMR spectroscopy, showing two peaks at $\delta = -23.3$ (P_{out}) and -34.0 ppm (P_{in})





Scheme 2. Structures of $[Au_4Cl_4(meso-dpmppm)]$ (2) and $[Au_4Cl_4(rac-dpmppm)]$ (3).

with ${}^{2}J_{P_{in}P_{out}} = 114.2$, ${}^{2}J_{P_{in}P_{in'}} = 105.4$, ${}^{4}J_{P_{out}P_{in'}} = 3.4$, and ${}^{6}J_{P_{out}P_{out'}} = 0.1$ Hz (Figure S1 b in the Supporting Information).

Each tetraphosphine was treated with [AuCl(tht)] in 1:4 ratio in an ethanol suspension to give colorless microcrystals of [Au₄Cl₄(*meso*-dpmppm)] (**2**) or [Au₄Cl₄(*rac*-dpmppm)] (**3**) quantitatively (Scheme 2), which were further recrystallized from DMF as colorless needle crystals of **2**·1.5 DMF and **3**·0.25 DMF·2 CH₂Cl₂, respectively. The ³¹P{¹H} NMR spectra of **2** and **3** exhibited two multiplets at $\delta = 25.6$ (P_{out}) and 22.2 ppm (P_{in}) for **2** and $\delta = 26.7$ (P_{out}) and 21.4 ppm (P_{in}) for **3**, which were assigned to AA'BB' spin systems with ²J_{PinPout} = 54.8, ²J_{PinPin} = 56.6, ⁴J_{PoutPin} = 1.7, and ⁶J_{PoutPout} = 0.1 Hz for **3** (Figure S1 d,e in the Supporting Information). Complexes **2** and **3** are sparingly soluble in usual organic solvents and soluble only in DMF and dimethyl sulfoxide (DMSO).

An X-ray diffraction analysis was performed on the crystals of 2 obtained from a DMSO/Et₂O mixed solvent (Figure 2). Four AuCl units are attached to the tetraphosphine ligand meso-dpmppm to form a neutral molecule composed of four P-Au-Cl linear fragments (av Au–Cl = 2.295, av Au–P = 2.233 Å, av P-Au-Cl = 174.01°). The flexible {PCH₂PCH₂PCH₂P} backbone disperses the four Au^I ions with interatomic distances of Au1---Au2 = 3.3392(6), Au2…Au3 = 3.3712(6), Au3 - Au4 =3.3402(7) Å, suggesting the presence of only a weak aurophilic interaction.^[1a,b,2] The outer Au-P-P-Au torsion angles indicate planar arrangements of Au1-P1-P2-Au2 (4.94°) and Au3-P3-P4-Au4 (1.88°), which are in contrast to the twisted arrangement of Au2-P2-P3-Au3 (58.61°) in the central part, these may be a result from a delicate balance between the attractive aurophilic interactions and electrostatic repulsions within the



Figure 2. ORTEP diagram of 2 with thermal ellipsoids at the 40% probability level. The hydrogen atoms are omitted for clarity.

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Ph₂



X' = PF₆ (4d), BF₄ (4e), TfO (4f)

Scheme 3. Synthesis of syn-[Au₄(meso-dpmppm)₂Cl]X₃ (X = Cl (4a), PF₆ (4b), BF_4 (4 c), syn-[Au₄(meso-dpmppm)₂]X₄ (X = PF₆ (4 d), BF₄ (4 e), TfO (4 f)), and syn-[Au₄(meso-dpmppm)₂I₂][PF₆]₂.

Au

Ph

4g

neighboring chloride anions (Cl1…Cl2=4.128(4), Cl2…Cl3= 4.894(5), and Cl3···Cl4 = 4.012(5) Å). The similar twisted structure was observed in $[Au_2Cl_2(dppm)]$ (Au-Au = 3.351(2) Å and $Au-P-P-Au = 67(1)^{\circ}$).^[15]

Synthesis and structures of syn-[Au₄(meso-dpmppm)₂Cl]X₃ $(X = CI (4a), PF_6 (4b), BF_4 (4c)), syn-[Au_4(meso-dpmppm)_2]X_4$ $(X = PF_6 (4 d), BF_4 (4 e), TfO (4 f)), and {syn-[Au_4(meso$ $dpmppm)_{2}I_{2}[PF_{6}]_{2}$ (4 g)

When meso-dpmppm was treated in dichloromethane with two equivalents of [AuCl(PPh₃)] in the presence of NH₄X, pale yellow tetragold(I) complexes, syn-[Au₄(meso-dpmppm)₂Cl]X₃ $(X = PF_6 (4b) BF_4 (4c))$ were obtained in moderate yields (Scheme 3). A similar reaction without NH₄X afforded syn-[Au₄(meso-dpmppm)₂Cl]Cl₃ (4a) in 67% yield. Complexes 4b and 4c were transformed by treating with AgPF₆ or AgBF₄ to give the anion-exchanged complexes syn-[Au₄(mesodpmppm)₂] X_4 (X = PF₆ (4d), BF₄ (4e)), respectively, in good yields. Reaction of 4b with excess NH₄OTf also yielded syn- $[Au_4(meso-dpmppm)_2]$ [TfO]₄ (**4 f**). When complex **4 b** was treated with 2.5 equivalents of KI in a CH₂Cl₂/MeOH mixed solvent, orange crystals of the octagold(I) complex syn-[{Au₄(mesodpmppm)₂ I_2 ₂[PF₆]₄ (**4g**) was isolated in 18% yield (Scheme 3). Complexes 4a-g were characterized by ¹H and ³¹P{¹H} NMR, ESI-MS, IR, and UV/Vis spectra and X-ray crystallography for 4b,d-g (the structures of 4b, 4d, and 4g have already been communicated).^[11a]

ORTEP diagrams for 4b and 4f are illustrated in Figure 3a, b (those for 4d and 4e are supplied as Figures S4 and S5 in the Supporting Information) and selected structural parameters are summarized in Table 1. Complexes 4b and 4d-f contain bent Au¹₄ chains bridged by two meso-dpmppm ligands, which





Figure 3. ORTEP diagrams for a) {syn-[Au₄(meso-dpmppm)₂]Cl}³⁺ of 4b and b) {syn-[Au₄(meso-dpmppm)₂]OTf}³⁺ of ${\bf 4} {\bf f}$ with thermal ellipsoids at the 40% probability level. The hydrogen atoms are omitted for clarity.

are recognized as deformed structures from the ideal syn-arrangement of two meso-dpmppm ligands (abbreviated as syn- $(meso-dpmppm)_2$ with $C_{2\nu}$ symmetry, Figure 1). In the structures of 4b and 4d, a terminal methylene unit of each mesodpmppm is flipped outside leading to a pseudo- C_2 axis passing through the midpoint of the central two Au atoms, Au2-Au3; the Au₄ chain is somewhat twisted with the Au-Au-Au-Au torsion angles of 32.95(6)° (4b) and 28.08(6)° (4d). In 4e and 4f, the central methylene unit of one meso-dpmppm is turned outside, resulting in pseudo-C_s symmetrical structures in which the four Au ions are constrained in a plane with the Au-Au-Au-Au torsion angles of 2.30(2) (4 e) and 5.15(2)° (4 f). These deformations may occur to avoid steric repulsions between the phenyl groups of two meso-dpmppm ligands, which could arise from incorporation of a counter anion into the bent Au₄ pocket (Figure 4).

In 4b, the Au-Cl interatomic distances of 3.664(6) (Au1…Cl1), 3.132(6) (Au2…Cl1), 3.162(6) (Au3…Cl1), and 3.803(6) Å (Au4---Cl1) suggest the presence of an electrostatic attraction between the inner two Au^l ions (Au2, Au3) and the Cl⁻ anion, in the light of the sum of van der Waals radii (3.26 Å); the outer gold atoms (Au1, Au4) are out of the secondary interaction range. The other anions PF_6^- (4d), BF_4^- (4e), and TfO⁻ (4 f) are housed in their shallow pockets with much weaker electrostatic interactions, presumably due to lower charge densities of the polyatomic anions; all the observed interatomic distances are longer than the sums of van der Waals



Table 1. Structural paramet	ers of <i>syn</i> -[Au ₄ (<i>meso-</i> dpmp	$pm)_2CI]X_3 (X = PF_6 (4b))$	and syn-[Au ₄ (meso-dpmpp)	m) ₂]X ₄ (X = PF ₆ (4 d), BF ₄ (4	4e), TfO (4f), I (4g)).
	P_{0}	Ph Ph Ph Ph Ph Ph Ph Ph Ph Ph	$\begin{array}{c c} Ph & Ph \\ & \vdots \\ Ph_2P & \\ Ph_2P & \\ Au_{in} & Au_{in} \\ Au_{out} & \\ Au_{out} & \\ Ph_2P & \vdots \\ Ph_2P & Ph \\ Ph_2P & even \\ Ph$	2+ 12 ut	
	4 b ^[a,f]	4b-f 4 d ^(b,f)	4g 4 e ^[c]	4 f ^[d]	4 g ^[e,f]
X Au _{out} …Au _{in} [Å]	Cl 2.948(1) 2.924(1)	PF ₆ 2.9743(2) 2.9700(5)	BF ₄ 2.9704(2) 2.9774(2)	TfO 2.9388(3) 3.0080(3)	l 3.0867(6) 2.954(1)
Au _{in} ···Au _{in} [Å] Au _{out} ···Au _{out} [Å]	av 2.936 2.953(1) 7.281	av 2.9722 2.9595(3) 8.274	av 2.9739 2.9562(2) 7.599	av 2.9734 2.9036(3) 7.942	av 3.020 3.0243(8) 8.744
av Au _{out} P _{out} [A] av Au _{in} P _{in} [Å] Au _{out} Au _{in} Au _{out} [°]	2.303 2.306 134.98(4) 137.37(3)	2.312 2.316 143.19(1) 163.89(1)	2.3238 2.3166 140.746(7) 141.866(8)	2.3187 2.3177 149.583(8) 146.231(0)	2.322 2.307 156.20(3) 166.90(3)
av P _{out} -Au _{out} -P _{out} [°] av P _{in} -Au _{in} -P _{in} [°]	av 136.18 175.5 178.5	av 153.54 178.19 178.02	av 141.306 177.98 177.52	av 147.907 175.59 175.63	av 161.55 165.06 172.15
av P _{out} -Au _{out} -Au _{in} -P _{in} [°] av P _{in} -Au _{in} -Au _{in} -P _{in} [°] Au _{out} -Au _{in} -Au _{in} -Au _{out} [°]	1.6 21.2 32.95(6)	10.57 18.99 28.08(6)	20.73 2.63 2.30(2)	18.00 2.58 5.15(2)	4.9 0.8 3.8(1)
av Au _{in} …X [Å]	3.132(6) (Au2–Cl1) 3.162(6) (Au3–Cl1) av 3.147	3.077(6) (Au2–F2) 3.081(6) (Au3–F1) av 3.080	3.349(4) (Au2–F1) 3.388(4) (Au3–F1) 3.449(5) (Au3–F3) 3.351(3) (Au2–F2) av 3.384	3.204(4) (Au2–O2) 3.458(4) (Au3–O1) 3.531(4) (Au2–O3) av 3.332	3.017(1) (Au2–I1) 3.232(1) (Au3–I2) av 3.125
av Au _{out} …X [Å]	3.664(6) (Au1—Cl1) 3.803(6) (Au4—Cl1) av 3.734	3.393(6) (Au1–F2) 3.738(5) (Au4–F1) av 3.566	3.151(3) (Au1–F2) 3.427(4) (Au4–F3) av 3.290	3.088(4) (Au1–O2) 3.818(4) (Au4–O1) av 3.453	3.160(1) (Au1–I1) 3.162(2) (Au2–I2) av 3.161

[a] See Figure 3a. [b] See Figure 54 in the Supporting Information. [c] See Figure 55 in the Supporting Information. [d] See Figure 3b in the Supporting Information. [e] See Figure 56 in the Supporting Information. [f] Reference [11a].



Figure 4. Perspective views showing interactions of *syn*-[Au₄(*meso*-dpmppm)₂]⁴⁺ with a) Cl⁻ (**4b**), b) PF₆⁻ (**4d**), c) BF₄⁻ (**4e**), and d) TfO⁻ (**4f**). The tetragold parts and the counter anions are illustrated with space-filling models.

radii (2.81–2.86 Å) (Table 1). While the large PF_6 anion of **4d** fits well the Au₄ chain with rather short separations between the central two Au_{in} ions (Au2···F2=3.077(6), Au3···F1=3.081(6) Å),

the BF₄ and TfO anions have shorter contacts to the Au_{out} ions (Au1--F2=3.151(3) (4e), Au1--O2=3.088(4) Å (4f)). The average Au---Au angles vary from 136.18 (4b) to 141.31 (4e), 147.91 (4f), to 153.54° (4d), depending on the size of the trapped counter anions (Figure 4). The Au---Au separations are not affected by the anions (av 2.942 (4b), 2.968 (4d), 2.968 (4e), and 2.950 Å (4f)) and indicate the presence of strong aurophilic interaction between them.^[1a,b,2] The intramolecular distances between the outer two Au ions are 8.274 (4d), 7.942 (4f), 7.599 (4e), and 7.281 Å (4b), which show an order similar to that for the Au--Au angles. These results demonstrated that the flexible Au₄ chains with a *syn-(meso-*dpmppm)₂ arrangement are likely to vary its bending form depending on the size of counter anions trapped.

The complex cation of **4g** was elucidated by X-ray crystallography to have a linear octagold(I) core comprised of two tetragold(I) units, *syn*-[Au₄(*meso*-dpmppm)₂I₂]²⁺ (Scheme 3), connected by two μ_3 -iodide bridges (Figure S6 in the Supporting Information).^[11a] The Au-Au separations (2.954(1)– 3.0867(6) Å, av 3.022 Å) are slightly longer than those of **4b**,**d**– **f**, and the average Au-Au-Au angle of 161.55° is larger than that of **4d**. The Au–I distances, ranging from 3.017(1) to 3.232(2) Å (av 3.125 Å), fall between the values for the sums of



Figure 5. ³¹P{¹H} NMR spectra for the *meso*-dpmppm region of a) **4 f**, b) **4e**, c) **4d**, d) **4a**, e) **4c**, f) **4b**, and g) **4g** in CD_2CI_2 at room temperature.

covalent bond (2.67 Å) and van der Waals radii (3.61 Å), suggesting the presence of a weak bonding interaction between the Au¹ and I⁻ ions. Whereas the octanuclear complex cation of **4g** possesses a crystallographically imposed inversion center, the tetragold(I) fragment itself has a pseudo- C_2 axis at the midpoint of the inner two gold ions as observed in **4b** and **4d**. In the solution state, the octanuclear complex cation is assumed to fragmentate into *syn*-[Au₄(*meso*-dpmppm)₂I₂]²⁺ (Scheme 3), which was confirmed by the ESI MS (*m/z*: 1149.05 for [Au₄-(dpmppm)₂I₂]²⁺) and the ³¹P{¹H} NMR spectrum (δ = 29.03 (P_{out}), 22.03 ppm (P_{in})).

The ³¹P{¹H} NMR spectra of **4a–g** in CD₂Cl₂ showed quite similar spectral patterns with two multiplets in 1:1 intensity ratio (Figure 5), consistent with the $C_{2\nu}$ symmetrical tetranuclear structure of *syn*-[Au₄(*meso*-dpmppm)₂]⁴⁺. Furthermore, the complexes can be classified into three groups from the δ values of their chemical shifts:

- 1) **4d** (δ = 36.5 (P_{out}), 32.3 ppm (P_{in})), **4e** (δ = 35.4 (P_{out}), 31.3 ppm (P_{in})), **4f** (δ = 35.1 (P_{out}), 31.3 ppm (P_{in})).
- 2) **4a** (δ = 33.1 (P_{out}), 27.7 ppm (P_{in})), **4b** (δ = 34.5 (P_{out}), 28.1 ppm (P_{in})), **4c** (δ = 34.0 (P_{out}), 27.8 ppm (P_{in})).
- 3) **4g** (δ = 29.03 (P_{out}), 22.03 ppm (P_{in})).

The second and third groups exhibited an upfield shift induced by appreciable interaction of the complex cations with the halide anions, suggesting that **4a**–**c** exist as an adduct of $\{syn-[Au_4(meso-dpmppm)_2]Cl\}^{3+}$ and **4g** as $\{syn-[Au_4(meso-dpmppm)_2]Cl\}^{2+}$, as observed in the crystal structures. Furthermore in **4a**–**c** with a nesting chloride anion, the degrees of higher field shift for the inner P atoms were more conspicuous than for the outer P atoms, referenced to the chemical shifts for **4d**–**f** with large counter anions (the first group). The values of chemical shifts for the first group complexes **4d**–**f** are almost identical irrespective of the counter anions of PF_6^- , BF_4^- , and TfO^- , indicating that the tetragold cations of **4d**–**f** exist in the solutions as $syn-[Au_4(meso-dpmppm)_2]^{4+}$ without remarkable interaction with the anions.

Synthesis and structures of *anti*- $[Au_4(meso-dpmppm)_2]X_4$ (X = PF₆ (5 d), BF₄ (5 e), TfO (5 f))

AgX (X = PF₆, BF₄, TfO) (4 equiv), *meso*-dpmppm (1 equiv), and 2,6-xylyl isocyanide (XylNC) (4 equiv) were added to a suspension of [Au₄Cl₄(*meso*-dpmppm)] (**2**) in toluene and the mixture was stirred at room temperature in the dark for 12 h. The resultant precipitate was crystallized from a dichloromethane/dieth-yl ether mixed solvent to afford pale yellow crystals of *anti*-[Au₄(*meso*-dpmppm)₂]X₄ in low yields (X = PF₆ (**5 d**, 29%), BF₄ (**5 e**, 25%), TfO (**5 f**, 11%)) (Scheme 4). Complex **5 f** was also obtained by reacting **2** with one equivalent of *meso*-dpmppm in the presence of AgOTf (4 equiv) in 11% yield. However, though the roles of XylNC are not clear, the reactions in the absence of the isocyanide led to a failure to isolate **5 d** and **5 e**.

The structures of **5 d**–**f** were determined by X-ray crystallography; ORTEP plot for the complex cation of **5 d** is shown in Figure 6 (those for **5 e** and **5 f** are deposited in Figure S7 in the Supporting Information), and the structural parameters are listed in Table 2. The structures of **5 d**–**f** have crystallographically imposed inversion centers at the midpoint of the central two Au_{in} atoms and have almost linearly aligned tetranuclear Au¹ ions supported by two *meso*-dpmppm ligands in the *anti*arrangement as shown in Figure 1 (abbreviated as *anti-(meso*dpmppm)₂). The Au-Au-Au angles are 177.78(2) (**5 d**), 177.99 (av, **5 e**), and 171.34(1)° (**5 f**), which definitely demonstrate linear alignment of the tetragold chains and are in contrast to the flexible bent structures of **4** with a *syn-(meso-*dpmppm)₂ arrangement. The Au-Au distances of **5** are shorter than those of **4**, suggesting the presence of stronger aurophilic interac-



Scheme 4. Preparations of *anti*- $[Au_4(meso-dpmppm)_2]X_4$ (X = PF₆ (5 d), BF₄ (5 e), TfO (5 f)).

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tion; in particular the Au_{in}···Au_{in} distances (2.8658(2) (5 d), 2.8833 (av, 5 e), 2.8981(3) Å (5 f)) are appreciably shorter than those of the Au_{in}···Au_{out} distances (2.9106(3) (5 d), 2.9390 (av, 5 e), 2.9511(3) Å (5 f)). Due to the linearity, the Au_{out}···Au_{out} separations (8.686 (5 d), 8.763 (av, 5 e), 8.778 Å (5 f)) are large compared with those for complexes 4b and 4d–f. The P-Au-P linear moieties are rather twisted between the Au_{out} and Au_{in} centers (P-Au-Au-P torsion angles are 14.54–18.27°) and in parallel between the two Au_{in} centers (P-Au-Au-P torsion angles are 0.52–4.38°). The two counter anions very weakly contact to the central Au_{in} centers (> ca. 3.2 Å).

In the solution state, the *anti* complexes **5** are not stable and slowly isomerize into *syn*-[Au₄(*meso*-dpmppm)₂]⁴⁺ (**4**); this process was monitored by ³¹P{¹H} NMR spectroscopy. The ³¹P{¹H} NMR spectrum of **5 f** in CD₃CN consists of two broad multiplets in a narrow range around δ =35–36 ppm; however, resonances for the *syn* complex **4 f** appeared after several hours, and finally, the spectral patters mostly changed to those of **4 f** after several days (Figure S8a in the Supporting Information). The isomerization was analyzed with first-order kinetics for the concentration^[5f] to give an apparent rate constant *k*=2.54 × 10⁻⁶ s⁻¹ and a half-life time $t_{1/2}$ =2.73×10⁵ s (Figure S8b, c in the Supporting Information). In CD₂Cl₂, the *anti*-to-*syn* isomerization proceeded very slowly



Figure 6. a) ORTEP view for the complex cation of *anti*-[Au₄(*meso*-dpmppm)₂][PF₆]₄ (**5** d) with thermal ellipsoids at the 40% probability level. The hydrogen atoms are omitted for clarity. b) A diagram in which the tetra-gold ions are illustrated with space-filling models to show the linear arrangement.



to afford an approximate 1:1 mixture of **5 f** and **4 f** after three weeks.

Synthesis and structures of syn-[Au₄(rac-dpmppm)₂Cl₂]X₂ (X = Cl (6a), PF₆ (6b), BF₄ (6c)) and syn-[Au₄(rac-dpmppm)₂]X₄ (X = PF₆ (6d), BF₄ (6e), TfO (6f))

Reaction of *rac*-dpmppm with [AuCl(PPh₃)] (2 equiv) in CH₂Cl₂ at room temperature afforded *syn*-[Au₄(*rac*-dpmppm)₂Cl₂]Cl₂ (**6a**) in 62% yield. Similar reactions using [AuCl(tht)] in the presence of NH₄X (X=PF₆, BF₄) also gave *syn*-[Au₄(*rac*dpmppm)₂Cl₂]X₂ (X = PF₆ (**6b**), BF₄ (**6c**)) in 47 and 63% yields, respectively (Scheme 5), and that with NH₄OTf yielded *syn*-[Au₄(*rac*-dpmppm)₂][TfO]₄ (**6 f**) in 14% yield. When complex **6 f** was treated with NH₄X (X = PF₆, BF₄), the TfO anions were replaced by the respective large anions to afford pale yellow crystals of *syn*-[Au₄(*rac*-dpmppm)₂]X₄ (X = PF₆ (**6d**), BF₄ (**6e**)). Complexes **6a**-**f** were characterized by IR, UV/Vis, ³¹P{¹H} and ¹H NMR spectroscopy and ESI mass spectrommetry, and for **6a**-**c**,**e**,**f** in addition by X-ray crystallographic analyses.

ORTEP plots for the complex cations of **6b** and **6f** are illustrated in Figure 7a, b (those for **6a,c,e** are supplied in the Supporting Information, Figure S9a–c), and the structural parameters are summarized in Table 3. In the crystal structures of **6a**–**c,e,f**, four two-coordinate gold(I) ions are bridged by two *rac*-

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Scheme 5. Preparations of syn-[Au₄(rac-dpmppm)₂Cl₂]X₂ (X = Cl (6a), PF₆ (6b), BF₄ (6c)) and syn-[Au₄(rac-dpmppm)₂]X₄ (X = PF₆ (6d), BF₄ (6e), TfO (6 f)).



Figure 7. ORTEP diagrams for a) $\{syn-[Au_4(rac-dpmppm)_2]Cl_3\}^{2+}$ of **6 b** and b) $\{syn-[Au_4(rac-dpmppm)_2](OTf)_2\}^{2+}$ of **6 f** with thermal ellipsoids at the 40% probability level. The hydrogen atoms are omitted for clarity.

dpmppm ligands in a *syn*-arrangement as shown Figure 1 (abbreviated as *syn*-(*rac*-dpmppm)₂) with an inversion center. The array of Au_4 ions is not linear, but a zigzag form with the

Au---Au angles of 138.37(1) (6a), 134.50(2) (6b), 142.83(2) (6c), 145.35(2) (6e), and 148.58(2)° (6f), which are comparable to those of 4 with bent structures by syn-(meso-dpmppm)₂ arrangement. The crystallographic C_i symmetry constrains the zigzag Au₄ chains as planar. Two counter anions are trapped into each zigzag pocket of the Au₄ structures (Figure 8a, b). Like in complexes 4, the chloride ions in 6a-c should be more tightly incorporated with the interatomic distances of 2.974(2)-3.089(3) Å to the Au_{in} ions and 3.017(2)-3.218(3) Å to the Au_{out} ones, which are notably shorter than the sum of van der Waals radii (3.26 Å). The BF₄⁻ and TfO⁻ ions are also placed in the position with the shortest contacts to Au: Au_{in} ...F1 = 3.121(8) (6e) and Au_{in} ...O2 = 3.151(11) Å (6 f); these electrostatic interactions should be very weak in comparison with that with the chloride anions in **6a-c**, which were evidenced by the higher field shift in the ³¹P{¹H} NMR spectra. Whereas the ³¹P{¹H} NMR spectrum of **6f** showed two broad multiplets at $\delta = 35.5$ (P_{out}) and 31.1 ppm (Pin) in 1:1 intensity ratio, those of 6a-c exhibited two peaks at $\delta = 32.5$ (P_{out}) and 28.1 (P_{in}) (**6**a), 31.9 (P_{out}) and 27.2 (P_{in}) (**6 b**), and 31.6 (P_{out}) and 26.3 ppm (P_{in}) (**6 c**), both the peaks for Pout and Pin suffering some higher field shifts, implying that the Au2...Cl weak interaction in the Au4 zigzag pockets are retained even in the solution state. The Au-Au distances of 6 are also similar to those of 4; the Auin-Auin distances (2.956(2) (6a), 2.9713(4) (6b), 3.0065(7) (6c), 2.9585(6) (6e), 2.9545(6) Å (6 f)) are almost identical to those of the Auin-Auout distances (2.973(2) (6a), 2.9635(4) (6b), 2.9736(7) (6c), 2.9442(6) (6e), 2.9080(4) Å (6f)), suggesting the presence of aurophilic interactions. The Au_{out}···Au_{out} separations (8.370 (6a), 8.294 (6b), 8.573 (6c), 8.505 (6e), 8.527 Å (6f)) fall between the values for the linear anti complexes 5d-f and for the bent syn complexes 4b,d-f. The P-Au-P linear moieties are rather twisted between the Au_{out} and Au_{in} centers (P-Au-Au-P torsion angle is 13.56–20.14°) and in parallel between the two Au_{in} centers (P-Au-Au-P torsion angle is 0.26-4.70°).

Electronic absorption and emission spectra and theoretical calculations

The UV/Vis absorption and emission spectroscopic data of complexes 4a-f, 5d-f, and 6a-f are listed in Table 4. The absorption spectra of 4d-f, 5d-f, and 6d-f in CH₂Cl₂ (Figure 9ac) show a characteristic intense bands around 363-370 nm $(\log \varepsilon = 4.51 - 5.07)$ for **4d-f**, 387-389 nm $(\log \varepsilon = 4.81 - 5.11)$ for **5 d-f**, and 358–360 nm (log ε = 4.53–4.95) for **6 d-f**, together with broad absorptions at $\lambda < 300$ nm by phenyl groups of the phosphine ligands. On the basis of TD-DFT calculations on the models, syn-[Au₄(meso-H₂PCH₂P(H)CH₂P(H)CH₂PH₂)₂]⁴⁺ (**M** 4), anti- $[Au_4(meso-H_2PCH_2P(H)CH_2P(H)-CH_2PH_2)_2]^{4+}$ (M 5), and syn- $[Au_4(rac-H_2PCH_2P(H)CH_2P(H)CH_2PH_2)_2]^{4+}$ (**M6**), which were optimized by DFT calculations using MPWPW91 functions^[16] with Stuttgart-Dresden ECP basis set (SDD, the 19-valence electron Wood-Boring quasi-relativistic pseudopotentials were used for Au),^[17] the lowest energy bands are assigned to as spin-allowed ¹[5d_{$\sigma^*\sigma^*\sigma^*$} \rightarrow 6p_{$\sigma\sigma\sigma$}] (HOMO \rightarrow LUMO) transition (λ = 365 nm, f (oscillator strength) = 0.383 for M4, λ = 365 nm, f = 0.581 for M5, and $\lambda = 361$ nm, f = 0.433 for M6). The HOMOs of M4–6



Table 3. Structural parame	Table 3. Structural parameters of syn -[Au ₄ (rac -dpmppm) ₂ Cl ₂]X ₂ (X = Cl (6a), PF ₆ (6b), BF ₄ (6c)) and syn -[Au ₄ (rac -dpmppm) ₂]X ₄ (X = BF ₄ (6e), TfO (6f)).							
$\begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$								
	6 a ^[a]	6a–c,e, 6 b ^[b]	f 6 c ^[c]	6 e ^[d]	6 f ^[e]			
$ \begin{array}{l} X \\ X' \\ Au_{out} \cdots Au_{in} \left[\mathring{A} \right] \\ Au_{in} \cdots Au_{in} \left[\mathring{A} \right] \\ Au_{out} \cdots Au_{out} \left[\mathring{A} \right] \\ av Au_{out} - P_{out} \left[\mathring{A} \right] \\ av Au_{in} - P_{in} \left[\mathring{A} \right] \\ Au_{out} \cdots Au_{in} \cdots Au_{out} \left[\mathring{C} \right] \\ P_{out} - Au_{out} - P_{out} \left[\mathring{C} \right] \\ P_{out} - Au_{out} - P_{in} \left[\mathring{C} \right] \\ P_{out} - Au_{out} - Au_{in} - P_{in} \left[\mathring{C} \right] \\ P_{out} - Au_{in} - Au_{in} - P_{in} \left[\mathring{C} \right] \\ Au_{out} \cdots Au_{in} - Au_{out} \left[\mathring{C} \right] \\ Au_{out} \cdots X \left[\mathring{A} \right] \\ \end{array} $	Cl Cl 2.956(2) 2.973(2) 8.370 2.307 2.315 138.37(1) 171.83(7) 176.27(6) 13.56(6) 2.21(4) 0.0 2.974(2)(Au2-Cl1) 3.017(2)(Au1-Cl1)	Cl PF ₆ 2.9713(4) 2.9635(4) 8.294 2.310 2.311 134.50(2) 171.7(1) 177.4(1) 18.4(1) 0.26(8) 0.0 3.089(3)(Au2-Cl1) 3.044(3)(Au1-Cl1)	Cl BF ₄ 3.0065(7) 2.9736(7) 8.573 2.344 2.339 142.83(2) 176.5(1) 175.3(1) 19.5(1) 3.24(1) 0.0 3.032(2)(Au2-Cl1) 3.218(3)(Au1-Cl1)	BF ₄ BF ₄ 2.9585(6) 2.9442(6) 8.505 2.330 2.331 145.35(2) 169.38(9) 176.53(10) 13.76(10) 1.44(9) 0.0 3.121(8)(Au2–F1) 3.349(6)(Au2–F2*) 3.283(8)(Au1–F1)	TfO TfO 2.9545(6) 2.9080(4) 8.527 2.325 2.327 148.58(2) 176.82(13) 173.41(9) 20.14(11) 4.70(12) 0.0 3.151(11)(Au2–O1) 3.566(16)(Au2–O2*) 3.255(13)(Au1–O3)			

[a] See Figure S9a in the Supporting Information. [b] See Figure 7a. [c] See Figure S9b in the Supporting Information. [d] See Figure S9c in the Supporting Information. [e] See Figure 7b.



Figure 8. Perspective views showing interactions of *syn*-[Au₄(*rac*-dpmppm)₂]⁴⁺ with a) Cl⁻ (**6** b), and b) TfO⁻ (**6** f) ions. The tetragold parts and the counter anions are illustrated with space-filling models.

are mainly composed of *anti*-bonding d_o orbitals of the four Au ions (5d_{o*o*o*}) and the LUMOs are derived from the bonding interactions of the p_o orbitals of the four Au atoms (6p_{oro}) mixed with the orbitals of phosphine ligands (Figure 10a and b, and Figures S10-S12 in the Supporting Information). Hence, the $^1\![5d_{\sigma^*\sigma^*\sigma^*}\!\!\rightarrow\!\!6p_{\sigma\sigma\sigma}]$ absorption might be partially mixed with metal-to-metal-to-ligand charge transfer (¹MMLCT) character. The absorption energy of 4d-f, 5d-f, and 6d-f is appreciably red-shifted with respect to the $5d_{a^*} \rightarrow 6p_a$ transition reported for digold(I) complexes with dppm and dcpm (ca. 270-300 nm)^[5,7a] and the $5d_{\sigma^*\sigma^*} \rightarrow 6p_{\sigma\sigma}$ transition for trigold(I) complexes with dpmp and dcmp (ca. 329–350 nm).^[7b] In relation to $[Au_2(dcpm)_2]^{2+}$ and $[Au_3(dcmp)_2]^{3+}$ together with our compound syn-[Au₄(meso-dpmppm)₂]⁴⁺, Che and his co-workers carried out TD-DFT calculations on the linear models of [Au_n- $\{H_2P(CH_2PH)_{n-2}CH_2PH_2\}_2]^{n+}$ (n=2-4) to assign the absorption bands to spin-allowed metal-centered HOMO-LUMO transitions 1 [5d_{σ^*} \rightarrow 6p_{σ}] partially mixed with 1 MMLCT character. In the present study, the optimized model structures of the singlet ground state (S₀) slightly differ from each other depending on the arrangement and configuration of the two phosphine ligands H₂PCH₂P(H)CH₂P(H)CH₂PH₂, although the steric factors are neglected by replacing phenyl groups with hydrogen atoms (Table 5). The calculated Au-Au separations are all indicative of aurophilic interaction (Au-Au = 3.064–3.132 Å). Whereas the optimized structures of the models M4 and M6 are rather linear compared with the corresponding crystal ones, they converge at slightly bent (M4, Au-Au-Au = 171.1°) and zigzag (M6, Au-Au-Au-160.4°) structures, which are interestingly in contrast with the linear Au₄ alignment of M5 (Au-Au-Au = 180.0°), all the structures being reminiscent of

Table 4. Photophysic	cal data of	Table 4. Photophysical data of complexes 4 b-f, 5 d-f, and 6 b-f									
	Medium	λ_{abs} [nm] (ε [dm ³ mol ⁻¹ cm ⁻¹])	λ _{em} [nm]	τ [μs]	$\Phi_{ m em}$						
syn-[Au₄(meso-dpmp	pm) ₂]XX′ ₃										
4 a (X = X' = CI)	CH₃CN	398 (4.73×10 ⁴)	486	1.0	0.003						
	CH_2CI_2	382 (2.59×10 ⁴)	476	1.9							
	solid		510		0.01						
4b (X = Cl, X' = PF ₄)	CH₃CN	383 (4.14×10 ⁴)	512	4.6	0.02						
	CH_2CI_2	372 (2.32×10 ⁴)	509	4.4							
	solid	,	484		0.09						
4c (X = Cl, X' = BF ₄)	CH₃CN	388 (2.65×10 ⁴)	503	4.9	0.01						
	CH ₂ Cl ₂	367 (1.95×10⁴)	504	3.4							
	solid	201 (1 00 10 ⁵)	481		0.17						
4d $(X = X' = PF_6)$	CH ₃ CN	$384(1.02 \times 10^{3})$	520	6.8	0.45						
	CH ₂ Cl ₂	$3/0(3.23\times10^{-1})$	510	4.0	0.74						
	SOLIC	$269(280 \times 10^{4})$	508	74	0.76						
$4e (X = X = Dr_4)$		$308(3.89 \times 10)$	508	7.4	0.85						
		505 (5.87 × 10)	501	4.2	0.72						
$\mathbf{A} \mathbf{f} (\mathbf{Y} - \mathbf{Y}' - \mathbf{T} \mathbf{f} \mathbf{O})$		272 (2 80 × 10 ⁴)	504	5.0	0.72						
41(x - x - 10)		$373(3.09 \times 10)$	507	J.9 4.0	0.09						
	solid	500 (1.17 × 10)	475	4.0	0.85						
	30110		475		0.05						
anti-[Au](meso-dpmr	nm) ₂]X										
5 d $(X = PF_{\epsilon})$	CH ₂ CN	383 (9.55×10⁴)	514	6.7	0.36						
	CH ₂ Cl ₂	387 (1.29×10 ⁵)	511	4.7							
	solid	())	515		0.78						
5 e (X = BF ₄)	CH₃CN	382 (6.76×10 ⁴)	514	6.9	0.38						
	CH₂Cl₂	387 (6.46×10 ⁴)	512	3.0							
	solid		513		0.68						
5 f (X = TfO)	CH₃CN	378 (4.47×10 ⁴)	512	6.1	0.33						
	CH_2CI_2	389 (7.18×10 ⁴)	514	5.1							
	solid		515		0.67						
syn-[Au ₄ (rac-dpmppr	$n)_{2}X_{2}X_{2}'$										
6a (X = X' = CI)	CH ₃ CN	369 (1.90×10 ⁴)	510	2.8	0.02						
	CH ₂ Cl ₂	375 (3.40×10 ⁺)	495	1.5							
	solid	24E (2 40 - 10 ⁴)	505	1.0	0.08						
$(X = CI, X = PF_6)$		545 (2.40×10')	499	1.0	0.05						
		507 (1.50 X 10')	490 100	3.9	0.24						
		$370(371 \times 10^4)$	403 [a]		0.24						
$(\Lambda - C_1, \Lambda - D_{-4})$		$369(3.71\times10)$	503	36							
	solid	509 (2.02 × 10)	205 487	5.0	0.05						
6d $(X = X' = PF_{c})$		352 (4.39×10 ⁴)	501	6.7	0.85						
	CH ₂ CL	$358 (3.39 \times 10^4)$	490	3.5	0.00						
	solid	(0.027.107)	485	0.0	0.75						
6e $(X = X' = BF_{a})$	CH₃CN	353 (4.19×10 ⁴)	500	6.7	0.97						
	CH ₂ Cl ₂	358 (5.13×10 ⁴)	492	4.1							
	solid	· · ·	494		0.85						
6 f (X = X' = TfO)	CH₃CN	356 (5.45×10 ⁴)	491	7.1	0.75						
	CH ₂ Cl ₂	360 (8.91×10 ⁴)	486	3.5							
	solid		485		0.67						
[a] Not observed											
[a] NOL ODSERVED.											

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their parent crystal structures. As a result, the HOMO-LUMO energy gap of **M5** is smaller by 0.04–0.07 eV than those of **M4** and **M6** (Figure S13a in the Supporting Information). The linear Au₄ arrangement is likely to destabilize the $5d_{\sigma^*\sigma^*}$ antibonding interaction and instead stabilize the $6p_{\sigma\sigma\sigma}$ in-phase orbital, and thus, responsible for the lower absorption energy of **5 d–f** than those of **4 d–f** and **6 d–f**.

Complexes **4d**–**f**, **5d**–**f**, and **6d**–**f** containing large counter anions are all strongly luminescent both in the solid states and

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in the acetonitrile (Figure 9d-i, Table 4). In the solid state at room temperature, intense visible (blue to bluish-green) emissions were observed with quantum yields of 0.67-0.85 (Figures 9 d-f and 11), and their energies are red-shifted 485-494 (6d-f) < (475-)508 (4d-f) < 513-515 nm (5d-f), depending on the Au₄ structures. In CH₂Cl₂ (298 K), they are also luminous with the emission band maxima around 500 nm with a weak band at 440 nm (for 4d-f and 5d-f). When the solutions were exposed to air, the emission at 500 nm was slowly guenched, whereas the higher energy band (ca. 440 nm), presumably an intraligand fluorescence, was almost intact. In CH₃CN (298 K), intense bluish-green emissions were observed at 491-520 nm with microsecond lifetimes $(5.9-7.4 \,\mu s)$ (Figure 9g-i). In the light of the long lifetime and the DFT calculations, the emission is assigned to come from a triplet excited state, ${}^{3}[5d_{a^{*}a^{*}a^{*}}6p_{aaa}]$. The Stokes shifts between the ${}^{1}[5d_{\sigma^{*}\sigma^{*}\sigma^{*}}\rightarrow 6p_{\sigma\sigma\sigma}]$ absorption and 3 [5d_{$\sigma^{*}\sigma^{*}\sigma^{*}\rightarrow$} 6p_{$\sigma\sigma\sigma$}] emission are about 6.4–7.7×10³ cm⁻¹, comparable to those observed in $[Au_3(dcmp)_2]^{3+}$ (ca. 7.5-8.0× $10^{3} \text{ cm}^{-1})^{[7b]}$ and $K_{4}[Pt_{2}(P_{2}O_{5}H_{2})_{4}]$ (7.8×10³ cm⁻¹).^[18] The emission bands of the tetragold(I) complexes are significantly redshifted in energy relative to those of the trigold(I) complexes $[Au_3(dcmp)_2]^{3+}$ (442–452 nm)^[7b] and the digold(I) complexes $[Au_2(dcpm)_2]^{2+}$ (360–368 nm); this shift should be ascribed to a smaller $5d_{a^*} \rightarrow 6p_a$ gap for higher nuclearity of the complexes as discussed by Che et al. $^{\left[7b\right] }$ The lowest triplet (T1) excited states for M4-M6 were analyzed by DFT optimizations with MPWPW91/SDD methods (Table 5). In the T_1 excited states, α -HOMO and $\alpha\text{-HOMO}{-1}$ correspond to LUMO and HOMO of the S₀ ground states, respectively (Figure 10 d, and Figures S10-S12 in the Supporting Information), clearly indicative of its generation through intersystem crossing from the $^1[5d_{\sigma^*\sigma^*\sigma^*}6p_{\sigma\sigma\sigma}]$ state. The Au-Au distances (2.748–2.982 Å) in the T₁ states are appreciably shorter than those in the S₀ states (3.064-3.132 Å) owing to singly occupied $6p_{\sigma\sigma\sigma}$ bonding and $5d_{\sigma^*\sigma^*\sigma^*}$ antibonding orbitals. The calculated emission wavelengths are 453 (M6), 459 (M4), and 462 nm (M5) (Figure S13 b in the Supporting Information); the order is roughly in agreement with the observed data.

In order to obtain more accurate theoretical consideration, the DFT full optimization for syn-[Au₄(meso-dpmppm)₂]⁴⁺, anti- $[Au_4(meso-dpmppm)_2]^{4+}$, and $syn-[Au_4(rac-dpmppm)_2]^{4+}$ were carried out with B3LYP-D^[19,20] functionals with Lanl2tzf^[21] (Au) and 6-31G* (others) basis sets for the $S_{\rm 0}$ ground and lowest $T_{\rm 1}$ excited states (the initial coordinates were derived from 4d, 5e, and 6e, respectively). The PCM model^[22] was employed to approximate the solvent dichloromethane. The converged structures for the S₀ states are in agreement with the respective crystal structures (Table 6 and Figures S14-16 in the Supporting Information), which still showed slight elongation of Au-Au distances by 0.08-0.28 Å, although the hybrid functionals include an empirical correction term for long-range dispersion interactions.^[20] Notably, the qualitative order of the Au-Au distances (5e < 6e < 4d) is consistent with the observed distances. The characters of HOMO and LUMO are essentially identical to the results from the primitive calculations on M4–M6, consisting of $5d_{a^*a^*a^*}$ and $6p_{aga}$ orbitals, respectively, partially mixed with the ligand orbitals (Figure 12). The DFT



Figure 9. Absorption spectra of a) *syn*-[Au₄(*meso*-dpmppm)₂]X₄ (X = PF₆ (**4d**, blue), BF₄ (**4e**, red), TfO⁻ (**4** f, green), b) *anti*-[Au₄(*meso*-dpmppm)₂]X₄ (X = PF₆ (**5d**, blue), BF₄ (**5e**, red), TfO⁻ (**5** f, green), and c) *syn*-[Au₄(*rac*-dpmppm)₂]X₄ (X = PF₆ (**6d**, blue), BF₄ (**5e**, red), TfO⁻ (**6** f, green), in CH₂Cl₂ at room temperature. Solid-state emission spectra of d) *syn*-[Au₄(*meso*-dpmppm)₂]X₄ (X = PF₆ (**4d**, blue), BF₄ (**4e**, red), TfO⁻ (**4f**, green), e) *anti*-[Au₄(*meso*-dpmppm)₂]X₄ (X = PF₆ (**5d**, blue), BF₄ (**5e**, red), TfO⁻ (**6f**, green), at room temperature. Solution-state emission spectra of g) *syn*-[Au₄(*meso*-dpmppm)₂]X₄ (X = PF₆ (**4d**, blue), BF₄ (**4e**, red), TfO⁻ (**6f**, green), at room temperature. Solution-state emission spectra of g) *syn*-[Au₄(*meso*-dpmppm)₂]X₄ (X = PF₆ (**4d**, blue), BF₄ (**4e**, red), TfO⁻ (**4f**, green), h) *anti*-[Au₄(*meso*-dpmppm)₂]X₄ (X = PF₆ (**5d**, blue), BF₄ (**5e**, red), TfO⁻ (**6f**, green), at room temperature. Solution-state emission spectra of g) *syn*-[Au₄(*meso*-dpmppm)₂]X₄ (X = PF₆ (**6d**, blue), BF₄ (**4e**, red), TfO⁻ (**4f**, green), h) *anti*-[Au₄(*meso*-dpmppm)₂]X₄ (X = PF₆ (**5d**, blue), BF₄ (**5e**, red), TfO⁻ (**6f**, green), at room temperature. Solution-state emission spectra of g) *syn*-[Au₄(*rac*-dpmppm)₂]X₄ (X = PF₆ (**6d**, blue), BF₄ (**6e**, red), TfO⁻ (**6f**, green), and i) *syn*-[Au₄(*rac*-dpmppm)₂]X₄ (X = PF₆ (**6d**, blue), BF₄ (**6e**, red), TfO⁻ (**6f**, green), in CH₃CN at room temperature.



Figure 10. MO surface diagrams for a) LUMO and b) HOMO of syn-[Au₄(meso-C₃H₁₂P₄)₂]⁴⁺ (**M4**, singlet ground state S₀) and c) α -HOMO and d) α -HOMO-1 of syn-[Au₄(meso-C₃H₁₂P₄)₂]⁴⁺ (**M4**, lowest triplet excited state T₁).

Table 5. Optimized structures and photophysical data of the ground singlet (S₀) and lowest triplet (T₁) excited states for model complexes, *syn*- $[Au_4(meso-L)_2]^{4+}$ (**M 4**), *anti*- $[Au_4(meso-L)_2]^{4+}$ (**M 5**), and *syn*- $[Au_4(rac-L)_2]^{4+}$ (**M 6**) (L = H₂PCH₂P(H)CH₂P(H)CH₂PH₂) from DFT calculations.

	M 4		м	M 5		M6	
	S ₀	T ₁	S ₀	T ₁	S ₀	T ₁	
Au _{out} …Au _{in} [Å]	3.127	2.973	3.099	2.949	3.124	2.961	
Au _{in} …Au _{in′} [Å]	3.132	2.982	3.094	2.821	3.064	2.784	
av Au…Au [Å]	3.130	2.978	3.097	2.885	3.094	2.873	
Au _{out} –P [Å]	2.406	2.442	2.412	2.447	2.406	2.443	
Au _{in} —P [Å]	2.417	2.431	2.416	2.429	2.423	2.433	
Au _{out} …Au _{int} …Au _{in} [°]	171.1	174.0	180.0	180.0	160.4	172.3	
P-Au _{out} -P, [°]	177.2	165.7	176.3	165.5	177.1	165.5	
P-Au _{in} -P, [°]	177.4	171.7	178.4	172.5	172.8	164.5	
$\Delta E_{\text{HOMO-LUMO}}$ [eV]	3.08		3.04		3.11		
calcd λ_{abs} [nm] ^[a]	365		365		361		
calcd $\lambda_{ m em}$ [nm] ^[b]	459		462		453		
[a] Calculated with TD-DFT methods on the S_0 optimized structures with with MPWPW91/SDD. [b] Calculated from energy difference, Δ SCF = E(T ₁) -E(S ₀) on the T ₁ optimized structures.							







Figure 11. Photographs of solid samples 4d–f, 5d–f, and 6d–f under UV irradiation (365 nm) at room temperature.



Figure 12. MO surface diagrams for HOMO and LUMO of *syn*-[Au₄(*meso*-dpmppm)₂]⁴⁺ (**4** d), *anti*-[Au₄(*meso*-dpmppm)₂]⁴⁺ (**5** e), and *syn*-[Au₄(*rac*-dpmppm)₂]⁴⁺ (**6** e) in the ground state S₀, the structures of which are optimized by DFT calculations with RB3LYP-D functionals.

single-point calculations on the crystal structures with the same methods B3LYP-D/Lanl2tzf (Au) and 6-31G* (others) also indicated the similar HOMO–LUMO characters. The HOMO–LUMO energy gaps for the optimized and X-ray structures exhibited the same tendency of **5e** (*anti-(meso-*dpmppm)₂) < **4d**(*syn-(meso-*dpmppm)₂) < **6e**(*anti-(rac-*dpmppm)₂) as observed for the model compounds. The TD-DFT calculations on the optimized and X-ray structures of **4d**, **5e**, and **6e** clearly indicated that the electronic absorptions around 360–390 nm are assignable to HOMO–LUMO transitions; the values for the optimized structures, 332 (f=0.771) (**4d**), 365 (f=1.092) (**5e**), and 325 nm (f=0.588) (**6e**), are relatively comparable with those for the X-ray structures, 366 (f=0.933) (**4d**), 378 (f=

1.173) (**5**e), and 366 nm (f=0.849) (**6**e) (Table 6). The structures for the lowest triplet excited states (T₁) of **4d**, **5**e, and **6**e were optimized with UB3LYP-D/Lanl2tzf (Au) and 6–31G* (others), in which the Au-Au distances are appreciably reduced due to partial bonding interactions of the ³[5d_{0⁺0⁺0⁺0⁺0⁺0⁻0⁻0]} excited state; average Au-Au = 2.825 Å (**4d**), 2.861 (**5e**), and 2.811 (**6e**). In the T₁ states of **4d** and **6e**, the average Au-Au distances are reduced dramatically by 0.324 (**4d**) and 0.302 Å (**6e**) with distinct increases of the average Au-Au angles by 14.6 (**4d**)}

Table 6. Optimized structures and photophysical data of the ground singlet (S ₀) and lowest triplet (T ₁) excit
states for syn-[Au ₄ (meso-dpmppm) ₂] ⁴⁺ (4d), anti-[Au ₄ (meso-dpmppm) ₂] ⁴⁺ (5e), and syn-[Au ₄ (rac-dpmppm) ₂
(6 e) from DFT calculations.

	4 d		5 e		бе	
	So	T ₁	So	Τ ₁	S ₀	T ₁
Au1Au2 [Å]	3.256	2.857	3.042	2.897	3.112	2.850
Au2…Au3, [Å]	3.067	2.744	2.967	2.789	3.100	2.736
Au3…Au4, [Å]	3.123	2.875	3.043	2.897	3.127	2.848
av Au…Au [Å]	3.149	2.825	3.017	2.861	3.113	2.811
obsd. av Au…Au [Å]	2.968		2.916		2.953	
Au _{out} –P [Å]	2.336	2.346	2.339	2.342	2.335	2.349
Au _{in} —P [Å]	2.330	2.339	2.330	2.334	2.331	2.334
Au1…Au2…Au3 [°]	133.3	158.9	178.5	179.2	133.1	157.9
Au2…Au3…Au4 [°]	164.6	168.3	179.2	179.5	129.8	158.5
av Au…Au…Au [°]	149.0	163.6	178.9	179.4	131.5	158.2
obsd. av Au…Au…Au [°]	153.6		176.6		145.4	
P-Au _{ou} -P [,] [°]	171.8	170.9	177.3	169.2	174.2	173.9
P-Au _{in} -P [°]	173.4	174.4	177.6	174.2	172.6	170.3
$\Delta E_{\text{HOMO-LUMO}}$ [eV]	4.33 ^[a] (3.95) ^[b]		3.95 ^[a] (3.81) ^[b]		4.45 ^[a] (3.97) ^[b]	
calcd λ_{abs} [nm]	332 ^[a,c] (366) ^[b,c]		365 ^[a,c] (378) ^[b,c]		325 ^[a,c] (366) ^[b,c]	
obsd λ_{abs} [nm] in CH ₂ Cl ₂	370		387		358	
calcd λ_{em} [nm]	476 ^[a,d] (486) ^[b,e]		479 ^[a,d] (488) ^[b,e]		473 ^[a,d] (481) ^[b,e]	
obsd λ_{abs} [nm] in CH ₂ Cl ₂	510		512		492	

[a] For DFT optimized structures with B3LYP-D/Lanl2tzf (Au) and 6–31G*(others). [b] For X-ray determined structures. [c] Calculated with TD-DFT methods on the S₀ optimized structures with B3LYP-D/Lanl2tzf (Au) and 6–31+G*(others). [d] Calculated from energy difference, Δ SCF = E(T₁)-E(S₀) on the T₁ optimized structures. [e] Calculated with TD-DFT methods on the T₁ optimized structures with UB3LYP-D/Lanl2tzf(Au) and 6–31+G* (others).

and 26.7° (6e), showing a lightinduced elasticity of the bent and zigzag Au₄ chains. On the other hand, the structural difference between the T_1 and S_0 states of 5e is quite small with $\Delta(av Au - Au) = 0.156 \text{ Å and } \Delta(av)$ $Au \cdot Au \cdot Au = 0.5^{\circ}$ owing to the linearly constrained Au₄ structure. The SCF energy differences between the S_0 and T_1 states at the T₁ optimized structures afford emissions originating from the 3 [5d_{$\sigma^{*}\sigma^{*}\sigma^{*}$ 6p_{$\sigma\sigma\sigma$}] excited} states at 476 (4d), 479 (5e), and 473 nm (6e) (Figure S17 in the Supporting Information), and the TD-DFT methods on the T₁ optimized structures gave values of 486 (4d), 488 (5e), and 481 nm (6e) (Table 6); these results show a same order of the observed emission of 492 (6e) < 510 (4d) < 512 nm (5 e) and can be compared with 4d-f (501-510 nm), 5d-f (511-514 nm), and 6d-f (486-492 nm) in dichlorome-

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thane. Interestingly, the photochemical properties are predominantly determined by the HOMO and LUMO characters of the Au₄ arrays, which are essentially identical in the S₀, S₁, and T₁ states.

Emission quenching by chloride anions

The solid-state emissions are appreciably quenched in complexes **4b** (Φ =0.09) and **4c** (Φ =0.17), referenced to **4d** (Φ =0.76) and **4e** (Φ =0.72), presumably due to interaction of the Au₄ chain with a chloride

Table 7. Photophysical parameters for the emission quenching of 4d ,e, 5d ,e, and 6d ,e by chloride ions at room temperature in CH ₃ CN, determined from the Stern–Volmer plots for I_0/I and τ_0/τ , and UV/Vis titration.								
	4 d	4e	5 d	5 e	6 d	6 f		

$K_{\rm SV}^{\rm app}[{\rm mol}^{-1}{\rm dm}^3]^{[a]}$	5.7×10⁵	1.4×10 ⁶	9.3×10⁵	7.6×10⁵	2.3×10 ⁶	1.0×10 ⁶
$k_{\rm q}^{\rm app}$ [mol ⁻¹ dm ³ s ⁻¹] ^[b]	8.4×10 ¹⁰	1.9×10 ¹¹	1.4×10 ¹¹	1.1×10 ¹¹	3.4×10 ¹¹	1.5 x10 ¹¹
K_{sv}^{D} [mol ⁻¹ dm ³] ^[c]	2.0×10⁵	2.1×10 ⁵	2.0×10⁵	1.8×10⁵	3.5×10⁵	6.3×10 ⁵
k ^D _a [mol ⁻¹ dm ³ s ⁻¹] ^[d]	2.9×10 ¹⁰	2.8×10 ¹⁰	3.0×10 ¹⁰	2.6×10 ¹⁰	5.2×10 ¹⁰	9.4 x10 ¹⁰
K ^s _{AB} [mol ⁻¹ dm ³] ^[e]	2.7×10⁵	3.0×10 ⁵	1.8×10 ⁴	5.4×10 ⁴	2.1×10^{4}	5.5×10 ⁴
$K_{P}^{S} [mol^{-1}dm^{3}]^{[f]}$	3.2×10⁵	9.7×10⁵	7.5×10⁵	5.8×10⁵	1.5×10^{6}	5.2×10 ⁵
$V_{q} [dm^{3}]^{[g]}$	5.3×10 ⁻¹⁹	1.6×10^{-18}	1.2×10^{-18}	9.6×10 ⁻¹⁹	2.5×10^{-18}	8.6×10 ⁻¹⁹
$K_{SV}^{D} + K_{AB}^{S} + K_{P}^{S}$	7.9×10⁵	1.5×10 ⁶	9.7×10⁵	8.1×10 ⁵	1.9×10 ⁶	1.2×10 ⁶

[a] Calculated from the extrapolated line with $l_0/I = 1 + K_{SV}^{appr}[Cl^-]$ at very low quencher concentration range. [b] Derived with a tentative equation of $K_{SV}^{app} = k_q^{appr} \tau_0$ (τ_0 is lifetime without quencher). [c] Derived from the Stern–Volmer plots $\tau_0/\tau = 1 + K_{SV}^{b}[Cl^-]$ (τ_0 and τ are lifetime without and with quencher, respectively). [d] Derived with an equation of $K_{SV}^{b} = k_q^{b} \tau_0$ (τ_0 is lifetime without quencher). [e] K_{AB}^{s} is the first chloride binding constants for *syn/anti*-[Au₄(*meso/rac*-dpmppm)₂]²⁺ + Cl⁻ \Rightarrow {*syn/anti*-[Au₄(*meso/rac*-dpmppm)₂]Cl]³⁺ determined by titration with adding *n*Bu₄NCl monitored by UV/Vis spectra. [f] Derived from the Stern–Volmer plots for l_0/l with an equation of $\ln[l_0/[l(1 + K_{SV}^{b}[Cl^-])(1 + K_{AB}^{s}[Cl^-])] = K_{P}^{s}[Cl^-]$. [g] $K_{P}^{s} = V_q N_a$; V_q is volume for the sphere of effective quenching, and N_a is Avogadro's constant.



Figure 13. a) Emission spectral changes of *syn*-[Au₄(*meso*-dpmppm)₂][BF₄]₄ (**4e**) in CH₃CN at room temperature by successive titration with 0.1 equiv of [*n*Bu₄N]Cl. b) Plot of *l*₀// at 508 nm versus [Cl⁻] (black circle), along with an extrapolated line at very low quencher concentration (blue), $l_0/I = (1 + K_{SV}^{app}[Cl^-])$, and the Stern–Volmer plot for τ_0/τ (red circle) along with a fitted line of $\tau_0/\tau = (1 + K_{SV}^b[Cl^-])$. c) Plot of $\ln[l_0/[l(1 + K_{SV}^b[Cl^-])(1 + K_{AB}^s[Cl^-])]$ } versus [Cl⁻], the slope of which give a fitted value of K_P^{-5} for equation of $l_0/I = (1 + K_{SV}^b[Cl^-])(1 + K_{AB}^s[Cl^-])$.

anion as observed in the crystal structure of 4b (Figure 3a). Even in acetonitrile, the intensities of the metal-centered emission for 4d (Φ = 0.45) and 4e (Φ = 0.83) distinctly decreased when nBu₄NCl was added to the solution (Figure 13 a and Figure S18 in the Supporting Information). Similar sensitive quenching by chloride ions was also observed for the other isomeric Au₄ chains of 5d,e and 6d,e (Figure S18 in the Supporting Information). In particular, more than 90% of emission for 6d,e was effectively quenched by adding 0.5 equivalents of Cl^- at a concentration ca. 1.5 μ M. These results revealed that the luminous tetragold(I) units supported by two dpmppm ligands have the potential ability to detect chloride anions in the solution state, which perturbed their metal-centered emission. Che et al. reported similar halide-quenching phenomena of $[Au_2(dcpm)_2]^{2+}$ and $[Au_3(dcmp)_2]^{3+}$, which were elucidated to result from substrate-binding of their ${}^3\![d_{\sigma^*\sigma^*}\!p_{\sigma\sigma}]$ excited states.^[7]

The observed decreases in emission intensity with varying $[Cl^{-}]$ do not follow the linear Stern–Volmer equation, $l_0/l = 1 + 1$ $K_{sy}[CI^{-}]$, and the I_0/I plots show upward curvatures at high quencher concentrations (Figure 13b (black circles), Figure S18 in the Supporting Information), demonstrating that simultaneous dynamic and static quenching processes are involved in the present systems.^[23a] The apparent Stern–Volmer constants are derived from the extrapolated line at very low quencher concentration range as $K_{SV}^{app} = 5.7 \times 10^5 - 2.3 \times 10^6 \text{ mol}^{-1} \text{ dm}^3$ (Figure 13 b (blue line), Figure S18, Table 7). These values result in apparent quenching rate constants, $k_q^{app} = 8.4 \times 10^{10} - 3.4 \times$ $10^{11} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ ($K_{\text{SV}} = k_{\text{q}} \tau_0$, τ_0 is lifetime without quencher), which are appreciably higher than the diffusion-controlled limit (ca. 10¹⁰ mol⁻¹ dm³ s⁻¹) and suggested that static quenching processes are also substantial. In general, static quenching involves two mechanisms, 1) static binding between chromophore and quencher in ground states and 2) static bonding in excited states of chromophore. To evaluate simultaneous dynamic and static quenching, the former case 1 is treated by an equation of [Equation (1)], in which K_{SV}^{D} [mol⁻¹ dm³] is the



Stern–Volmer constant for dynamic quenching, and K_{AB}^{S} [mol⁻¹ dm³] is the static ground-state bimolecular binding constant.

$$I_0/I = (1 + K_{SV}^{D}[CI^{-}])(1 + K_{AB}^{S}[CI^{-}])$$
(1)

In the latter case 2, Perrin's sphere of effective quenching model is often used to approximate the static quenching of excited species, and then the plot for I_0/I can be represented by Equation (2) in which K_p^S [mol⁻¹dm³] (= V_qN_a) is static quenching constant for excited chromophore, V_q [dm³] is volume for the sphere of effective quenching, and N_a is Avogadro's constant.^[23a]

$$I_0/I = (1 + K_{SV}^{D}[CI^{-}])\exp(K_{P}^{S}[CI^{-}])$$
⁽²⁾

Notably, K_{SV}^D can be determined from Stern–Volmer plot for τ_0/τ (τ_0 and τ are lifetimes without and with quencher), and K_{AB}^S is determined by electronic absorption spectral titration.

At first, the Stern–Volmer plots for au_0/ au were analyzed with $\tau_0/\tau = 1 + K_{sv}^{D}[CI^{-}]$ (Figure 13 b, red) to afford $K_{sv}^{D} = 1.8 - 6.3 \times$ 10⁵ mol⁻¹dm³ (Table 7, Figure 13 b (red line), Figure S18 in the Supporting Information). The obtained K_{sv}^{D} values are notably smaller than the apparent Stern–Volmer constant K_{SV}^{app} (5.7× 10^{5} –2.3×10⁶ mol⁻¹ dm³) (Table 7, Figure 13 b (blue line), Figure S18 in the Supporting Information), and result in the quenching rate constants k_q^D of 2.6–9.4×10¹⁰ mol⁻¹ dm³ s⁻¹, which are comparable or slightly higher than diffusion controlled rate constants. The ground-state binding constants for the first chloride association, syn/anti-[Au₄(meso/racdpmppm)₂]⁴⁺ + Cl⁻ \rightleftharpoons {*syn/anti*-[Au₄(*meso/rac*-dpmppm)₂]Cl}³⁺, were determined by UV/Vis titration with nBu₄NCI to afford $K_{AB}^{S} = 1.8 \times 10^{4} - 3.0 \times 10^{5} \text{ mol}^{-1} \text{ dm}^{3}$ (Table 7, Figure 14, Figure S19 in the Supporting Information). These values are significantly larger than that found for $[Au_2(dcpm)_2]^{2+}$ with Cl⁻ (1.8× 10³ mol⁻¹ dm³)^[7a] and slightly larger than those foudn for for $[Au_2(dmpm)_2]^{2+}$ and $[Au_2(dmpe)_2]^{2+}$ (ca. $10^4 \text{ mol}^{-1} \text{ dm}^3)$.^[24] It should be noted that the K_{AB}^{S} values for **4d**,**e** (2.7–3.0× 10⁵ mol⁻¹ dm³) are one order of magnitude larger than those of **5e**,**d** and **6e**,**d** $(1.8-5.5\times10^4 \text{ mol}^{-1} \text{ dm}^3)$, which may be attributed to high affinity of the bent Au₄ pocket toward a chloride ion as observed in the X-ray structure of 4b.

Even by using the independently determined K_{SV}^{D} and K_{AB}^{S} values, the observed I_0/I data could not be fitted to Equation (1). On the other hand, the K_{P}^{S} values obtained by using Equation (2) with the pre-determined K_{SV}^{D} were sufficiently large (ca. $10^{5}-10^{6}$ mol⁻¹dm³), suggesting the effective sphere of binding for the excited chromophore is the main quenching process. Nevertheless, the K_{P}^{S} values for **4d,e** were fairly comparable to the K_{AB}^{S} values (ca. 10^{5} mol⁻¹dm³), while those for **5d,e** and **6d,e** were one order of magnitude larger than the corresponding K_{AB}^{S} values (ca. 10^{4} mol⁻¹dm³). In the light of these preliminary results, both the ground- and excited-state static quenching process and the I_0/I data were analyzed by using Equation (3).



Figure 14. a) Absorption spectral changes of *syn*-[Au₄(*meso*-dpmppm)₂][BF₄]₄ (**4e**) in CH₃CN at room temperature by titrating with [*n*Bu₄N]Cl and b) plot of $A_0/(A_0-A)$ versus 1/[Cl⁻], which afford the ground-state binding constant K_{AB}^{S} for *syn*-[Au₄(*meso*-dpmppm)₂]⁴⁺ + Cl⁻ \rightleftharpoons {*syn*-[Au₄(*meso*-dpmppm)₂]Cl]³⁺.

$$I_0/I = (1 + K_{SV}^{D}[CI^{-}])(1 + K_{AB}^{S}[CI^{-}])exp(K_{P}^{S}[CI^{-}])$$
(3)

Since $\exp(K_{P}^{S}[CI^{-}]) \approx 1 + K_{P}^{S}[CI^{-}]$ at low quencher concentrations, the extrapolated apparent Stern–Volmer constant K_{SV}^{app} should approximately correspond to a summation $K_{SV}^{D} + K_{AB}^{S} +$ K_{P}^{S} . By using the K_{SV}^{D} and K_{AB}^{S} values, the static quenching constants for the excited species (K_p^S) were derived according to Equation (3); namely, the plots of $\ln\{I_0/[I(1+K_{SV}^D[CI^-])(1+$ $K_{AB}^{S}[CI^{-}])$]} versus [CI⁻] exhibited a linear correlation, and from the slope K_P^S are estimated as $3.2 \times 10^5 - 1.5 \times 10^6 \text{ mol}^{-1} \text{ dm}^3$ (Table 7 and Figure 13, and Figure S18 in the Supporting Information), which lead to unusually large sphere volumes of effective quenching V_{q} . From these results, the phosphorescence of 4d,e-6d,e is estimated to guench through simultaneous static and dynamic processes; in particular, static association of chloride ions to the excited-state Au₄ centers is significant for the sensitive quenching. The contribution of ground-state static quenching for 4d,f is notably higher than that for 5d,f and 6d,f. The detailed mechanisms for the excited-state quenching will be investigated in our subsequent studies.

Conclusion

In the present study, a series of Au_4^1 complexes with new tetraphosphine ligands, *meso-* and *rac-bis*[(diphenylphosphinomethyl)phenylphosphino]methane (*meso-* and *rac-dpmppm*) were synthesized to demonstrate that the tetranuclear Au^1 alignment varies depending on *syn-* and *anti-arrangements* of the two dpmppm ligands as bent (*syn-*[Au₄(*meso-dpmppm*)₂]⁴⁺

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(4)), linear $(anti-[Au_4(meso-dpmppm)_2]^{4+}$ (5)), and zigzag (syn- $[Au_4(rac-dpmppm)_2]^{4+}$ (6)) structures. Complexes 4–6 with non-coordinative large anions (PF₆⁻, BF₄⁻, TfO⁻) are strongly luminescent in the sold state ($\lambda_{max} = 475-508$ (4), 513-515 (5), 485–494 nm (6)) with quantum yields $\Phi = 0.67-0.85$, which were assigned to phosphorescence from the ${}^3[5d_{\sigma^*\sigma^*\sigma^*}\!6p_{\sigma\sigma\sigma}]$ excited state of the cluster centers on the basis of DFT calculations as well as the long lifetimes. The emission energy clearly relates to the HOMO (5d_{\sigma^*\sigma^*\sigma^*})-LUMO (6p_{\sigma\sigma\sigma}) energy gaps, which are systematically altered depending on the Au₄ core structures. In the light of DFT optimization of 4d, 5e, and 6e in the lowest triplet excited states, an interesting light-induced elasticity of the bent and zigzag Au₄ chains was observed for **4d** and **6e**, while the structural difference between the T_1 and S₀ states of **5e** is guite small, owing to the linearly constrained Au₄ structure. In addition, the intense emission was sensitively quenched by chloride anions through both the dynamic and static quenching processes. For the static quenching, effective sphere binding of chloride ions to the Au₄ excited species is assumed to be predominant for the linear and zigzag Au₄ chains of 5 and 6, while formation of ground-state non-luminescent complexes is also substantial for the quenching of the bent Au₄ chains of 4. These results are quite interesting as strongly luminescent properties intrinsic to the fine tunable linear tetragold(I) chains, and could lead to their application for anion sensing systems by utilizing their ${}^{3}[5d_{\sigma^{*}\sigma^{*}\sigma^{*}}6p_{\sigma\sigma\sigma}]$ excited states.

Experimental Section

General procedures

All reactions were carried out under a nitrogen atmosphere by using standard Schlenk techniques. Solvents were dried by standard procedures and freshly distilled prior to their use. Other reagents were of the best commercial grade and no further purifica-Bis(phenylphosphino)methane,^[8c, 12] were performed. tions $[AuCl(PPh_{3})],^{[25]}$ and [AuCl(tht)] $(tht = tetrahydrothiophene)^{[25]}$ were prepared according to the literature procedures. ¹H NMR spectra were recorded on a Varian Gemini 2000 instrument or a Bruker AV-300N spectrometers at 300 MHz, and the chemical shifts are referenced to the residual resonances of the deuterated solvent. ³¹P{¹H} NMR spectra were recorded on the same instruments at 121 MHz with chemical shifts calibrated to 85% H₃PO₄ as an external reference. Electronic absorption spectra were recorded on a Shimadzu UV-3000 and HP Agilent 8453 spectrophotometers in dichloromethane or acetonitrile. The solution and solid-state emission spectra were measured on a Shimadzu RF-5300PC spectrofluorometer, or JASCO FP-6600 and FP-6200 spectrofluorometers. Solvents (spectroscopic-grade acetonitrile and dichloromethane) were degassed by repeated freeze-pump-thaw procedures under nitrogen. The quantum yields for solid-state and acetonitrile solution samples were determined by the measurements at room temperature using ILF-533 (100 mm diameter) integrating photometer. Luminescence decay curves were measured with N₂ laser (337 nm) on a Hamamatsu R-928 with a Jovin-Ybon H-20 monochromator or a Horiba TemPro Fluorescence Lifetime System. IR spectra (KBr) were recorded on a Jasco FT/IR-410 spectrometer. ESI-TOF-mass spectra were obtained with an Applied Biosystems Mariner high resolution mass spectrometer or a JEOL JMS-T100 LC high-resolution mass spectrometer with positive ionization mode.

Syntheses

Bis[(trimethylsilylmethyl)phenylphosphino]methane (tmsmppm): In a dry ice-methanol bath, nBuLi-hexane solution (1.61 M, 44 mL, 71 mmol) in THF (20 mL) was added slowly to a solution of bis(diphenylphosphino)methane (7.32 g, 31.5 mmol) in THF (100 mL). The reaction mixture was gradually warmed to room temperature to result in a clear yellow-orange solution after stirring for 1 h. Then, chloromethyltrimethylsilane (9.7 mL, 69 mmol) in THF (20 mL) was added to the solution, which was cooled in a dry icemethanol bath. The reaction mixture was warmed again to room temperature and then refluxed at 80°C for 1 h to give a pale yellow suspension. After cooling to room temperature, degassed H₂O (30 mL) was added to the mixture. The resultant organic layer was extracted with diethyl ether and the solvent was removed under reduced pressure to afford clear oil of bis[(trimethylsilylmethyl)phenylphosphino]methane (tmsmppm) (11.8 g, yield: 92%). ¹H NMR (300 MHz, CDCl₃, RT): δ = 7.59–7.23 (m, 10 H; Ph), 2.03 (m, 2H; CH₂), 1.40-1.23 (m, 1H; CH₂), 0.23-0.05 ppm (m, 18H; SiMe₃); $^{31}P{^{1}H}$ NMR (121 MHz, CDCl₃, RT): $\delta = -34.2$ (s, 1P), -35.3 ppm (s, 1 P); ESI-MS (in CH₃CN): m/z: 405.192 [tmsmppm+H]⁺ (calcd: 405.175).

meso-Bis[(diphenylphosphinomethyl)phenylphosphino]methane (meso-dpmppm): A mixture of Ph₂PCI (12 mL, 58 mmol) and tmsmppm (11.8 g, 29.1 mmol) was refluxed at 95 °C for 1 h to give a white viscous liquid. After cooling down to room temperature, the remaining chlorotrimethylsilane was removed under reduced pressure to give a meso-rich mixture of dpmppm. The mixture was dissolved in acetone and cooled at 2°C to afford pure white powder of meso-dpmppm, which was washed with methanol and dried under vacuum (9.22 g, yield: 50%). IR (KBr): $\tilde{\nu} = 1433$ (s, P–C), 1096 (w), 774 (w), 732 (s), 694 cm⁻¹ (s); ¹H NMR (300 MHz, in CDCl₃, RT): $\delta = 7.70-7.19$ (m, 30H; Ph), 2.56 (d, ${}^{2}J_{HH} = 13$ Hz, 2H), 2.42 (d, $^{2}J_{HH} = 13$ Hz, 2 H), 2.37 (d, $^{2}J_{HH} = 16$ Hz, 1 H), 2.20 ppm (d, $^{2}J_{HH} =$ 14 Hz, 1 H); ³¹P{¹H} NMR (121 MHz, in CDCl₃, RT): $\delta = -23.0$ (m, 2 P; P_{out}), -34.7 ppm (m, 2P; P_{in}) (${}^{2}J_{P_{in}P_{out}} = 117.06$ Hz, ${}^{2}J_{PinPin'} = 92.10$ Hz, ⁴J_{PoutPin}=3.85 Hz, ⁶J_{PoutPout}=0.09 Hz, simulated by gNMR with AA'BB' system); ESI-MS (in CH₃CN): m/z: 629.199 [dpmppm+H]⁺ (calcd: 629.184).

meso/rac-Bis[(diphenylphosphinomethyl)phenylphosphino]me-

thane mixture (*meso/rac-dpmppm***)**: The white solid of *meso-*dpmppm (200 mg, 0.32 mmol) was heated at 165 °C for about 1 h under an argon atmosphere. Then, the mixture was cooled to room temperature to afford white oily product of an approximate 1:1 mixture of *meso-* and *rac-dpmppm*, which was analyzed by ¹H and ³¹P{¹H} NMR spectra.

[Pd₂Cl₄(*rac***-dpmppm)]-0.5 CH₂Cl₂ (1-0.5 CH₂Cl₂): The 1:1 mixture of** *meso***- and** *rac***-dpmppm (derived from 500 mg (0.80 mmol) of** *meso***-dpmppm) was dissolved in CH₂Cl₂ (13 mL) at room temperature, and a portion of [PdCl₂(cod)] (671 mg, 2.35 mmol) was added to the solution. After stirring for 30 s, white powder was precipitated and the resultant pale orange suspension was further stirred for 12 h. The product of [Pd₂Cl₄(***rac***-dpmppm)]-0.5 CH₂Cl₂ was separated by filtration, washed with CHCl₃ (3 mL×3) and diethyl ether (3 mL×3), and dried under vacuum (341 mg, yield: 43% vs.** *meso***-dpmppm). Elemental analysis calcd (%) for C₃₉₅H₃₇P₄Cl₅Pd₂ (1025.72): C 46.25, H 3.64; found: C 46.63, H 3.59; IR (KBr): v = 1435 (s, P–C), 1098 (m), 807 (m), 793 (w), 744 (m), 692 cm⁻¹ (s); ¹H NMR (300 MHz, in [D₇]DMF, RT): \delta = 8.39–7.40 (m, 30H; Ph), 4.44 (dt, J_{HH} = 2, 6 Hz, 2 H), 4.01–3.87 (m, 2 H), 3.55–3.40 ppm (m, 2 H);**

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³¹P{¹H} NMR (121 MHz, in [D₇]DMF, RT): δ = 19.4 (m, 2 P; P_{out}) 17.7 ppm (m, 2 P; P_{in}), (²J_{PmPout} = 45.68 Hz, ²J_{PmPin} = 38.63 Hz, ⁴J_{PoutPin} = 0.29 Hz, ⁶J_{PmuPout} = 0.12 Hz, simulated by gNMR with AA'BB' system).

rac-Bis[(diphenylphosphinomethyl)phenylphosphino]methane

(*rac-dpmppm*): A solution of NaCN (503 mg, 19.3 mmol) in water (1.1 mL) was added to a suspension of 1 (51 mg, 0.0052 mmol) in CH₂Cl₂ (7 mL), and the mixture was stirred for 1 h. Then, the organic layer was separated, washed with degassed water (3 mL×3), and dried over Na₂SO₄ for 2 h. The organic solution was removed by filtration, and the inorganic salts were washed with CH₂Cl₂ (3 mL×3). The extracts were combined and concentrated to dryness under reduced pressure, resulting in colorless oil of *rac-*dpmppm in a quantitative yield. ¹H NMR (300 MHz, in CDCl₃, RT): δ =7.19–7.75 (m, 30H; Ph), 2.50 (dd, 4H; *J*_{PH}=32, 13 Hz), 2.45 ppm (s, 2H;); ³¹P{¹H} NMR (121 MHz, in CDCl₃, RT): δ =-23.3 (m, 2P; P_{out}), -34.0 ppm (m, 2P; P_{inn}), (²*J*_{PHPout}=114.21 Hz, ²*J*_{PHPir}=105.43 Hz, ⁴*J*_{PoutPir}=3.44 Hz, ⁶*J*_{PoutPire}=0.12 Hz, simulated by gNMR with AA'BB' system).

[Au₄Cl₄(meso-dpmppm)]·1.5 DMF (2·1.5 DMF): meso-dpmppm (115 mg, 0.183 mmol) was added to a suspension of [AuCl(tht)] (240 mg, 0.748 mmol) in ethanol (8 mL), and the reaction mixture was stirred at room temperature overnight. The mother liquor was separated by filtration and the solid was washed with diethyl ether and dried under vacuum. The colorless product was extracted with DMF (5 mL), which was passed through a membrane filter. Addition of diethyl ether to the extract afforded colorless needle crystals of 2.1.5 DMF (yield: 184 mg, 76% vs. Au). Elemental analysis calcd (%) for $C_{43.5}H_{46.5}N_{1.5}O_{1.5}P_4Cl_4Au_4$ (1667.92): C 31.32, H 2.81, N 1.26; found: C 31.19, H 2.77, N 1.60; IR (KBr): v=1647 (s, DMF), 1437 (s, P–C), 1103 (m), 802 cm⁻¹ (m); ¹H NMR (300 MHz, in $[D_7]DMF$, RT): $\delta =$ 7.13–7.93 (m, 30H; Ph), 4.45–4.47 (m, 4H), 4.14– 4.21 ppm (m, 2 H); $^{\rm 31}{\rm P}\{^{\rm 1}{\rm H}\}$ NMR (121 MHz, in [D₆]DMSO, RT): $\delta\!=$ 25.6 (m, 2 P; P_{out}) 22.2 ppm (m, 2 P; P_{in}), (${}^{2}J_{P_{in}P_{out}}$ = 54.79 Hz, ${}^{2}J_{P_{in}P_{in}}$ = 56.63 Hz, ${}^{4}J_{P_{out}P_{in'}} = 2.18$ Hz, ${}^{6}J_{P_{out}P_{out'}} = 0.15$ Hz, simulated by gNMR with AA'BB' system); ${}^{31}P{}^{1}H$ NMR (121 MHz, in [D₇]DMF, RT): $\delta =$ 25.1 (m, 2P; P_{out}) 20.5 ppm (m, 2P; P_{in}); ESI-MS (in DMF): *m/z*: 1520.730 [Au₄Cl₃(dpmppm)]⁺ (calcd: 1520.950), 1484.756 [Au₄Cl₂(dpmppm)–H]⁺ (calcd: 1484.973).

[Au₄Cl₄(*rac***-dpmppm)]-0.25 DMF-2 CH₂Cl₂ (3-0.25 DMF-2 CH₂Cl₂):** By a procedure similar to that for **2**, complex 3-0.25 DMF-2 CH₂Cl₂): By was obtained from *rac*-dpmppm (30 mg, 0.048 mmol) (yield: 70 mg, 95% vs. Au). Elemental analysis calcd (%) for C_{41.75}H_{41.75}N_{0.25}O_{0.25}P₄Cl₈Au₄ (1746.41): C 28.71, H 2.41, N 0.20; found: C 28.41, H 1.98, N 0.11; IR (KBr): $\tilde{\nu} = 1647$ (s, DMF), 1436 (s, P–C), 1104 (m), 796 cm⁻¹(m); ¹H NMR (300 MHz, in [D₆]DMSO, RT): $\delta =$ 7.26–8.07 (m, 30 H; Ph), 3.83–3.99 (m, 4 H; CH₂), 4.33–4.46 ppm (m, 2 H; CH₂); ³¹P{¹H} NMR (121 MHz, in [D₆]DMSO, RT): $\delta = 26.7$ (m, 2 P; P_{out}) 21.4 ppm (m, 2 P; P_{in}) (²J_{PmPout} = 56.66 Hz, ²J_{PmPin} = 48.01 Hz, ⁴J_{PoutPin} = 1.66 Hz, ⁶J_{PoutPint} = 0.05 Hz, simulated by gNMR with AA'BB' system).

syn-[Au₄(*meso*-dpmppm)₂CI]Cl₃·3H₂O (4a·3H₂O): *meso*-dpmppm (95 mg, 0.151 mmol) was added to a solution of [AuCl(PPh₃)] (150 mg, 0.303 mmol) in CH₂Cl₂ (10 mL), and the reaction mixture was stirred for 6 h at room temperature. The color of the solution changed from colorless to yellow and the solution was evaporated to dryness. After washing with diethyl ether, the residue was crystallized from an CH₂Cl₂/diethyl ether mixed solvent to afford pale yellow powder of 4a·3H₂O (110 mg, yield: 67%). Elemental analysis calcd (%) for C₇₈H₇₈O₃P₈Au₄Cl₄ (2240.92): C 41.81, H 3.51; found: C 41.60, H 3.90; IR (KBr pellet): v = 1436 (s, P–C), 1104 (w), 786 (w), 740 (s), 688 cm⁻¹ (s); ¹H NMR (300 MHz, CDCl₃, RT): $\delta = 7.07-7.87$ (m, 60H; Ph), 5.12–5.15 (br, 4H; CH₂), 4.52–4.63 (br, 4H; CH₂), 2.61 ppm (br, 4H; CH₂); ³¹P{¹H} NMR (121 MHz, CDCl₃, RT): $\delta = 33.1$

(m, 4P; P_{out}), 27.7 ppm (m, 4P; P_{inn}); ESI-MS (CH₂Cl₂): *m/z*: 2151.184 [Au₄(dpmppm)₂Cl₃]⁺ (calcd: 2151.126).

syn-[Au₄(meso-dpmppm)₂Cl][PF₆]₃·CH₂Cl₂ (4 b·CH₂Cl₂): mesodpmppm (115 mg, 0.183 mmol) and NH₄PF₆ (127 mg, 0.779 mmol) were added to a solution of [AuCl(PPh₃)] (150 mg, 0.303 mmol) in CH_2CI_2 (15 mL), and the reaction mixture was stirred for 6 h at room temperature. The solution was evaporated to dryness. After washing with diethyl ether, the residue was crystallized from an acetone/diethyl ether mixed solvent to afford pale yellow crystals of 4b·CH₂Cl₂ (90 mg, yield: 46%). Elemental analysis calcd (%) for C₇₉H₇₄P₁₁Au₄Cl₃F₁₈ (2600.34): C 36.49, H 2.87; found: C 36.78, H 2.79; IR (KBr pellet): $\tilde{\nu} = 1437$ (s, P–C), 1105 (m), 837 (s, P-F), 795 (m), 739 (s), 687 (s), 557 (s), 520 (m), 511 cm⁻¹ (m); UV/Vis (CH₂Cl₂): λ_{max} (ε) = 372 nm (2.32 \times 10⁴ L cm⁻¹ mol⁻¹); ¹H NMR (300 MHz, CD₂Cl₂, RT): δ = 7.86-7.95 (m, 60 H; Ph), 4.32-4.23 (br, 6 H; CH₂), 3.93 (br, 2 H; CH₂), 1.81 ppm (br, 4H; CH₂); ³¹P{¹H} NMR (121 MHz, CD₂Cl₂, RT): δ = 34.5 (m, 4P; P_{out}), 28.1 (m, 4P; P_{in}), -144.7 ppm (sept, 3P, $PF_{6'}$, ${}^{1}J_{PF} =$ 713 Hz); ESI-MS (CH₂Cl₂): *m/z*: 2369.227 [Au₄(dpmppm)₂Cl+2PF₆]⁺ (calcd: 2369.116), 1112.090 $[Au_4(dpmppm)_2CI + PF_6]^{2+}$ (calcd: 1112.076), 693.063 [Au₄(dpmppm)₂Cl]³⁺ (calcd: 693.062).

syn-[Au₄(meso-dpmppm)₂Cl][BF₄]₃ (4c): A procedure similar to that for **4b** using NH₄BF₄ was adopted for the preparation of **4c**. Crystallization from an acetone/diethyl ether mixed solvent afforded pale yellow powder of **4c** (yield: 47%). Elemental analysis calcd (%) for C₇₈H₇₂P₈Au₄B₃ClF₁₂ (2340.20): C 40.02, H 3.10; found: C 39.80, H 3.05; IR (KBr pellet): $\ddot{\nu} = 1437$ (s, P–C), 1103 (s), 1083 (s, B–F), 793 (m), 741 (s), 688 (s), 522 (m), 512 cm⁻¹ (m); UV/Vis (CH₂Cl₂): λ_{max} (ε) = 367 nm (1.95×10⁴ Lcm⁻¹ mol⁻¹); ¹H NMR (300 MHz, CD₂Cl₂, RT): δ = 7.84–7.12 (m, 60 H; Ph), 4.8–4.7 (br, 4H; CH₂), 4.4–4.2 (br, 5H; CH₂), 3.82 (br, 1H; CH₂), 1.73 ppm (br, 2H; CH₂); ³¹P{¹H} NMR (121 MHz, CD₂Cl₂, RT): δ = 34.0 (m, 4P; P_{out}), 27.8 ppm (m, 4P; P_{in}); ESI-MS (acetone): *m/z*: 2254.287 [Au₄(dpmppm)₂Cl+2BF₄]⁺ (calcd: 2254.198), 1083.093 ([Au₄(dpmppm)₂Cl]³⁺ (calcd: 693.062).

syn-[Au₄(meso-dpmppm)₂][PF₆]₄ (4d): AgPF₆ (49 mg, 0.19 mmol) was added to a solution of complex $4b \cdot CH_2CI_2$ (100 mg, $3.86 \times$ 10⁻² mmol) in acetone (10 mL), and the reaction mixture was stirred overnight. The solution was filtered and evaporated to dryness. The residue was crystallized from an acetone/diethyl ether mixed solvent to afford pale yellow crystals of 4d (85 mg, yield: 84%). Elemental analysis calcd (%) for C₇₈H₇₂P₁₂Au₄F₂₄ (2624.92): C 35.69, H 2.76; found: C 35.57, H 3.01; IR (KBr pellet): $\tilde{v} = 1438$ (s, P-C), 1105 (m), 837 (s, P-F), 793 (m), 738 (s), 687 (s), 557 (s), 521 (m), 512 cm^{-1} (m); UV/Vis (CH₂Cl₂): λ_{max} (ε) = 370 nm (3.23× $10^4 \text{ L cm}^{-1} \text{ mol}^{-1}$); ¹H NMR (300 MHz, [D₆]acetone, RT): $\delta = 7.93 - 7.11$ (m, 60 H; Ph), 4.92-4.89 (br, 6 H; CH₂), 4.45 (br, 4 H; CH₂), 3.68 ppm (br, 2H; CH_2); $^{\rm 31}{\rm P}\{^{\rm 1}{\rm H}\}$ NMR (121 MHz, [D_6]acetone, RT): $\delta\!=\!36.5$ (m, 4P; P_{out}), 32.3 (m, 4P; P_{in}), -144.4 ppm (sept, 4P; $PF_{6'}$ ¹ J_{PF} = 716 Hz); ESI-MS (acetone): m/z: 2479.163 $[Au_4(dpmppm)_2 + 3PF_6]^+$ (calcd: 2479.112), 1167.083 $[Au_4(dpmppm)_2 + 2PF_6]^{2+}$ (calcd: 1167.074), 729.736 [Au₄(dpmppm)₂ + PF₆]³⁺ (calcd: 729.727).

syn-[Au₄(meso-dpmppm)₂][BF₄]₄·CH₂Cl₂ (4e·CH₂Cl₂): AgBF₄ (48 mg, 0.25 mmol) was added to a solution of complex **4c** (130 mg, 5.5 × 10⁻² mmol) in CH₂Cl₂ (10 mL), and the reaction mixture was stirred overnight in the dark. The solution was filtered and addition of Et₂O at 5 °C gave pale yellow crystals of **4e**·CH₂Cl₂ (98 mg, yield: 72%). Elemental analysis calcd (%) for C₇₉H₇₄P₈Au₄F₁₆B₄Cl₂ (2477.21): C 38.30, H 3.01; found: C 38.61, H 3.15; IR (KBr pellet): $\tilde{\nu}$ = 1438 (s, P–C), 1104 (br), 1057 (br, B–F), 998 (br), 796 (m), 741 (s), 688 (s), 557 (s), 521 cm⁻¹ (m); UV/Vis (CH₃CN): λ_{max} (ε) = 368 nm (3.89× 10⁴ L cm⁻¹ mol⁻¹); ¹H NMR (300 MHz, CD₂Cl₂, RT): δ = 6.98–7.76 (m, 60H; Ph), 4.49–4.61 (br, 6H; CH₂), 3.98–4.03 (br, 4H; CH₂), 3.64–3.72 ppm (br, 2H; CH₂); ³¹P{¹H} NMR (121 MHz, CD₂Cl₂, RT): δ = 35.4

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 $\begin{array}{ll} (m, \, 4\,P; \, P_{out}), \, 31.3 \, ppm \, (m, \, 4\,P; \, P_{in}); \, ESI-MS \, (CH_2Cl_2): \, \textit{m/z:} \, 2304.906 \\ [Au_4(dpmppm)_2 + 3\,BF_4]^+ & (calcd: \, 2305.232), \quad 1108.964 \\ [Au_4(dpmppm)_2 + 2\,BF_4]^{2+} \, (calcd: \, 1109.114). \end{array}$

syn-[Au₄(meso-dpmppm)₂][TfO]₄·0.5 CH₂Cl₂ (4 f·0.5 CH₂Cl₂): NH₄OTf (99 mg, 0.59 mmol) was added to a solution of complex $4 b \cdot CH_2 CI_2$ (175 mg, 7.23×10^{-2} mmol) in CH₂Cl₂ (10 mL), and the reaction mixture was stirred overnight. The solution was filtered and evaporated to dryness. The residue was crystallized from a CH₂Cl₂/diethyl ether mixed solvent to afford pale yellow crystals of 4 f 0.5 CH₂Cl₂ (132 mg, yield: 69%). Elemental analysis calcd (%) for $C_{82.5}H_{73}O_{12}F_{12}P_8S_4ClAu_4$ (2683.81): C 36.92, H 2.74; found: C 36.87, H 2.58; IR (KBr pellet): $\tilde{\nu} = 1439$ (s, P–C), 1253 (br, C–F), 1160 (br, S= O), 1103 (m), 1028 (s), 792 (br), 741 (m), 689 (m), 518 cm⁻¹ (m); UV/ Vis (CH₂Cl₂): λ_{max} (ϵ) = 366 nm (1.17×10⁵ L cm⁻¹ mol⁻¹); (CH₃CN): λ_{max} (ε) = 373 (3.89×10⁴ L cm⁻¹ mol⁻¹); ¹H NMR (300 MHz, CD₂Cl₂, RT): $\delta = 6.97-7.79$ (m, 60 H; Ph), 4.85 (dt, J = 14, 4 Hz, 2 H; CH₂), 4.69 (d, J=14 Hz, 4 H), 4.26 (d, J=11 Hz, 4 H), 4.03 ppm (dt, J=14, 3 Hz, 2H; CH₂); ³¹P{¹H} NMR (121 MHz, CD₂Cl₂, RT): $\delta = 35.1$ (m, 4P; P_{out}), 31.3 ppm (m, 4P; P_{in}); ESI-MS (CH₂Cl₂): m/z: 2491.228 $[Au_4(dpmppm)_2 + 3TfO]^+$ (calcd: 2491.076), 2377.217 $[Au_4(dpmppm)_2 + Cl + 2\,TfO]^+$ (calcd: 2377.093), 1021.129 $[Au_4(dpmppm)_2 - 2H]^{2+}$ (calcd: 1021.102).

syn-[Au₄I₂(*meso*-dpmppm)₂][PF₆]₂·3.5 CH₂CI₂ (4 g·3.5 CH₂CI₂): KI (7.9 mg, 4.7×10^{-2} mmol) was added to a solution of complex 4b·CH₂Cl₂ (50.2 mg, 1.93×10^{-2} mmol) in a CH₂Cl₂/methanol mixed solvent. The color of solution gradually changed from yellow to orange. After stirring for 10 h, the solution was evaporated to dryness. The residue was crystallized from an acetone/diethyl ether mixed solvent to afford pale orange crystals of 4g·3.5CH₂Cl₂ (9.1 mg, yield: 18%). Elemental analysis calcd (%) for C₁₅₉H₁₅₀P₂₀Au₈Cl₆F₂₄I₄ (5433.77): C 35.15, H 2.78; found: C 34.96, H 2.68; IR (KBr pellet): $\tilde{\nu} = 1437$ (s, P–C), 1101 (m), 839 (s, P–F), 795 (m), 737 (s), 687 (s), 557 (s), 511 cm⁻¹ (m); UV/Vis (CH₂Cl₂): λ_{max} (ε) = 450 (1.25×10^4) , 362 (5.69×10^4) , 320 nm $(6.98 \times 10^4 \text{ Lcm}^{-1} \text{ mol}^{-1})$; ¹H NMR (300 MHz, CD₂Cl₂, RT): $\delta = 7.92-6.98$ (m, 60 H; Ph), 4.93-4.23 (m, 3H; CH₂), 4.67 (br, 1H; CH₂), 4.50 (br, 3H; CH₂), 4.26 ppm (br, 1 H; CH₂); ${}^{31}P{}^{1}H$ NMR (121 MHz, CD₂Cl₂, RT): $\delta = 29.0$ (m, 4 P; P_{out}), 22.0 (m, 4P; P_{in}), -144.5 ppm (sept, 2P; PF₆, ¹J_{PF}=708 Hz); ESI-MS (CH₂Cl₂): m/z: 2444.078 [Au₄l₂(dpmppm)₂+2PF₆]⁺ (calcd: 2443.946), 1149.059 [Au₄l₂(dpmppm)₂]²⁺ (calcd: 1149.014).

anti- $[Au_4(meso-dpmppm)_2]$ [PF₆]₄·3 CH₂Cl₂ (5 d·3 CH₂Cl₂): AgPF₆ (70 mg, 0.27 mmol), *meso*-dpmppm (28 mg, 4.4×10^{-2} mmol), and 2,6-xylyl isocyanide (22 mg, 0.17 mmol) were added to a suspension of 2 (66 mg, 4.2×10^{-2} mmol) in toluene (8 mL), and the reaction mixture was stirred overnight in the dark. The solution was filtered and evaporated to dryness. The residue was crystallized from a CH₂Cl₂/diethyl ether mixed solvent at 4°C to yield pale greenish yellow crystals of 5d·3CH₂Cl₂ (35 mg, yield: 29%). Elemental analysis calcd (%) for C₈₁H₇₈P₁₂Au₄F₂₄Cl₆ (2879.72): C 33.78, H 2.73; found: C 33.79, H 2.83; IR (KBr pellet): v=1485 (w), 1439 (s, P-C), 1297 (br), 1133 (w), 1106 (m), 841 (s, P-F), 740 (m), 688 (m), (w); UV/Vis (CH₂Cl₂): λ_{max} (ε) = 387 nm 558 cm^{-1} (1.29× $10^{5} L cm^{-1} mol^{-1}$), (CH₃CN): λ_{\max} $(\varepsilon) = 383 \text{ nm}$ (9.55× $10^4 \text{ L cm}^{-1} \text{ mol}^{-1}$); ¹H NMR (300 MHz, CD₂Cl₂, RT): δ = 7.62–6.83 (m, 60 H; Ph), 4.68 (d, J=15 Hz, 4H; CH₂), 4.59 (d, J=16 Hz, 2H; CH₂), 4.35 (br, 2 H; CH_2), 4.09 ppm (br, 4 H; CH_2); $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CD_2Cl_2, RT): $\delta\!=\!35.6$ (m, 4P; P_{out}), 35.2 (m, 4P; P_{in}), -143.9 \, ppm (sept, 4P; PF_{6} , ${}^{1}J_{PF} = 712 \text{ Hz}$); ESI-MS (CH₂Cl₂): m/z: 2477.627 $[Au_4(dpmppm)_2 + 3PF_6 - H]^+$ 2478.104), 1166.345 (calcd: $[Au_4(dpmppm)_2 + 2PF_6 - 3H]^{2+1}$ (calcd: 1166.570), 1093.390 $[Au_4(dpmppm)_2 + PF_6 - 4H]^{2+}$ (calcd: 1093.539), 1020.641 $[Au_4(dpmppm)_2 - 5H]^{2+}$ (calcd: 1020.598).

anti-[Au₄(meso-dpmppm)₂][BF₄]₄ (5e): AgBF₄ (70 mg, 0.36 mmol), meso-dpmppm (38 mg, 6.0×10^{-2} mmol), and 2,6-xylyl isocyanide (34 mg, 0.26 mmol) were added to a suspension of ${\bf 2}$ (93 mg, 6.0 \times 10⁻² mmol) in toluene (10 mL), and the reaction mixture was stirred overnight in the dark. The solution was filtered and evaporated to dryness. The residue was crystallized from a CH₂Cl₂/diethyl ether mixed solvent at 4 °C to yield pale greenish yellow crystals of 5e (37 mg, yield: 25%). Elemental analysis calcd (%) for C₇₈H₇₂P₈Au₄B₄F₁₆ (2392.28): C 39.16, H 3.03; found: C 38.33, H 2.86; IR (KBr pellet): $\tilde{v} = 1485$ (w), 1438 (s, P–C), 1375 (w), 1083 (br, B–F), 806 (m), 740 (s), 688 (s), 523 cm⁻¹ (m); UV/Vis (CH₂Cl₂): λ_{max} (ε) = 387 nm (6.46 × 10⁴ L cm⁻¹ mol⁻¹); UV/Vis (CH₃CN): λ_{max} (ϵ) = 382 nm (6.76 \times 10⁴ L cm $^{-1}$ mol $^{-1}$); 1 H NMR (300 MHz, CD $_{2}$ Cl $_{2}$, RT): δ = 6.78 -7.71 (m, 60H; Ph), 4.94 (m, 2H; CH₂), 4.85 (d, J=17 Hz, 4H; CH₂), 4.30 (br, 2H; CH₂), 4.08 ppm (br, 4H; CH₂); ³¹P{¹H} NMR (121 MHz, CD_2CI_2 , RT): $\delta = 36.1$ (m, 4P; P_{out}), 35.0 ppm (m, 4P; P_{in}); ESI-MS (CH_2CI_2) : m/z: 2303.834 $[Au_4(dpmppm)_2 + 3BF_4 - H]^+$ (calcd: 2304.221), 1108.416 $[Au_4(dpmppm)_2 + 2BF_4 - 4H]^{2+}$ (calcd: 1108.608), 1064.435 $[Au_4(dpmppm)_2 + BF_4 - 4H]^{2+}$ (calcd: 1064.603), $1020.641 [Au_4(dpmppm)_2 - 5 H]^{2+}$ (calcd: 1020.598).

anti-[Au₄(meso-dpmppm)₂][TfO]₄·0.5 Et₂O (5 f·0.5 Et₂O): AgOTf (80 mg, 0.31 mmol), meso-dpmppm (32 mg, 5.1×10⁻² mmol), and 2,6-xylyl isocyanide (31 mg, 0.24 mmol) were added to a suspension of 2 (80 mg, 5.2×10^{-2} mmol) in toluene (8 mL), and the reaction mixture was stirred overnight in the dark. The solution was filtered and evaporated to dryness. The residue was crystallized from a CH₂Cl₂/diethyl ether mixed solvent at 4°C to yield pale greenish yellow, needle crystals of 5 f 0.5 Et₂O (16 mg, yield: 11 %). Elemental analysis calcd (%) for $C_{84}H_{77}O_{12.5}P_8S_4Au_4F_{12}$ (2678.40): C 37.67, H 2.90. found: C 37.83, H 2.78; IR (KBr pellet): $\tilde{\nu} = 1486$ (w), 1438 (s, P-C), 1259 (br, OTf), 1161 (br, OTf), 1105 (m), 1029 (m), 804 (m), 741 (m), 688 (m), 637 (s), 522 cm⁻¹ (m); UV/Vis (CH₂Cl₂): λ_{max} (ε) = 389 nm (7.18 \times 10⁴ L cm $^{-1}$ mol $^{-1}$); UV/Vis (CH₃CN): $\lambda_{\rm max}$ (ε) = 378 nm (4.47 $\times\,10^4\,L\,cm^{-1}\,mol^{-1}$); $\,^1\text{H}$ NMR (300 MHz, $\,\text{CD}_2\text{Cl}_2$, RT): $\delta\,{=}\,7.65{-}$ 6.82 (m, 60H; Ph), 4.89-4.86 (br, 4H; CH₂), 4.31-4.28 (br, 4H; CH₂), 0.9 ppm (br, 4H; CH₂); ${}^{31}P{}^{1}H{}$ NMR (121 MHz, CD₂Cl₂, RT): $\delta =$ 35.8 ppm (m, 8P; P_{outin}); ESI-MS (CH₂Cl₂): m/z: 2489.526 $[Au_4(dpmppm)_2 + 3 OTf - 2H]^+$ (calcd: 2489.060), 1170.326 $[Au_4(dpmppm)_2 + 2 OTf - 4 H]^{2+1}$ (calcd: 1170.054), 1095.395 $[Au_4(dpmppm)_2 + OTf - 4H]^{2+}$ (calcd: 1095.578), 1020.641 $[Au_4(dpmppm)_2 - 5H]^{2+}$ (calcd: 1020.598).

syn-[Au₄(rac-dpmppm)₂Cl₂]Cl₂·1.5 CH₂Cl₂ (6 a · 1.5 CH₂Cl₂): [AuCl(PPh₃)] (84 mg, 0.17 mmol) was added to a solution of racdpmppm (50 mg, 0.080 mmol) in CH₂Cl₂ (10 mL) and the reaction mixture was stirred for 12 h at room temperature, resulting in a pale yellow suspension. The solution was evaporated to dryness. After washing with diethyl ether, the residue was crystallized from a concentrated CH₂Cl₂ solution at 4°C to afford pale yellow crystals of **6a**·1.5 CH₂Cl₂ (60 mg, yield: 62%). Elemental analysis calcd (%) for $C_{79.5}H_{75}P_8Au_4Cl_7$ (2314.27): C 41.26, H 3.27; found: C 41.22, H 2.89; IR (KBr pellet): $\tilde{\nu} = 1436$ (s, P–C), 1103 (s), 798 (br), 742 (m), 692 cm $^{-1}$; UV/Vis (CH_2CI_2) : λ_{\max} $(\varepsilon) = 375 \text{ nm}$ $(3.40 \times$ $10^4 \text{ L cm}^{-1} \text{ mol}^{-1}$; ¹H NMR (300 MHz, [D₆]DMSO, RT): $\delta = 7.24-8.06$ (m, 60 H; Ph), 4.65 (d, J = 14 Hz, 4H; CH₂), 4.20 (br s, 4H; CH₂), 3.47 ppm (m, 4H; CH₂); ${}^{31}P{}^{1}H$ NMR (121 MHz, [D₆]DMSO, RT): $\delta =$ 32.5 (m, 4P; Pout), 28.1 ppm (m, 4P; Pin); ESI-MS (CH2Cl2): m/z: 2151.415 $[Au_4(dpmppm)_2 + 3Cl]^+$ (calcd: 2151.126), 1021.185 $[Au_4(dpmppm)_2 - 2H]^{2+}$ (calcd: 1021.102).

syn-[Au₄(rac-dpmppm)₂Cl₂][PF₆]₂·4 CH₂Cl₂ (6b·4 CH₂Cl₂): [AuCl(tht)] (34 mg, 0.10 mmol) and NH₄PF₆ (46 mg, 0.28 mmol) were added to a solution of *rac*-dpmppm (35 mg, 0.055 mmol) in CH₂Cl₂ (5 mL) and the reaction mixture was stirred for 12 h at room temperature. The solution was evaporated to dryness. After washing with diethyl

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ether, the residue was crystallized from a concentrated CH₂Cl₂ solution at 4°C to afford pale yellow crystals of **6b**·4CH₂Cl₂ (28 mg, yield: 47%). Elemental analysis calcd (%) for C₈₂H₈₀P₁₀Au₄Cl₁₀F₁₂ (2745.63): C 35.85, H 2.94; found: C 35.97, H 2.60; IR (KBr pellet): $\tilde{\nu} = 1485$ (w), 1438 (s, P–C), 1104 (s), 841 (s, P–F), 797 (m), 741 (m), 689 (m), 557 (s), 521 cm⁻¹ (w); UV/Vis (CH₂Cl₂): λ_{max} (ε) = 367 nm (1.50×10⁴ L cm⁻¹ mol⁻¹); ¹H NMR (300 MHz, CD₂Cl₂, RT): δ = 7.23–7.92 (m, 60 H; Ph), 3.15 (br, 4H; CH₂), 3.90 (br, 4H; CH₂), 3.0–3.7 ppm (br, 4H; CH₂); ³¹P{¹H} NMR (121 MHz, CD₂Cl₂, RT): δ = 31.90 (m, 4P; P_{out}), 27.2 (m, 4P; P_{in}), -144.3 ppm (sept, 3P; PF₆, ¹J_{PF}= 713 Hz); ESI-MS (CH₃OH): *m/z*: 1020.424 [Au₄(dpmppm)₂–5H]²⁺ (calcd: 1020.598).

syn-[Au₄(rac-dpmppm)₂Cl₂][BF₄]₂·CH₂Cl₂ (6 c·CH₂Cl₂): [AuCl(tht)] (31 mg, 0.097 mmol) and NH_4BF_4 (29 mg, 0.28 mmol) were added to a solution of rac-dpmppm (35 mg, 0.055 mmol) in CH₂Cl₂ (7 mL) and the reaction mixture was stirred for 12 h at room temperature. The solution was evaporated to dryness. After washing with diethyl ether, the residue was crystallized from a concentrated CH₂Cl₂ solution at 4°C to afford pale yellow crystals of 6c·CH₂Cl₂ (35 mg, yield: 63%). Elemental analysis calcd (%) for $C_{79}H_{74}P_8Au_4Cl_4B_2F_8$ (2374.51): C 39.96, H 3.14; found: C 40.14, H 2.95; IR (KBr pellet): $\tilde{\nu} = 1483$ (w), 1437 (s, P–C), 1104 (m), 1062 (br, BF₄), 798 (m), 744 (m), 690 (m), 523 (w), 513 cm⁻¹ (w); UV/Vis (CH₂Cl₂): λ_{max} (ε) = 369 nm (2.82×10⁴ L cm⁻¹ mol⁻¹); UV/Vis (CH₃CN): λ_{max} (ϵ) = 370 nm (3.71 $\times\,10^4\,L\,cm^{-1}\,mol^{-1}$); $\,^1\text{H}$ NMR (300 MHz, CD_2Cl_2, RT): $\delta\!=\!7.21\text{--}$ 8.01 (m, 60H; Ph), 4.33-4.45 (m, 4H; CH₂), 3.93-3.97 (m, 4H; CH₂), 3.41–3.52 ppm (m, 4H; CH₂); ³¹P{¹H} NMR (121 MHz, CD₂Cl₂, RT): $\delta = 31.6$ (m, 4P; P_{out}), 26.3 ppm (m, 4P; P_{in}); ESI-MS (CH₃OH): *m/z*: 2179.748 $[Au_4(dpmppm)_2 + 2CI + BF_4 - H]^+$ (calcd: 2200.153), 1020.424 [Au₄(dpmppm)₂-5 H]²⁺ (calcd: 1020.598).

syn-[Au₄(*rac*-dpmppm)₂][PF₆]₄ (6d): NH₄PF₆ (136 mg, 0.83 mmol) was added to a solution of 6f (28 mg, 0.010 mmol) in acetone(15 mL), and the mixture was stirred at room temperature for 12 h. The solvent was then removed under reduced pressure and the residue was extracted with CH_2CI_2 (10 mL) and H_2O (10 mL). The organic layer was separated and concentrated to dryness, which was dissolved again in acetone (7 mL) and dried over Na₂SO₄. The solution was filtered and concentrated, and was allowed to stand at 4°C after addition of diethyl ether, to afford pale yellow crystals of 6d (9.3 mg, yield: 35%). Elemental analysis calcd (%) for $C_{78}H_{72}P_{12}Au_4F_{24}$ (2624.92): C 35.69, H 2.76; found: C 35.79, H 2.44; IR (KBr pellet): $\tilde{\nu} = 1485$ (w), 1439 (s, P–C), 1104 (s), 842 (s, P– F), 799 (m), 741 (m), 688 (m), 558 cm⁻¹ (s); UV/Vis (CH₂Cl₂): λ_{max} $(\varepsilon) = 358 \text{ nm} (3.39 \times 10^4 \text{ L cm}^{-1} \text{ mol}^{-1}); {}^{1}\text{H NMR} (300 \text{ MHz}, [D_{e}]\text{DMSO},$ RT): $\delta =$ 7.30–7.91 (m, 60 H; Ph), 4.88–4.92 (br, 4H; CH₂), 4.25 (br s, 4H; CH₂), 3.23-3.26 ppm (br, 4H; CH₂); ³¹P{¹H} NMR (121 MHz, [D₆]DMSO, RT): $\delta\!=\!$ 34.8 (m, 4P; P_{out}), 32.9 (m, 4P; P_in), -143.0~ppm(sept, 4P; PF₆, ¹J_{PF}=713 Hz); ESI-MS (CH₂Cl₂): *m/z*: 2479.262 $[Au_4(dpmppm)_2 + 3PF_6]^+$ (calcd: 2479.112), 2369.133 $[{\rm Au}_4({\rm dpmppm})_2 + {\rm CI} + 2\,{\rm PF}_6]^+$ (calcd: 2369.117), 1021.121 [Au₄(dpmppm)₂]²⁺ (calcd: 1021.102).

syn-[Au₄(*rac*-dpmppm)₂][BF₄]₄·CH₂Cl₂ (6e·CH₂Cl₂): NH₄BF₄ (97 mg, 0.92 mmol) was added to a solution of **6f** (24 mg, 0.0089 mmol) in acetone (10 mL), and the mixture was stirred at room temperature for 12 h. The solvent was then removed under reduced pressure and the residue was extracted with CH₂Cl₂ (8 mL) and H₂O (5 mL). The organic layer was separated and concentrated to dryness, which was dissolved again in acetone (7 mL) and dried over Na₂SO₄. The solution was filtered and concentrated, and was allowed to stand at 4 °C after addition of diethyl ether, to afford pale yellow crystals of **6e**·CH₂Cl₂ (7.0 mg, yield: 32%). Elemental analysis calcd (%) for C₇₉H₇₄P₈Au₄Cl₂B₄F₁₆ (2477.21): C 38.30, H 3.01; found: C 38.18, H 3.12; IR (KBr pellet): $\tilde{\nu} = 1485$ (w), 1438 (s, P–C), 1054 (br,

 $\begin{array}{l} \mathsf{BF}_4 \mbox{, 797 (m), 743 (m), 689 cm^{-1} (m); UV/Vis (CH_2Cl_2): λ_{max} ($$\epsilon$) = $359 nm (4.17 \times 10^4 L cm^{-1} mol^{-1}); 1H NMR (300 MHz, [D_6]DMSO, RT): δ = $7.30 - 7.93 (m, 60 H; Ph), 4.90 (br, 4 H; CH_2), 4.27 (br s, 4 H; CH_2), $3.21 ppm (br, 4 H; CH_2); $^{31}P{}^1$H NMR (121 MHz, [D_6]DMSO, RT): δ = $34.8 (m, 4 P; P_{out}), $32.8 ppm (m, 4 P; P_{inn}); $ESI-MS (CH_3CN): m/z: $2305.224 [Au_4(dpmppm)_2 + 3 BF_4]^+$ (calcd: $2305.232), $1021.097 [Au_4(dpmppm)_2 - 2 H]^{2+}$ (calcd: $1021.102). $ \end{array}$

syn-[Au₄(rac-dpmppm)₂][TfO]₄·0.5 CH₂Cl₂ (6 f·0.5 CH₂Cl₂): [AuCl(tht)] (35 mg, 0.108 mmol) and NH₄OTf (49 mg, 0.29 mmol) were added to a solution of rac-dpmppm (34 mg, 0.055 mmol) in CH₂Cl₂ (10 mL) and the reaction mixture was stirred for 12 h at room temperature. The solution was evaporated to dryness. After washing with diethyl ether, the residue was crystallized from a concentrated CH₂Cl₂ solution at 4 °C to afford pale yellow needle crystals of 6 f 0.5 CH₂Cl₂ (12 mg, yield: 17%). Elemental analysis calcd (%) for $C_{82.5}H_{73}O_{12}F_{12}S_4P_8Au_4CI$ (2683.81): C 36.92, H 2.74; found: C 36.92, H 2.93; IR (KBr pellet): $\tilde{\nu} =$ 1438 (s, P–C), 1255 (br, OTf), 1160 (br, OTf), 1104 (m), 1029 (s), 800 (m), 742 (m), 689 (m), 636 cm⁻¹ (s); UV/Vis (CH₂Cl₂): λ_{max} (ε) = 360 nm (8.91 × 10⁴ L cm⁻¹ mol⁻¹); UV/Vis (CH₃CN): λ_{max} (ϵ) = 356 nm (5.45 × 10⁴ L cm⁻¹ mol⁻¹); ¹H NMR (300 MHz, CD_2Cl_2 , RT): δ = 7.19–8.00 (m, 60 H; Ph), 4.665 (br, 4 H; CH₂), 4.34–4.38 (m, 4H; CH₂), 3.64–3.67 ppm (m, 4H; CH₂); ³¹P{¹H} NMR (121 MHz, CD_2CI_2 , RT): $\delta = 35.5$ (m, 4P; P_{out}), 31.1 ppm (m, 4P; P_{in} ; ESI-MS (CH₂Cl₂): m/z: 2489.438 [Au₄(dpmppm)₂+3OTf-2H]⁺ (calcd: 2489.060)), 1170.305 $[Au_4(dpmppm)_2 + 2OTf - 4H]^{2+}$ (calcd: 1170.054), 1095.375 [Au₄(dpmppm)₂+OTf-4H]²⁺ (calcd: 1095.578), 1020.443 $[Au_4(dpmppm)_2 - 5H]^{2+}$ (calcd: 1020.598).

X-ray crystallographic analyses of 1, 2, 4e, 4f, 5d–5f, 6a–6c, 6e, and 6f

Crystals of 1, 2, 4e,f, 5d-f, 6a-c, 6e, and 6f were quickly coated with Paratone N oil and mounted on top of a loop fiber at room temperature. The X-ray reflection data were measured with a Rigaku VariMax Mo/Saturn CCD diffractometer equipped with graphite-monochromated confocal $Mo_{K\alpha}$ radiation using a rotatinganode X-ray generator RA-Micro7 (50 kV, 24 mA). Crystal and experimental data are summarized in Tables S1-S3 in the Supporting Information. All data were collected at $-120\,^\circ\text{C}$ and a total of 2160 oscillation images, covering a whole sphere of $6 < 2\theta < 55^{\circ}$, were corrected by the ω -scan method (-62 < ω < 118°) with $\Delta \omega$ of 0.25°. The crystal-to-detector (70×70 mm) distance was set at 60 mm. The data were processed using the Crystal Clear 1.3.5 program (Rigaku/MSC)^[26] and corrected for Lorentz-polarization and absorption effects.^[27] The structures of complexes were solved by direct methods with SHELXS-97^[28] and were refined on F^2 with fullmatrix least-squares techniques with SHELXL-97^[28] using the Crystal Structure 3.7 package.^[29] All non-hydrogen atoms were refined with anisotropic thermal parameters, and the C-H hydrogen atoms were calculated at ideal positions and refined with riding models. In both the structures of 1 and 4e, a solvent molecule of crystallization is disordered (DMF for 1 and CH₂Cl₂ for 4e). All calculations were carried out on a Windows PC with Crystal Structure 3.7 package.^[29] The crystal data for **4b**, **4d**, and **4g** were already reported.^[11a]

CCDC-959320 (1), CCDC-959321 (2), CCDC-959322 (4e), CCDC-959323 (4 f), CCDC-959324 (5 d), CCDC-959325 (5 e), CCDC-959326 (5 f), CCDC-959327 (6 a), CCDC-959328 (6 b), CCDC-959329 (6 c), CCDC-959330 (6 e), and CCDC-959331 (6 f) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Theoretical calculations

Gas-phase DFT calculations were performed on model compounds (M4-M6) using the MPWPW91^[15] functions with Stuttgart-Dresden ECP basis set, SDD (the 19-valence electron Woodpseudopotentials Boring guasirelativistic were used for Au).^[16] The DFT optimization were carried out on the models, syn- $[Au_4(meso-H_2PCH_2P(H)CH_2P(H)CH_2PH_2)_2]^{4+}$ (**M 4**), anti- $[Au_4(meso-H_2PCH_2P(H)CH_2PH_2)_2]^{4+}$ $H_2PCH_2P(H)CH_2P(H)CH_2PH_2)_2]^{4+}$ (M 5), and svn-[Au₄(rac- $H_2PCH_2P(H)CH_2P(H)CH_2PH_2)_2]^{4+}$ (M6), the initial coordinates being derived from the crystal structures of 4d, 5e, and 6e by replacing phenyl groups by hydrogen atoms. TD-DFT calculations^[30] were also performed with the optimized structures. The lowest triplet (T₁) excited states for M4–M6 were analyzed by DFT optimizations with the unrestricted MPWPW91/SDD methods.

Geometry optimizations and frequency analyses for the complexes (4d, 5e and 6e) of the singlet (S_0) and the triplet (T_1) states were carried out by the DFT method with B3LYP^[19] functional set and Grimme's D2 empirical dispersion (B3LYP-D)^[20] parameter. The polarizable continuum model (PCM)^[22] was employed for all calculations to approximate the solvent (CH₂Cl₂). For the geometry optimization, the basis set that consists of the effective core potential (ECP) of LANL2TZ(f)^[21] and 6–31G* for Au and other atoms, respectively was employed. All optimized structures were verified that they did not have any negative frequencies. After the geometry optimizations, the single-point calculations and the time-dependent DFT (TD-DFT) calculations were carried out with the larger basis set that consisted of LANL2TZ(f) and $6-31+G^*$ for Au and other atoms, respectively. To examine absorption spectra of the complexes, ten excited states $(\mathsf{S}_1 \text{-} \mathsf{S}_{10})$ were calculated by TD-DFT calculations with B3LYP functional set at the optimized S₀ structures. The emission energy was estimated by both ΔSCF and TD-DFT calculations with B3LYP-D functional set at the optimized triplet (T₁) structures. The atomic charges were calculated by population analyses of Mulliken^[31] and Hirshfeld^[32] methods with the B3LYP functional set. All calculations were carried out on a UNIX Station with Gaussian 03/09 program packages.^[33]

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