

Diarsine Ligands Dinuclear Gold(I) Chloride Complexes with Diarsine Ligands

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Abstract: Recently, we have developed synthetic methods for preparing diarsenic ligands. Herein, dinuclear gold(I) chloride complexes with various kinds of diarsenic ligands [Au₂Cl₂(diars)] were synthesized (diars = dpae, dpap, dpab, *cis*-dpav, *trans*-dpav, dpapz, and dpaq). X-ray crystallography revealed that they can form intra- or intermolecular aurophilic interactions depending on the ligand structure except for dpab. Crystal polymorphs of Au₂Cl₂(dpae) and Au₂Cl₂(dpap) were observed

Introduction

Trivalent arsenic atom has soft Lewis basicity, large atomic size, weak σ -donation, and high air-stability, when compared with phosphorus one.^[1] Accordingly, transition metal complexes with arsenic ligands can show excellent functions and interesting behaviors as catalyst,^[2] luminophore,^[3] stimuli-responsive material,^[4] etc. Gold(I) complexes with arsenic ligands in particular have unique structures and properties because the soft Lewis basicity of arsenic atom can enhance Au---Au interactions, called aurophilic interactions.^[5] Aurophilic interaction often exhibits phosphorescence due to $5d\sigma^*$ -6p σ electron transition, which is dependent on the Au---Au distance. Since bonding energy of aurophilic interaction is comparable to that of hydrogen bond, external stimuli can induce elongation, shortening, formation, or cleavage of Au---Au bonds to cause emission color change.^[6] Aurophilic networks are thus promising candidates as stimuli-responsive materials. Since bidentate ligand structure is suitable for construction of intra- and/or intermolecular aurophilic interactions, some bidentate arsenic ligands have been applied for aurophilic architectures.[3a,3e,3f,4c,7] Gold(I) halide (AuX, X = CI, Br, I) complexes with 1,2-bis(diphenylarsanyl)ethane (dpae) varies luminescent properties depending on crystal polymorphs.^[3a] We also previously reported that one-dimensional aurophilic chains of AuCl complexes are supported by 1,4-dihydro-1,4-diarsinines, and the substituents of the ligands

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because of the flexible alkylene linkers of the diarsine ligand. The emission behaviors of the complexes were drastically changed by the ligands, which should affect the energy barrier for internal conversion from the intraligand excitation state to the halide-to-ligand charge transfer one. Some of the complexes accordingly showed luminescent mechanochromism and/or thermochromism.

highly affect the electron transition energies via conformational change. $^{\rm [4c,7]}$

Despite the pioneering works, structures and properties of gold(I) complexes with bidentate arsenic ligands have never been systematically studied because of a lack of practical synthetic methods for organoarsenic compounds. That is, there is a serious concern to the danger of arsenic precursors such as arsenic hydrides or chlorides, which were miserably misused as chemical weapons. To address this issue, we have developed practical synthetic routes that employ only non-volatile arsenic precursors.^[8] Cyclooligoarsines, which can be readily prepared from inorganic arsenic precursors,^[9] are key intermediates for these strategies. Their As–As bonds are cleaved to generate various reactive species such as radical,^[10] electrophile,^[11] and nucleophile.^[12] The subsequent As–C bond formation reactions efficiently produce various organoarsenic compounds.

We recently reported bidentate arsenic ligand library by fully utilizing our synthetic protocols, and the ligands were applied to Suzuki–Miyaura coupling reaction to elucidate the structurecatalytic activity relationships.^[13] In this work, we prepared bidentate ligands with flexible (dpae, dpap, and dpab) or rigid (*cis*-dpav, *trans*-dpav, dpapz, and dpaq) linkers as summarized in Scheme 1. The dinuclear AuCl complexes with these ligands were synthesized and the structures were analysed by X-ray crystallography. The relationship between structures and luminescent behaviors were studied. This is the first systematic study on AuCl complexes with arsenic ligands.



Scheme 1. Chemical structures of bidentate arsenic ligands examined in the present work.



Results and Discussion

Bidentate arsenic ligands were synthesized following the literature procedure (Scheme 2).^[12,13] Diphenylarsanyllithium (Ph₂AsLi) was generated from hexaphenylhexaarsine (As₆Ph₆) and phenyllithium (PhLi). Without isolation, the solution of Ph₂AsLi was utilized for the substitution reaction with alkyl, vinyl, or aryl dichlorides to give corresponding bidentate ligands. The newly synthesized ligands, *trans*-dpav and dpapz, were characterized by NMR spectroscopy, high resolution mass analysis, and single-crystal X-ray diffraction analysis.



Scheme 2. Syntheses of bidentate arsenic ligands. The isolated yields of dpae, dpap, dpab, *cis*-dpav, and dpaq were cited from previous papers.^[12,13]

The gold(I) metalation of the diarsine ligands afforded adduct complexes Au₂Cl₂(diars). The coordination was confirmed by NMR spectroscopy; the signals were shifted to lower magnetic field because of lowering the electron density by the coordination. The obtained complexes were recrystallized by slow mixing of a solution (dichloromethane or chloroform) and poor solvent (methanol or hexane). The ligands with flexible linker, i.e., dpae, and dpap, tended to give polymorphs, whereas only one type of crystalline structure was obtained in the cases of those with rigid one.

The single crystals were fabricated for X-ray diffraction (XRD) analysis. The results of the analyses are summarized in Table 1. The gold(I) formed linear coordination considering the wide As–Au–Cl angles [> $171.9(2)^{\circ}$]. There are negligible differences in coordination bond lengths for Au–As and Au–Cl, implying that coordination abilities including σ -donation and π -accept-

ance of the ligands were quite similar. It is thus evident that the series of the arsenic ligands are suitable for studying structural effects of ligand backbone on aurophilic interactions without changing the electron density on the gold(I) center. The ligand structure drastically affected the form of aurophilic interactions. Unlikely to the others, Au₂Cl₂(dpab) had no aurophilic interactions in the crystalline state (Figure 1); the nearest intraand intermolecular Au-Au distances were 8.612(3) and 5.788(2) Å, respectively. This is probably because the competing intermolecular interactions such as hydrogen bondings [2.900(4) Å] and CH– π interactions (2.980 Å) were formed instead of aurophilic interaction.



Figure 1. Results of X-ray crystallography of Au₂Cl₂(dpab). (a) Intramolecular Au···Au distance. (b) Intermolecular Au···Au distance and selected intermolecular interactions such as hydrogen bond and CH– π interaction. Red dot represents the centroid of the benzene ring.

Intermolecular aurophilic interactions were observed for the ligands with flexible linkers such as dpae and dpap, and they offered polymorphs to their Au₂Cl₂(diars) complexes. The crystal polymorphs of Au₂Cl₂(dpae) was reported by the Balch's group; the space groups of the crystals that they obtained were $P2_1/c$ and P1.^[3a] On the other hand, the results of our present analyses showed $P2_1/c$ [α -Au₂Cl₂(dpae)] and $C2/_c$ [β -Au₂Cl₂(dpae)] space groups. While the formar corresponds to the Balch's report, the latter should be the third polymorphic form. The packing structures of α - and β -Au₂Cl₂(dpae) were completely different. In the α -form, dimerization occurred via intermolecular aurophilic interactions (Figure 2a), while 1D-polymers were formed in the β -one (Figure 2b). On the other hand, α -Au₂Cl₂(dpap) (space group: P2₁/c) and β -Au₂Cl₂(dpap) (space group: Pbcn) were composed of 1D-polymers through intermolecular aurophilic interactions with similar bond lengths, bond angles, and torsion angles (Figure 2c and Figure 2d).

The complexes with the rigid ligands did not show crystal polymorphs in contrast to those with flexible ones. (Figure 3). The *cis*- or *ortho*-linked ligands, i.e., *cis*-dpav, dpapz, and dpaq,

Table 1. Selected bond length [Å] and angles [°] of Au₂Cl₂(diars) complexes.

As-Au-Cl
07 69(3)
97.00(J)
116.07(3)
119.61(5)
117.49(3)
-
50.6(1)
94.88(3)
60.62(2)
63.13(2)

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Figure 3. Results of X-ray crystallography of (a) $Au_2Cl_2(cis-dpav)$, (b) $Au_2Cl_2(trans-dpae)$, (c) $Au_2Cl_2(dpapz)$, and (d) $Au_2Cl_2(dpaq)$. Intra- and intermolecular Au--Au distances are displayed.

Figure 2. Results of X-ray crystallography of (a) α -Au_2Cl_2(dpae), (b) β -Au_2Cl_2(dpae), (c) α -Au_2Cl_2(dpap), and (d) β -Au_2Cl_2(dpap). Intermolecular Au--Au distances are displayed.

supported intramolecular aurophilic interactions because the coordination directions of the ligands were fixed by the vinylene or arylene linkers. The Au···Au distances of the complexes were similar to each other; Au₂Cl₂(*cis*-dpav): 3.079(1) Å, Au₂Cl₂(dpapz): 2.965(1) Å, and Au₂Cl₂(dpaq): 2.9784(5) Å. On the other hand, 1D-polymer was formed for Au₂Cl₂(*trans*-dpav) via intermolecular aurophilic interactions. The Au···Au distance [3.025(1) Å] was similar to those of other complexes with the rigid ligands.

We then examined photoluminescence (PL) properties of the obtained Au₂Cl₂(diars) complexes in the solid-states. Generally, origins of emission of dinuclear gold(I) complexes are classified into two triplet excitation states. In reference to the detailed discussion on Au₂I₂ complexes with diphosphine ligands,^[14] the low-energy (LE) one has contribution of halide and metal-centered and halide-to-ligand charge transfer [3(X+M)C/3XLCT] excitation states, and the high-energy (HE) emission is attributed to intraligand ${}^{3}\pi\pi^{*}$ excitation state. There is energy barrier for internal conversion form the ${}^{3}\pi\pi^{*}$ excitation state to the ³(X+M)C/³XLCT one. Accordingly, the HE emission is favorable at lower temperature, while the LE emission is favorable at higher temperature. It is notable that energy level of the ³(X+M)C/ ³XLCT excitation state is affected by the Au-Au distance, meaning that mechanical stimuli such as grinding can change color of the LE emission. It has been reported that through crystalto-amorphous transition, HE emission is weakened and LE one is enhanced gradually as grinding time is longer.^[15] Herein, the PL spectra were measured at room temperature and 77 K for the crystalline and amorphous samples; the amorphous samples were prepared by grinding crystalline ones in a mortar. In addition, the PL spectra of the bare ligands were also measured for understanding the origins of the emissions (Figure S15).

Initially, we investigated Au₂Cl₂(dpae) (Figure 4a and 4b). In the α -form, the HE emission of Au₂Cl₂(dpae) at 77 K was observed around 489 nm, while the LE emission appeared around 723 nm at room temperature (Figure 4a). On the other hand, β -Au₂Cl₂(dpae) showed dual emission due to the ${}^{3}\pi\pi^{*}$ (485 nm) and ³(X+M)C/³XLCT (700-770 nm) excitation states except for the ground sample at room temperature (Figure 4b). It is known that Cl-Au-Au-Cl torsion angle as well as Au-Au bond length affect the photophysical properties of aurophilic interaction.^[7] Although the Au-Au bond lengths of α - and β -Au₂Cl₂(dpae) are similar [3.129(2) and 3.162(3) Å, respectively], their Cl-Au····Au-Cl torsion angles were different [α -form: 100.3(1)°, β -form: 114.67(8)°], which possibly caused the different emission behaviors. Then after grinding, the LE emissions were enhanced for both the α - and β -forms at room temperature. Negligible spectral change occurred after grinding the crystal sample of the bare ligand, thus the HE emission was not affected by the grinding procedure (Figure S15a). The powder XRD (PXRD) measurements revealed that the grinding caused crystal-toamorphous transitions (Figure S14a and Figure S14b). For Au₂Cl₂(dpae), aurophilic interactions might be readily formed in the amorphous states in contrast to the conformationally restricted crystal phases.

Although polymorphism was also observed for Au₂Cl₂(dpap), sufficient amounts of the β -form crystals for PL measurement were not collected. We thus analyzed only the α -form (Figure 4c). The emission of the crystalline sample at 77 K was derived from the ${}^{3}\pi\pi^{*}$ excitation state, whereas the emission





Figure 4. PL spectra of AuCI complexes in the solid states. The data of the non-emissive samples were omitted for clarity.

due to the XLCT was dominant at room temperature. This result indicates that the energy barrier from ${}^{3}\pi\pi^{*}$ to ${}^{3}(X+M)C/{}^{3}XLCT$ of Au₂Cl₂(dpap) was lower than that of Au₂Cl₂(dpae). After grinding, the emission due to the XLCT was observed at room temperature likely to α -Au₂Cl₂(dpae). In the case of Au₂Cl₂(dpab) (Figure 4d), the emission in the crystalline state was only HE one because there is no aurophilic interaction in reference to the X-ray crystallographic data. On the other hand, the LE emission was observed after grinding whether at room temperature and 77 K. This is probably because the grinding assisted the formation of aurophilic interactions via crystal-toamorphous transition, though the PXRD indicated that crystals remained to some extent even after grinding (Figure S14d).

The emission of Au₂Cl₂(*cis*-dpav) and Au₂Cl₂(*trans*-dpav) was not observed in the crystalline state at room temperature (Figure 4e and Figure 4f). The reason for the negligible emission is still unclear, but it is possible that molecular motions were not fully restricted at room temperature to cause non-emissive deactivation of the excitons. This hypothesis was supported by the fact that the LE emission was observed in the crystalline state at 77 K, implying that the molecular motions were frozen by cooling. PXRD measurements revealed that grinding in a mortar cannot cause crystal-to-amorphous transition for Au₂Cl₂(*cis*-dpav) and Au₂Cl₂(*trans*-dpav); sharp signals due to crystals were still observed after grinding for several minutes (Figures S14e and S14f). Therefore, the emission properties were not changed by grinding.

For the crystal samples of Au₂Cl₂(dpapz) (Figure 4g) and Au₂Cl₂(dpaq) (Figure 4h), no emission was observed at room temperature likely to Au₂Cl₂(*cis*-dpav) and Au₂Cl₂(*trans*-dpav), but only the HE emissions were observed at 77 K. Pyrazine and quinoxaline moieties had more expanded π -conjugated systems than the vinylene moieties of *cis*- and *trans*-dpav, resulting in the stabilized IL states to give higher energy barrier from ${}^3\pi\pi^*$ to ${}^3(X+M)C/{}^3XLCT$. Moreover, after grinding, Au₂Cl₂(dpapz) showed the LE emission was exhibited even at 77 K, whereas Au₂Cl₂(dpaq) showed the LE and HE emissions at room temperature and 77 K, respectively. This is because the more expanded π -conjugation of dpaq further raised the energy barrier for the

internal conversion of ${}^3\pi\pi^*\text{-to-}{}^3(X+M)C/{}^3XLCT$ when compared with dpapz.

Conclusion

Diarsenic ligands were prepared by practical synthetic method that we have recently developed. The Au₂Cl₂ complexes with the diarsenic ligands were synthesized, and their structures were analyzed by X-ray crystallography. The diarsenic ligands worked as templates for construction of intra- or intermolecular aurophilic interaction except for dpab. The flexible ligands such as dpae and dpap produced crystal polymorphs of the resultant Au₂Cl₂(diars) complexes. The rigid ligands cis-dpav, dpapz, and dpag supported intramolecular aurophilic interaction while Au₂Cl₂(trans-dpav) formed 1D-polymeric structure; their coordination directions were fixed by the vinylene or arylene linkers. The emission behaviors were drastically changed according to the ligand structures. The ${}^{3}\pi\pi^{*}$ and ${}^{3}(X+M)C/{}^{3}XLCT$ excitation states, being responsible for the emissions, were affected by π -conjugation, Au---Au distance and torsion, rigidity, and molecular packing, resulting in stimuli-responsiveness of the complexes: luminescent mechanochromism and/or thermochromism. The present study on arsenic-gold complexes will open new venue towards the further development of other metal complexes with various functions. The relationships between arsenic ligand structure and photophysical properties in other metal complexes are now under investigation.

Experimental Section

Materials

Chloroform (CHCl₃), dichloromethane (CH₂Cl₂), tetrahydrofuran (THF), methanol (MeOH), 1,2-dichloroethane, sodium sulfate (Na₂SO₄), 2-propanol and *cis*-1,2-dichloroethylene were purchased from Nacalai Tesque, Inc. Hexane was purchased from Wako Pure Chemical Industry, Ltd. Phenyllithium (PhLi, 1.1 μ in cyclohexane and diethyl ether) was purchased from Kanto Chemical Co., Inc. 1,3-Dichloropropane, 1,4-dichlorobutane, 2,3-dichloropyrazine, and 2,3-dichloroquinoxaline were purchased from Tokyo Chemical Industry



Co., Ltd. *trans*-1,2-dichloroethylene and gold(I) chloride (AuCI) were purchased from Sigma Aldrich. Hexaphenylcyclohexaarsine (Ph₆As₆)^[9b] and arsenic ligands dpae,^[12] dpap,^[13] dpab,^[13] *cis*-dpav,^[12] and dpaq^[13] were prepared according to literature procedures.

Measurement

¹H (400 MHz) and ¹³C (100 MHz) nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE III 400 NMR spectrometer. High resolution mass spectra (HRMS) were obtained on a JEOL JMS-SX102A spectrometer. Emission and excitation spectra were obtained on an FP-8500 (JASCO) spectrometer and the absolute PL quantum yields (Φ) were determined by using a JASCO ILFC-847S; the quantum yield of quinine sulfate as reference was 0.52, which is in agreement with the literature value.^[16] Powder X-ray diffractometer with CuK_{α} radiation (λ = 1.5406 Å) in the 2 θ/θ mode at room temperature. The 2 θ scan data were collected at 0.01° intervals and the scan speed was 10° (2 θ) / min.

X-ray Crystallographic Data for Single Crystalline Products

The single crystal was mounted on a nylon loop. Intensity data were collected at room temperature on a Rigaku XtaLAB mini with graphite-monochromated MoK_{α} radiation. The readout was performed in the 0.073 mm pixel mode. The data were collected at room temperature to a maximum 2θ value of 55.0°. Data were processed by Crystal Clear.^[17] An empirical absorption correction^[18] was applied. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods^[19] and expanded by using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined by using the riding model. The final cycle of the full-matrix least-squares refinement on F^2 was based on observed reflections and variable parameters. All calculations were performed by using the CrystalStructure^[19] crystallographic software package except for the refinement, which was performed by using SHELXL2013.^[20] The disordered structures were refined with SHELXL2016^[21] by using Olex₂^[22] as the graphical interface. Crystal data and more information on the X-ray data collection are summarized in Table 1 and S1-S14.

Deposition Numbers 2034893 (for *trans*-dpav), 2034892 (for dpapz), 2017062 [for α -Au₂Cl₂(dpae)], 2017060 [for β -Au₂Cl₂(dpae)], 2017061 [for α -Au₂Cl₂(dpap)], 2017063 [for β -Au₂Cl₂(dpap)], 2017059 [for Au₂Cl₂(dpab)], 2017058 [for Au₂Cl₂(*cis*-dpav)], 2017065 [for Au₂Cl₂(*trans*-dpav)], 2017064 [for Au₂Cl₂(dpapz)], 2017066 [for Au₂Cl₂(dpaq)] contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Synthesis

trans-dpav: A THF (20 mL) dispersion of Ph₆As₆ (524 mg, 0.574 mmol) was cooled to 0 °C under N₂ atmosphere, and PhLi (1.12 m in cyclohexane and Et₂O, 3.1 mL, 3.47 mmol) was slowly added. The reaction mixture was warmed to room temperature and stirred for 2 h. Again, the reaction mixture was cooled to 0 °C, and *trans*-1,2-dichloroethylene (130 μ L, 1.71 mmol) was slowly added. After stirring at room temperature overnight, the reaction was quenched by distilled water. The resultant solution was extracted with CH₂Cl₂ three times, and the combined organic layers were dried with Na₂SO₄. After filtration, the volatiles were removed in vacuo. The obtained products were purified by recrystallization from CH₂Cl₂/MeOH to obtain colorless solid of *trans*-dpav (0.1648 g, 0.340 mmol, 20 %). ¹H-NMR (CDCl₃, 400 MHz): δ = 7.40–7.30 (m, 20

H), 7.06 (s, 2H) ppm; ¹³C-NMR (CDCl₃, 100 MHz): δ = 145.43, 140.22, 133.25, 128.69, 128.48 ppm. HR-MS (FAB) *m/z*: calculated for C₂₆H₂₂As₂: 484.0153; found [M]⁺: 484.0148.

dpapz: A THF (30 mL) dispersion of Ph₆As₆ (500 mg, 0.548 mmol) was cooled to 0 °C under N₂ atmosphere, and PhLi (1.10 M in cyclohexane and Et₂O, 3.0 mL, 3.30 mmol) was slowly added. The reaction mixture was warmed to room temperature and stirred for 2 h. Again, the reaction mixture was cooled to 0 °C, and a THF solution (5 mL) of 1,2-dichloropyrazine (244 mg, 1.64 mmol) was slowly added. After stirring at room temperature overnight, the reaction was guenched by distilled water. The resultant solution was extracted with CH₂Cl₂ three times, and the combined organic layers were dried with Na2SO4. After filtration, the volatiles were removed in vacuo. The obtained products were purified by recrystallization from CH₂Cl₂/MeOH to obtain colorless solid of dpapz (361 mg, 0.673 mmol, 41 %). ¹H-NMR ([D₆]Acetone, 400 MHz): δ = 8.55 (s, 2 H), 7.34–7.21 (m, 20 H) ppm; ¹³C-NMR (CDCl₃, 100 MHz): δ = 168.52, 144.84, 139.02, 134.34, 128.76, 128.65 ppm. HR-MS (FAB) m/z: calculated for C₂₈H₂₂As₂N₂: 536.0215; found [M]⁺: 536.0226.

General Procedure for Gold(I) Chloride Complexes: A CH_2Cl_2 solution of arsenic ligands and AuCl was stirred under a N_2 atmosphere at room temperature for 2 h. After filtration with a membrane filter, recrystallization gave crystals of AuCl complexes.

Au₂Cl₂(dpae): A CH₂Cl₂ solution (10 mL) of dpae (49 mg, 0.10 mmol) and AuCl (50 mg, 0.22 mmol) was used to obtain colorless solid of Au₂Cl₂(dpae) (69 mg, 0.073 mmol, 73 %). Recrystallization: slow evaporation of CH₂Cl₂ for α-form, slow diffusion to mix MeOH with a CH₂Cl₂ solution for β-form. ¹H-NMR spectrum well corresponded to literature data.^[3a]

Au₂Cl₂(dpap): A CH₂Cl₂ solution (10 mL) of dpap (99 mg, 0.20 mmol) and AuCl (94 mg, 0.40 mmol) was used to obtain colorless solid of Au₂Cl₂(dpap) (140 mg, 0.145 mmol, 73 %). Recrystallization: slow diffusion to mix MeOH with a CH₂Cl₂ solution. ¹H-NMR (CDCl₃, 400 MHz): δ = 7.61–7.45 (m, 20 H), 2.76 (t, *J* = 7.4 Hz, 4 H), 2.05 (quint, *J* = 7.4 Hz, 2 H) ppm; ¹³C-NMR (CDCl₃, 100 MHz): δ = 132.7 131.7, 130.4, 129.9 28.5, 21.6 ppm.

Au₂Cl₂(dpab): A CH₂Cl₂ solution (10 mL) of dpap (299 mg, 0.582 mmol) and AuCl (274 mg, 1.18 mmol) was used to obtain colorless solid of Au₂Cl₂(dpab) (398 mg, 0.406 mmol, 70 %). Recrystallization: slow diffusion to mix MeOH with a CH₂Cl₂ solution. ¹H-NMR (CDCl₃, 400 MHz): δ = 7.58–7.45 (m, 20 H), 2.44 (t, *J* = 7.4 Hz, 4 H), 1.80 (quint, *J* = 3.9 Hz, 4 H) ppm; ¹³C-NMR (CDCl₃, 100 MHz): δ = 132.6, 131.6, 131.0, 129.8, 27.7, 27.4 ppm.

Au₂Cl₂(cis-dpav): A CH₂Cl₂ solution (10 mL) of *cis*-dpav (485 mg, 0.100 mmol) and AuCl (476 mg, 2.04 mmol) was used to obtain colorless solid of Au₂Cl₂(*cis*-dpav) (533 mg, 0.562 mmol, 56%). Recrystallization: slow diffusion to mix hexane with a CH₂Cl₂ solution. ¹H-NMR (CDCl₃, 400 MHz): δ = 7.62 (s, 2 H), 7.57–7.41 (m, 20 H) ppm; ¹³C-NMR (CDCl₃, 100 MHz): δ = 142.4, 132.8, 131.9, 131.2, 130.0 ppm.

Au₂Cl₂(trans-dpav): A CH₂Cl₂ solution (10 mL) of *trans*-dpav (25 mg, 0.050 mmol) and AuCl (24 mg, 0.10 mmol) was used to obtain colorless solid of Au₂Cl₂(*trans*-dpav) (32 mg, 0.030 mmol, 65 %). After the reaction, colorless precipitates were collected and purified by recrystallization: (slow diffusion to mix hexane with a CHCl₃ solution). ¹H-NMR (CDCl₃, 400 MHz): δ = 7.59–7.51 (m, 20 H), 7.36 (s, 2H) ppm. ¹³C-NMR cannot be measured because of the low solubility.

 $Au_2Cl_2(dpapz)$: A CH₂Cl₂ solution (20 mL) of dpapz (80 mg, 0.150 mmol) and AuCl (70 mg, 0.30 mmol) was used to obtain color-



less solid of Au₂Cl₂(dpapz) (90 mg, 0.090 mmol, 60 %). Recrystallization: slow diffusion to mix MeOH with a CH₂Cl₂ solution. ¹H-NMR (CDCl₃, 400 MHz): δ = 8.71 (s, 2 H), 7.60–7.58 (m, 8 H), 7.52–7.48 (m, 4 H), 7.44–7.40(m, 8 H). ¹³C-NMR cannot be measured because of the low solubility.

Au₂Cl₂(dpaq): A CH₂Cl₂ solution (20 mL) of dpaq (80 mg, 0.140 mmol) and AuCl (64 mg, 0.28 mmol) was used to obtain yellow solid of Au₂Cl₂(dpaq) (69 mg, 0.066 mmol, 48 %). Recrystallization: slow diffusion to mix MeOH with a CH₂Cl₂ solution. ¹H-NMR (CDCl₃, 400 MHz): δ = 8.02–8.00 (m, 2H), 7.89–7.86 (m, 2H), 7.64 (d, J = 8 Hz, 8H), 7.48 (t, J = 6 Hz, 4H), 7.41 (t, J = 8 Hz, 8H). ¹³C-NMR cannot be measured because of the low solubility.

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