Gold(I) and Platinum(II) Tetracenes and Tetracenyldiacetylenes: Structural and Fluorescence Color Changes Induced by \( \sigma \)-Metalation

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Received January 21, 2010

\( \sigma \)-Metalation of tetracene can change the emission color of and introduce new structural dimensionality to the organic chromophore. Two synthetic entries to \( \sigma \)-metallotetracenes have been explored, leading to emissive mononuclear (Ph\(_3\)PAu\(^{+}\))-tetracene (1) and cis-[Br(Et\(_3\)P)\(_2\)Pt\(^{II}\)]-tetracene (2) and binuclear (R\(_3\)PAu\(^{+}\))-tetracenyldiacetylene (R = Ph (Me) (5) and trans-[Et(Et\(_3\)P)\(_2\)Pt\(^{II}\)]-tetracenyldiacetylide (6). Metalation can lower the emission energy of tetracene up to 0.53 eV. The X(Et\(_3\)P)\(_2\)Pt\(^{II}\) group (X = Br, I) has stronger perturbations on the tetracenyl ring than the R\(_3\)PAu\(^{+}\) group. \( \sigma \)-Metalation also leads to different crystal packing of the complexes and thus arrangements of the tetracenylic rings. Aurophilic attraction operates in 5, leading to self-assembly of the molecules into a novel honeycomb structure composed of helical Au\(^{III}\) chains. In contrast to the other complexes, the crystal of 5 is not emissive, possibly due to efficient excitation delocalization.

Introduction

Larger acenes (LA), especially tetracene and pentacene, have important applications in advanced materials because of their strong visible \( \pi \)–\( \pi ^* \) absorptions, intense luminescence, and high charge mobility in the solid state.\(^1\)-\(^6\) The electronic structure, photophysics, and solid-state assembly of LA, which are related to the performance of LA-based devices, can be changed by functionalization of the rings.\(^2\) For example, the recent work of Anthony showed that the emission of tetracene can be red-shifted up to 5310 cm\(^{-1}\) (0.66 eV) by attaching substituted ethynyl groups at the C5 and C12 positions.\(^3\) While many organic derivatives of LA have been reported,\(^4\)-\(^6\) the coordination chemistry of LA remains to be fully explored. Notable examples of metal–LA complexes are sandwich cobalt\(^4a\) and palladium tetracene\(^4b\) \( \pi \)-complexes. To our knowledge, no \( \sigma \)-metallotetracene complex has ever been reported. It has been demonstrated that attaching metal ions such as Au\(^{III}\) and Pt\(^{II}\) to the rims of anthracene and pyrene has significant effects on the spectroscopy or the reactivity of the acenes.\(^5\) It is therefore possible that metalation of LAs and their derivatives can be a mechanism for tuning the ground-state and excited-state

properties of the organic molecules. Apart from their electronic effects, metals can increase the structural dimensionality of LA. A herringbone structure is a common packing motif for tetracene and some of its derivatives, but in some cases, \( \pi-\pi \) stacking is observed. It is possible that new patterns will emerge in tetracene modified with metals which have geometry and secondary interactions (e.g., metallophilicity) different from those of organic substituents.

As part of our ongoing effort to develop heavy metal alternant hydrocarbon \( \sigma \)-complexes into a new class of luminescent materials and near-infrared emitters, we embarked on a study of the synthesis and spectroscopy of \( \sigma \)-metallotetracenes. Reported in this paper are two synthetic entries into metalated tetracene and its derivatives. The first approach is direct metallation of tetracene, which resulted in the two mononuclear complexes \( \text{Ph}_3\text{PAu}^+\text{tetracene} (1) \) and cis-Br(\( \text{Et}_3\text{P} \))\( \text{Pt}^{\text{II}} \)-tetracene (2) (Chart 1). 5,12-Bis((triisopropylsilyl)ethynyl)tetracene (5), first synthesized by Anthony, was used in the second approach as a precursor for the dianionic ligand 5,12-tetracenediyldiacetylide, with which the three binuclear complexes [\( \text{Ph}_3\text{PAu} \)]\( \text{Au}^{\text{I}} \)-tetracene (3), first synthesized by Anthony, and Au \( \text{I} \) aryldiacetylide, which have been observed to have rich photophysics and optoelectronics. Aurophilic interactions, “super van der Waals bonding”, are responsible for the formation of intricate supramolecular structures such polymers, helicates, and catenanes. Interestingly, our results showed that the auxiliary phosphine from \( \text{Ph}_3\text{P} \) to \( \text{Me}_3\text{P} \) induced aurophilic interactions, leading to self-assembly of an intriguing honeycomb network.

Results and Discussion

Structures of \( \text{Au}^{\text{I}} \) and \( \text{Pt}^{\text{II}} \) Tetracene. The complex 1 was prepared from lithiation of 5-bromotetracene followed by addition of \( \text{Ph}_3\text{PAuCl} \), while the complex 2 was prepared from oxidative addition of \( \text{Pt}(\text{PEt}_3)_2 \) to 5-bromotetracene. Both compounds are unstable and slowly decompose in organic solvents after 2 days in air to give tetracene and metal colloids. The structure of 1 shows a \( \text{Ph}_3\text{PAu}^{\text{I}} \) group attached to a planar tetracene ring at its C5 carbon atom (Figure 1 and Table 1). The Au–C\(_{\text{ipso}}\) (2.075(6) \( \text{Å} \)) and Au–P (2.2956(16) \( \text{Å} \)) bond lengths are similar to those observed in other arylgold(I) phosphine complexes. The P–Au–C\(_{\text{ipso}}\) (169.81(1)) is distorted from linearity, and as a result, the Au and P atoms deviate from the mean plane of the tetracene by 0.56 and 1.32 \( \text{Å} \). The distortion could be due to steric repulsion between one of the phenyl rings and the tetracenylic ring in the neighboring molecule (Figure 1b). Similar to the case for tetracene and its derivatives, the molecules of 1 are assembled into a herringbone structure in the crystal via edge-to-face interactions between adjacent tetracenylic rings (Figure 1b). The dihedral angle (55.39\( ^\circ \)) between two interacting rings and the calculated (edge)H–C\(_{\text{ipso}}\) (face) distance (2.801 \( \text{Å} \)) are close to those of tetracene (51.40\( ^\circ \), 2.761 \( \text{Å} \)). While the herringbones in the crystal of tetracene interlock and extend two-dimensionally, each herringbone in 1 is isolated from the adjacent ones by \( \text{AuPh}_3 \) groups.

The crystal structure of 2 (Figure 2 and Table 1) shows a Pt\(^{\text{II}}\) ion coordinated to two \( \text{PEt}_3 \) ligands and a \( \text{Br}^- \) ion and...
the C5 atom of the tetracene, showing a distorted-square-planar geometry.

The two PEt₃ are in a cis configuration, and in accord with the solid-state structure, the ³¹P NMR spectrum shows two doublets at δ 8.96 (¹J_P-P1 = 1580 Hz) and 2.94 (¹J_P-P1 = 4070 Hz) with a ²J_P-P value of 18 Hz, which are assigned to the P atoms trans and cis to the metalated carbon atom, respectively, according to their different ¹J_P-P values and Pt–P distances. The coordination plane of the Pt ion and the plane of the tetracene ring make a dihedral angle of 89.6°. The Pt–Cipso bond length is 2.066(7) Å, typical for platinated polycyclic aromatic hydrocarbons. ¹⁶ Because of the strong trans influence of the carbanion, the Pt(1)–P(1) bond (2.355(2) Å) is notably longer than the Pt(1)–P(2) bond (2.2354(13) Å). Similarly, the P1–Pt–P2 angle is distorted (∠P1–Pt–P2 = 99.67°), possibly due to steric repulsion between the ethyl groups in the phosphines. The molecules of 2 are aligned along the c axis (Figure 2b) with their tetracynyl rings in parallel and separated by ~6.8 Å. There is no overlap between the tetracene rings in adjacent columns. Tetracene and some of its derivatives such as 1 aggregate into a herringbone structure in the solid state. Possibly the structure is disfavored in 2 because of the bulky PEt₃ ligands, especially the ligand close to the ring.

Structures of Au and Pt Tetracynylacetyldiyls. The complexes 4 and 5 were synthesized by reacting 2 mol equiv of Ph₃PAuCl and Me₃PACl, respectively, with 5,12-diethynyltetracene in CH₂Cl₂ in the presence of NaOMe. 5,12-Diethynyltetracene was generated in situ by reacting 5,12-bis(triisopropylsilyl)ethyl(tetracene (3) with n-Bu₃NF. The crystal structures of 4 and 5 are depicted in Figure 3.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 4-3.5CHCl₃ and 5

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond Length/Å</th>
<th>Angle/deg</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-3.5CHCl₃</td>
<td>Au(1)–P(1) = 2.277(3)</td>
<td>C(1)–Au(1)–C(1) = 175.8(4)</td>
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<tr>
<td></td>
<td>Au(1)–C(1) = 1.9829(14)</td>
<td>C(1)–Au(1)–C(1) = 177.3(12)</td>
</tr>
<tr>
<td>5</td>
<td>Au(1)–P(1) = 2.287(4)</td>
<td>P(1)–Au(1)–C(1) = 171.6(3)</td>
</tr>
<tr>
<td></td>
<td>Au(1)–P(1A) = 2.327(8)</td>
<td>P(1A)–Au(1)–C(1) = 164.1(5)</td>
</tr>
<tr>
<td></td>
<td>Au(1)–C(1) = 1.968(8)</td>
<td>C(2)–C(1)–Au(1) = 173.9(8)</td>
</tr>
</tbody>
</table>

and 4 (see Table 2 for selected bond lengths and angles), respectively.

The coordination of Au¹ ions in 4 and 5 is nearly linear and the Au–C and Au–P bond lengths are similar to those observed for phosphinegold(I) arylacetylides. The Me₂P ligands in 5 are disordered over two positions, and the corresponding P–Au–C angles are significantly bent (171.6(3) and 164.1(5)° for P(1) and P(1A)). The tetracynyl rings in the complexes are slightly curved. The C–C≡C≡C linkage between the tetracynyl ring and the acetylide group is nearly linear in 4 (∠C–C≡C≡C = 176.3(1)°) but is significantly bent in 5 (166.1(1)°). As a result of the distortion, the two acetylide groups and Au¹ ions are tilted slightly toward the longer end of the molecule. The ³¹P{¹H} NMR spectra of 4 and 5 display singlets at δ 42.9 and 1.58, respectively.

The crystal structure of 4 shows neither intermolecular Au–Au interactions (shortest intermolecular Au–Au distance 7.53(9) Å) nor π–π stacking. The tetracynyl rings are parallel to each other, forming a staircaselike array (Figure 3). Two adjacent molecules are associated through a C–H···π interaction involving the phenyl ring of PPh₃ and the tetracynyl ring, which are nearly perpendicular to each other (dihedral angle 88.8(7)°). The distance between the centroids of the rings is 4.92(7) Å, which is typical for edge-to-face interactions. ¹⁸

It has been demonstrated that intermolecular aurophilic interactions between Au¹ and phosphine can be induced by ¹⁸

References:
reducing the bulkiness of the phosphine.8 Indeed, aurophilic attraction operates in the crystal of 5, in which the molecules are assembled into a honeycomb network with the tetraceny1 rings and the Au ions forming the edges and vertices of hexagons (Figure 5).

The compound 5 was crystallized in the rhombohedral R3m space group. The crystal is highly porous with open channels extending along the c axis. No solvent molecule is found in the channels, which are lined with the edges of the tetraceny1 rings and have an estimated diameter of ∼8 Å. The honeycomb pores can be constructed by iterative stacking of three layers of molecules (pink, blue, and green), as shown in Chart 2.

The molecules in each layer are related by 3-fold rotation and reflection, and those in different layers are connected through their Au ions at the nodes of the network (or the “vertices” of the hexagonal pore). Parallel to the c axis and passing through vertices alternately are the 31 and 32 screw axes. The gold atoms form right-handed (Δ or P) and left-handed (Λ or M) helices that wind around the 31 and 32 axes, respectively (Figure 6). The Au atoms in the helix are equally spaced with a Au–Au distance of 3.26(8) Å, which falls into the range for aurophilic contacts.19 The Au–Au–Au angle is 134.2(3)°. Zigzag gold chains sustained by aurophilic interactions are known, but most of them display alternate

Figure 5. (a) Honeycomb-like framework of 5 viewed along the c axis showing the open channels. (b) Hexagonal pore showing stacking of molecules at the nodes.

Chart 2

Figure 6. (a) Right-handed and (b) left-handed Au helices. Au–Au bond distances.20 The present compound is a rare example of an undistorted helical gold chain.

A gold atom in the helix is separated from the C≡C bond coordinated to its adjacent gold atom by a distance of 3.42(9) Å, which is too long for any significant Au–I interactions.21 The network is therefore sustained mainly if not solely by aurophilic interactions. Au–Au attraction accounts for many novel solid-state assemblies of AuI complexes, but to our knowledge there is no example of a honeycomb structure arising from the metallophilic interaction. Metal–organic-based honeycomb frameworks are known,22 and they are usually assembled by stacking of hexagonal sheets which are conjoined by metal–ligand coordination or intermolecular association (i.e., π–π stacking)22b of individual molecules. The honeycomb network of 5 is distinctly different, as it arises from the Au–Au bonding between layers, but the molecules in each layer are not connected by covalent or any secondary bonding. The tetraceny1 rings stacking along the central axis of the helix are widely separated by 7.6 Å. Each tetraceny1 ring is surrounded by four neighboring rings with an angular separation of 60°.

The complex 6 was synthesized by Sonogashira coupling of trans-PtII(PEt3)2I and 5,12-diethynyltetracene. Although attempts to obtain the crystal structure of 3 failed,1H and 31P NMR, 1H–1H COSY, high-resolution ESI-MS, and elemental analysis results clearly showed that the complex has a C2v-symmetric structure whereby the two I(Et3 P)2PtII groups are coordinated to the two acetylide groups and the phosphines are in the trans configuration (Chart 3). The 31P{1H} NMR spectrum of the complex shows a singlet at δ 9.57 (Jp–p = 2323 Hz), and the 1H NMR spectrum shows aromatic signals including two double doublets (H1,4, H7,10) and one singlet (H6,11) and a multiplet arising from the overlap of the two double doublets for H2,3 and H8,9. The data are consistent with the proposed structure of C2v symmetry, which is further confirmed by the high-resolution


(e) Liu, R.-Y.; Schier, A.; Schmidbaur, H. Organometallics 2003, 22, 3199.


ESI-MS mass spectrum, which shows a cluster peak at m/z 1389.2 corresponding to [6]+ ion (Figure 7).

Absorption and Emission Spectroscopy. The UV-visible and emission spectra of the complexes are shown in Figure 8, and the spectroscopic data are summarized in Table 3. The absorption spectra display a moderately intense vibronic band at 400–550 nm for 1 (λ_{max} = 481 nm, ε_{max} = 7.70 × 10^3 M^{-1} cm^{-1}) and 2 (λ_{max} = 467 nm, ε_{max} = 1.05 × 10^4 M^{-1} cm^{-1}) and at 450–620 nm for 4 (λ_{max} = 553 nm, ε_{max} = 3.11 × 10^4 M^{-1} cm^{-1}), 5 (λ_{max} = 552 nm, ε_{max} = 2.23 × 10^4 M^{-1} cm^{-1}), and 6 (λ_{max} = 572 nm, ε_{max} = 2.62 × 10^4 M^{-1} cm^{-1}). The vibronic spacings are ∼1300–1400 cm^{-1}. Vibronic bands are commonly observed for the π → π* transitions of aromatic molecules, and in absorption bands with similar intensities, vibronic spacings, and shapes are found in the spectra of the parental tetracene and 3. Accordingly, the vibronic band is assigned to the lowest energy singlet π → π* (1A_g → 1B_2u) transition in the tetraceny1 ring, which is also known as the 1L_a band in Platt’s notation. Because of mixing of orbitals of tetracene and the metal ions (and ethynyl groups in 4–6), the transitions in the metalated tetracene are largely but not entirely tetracene-based. However, for the sake of clarity, the absorption band of the complexes is still labeled 1L_a in the following discussion.

Apart from the 1L_a band, the spectra of 3–6 display another intense vibronic band at 320–400 nm, which is too intense (ε_{max} = (1.38–2.32) × 10^4 M^{-1} cm^{-1}) to be a triplet component of a high-energy singlet excited state and is tentatively assigned to the 1L_b band, which arises from the pseudo-parity-forbidden 1A_g → 1B_2u− transition. Our recent work on the spectroscopy of metallocanthracene and pyrene showed that perturbations of metal ions can lead to the intensification of the 1L_b band. As no distinct 1L_b band is observed in the spectra of 1 and 2, it is reasonable to assume that the metalated ethynyl groups in 4–6 have stronger perturbations on the electronic structure of tetracene than the metal ions alone in 1 and 2.

The most notable feature of the spectra of the complexes is the significant red shift of the 1L_a band from that of tetracene, which follows the order 1 (1100 cm^{-1}) < 2 (1700 cm^{-1}) < 4 ≈ 5 (3000 cm^{-1}) < 6 (3700 cm^{-1}). The red shift is due to the perturbation of the substituents on the tetraceny1 ring. The emissions of 4–6 are lower in energy than those of 1 and 2 because two metalated ethynyl groups can exert stronger perturbation than a single metal center. In a first-order approximation, the 1L_a band arises from HOMO → LUMO of the tetracene, the energy of which can be lowered by destabilization of the HOMO and/or stabilization of the LUMO. As both the HOMO and the LUMO are π-symmetric, they should be more susceptible to the influence of π-interactions with the substituents. Notably, the compounds 4–6 exhibit a larger red shift than 3, indicating that the metal ions have stronger perturbation than the Si(Pr)3 group. Unlike the Si(Pr)3 group, which can only act as a π-acceptor, the metal ions can be both π-donating and π-accepting. The stronger perturbations observed for the metal ions suggest the importance of the metal-to-tetracene π-donation in influencing the energy of the 1L_a band. Notably, the 1L_a bands of the PtII complexes 2 and 6 are lower in energy than those of the corresponding AuI complexes 1, 4, and 5. Our previous study also showed that the energy of the 1L_a band of trans-Br(PEt3)2PtII-pyrene is lower than that of Ph3PAu−-pyrene. The X(PEt3)2PtII group (X = Br, I) has stronger perturbations than the R3PAu group (R = Ph, Me), possibly because it is a stronger π-donor with the electron-donating PEt3 and Br/ I ion. Anthony first demonstrated that attaching substituted ethynyl groups X’–C=C–X’ (X’ = substituent, i.e., Si(Pr)3) to the C5 and C12 positions of tetracene can red-shift its absorption and fluorescence. It is noted that the substituent that causes the largest red shift is X’ = 4-(N,N’-diethylamino)phenyl (emission maximum 643 nm), which is mainly π-donating.

All the complexes are emissive in solution (Figure 8 and Table 3). The emission bands show shoulders with a vibronic spacing of ∼1200 cm^{-1}. The metalated tetraceny1diacetylide 4, 5, and 6 are ≥10 times more emissive than the metalated tetracenes 1 and 2 (Table 3). Similar to the case for the 1L_a bands, the emissions are red-shifted from that of tetracene. The emission energy follows the order tetracene > 1 > 2 > 3 > 4 ≈ 5 > 6, and the fluorescence color changes from blue (tetracene) to yellow (1–3), orange (4, 5), and red (6) (Figure 9). The small Stokes shift (350–770 cm^{-1}) and short emission lifetimes (0.5–8.6 ns) suggest that the emissions are fluorescence arising from the 1L_a excited state. The emissions show very small solvent dependence (Supporting Information). For example, the emission of 4 is red-shifted by 300 cm^{-1} by changing the solvent from diethyl ether to DMSO. The complex 6 displays...
The excitation wavelength is 490 nm. The cause of the emission quenching is not certain, but it is probably due to the special orientation of the tetracenyl rings in the crystal of 5. As mentioned, the fluorescence of the complexes comes from the 1L_a excited state arising from the 1A_g → 1B_u transition, which is polarized along the long axis of the tetracene ring. Although the perturbations of the substituents would introduce a short-axis component to the overall transition moment, the major component should still lie along the long axis.26 The crystal packings of 1, 2, and 4 show that the long axes of the tetracenyl rings are parallel; i.e., the dihedral angle between the transition moments is 0°, which does not lead to exciton coupling. On the other hand, the angle between the transition moments of two adjacent tetracenyl rings is ~60° in the crystal of 5, which is close to 70° for maximum exciton coupling between two neighboring chromophores.27 In addition, each tetracenyl ring in 5 is surrounded by four tetracenyl rings. It is therefore possible that the exciton migration is efficient in the crystal of 5, leading to rapid transfer excitation energy to nonradiative traps present in the crystal. Exciton migration has been suggested to be the reason for the quenching of the solid-state emission of one crystal form of NO2-4-C6H4-C≡C–Au–PCy3 (Cy = cyclohexyl), in which the dihedral angle between the transition moments of two neighboring molecules is 79°.76

**Concluding Remarks**

In this study, two synthetic entries to σ-metallofullerendopentafulvene with COCl2. It has been demonstrated that auration and platination of tetracene and tetracenylacetylide can change the photophysical properties of the organic chromophore; particularly, metalation leads to a significant red shift of the 1L_a absorption band and the corresponding fluorescence. The X(Et3 P)2PtII group has greater perturbations on the electronic structure of tetracene than the R3 PAu I group, possibly due to its stronger π-donating character.25,26 The fluorescence of the complexes comes from the 1L_a excited state and ligand(π-orbital of iodide)-to-ligand(π*-orbital of tetracene)-charge-transfer excited state.

**Solid-State Emission.** Crystals of 1, 2, and 4 and powders of 6 are emissive at room temperature (Figure S1 in the Supporting Information). The solid emission energies of the complexes are all slightly red-shifted from the corresponding solution emissions by 1200–2200 cm⁻¹. Surprisingly, the crystal of 5 is virtually nonemissive, despite the strong solution luminescence. The cause of the emission quenching is not certain, but it is probably due to the special orientation of the tetracenyl rings in the crystal of 5. As mentioned, the fluorescence of the complexes comes from the 1L_a excited state arising from the 1A_g → 1B_u transition, which is polarized along the long axis of the tetracene ring. Although the perturbations of the substituents would introduce a short-axis component to the overall transition moment, the major component should still lie along the long axis.26 The crystal packings of 1, 2, and 4 show that the long axes of the tetracenyl rings are parallel; i.e., the dihedral angle between the transition moments is 0°, which does not lead to exciton coupling. On the other hand, the angle between the transition moments of two adjacent tetracenyl rings is ~60° in the crystal of 5, which is close to 70° for maximum exciton coupling between two neighboring chromophores.27 In addition, each tetracenyl ring in 5 is surrounded by four tetracenyl rings. It is therefore possible that the exciton migration is efficient in the crystal of 5, leading to rapid transfer excitation energy to nonradiative traps present in the crystal. Exciton migration has been suggested to be the reason for the quenching of the solid-state emission of one crystal form of NO2-4-C6H4-C≡C–Au–PCy3 (Cy = cyclohexyl), in which the dihedral angle between the transition moments of two neighboring molecules is 79°.76

**Table 3. Absorption and Emission Spectroscopic Data of the Complexes**

<table>
<thead>
<tr>
<th>complex</th>
<th>1L_a band/nm (ε, 10^4 M⁻¹ cm⁻¹)</th>
<th>1L_b band/nm (ε, 10^4 M⁻¹ cm⁻¹)</th>
<th>soln emission max/nm</th>
<th>emission lifetime τ/µs</th>
<th>emission quantum yield Φ</th>
<th>solid-state emission max/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>498 (1.10), 467 (1.05), 441 (0.56), 417 (0.22) (s)</td>
<td>a</td>
<td>509</td>
<td>0.5</td>
<td>0.05</td>
<td>573</td>
</tr>
<tr>
<td>2</td>
<td>512 (0.70), 481 (0.77), 455 (0.48)</td>
<td>a</td>
<td>532</td>
<td>3.9</td>
<td>0.06</td>
<td>582</td>
</tr>
<tr>
<td>4</td>
<td>553 (3.11), 515 (2.01), 481 (0.74), 453 (0.20) (s)</td>
<td>370 (0.86), 352 (2.32), 335 (1.43)</td>
<td>563</td>
<td>5.4</td>
<td>0.85</td>
<td>614</td>
</tr>
<tr>
<td>5</td>
<td>552 (2.23), 514 (1.56), 480 (0.59), 453 (0.19) (s)</td>
<td>368 (0.62), 348 (1.90), 332 (1.29)</td>
<td>562</td>
<td>5.5</td>
<td>0.73</td>
<td>b</td>
</tr>
<tr>
<td>6</td>
<td>572 (2.62), 532 (1.78), 498 (0.67) (s)</td>
<td>354 (1.38), 336 (1.20)</td>
<td>596</td>
<td>8.6</td>
<td>0.60</td>
<td>642</td>
</tr>
</tbody>
</table>

*No 1L_b band is observed. *Not emissive in the solid state.

**Figure 8.** (a) Absorption (solid line) and emission (broken line) spectra of tetracene (purple), 1 (orange), and 2 (purple) in THF at room temperature. The excitation wavelength is 420 nm. (b) Absorption (solid line) and emission (broken line) spectra of 3 (red), 4 (blue), 5 (green), and 6 (black) in CH2Cl2 at room temperature. The excitation wavelength is 490 nm.

**Figure 9.** Photograph showing the red shift of emission colors of the metalated tetracenes and tetracenylidiacetylenes.
their crystals. The typical herringbone structure is only observed in the crystal of Ph₃PAu⁻tetracene. An interesting result is that the crystal of (Me₃PAu)₂-tetracycladiene exhibits a honeycomb network which is mainly supported by aurophilic interactions. The finding highlights the potential of secondary interactions such as hydrogen bonding and metal-lphilicity in controlling the patterning of tetracyclyl rings in the solid state.

**Experimental Section**

**General Methods.** All syntheses were carried out under a N₂ atmosphere. All the solvents used for synthesis and spectroscopic measurements were purified according to the literature procedures. Pt(PEt₃)₄ trans-Pt(PEt₃)₂Br₂ Ph₃PAuCl, Me₃PAuCl₁₁b 5-bromotetracene, ᵇ₅ and 5,12-bis(triisopropyl-silyl)ethynyl)tetracene³ were prepared according to reported procedures.

**Physical Methods.** The UV/vis absorption and emission spectra of the complexes were recorded on a Hewlett-Packard HP8452A diode array spectrophotometer and a Perkin-Elmer LS-50D fluorescence spectrophotometer, respectively. Rhodamine 640 (also known as rhodamine 101)³² was used as a standard in measuring the emission quantum yields. Emission lifetimes were recorded on a Horiba Jobin-Yvon Fluorolog FL-10151 fluorometer. ¹H and ³¹P{¹H} NMR spectra were recorded on a Bruker ACF 300 spectrometer, ¹H COSY spectra were recorded on a Bruker DRX500 NMR spectrometer with a 5 mm Cryo TXI Probe. All chemical shifts are quoted relative to SiMe₄ (H) or H₂PO₄ (³¹P). Elemental analyses of the complexes were carried out by the microanalysis laboratory of the Department of Chemistry at the National University of Singapore.

**Synthesis of Ph₃PAu⁻Tetracene (1).** To a stirred solution of 5-bromotetracene (143 mg, 0.46 mmol) in freshly distilled THF (25 mL) was added 0.32 mL (0.5 mmol) of 1.6 M n-BuLi at −78 °C. After the mixture was stirred for 2 h at −78 °C, 0.23 g (0.46 mmol) of Ph₃PAuCl was added to the resulting deep red solution and the mixture was warmed to room temperature and stirred for 12 h. After the solvent was removed, excess hexane was added and the precipitate was filtered off. Needlelike crystals were obtained from the filtrate upon evaporation of the solvents. Yield: 31 mg, 10%. X-ray-quality crystals of I were grown by slow evaporation of an acetone solution at −20 °C. Anal. Calcd for C₃₆H₂₆AuP: C, 62.98; H, 3.82. Found: C, 63.20; H, 3.77. ¹H NMR (300 MHz, CDCl₃): δ 9.50 (s, 2H, H₧₋₁), 8.88 (dd, J = 3.3, 6.9 Hz, 2H, H₁₋₂), 8.11 (dd, J = 3.3, 6.7 Hz, 2H, H₁₋₂), 7.70 (s, 2H, H₁₋₂, Ph), 7.37 (dd, J = 3.3, 6.7 Hz, 2H, H₧₋₁). ³¹P{¹H} NMR (121.5 MHz, CDCl₃): δ 42.94 (s). FAB-MS: m/z 1192.3 [M⁺].

**Synthesis of Me₃PAu⁻Tetracene (2).** To a toluene solution (20 mL) of Pt(PEt₃)₂ (172 mg, 0.26 mmol) was added 5-bromotetracene (49 mg, 0.16 mmol). The resulting solution was stirred overnight, and an orange precipitate was produced. The solid was filtered and washed with cold toluene and ether. Yield: 60 mg, 51%. Slow evaporation of an acetone solution of 2 afforded orange-red crystals suitable for an X-ray crystallographic study. Anal. Calcd for C₃₆H₂₆Au₂P₂: C, 36.83; H, 3.25. ³¹P{¹H} NMR (300 MHz, CDCl₃): δ 10.29 (s, 2H, H₧₋₁), 9.95 (s, 2H, H₧₋₁). ¹H NMR (300 MHz, CDCl₃): δ 7.90 (s, 1H, H₧₋₁). ³¹P{¹H} NMR (121.5 MHz, CDCl₃): δ 45.62 (s). FAB-MS: m/z 686.1 [M⁺].

**Synthesis of cis-[Br(ET₃P)₂Pt(I)]⁻⁻Tetracene (3).** To a toluene solution (20 mL) of Pt(PEt₃)₂ (172 mg, 0.26 mmol) was added 5-bromotetracene (49 mg, 0.16 mmol). The resulting solution was stirred overnight, and an orange precipitate was produced. The solid was filtered and washed with cold toluene and ether. Yield: 60 mg, 51%. Slow evaporation of an acetone solution of 2 afforded orange-red crystals suitable for an X-ray crystallographic study. Anal. Calcd for C₃₆H₂₆Au₂P₂: C, 36.83; H, 3.25. ³¹P{¹H} NMR (300 MHz, CDCl₃): δ 10.29 (s, 2H, H₧₋₁), 9.95 (s, 2H, H₧₋₁). ¹H NMR (300 MHz, CDCl₃): δ 7.90 (s, 1H, H₧₋₁). ³¹P{¹H} NMR (121.5 MHz, CDCl₃): δ 45.62 (s). FAB-MS: m/z 686.1 [M⁺].


SHELXTL\textsuperscript{\textregistered} for space group determination, structure solution, and least-squares refinements on $|F|^2$. Anisotropic thermal parameters were refined for the rest of the non-hydrogen atoms. The hydrogen atoms were placed in their ideal positions. Some of the ethyl groups in 2 have large thermal motion, resulting in the observed shorter C–C bonds. The Me$_3$P ligand in 5 is disordered into two positions with 0.64 and 0.36 occupancies. There are some residual peaks in the voids of the crystal, but the peak heights are too low and do not fit any definite solvent. The crystal data and details of data collection and refinement are summarized in Table S1 in the Supporting Information.

**Acknowledgment.** We are grateful to Prof. Koh Lip Lin and Ms. Tan Geok Kheng for determining the X-ray structures. The Ministry of Education (Grant No. R-143-000-331-112) of Singapore and the National University of Singapore are thanked for financial support.

**Supporting Information Available:** CIF files giving crystal data for 1, 2, 4, and 5 and tables and figures giving solid state emission spectra, solution emission spectra in different solvents, and crystal data. This material is available free of charge via the Internet at http://pubs.acs.org.