Table of Contents

1. General Experimental Section S3
2. Experimental Procedures S4
2.1 General procedure of the synthesis of gold ortho-boronatephosphine chloride complexes 6, 7a S4
2.2 Procedure of the synthesis of gold complex 7b S4
2.3 General procedure of the synthesis of gold complexes 7c and 8 S5
2.4 General procedure of the synthesis of hexagold clusters 9 and 9’ S6
2.5 General Procedure for the cyclization of 1,6-enynes S7
2.6 Addition of indole to a 1,6-ene S7
2.7 Oxidative cyclization of alkynyl oxirane S8
2.8 General Procedure for cyclosiomerization of 7-alkynyl cycloheptatriene S8
Table 1. Cyclization of 1,6-enynes S7
Table 2. Cyclosiomerization of 7-alkynyl cycloheptatriene S8
2.9 General Procedure for hydration of phenylacetylene S8
Table 3. Hydration of phenylacetylene S9
2.10 General Procedure for [4+2] cyclization S9
Table 4. [4+2] cyclization S9
3. Kinetic study. General procedure S11
Figure 1. Kinetics study of 1,6-ene cyclization catalyzed by the complex 9 S11
4. Photophysical properties of hexagold cluster 9 S12
Figure 2. The absorption spectra of 9 in dichloromethane at room temperature S12
Table 5. The absorption spectrum data of 9 S12
Figure 3. The emission spectra of 9 in degassed dichloromethane and in solid state at room temperature S12
5. NMR Spectra S13
General methods

Reactions were carried out under Ar atmosphere in solvents dried by passing through an activated alumina column on a PureSolv™ solvent purification system (Innovative Technologies, Inc., MA). Analytical TLC was performed on precoated silica gel plates (0.2 mm thick, Gf234, Merck, Germany) and observed under UV light. Preparative TLC was performed on 20 cm × 20 cm silica gel plates (2.0 mm thick, catalogue number 02015, Analtech). NMR spectra were recorded at 298 K on Bruker Avance 400 Ultrashield or Bruker Avance 500 Ultrashield apparatus. Chemical shifts are reported in parts per million and referenced to residual solvent. Coupling constants (J) are reported in hertz (Hz). Mass spectra were recorded on a Waster LCT Premier Sp ectrometer (ESI and APCI), on an Autoflex B rokuer Daltonics (MALDI and LDI), or on an AgilentMSD-5975B (GC-MS). UV-Vis measurements were carried out on a Shimadzu UV-1700PC spectrophotometer equipped with a photomultiplier detector, double beam optics, and D₂ and W light source. Fluorescence measurements were carried out on a Aminco-Bowman Series 2 Luminescence spectrofluorimeter equipped with a high voltage PMT detector and continuum Xe light source. Lifetime measurements were carried out on a Edinburgh Instruments LifeSpec-II spectrometer based on the time-correlated single photon counting (TCSPC) technique, equipped with a PMT detector, double subtractive monochromator and picosecond pulsed diode lasers source.

Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification.

Au(tht)Cl (tht = tetrahydrothiophene), o-borylphosphines, 1,6-enynes, alkynyl oxirane, 7-alkynyl cycloheptatriene were prepared according to published procedures. The following compounds were reported: 12a, 12b, 15, 16, 17, 19, 21.

1. R. Usón, A. Laguna, M. Laguna, Inorg. Synth. 1989, 26, 85–91.
2. a) S. Porcel, G. Bouhadir, N. Saffon, L. Maron, D. Bourissou, Angew. Chem. Int. Ed. 2010, 49, 6186–6189; b) T. W. Hudnall, Y. - M. Kim, M. W. P. Bebbington, D. Bourissou, F. P. Gabbai, J. Am. Chem. Soc. 2008, 130, 10890–10891.
3. S. Kobayashi, S. Nishio, J. Org. chem. 1994, 59, 6620-6628.
4. M. Mendez, M.P. muñoz, A. M. Echavarren, J. Am. Chem. Soc. 2001, 123, 10511-10520;
5. C. Nevado, L. Charruault, V. Michelet, C. Nieto-Oberhuber, M. P. Muñoz, M. Mendez, M.-N. Rager, J.-P. Genet, A. M. Echavarren, Eur. J. Org. Chem. 2003, 706-713.
6. C. Nieto-Oberhuber, P. Perez-Galan, E. Herrero-Gomez, T. Lauterbach, C. Rodríguez, S. López, C. Bour, A. Rosellón, D. J. Cárdenas, A. M. Echavarren, J. Am. Chem. Soc. 2008, 130, 269-279.
7. C. Gronnier, S. Kramer, Y. Odabachian, F. Gagosz, J. Am. Chem. Soc. 2012, 134, 828–831.
8. P. R. McGonigal, C. de Leon, Y. Wang, A. Homs, C. R. Solorio-Alvarado, A. M. Echavarren, Angew. Chem. Int. Ed. 2012, 51, 13093-13096.
9. a) C. Nieto-Oberhuber, M. P. Muñoz, E. Buñuel, C. Nevado, D. J. Cárdenas, A. M. Echavarren, Angew. Chem. 2004, 116, 2456–2460; Angew. Chem. Int. Ed. 2004, 43, 2402–2406; b) C. Nieto-Oberhuber, M. P. Muñoz, S. López, E. Jiménez-Núñez, C.
Nevado, E. Herrero-Gómez, M. Raducan, A. M. Echavarren, *Chem. Eur. J.* **2006**, *12*, 1677–1693.

10. C. Nieto-Oberhuber, S. López, M. P. Muñoz, E. Jiménez-Núñez, E. Buñuel, D. J. Cárdenas, A. M. Echavarren, *Chem. Eur. J.* **2006**, *12*, 1694–1702.

11. C. H. M. Amijs, V. López-Carrillo, M. Raducan, P. Pérez-Galán, C. Ferrer, A. M. Echavarren, *J. Org. Chem.* **2008**, *73*, 7721–7730.
Experimental Procedures

2.1 Procedure of the synthesis of ortho-borinatephosphine gold chloride complexes 6, 7a

Au(tht)Cl (50.0 mg, 0.16 mmol) was dissolved in CH₂Cl₂ ortho-borinatephosphine ligand (63.6 mg, 0.17 mmol for 6, 81.7 mg, 0.17 mmol for 7a) was added. The reaction mixture was stirred for 1 h in the absence of light to give a nearly transparent colorless solution. The reaction mixture was passed through a layer of silica (2 cm) and evaporated. Recrystallization from CH₂Cl₂/hexane mixture at 23 ºC gave a crystalline colorless solid, which was collected, washed with pentane and vacuum dried. Yield: 89.3 mg (92%) for 6, 106.9 mg (90%) for 7a. Crystals suitable for X-ray analysis of both complexes were grown using a slow gas diffusion of Et₂O into the CH₂Cl₂ solution of the gold complexes at 5 ºC.

<chem>
\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{P} & \quad \text{Au} \quad \text{Cl}
\end{align*}
\]
</chem> 6

<chem>
\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{BMes}_2 & \quad \text{P} \quad \text{Au} \quad \text{Cl}
\end{align*}
\]
</chem> 7a

1H NMR (500 Hz, CDCl₃) δ 7.88-7.86 (m, 1H), 7.58-7.54 (m, 4H), 7.51-7.42 (m, 7H), 7.35-7.31 (m, 1H), 6.94-6.90 (m, 1H), 3.61 (s, 4H), 0.86 (s, 6H); 31P{1H} NMR (203 Hz, CDCl₃) δ 38.01 (s); 13C NMR (126 Hz, CDCl₃, PENDANT) δ 135.1 (d, J = 13.9 Hz, CH₃), 134.4 (d, J = 13.8 Hz, CH₃), 133.7 (C), 133.4 (d, J = 8.8 Hz, CH₃), 133.2 (C), 131.5 (d, J = 1.3 Hz, CH₃), 130.9 (C), 130.7 (d, J = 10.1 Hz, CH₃), 130.4 (C), 129.9 (d, J = 2.5 Hz, CH₃), 129.1 (d, J = 11.3 Hz, CH₃), 71.9 (CH₂), 31.8 (C), 22.2 (CH₃); MS-ESI: m/z for C₃₆H₃₆AuBClO₂P found 589.1 [M(H₂O)-Cl]⁺.

2.2 Procedure of the synthesis of gold complex 7b

Complex 7a (148.6 mg, 0.20 mmol) was dissolved in CH₂Cl₂ (1 mL) and AgOTf (51.4 mg, 0.20 mmol) was added. The reaction mixture was stirred for 30 min in the absence of light to give a colorless solution and a white precipitate. The mixture was filtered through 2 Teflon filters, evaporated, recrystallized from CH₂Cl₂/Et₂O at 5 ºC to give a colorless solid 7a, which was collected, washed with pentane and vacuum dried. Yield: 155.9 mg, 91%. Crystals suitable for X-ray analysis of 7a were grown using a slow gas diffusion of Et₂O into the CH₂Cl₂ solution of the gold complex at 5 ºC.
1H NMR (400 Hz, CDCl3) δ 7.45-7.18 (m, 14H), 6.77 (bs, 4H), 2.18 (bs, 18H); 
31P{1H} NMR (162 Hz, CDCl3) δ 34.39 (s); 
13C NMR (100 Hz, CDCl3, PENDANT) δ 157.2 (d, J = 19 Hz, Cipso,P), 140.3 (bs, C), 135.3 (d, J = 6.0 Hz, CHarom), 153.9 (d, J = 6.0 Hz, CHarom), 134.3 (d, J = 10.0 Hz, CHarom), 132.9 (s, C), 132.4 (s, C), 131.5 (d, J = 2.0 Hz, CHarom), 131.2 (bs, CH), 129.9 (d, J = 7.0 Hz, CHarom), 129.4 (d, J = 7.0 Hz, CHarom), 128.8 (d, J = 9.0 Hz, CHarom), 21.4 (s, CH3); MALDI+: m/z for C37H36AuBF3O3PS found 707.2 [M-OTf]+, 761.2 [M-OTf](NaOMe)+. 

Anal. calcd for C37H36AuBF3O3PS: C, 51.89; H, 4.24. Found: C, 52.65; H, 4.49.

2.3 Procedure of the synthesis of gold complexes 7c and 8

Complex 6 (84.9 mg, 0.14 mmol) or 7a (104.0 mg, 0.14 mmol) was dissolved in CH2Cl2 (1 mL) and AgNTf2 (54.3 mg, 0.14 mmol) was added. The reaction mixture was stirred for 30 min in the absence of light to give a colorless solution and a white precipitate. The mixture was filtered through 2 Teflon filters, evaporated, recrystallized from CH2Cl2/Et2O at 5 ºC to give 8 and 7c, which were collected, washed with pentane and vacuum dried. Yield: 129.9 mg (94%) for 7c, 80.9 mg (91%) for 8. Crystals suitable for X-ray analysis of 7c and 8 were grown using a slow gas diffusion of Et2O into the CH2Cl2 solution of the obtained gold complex at 5 ºC.

1H NMR (500 Hz, CDCl3) δ 7.50-7.44 (m, 4H), 7.42-7.35 (m, 5H), 7.25-7.13 (m, 5H), 6.57 (bs, Mes-CH, 4H), 2.18-1.94 (bs, 18H); 31P{1H} NMR (203 Hz, CDCl3) δ 30.88 (s); 13C NMR (126 Hz, CDCl3, PENDANT) δ 142.3 (s, C), 141.7 (s, C), 140.8 (C), 135.9 (d, J = 8.7 Hz, CHarom), 135.7 (d, J = 13.7 Hz, CHarom), 133.7 (d, J = 12.5 Hz, CHarom), 131.9 (CHarom), 131.7 (CHarom), 130.8 (s, C), 130.2 (s, C), 130.0 (d, J = 2.0 Hz, CHarom), 129.1 (d, J = 13.7 Hz, CHarom), 120.9 (s, C), 118.3 (s, C), 21.4 (CH3); MS-ESI: m/z for Au(C38H36BP)F6NO4S2 found 707.2 [M-F6NO4S2]+.

Anal. calcd for C38H36AuBF6NO4PS2: C, 46.22; H, 3.67; N, 1.42. Found: C, 45.67; H, 3.61; N, 1.59.
Hexagold cluster Anal. calcd for C_{130.2} (m, CH) 135.1 (m, CH) PENDANT 4H); 7.57 (m, 8H) suitable for X-ray analysis of salt were grown using a slow gas diffusion of Et_2O into the CH_2Cl_2 solution of the obtained gold complex at 5 ºC.

2.4 General procedure of the synthesis of hexagold clusters 9:

In a glove box, complex 6 (84.9 mg, 0.14 mmol) or 7a (104.0 mg, 0.14 mmol) was dissolved in CH_2Cl_2 (1 mL) and AgSbF_6 (50.0 mg, 0.14 mmol) was added. The reaction mixture was stirred for 30 min in the absence of light to give an intense dark green solution and a white precipitate. The mixture was filtered through 2 Teflon filters, the dark green filtrate was collected, passed through a layer of silica (2 cm, twice), evaporated, recrystallized from CH_2Cl_2/hexane at 5 ºC. Yield of 9: 28.3 mg (45%) from 7a, 20.8 mg (33%) from 6. Crystals suitable for X-ray analysis of 9 were grown using a slow gas diffusion of Et_2O into the CH_2Cl_2 solution of the obtained gold complex at 5 ºC.

Hexagold cluster 9' as a BF_4 salt was obtained by the reaction between 7a and AgBF_4 following the above described procedure. Yield of 9': 21.3 mg (38%). Crystals suitable for X-ray analysis of salt were grown using a slow gas diffusion of Et_2O into the CH_2Cl_2 solution of the obtained gold complex at 5 ºC.

\[ \text{SbF}_6^2+ \text{2 SbF}_6^- \]

\[ \begin{array}{c}
\text{Au} \quad \text{Au} \\
\text{Au} \quad \text{Au} \\
\text{Au} \quad \text{Au} \\
\text{Au} \quad \text{Au} \\
\text{Au} \quad \text{Au}
\end{array} \]

9: L = PPh_2

\[ ^1\text{H NMR} (500 \text{ Hz}, \text{CDCl}_3) \delta 8.07 (dd, J(H,H) = 7.0 \text{ Hz}, J(H,P) = 1.5 \text{ Hz}, 1H), 7.64-7.55 (m, 11H), 7.45 (td, J(H,H) = 7.5 \text{ Hz}, J(H,P) = 1.0 \text{ Hz}, 1H), 6.92 (q, J(H,H) = 5.4 \text{ Hz}, 1H), 2.99 (s, 4H), 0.45 (s, 6H); ^{31}\text{P} (^1\text{H}) \text{ NMR} (203 \text{ Hz}, \text{CDCl}_3) \delta 50.73 (s); ^{13}\text{C} \text{ NMR} (126 \text{ Hz}, \text{CDCl}_3, \text{PENDANT}) \delta 136.9 (t, J = 5.6 \text{ Hz}, \text{CH}_{\text{arom}}), 134.1 (t, J = 7.5 \text{ Hz}, \text{CH}_{\text{arom}}), 133.7 (t, J = 5.0 \text{ Hz}, \text{CH}_{\text{arom}}), 133.1 (t, J = 26.3 \text{ Hz}, \text{C}), 132.3 (s, \text{CH}_{\text{arom}}), 131.3 (m, \text{CH}_{\text{arom}}), 129.0 (s, \text{CH}_{\text{arom}}), 129.8 (t, J = 6.3 \text{ Hz}, \text{CH}_{\text{arom}}), 129.6 (s, \text{C}), 129.4 (s, \text{C}), 71.6 (s, \text{CH}_2), 31.1 (s, \text{C}), 20.1 (s, \text{CH}_3); \text{MALDI}^+: m/z \text{ for } C_{48}H_{47}AuB_2F_6NO_8P_2S_2 \text{ found 945.4 } [\text{M+}^+]^+.
\]

Anal. calcd for C_{49}H_{48}AuB_2F_6NO_8P_2S_2: C, 47.04; H, 3.95; N, 1.14. Found, C 46.62; H, 3.91; N, 1.25.

Hexagold cluster 9' has identical \(^1\text{H NMR}, ^{31}\text{P} (^1\text{H}) \text{ NMR,} \quad ^{13}\text{C} \text{ NMR spectra as the SbF}_6 \text{ salt 9.}
2.5 General Procedure for the cyclization of 1,6-enynes 11a-b

To a solution of the 1,6-enyne in 1,2-dichloroethane (0.1-0.05 M), the catalyst was added. The reaction was stirred at 23 °C until TLC showed total conversion. Then, the mixture was filtered through Celite, the solvent was evaporated, and the residue was purified by preparative TLC to give the cyclized product (SiO₂, EtOAc/cyclohexane).

Table 1. Cyclization of 1,6-enynes 11a-b.

| Entry | Substrate | Catalyst (mol%) | Time, h | Yield, % | Products, ratio |
|-------|-----------|-----------------|---------|----------|-----------------|
| 1     | 11a       | 9 (2.5 mol %)   | 0.3     | 85       | 1(12a):1.6(12b) |
| 2     | 11a       | 7c (2 mol %)    | 0.08    | 80       | 1(12a):1.6(12b) |
| 3     | 11b       | 9 (2.5 mol %)   | 12      | 90       | 1.5(15):1(16)   |

2.6 Addition of indole to 1,6-enyne 11c

To a solution of N-cinnamyl-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide (11c) (48.8 mg, 0.15 mmol) and indole (18.7 mg, 0.16 mmol 1.1 equiv) in 1,2-dichloroethane (2 ml) the catalyst 9 (10 mg, 0.0037 mmol, 2.5 mol%) was added. The reaction was stirred at 75 °C for 17 h, then it was filtered through Celite, the solvent was evaporated and the the residue was purified by preparative TLC to give the cyclized product 17 (42.5 mg, 64%) (SiO₂, EtOAc/cyclohexane).
2.7 Oxidative cyclization of alkynyl oxirane 18

![Chemical structure](image)

To a solution of alkynyl epoxide 18 (11.4 mg, 0.093 mmol) in CH$_3$CN (1 mL), pyridine oxide (18.1 mg, 0.19 mmol), and catalyst 9 (10 mg, 0.0037 mmol, 4 mol%) were added and the solution (0.1-0.05 M) was heated to 80 °C for 10 h. The mixture was filtered through a silica pad, which was rinsed with CH$_2$Cl$_2$ (2 times). The solvent was evaporated and lactone 19 (7.3 mg, 57%) was isolated by chromatography (SiO$_2$, EtOAc/cyclohexane).

2.8 Cyclosiomerization of 7-alkynyl cycloheptatriene 20

![Chemical structure](image)

To a solution of 7-alkynyl cycloheptatriene 20 in toluene (0.1-0.05 M), the catalyst was added. The reaction was stirred at 23 °C until TLC showed total conversion, then it was filtered through Celite, the solvent was evaporated and the residue was purified by preparative TLC to give exclusively 2-substituted indene 21 (SiO$_2$, EtOAc/cyclohexane).

| Table 2. Cyclosiomerization of 7-alkynyl cycloheptatriene 20 |
|-------------------------------------------------------------|
| Entry | Substrate | Catalyst (5 mol%) | Temperature, °C | Time, h | Yield, % |
|-------|-----------|-------------------|-----------------|--------|----------|
| 1     | 20        | 9                 | 23              | 1      | 72       |
| 2     | 20        | 7c                | 0               | 0.25   | 66       |

2.9 Procedure for hydration of phenylacetylene

![Chemical structure](image)

To a solution of phenylacetylene in MeOH (1 M), 4 equiv of water and the catalyst were added and the mixture was stirred at 23 °C until TLC showed total conversion. The mixture was diluted with CH$_2$Cl$_2$ and washed with water. The aqueous phase was extracted with CH$_2$Cl$_2$ and the combined organic phases were washed with brine, dried over MgSO$_4$, filtered and evaporated to yield acetophenone.
### Table 3. Hydration of phenylacetylene

| Entry | Substrate | Catalyst (1 mol%) | Time, h | Yield, % |
|-------|-----------|-------------------|---------|----------|
| 1     | 22        | 9                 | 18      | 87       |
| 2     | 22        | 7c                | 16      | 90       |

#### 2.10 Procedure for [4+2] cycloaddition of 1,6-ene 13

![Catalyst (2 mol%)](image1)

To a solution of 1,6-ene 13 in CH$_2$Cl$_2$ (0.1-0.05 M) the catalyst was added. The reaction was stirred at 23 °C until TLC showed total conversion, then it was filtered through Celite, the solvent was evaporated and the residue was purified by preparative TLC to give 14 (SiO$_2$, EtOAc/cyclohexane).

### Table 4. [4+2] cycloaddition

| Entry | Substrate | Catalyst (2 mol%) | Time, h | Yield, % |
|-------|-----------|-------------------|---------|----------|
| 1     | 13        | 9                 | 12      | 73       |
| 2     | 13        | 7c                | 0.75    | 71       |
| 3     | 13        | 2a                | 1.5     | 77       |

**Dimethyl 8-Methyl-4,4-dimethyl-3a,4-dihydro-1H-cyclopenta[b]naphthalene-2,2(3H)-dicarboxylate (14)**

![Dimethyl 8-Methyl-4,4-dimethyl-3a,4-dihydro-1H-cyclopenta[b]naphthalene-2,2(3H)-dicarboxylate (14)]

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.17 (d, $J = 6.1$, 1H), 7.08 (dd, $J = 6.1$, 6.0 Hz, 1H), 7.00 (d, $J = 6.1$ Hz, 1H), 6.58 (bs, 1H), 3.79 (s, 3H), 3.74 (s, 3H), 3.34 (d, $J = 12.8$ Hz, 1H), 3.03 (dt, $J = 14.4$, 2.4 Hz, 1H), 2.72-2.67 (m, 1H), 2.62 (dd, $J = 11.0$, 9.8 Hz, 1H), 2.34 (s, 3H), 2.16 (t, $J = 9.7$ Hz, 1H), 1.42 (s, 3H), 0.93 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.3, 172.1, 144.3, 143.1, 133.2, 132.3, 128.3, 126.6, 121.4, 116.2,
59.1, 53.0, 47.9, 39.8, 37.0, 35.0, 26.1, 21.8, 19.8; HRAPCI-MS $m/z = 351.1$ [M+Na]$^+$, calc. for C$_{20}$H$_{24}$O$_4$ = 328.17.

**Kinetic study. General procedure**

$$E = \text{CO}_2\text{Me}$$

![Chemical structure](image)

To a solution of 1,6- enyne 11a in CD$_2$Cl$_2$ (0.8 M) at 23 °C (for the experiment A) or at 0 °C (for the experiments B, C, D) complex 9 (for the experiments A, B) or a 1:1 ratio of complex 9 and PPh$_3$ (for the experiment C), or a 1:2 ratio of complex 9 and PPh$_3$ (for the experiment D) was added. The reaction was monitored by $^1$H NMR with 40 seconds delay between each of the measurements.

X: time, minutes
Y: conversion of 11a into 12a.

![Conversion plot](image)

**Figure 1.** Kinetic study of the 1,6- enyne cyclization catalyzed by complex 9.
Photophysical properties of hexagold cluster 9

The hexanuclear gold(I) complex shows room-temperature luminescent both in a dichloromethane solution and in a solid state under excitation at 355 nm. The UV-Vis spectrum measured in dichloromethane (Fig. 2) displays intense absorption ranging from ca. 220 to 300 nm that can be assigned to an IL ($\pi \rightarrow \pi^*$) transition localized at the phosphine ligand and less intensive band with the maximum at ca. 364 nm, that is likely a combination of the metal-centered 5$d$ $\rightarrow$ 6$s$/6$p$ transition due to the Au-Au interactions in the Au$_6$ core and the LM charge transfer transition.

![Figure 2. The absorption spectra of 9 in dichloromethane at room temperature](image)

Table 5. The absorption spectrum data of 9

| $\lambda$, nm | $\varepsilon$, $10^5$ mol$^{-1}$lcm$^{-1}$ |
|--------------|-------------------------------------|
| 239          | 0.4                                 |
| 320          | 0.1                                 |
| 364          | 0.06                                |

Complex 9 shows emission at room temperature in a degassed dichloromethane solution with the maximum at ca. 460 nm, the origin for this band can be proposed as an intraligand (IL) or/and metal-to-ligand transitions (Fig. 3) The lifetimes of the transition indicate a singlet origin of the emissive excited state ($\tau_1 = 1.93$ ns, $\tau_2 = 6.10$ ns). In the solid state the gold cluster 9 displays a more intense emission, which is substantially red-shifted with the maximum at ca. 550 nm, the origin for this band can be proposed as transitions in Au$_6$ core.

![Figure 3. The emission spectra of 9 in solid state and in degassed dichloromethane at room temperature](image)
