Supporting Information for

Solution versus Solid-State Dual Emission of the Au(I)-Alkynyl Diphosphine Complexes via Modification of Polyaromatic Spacer

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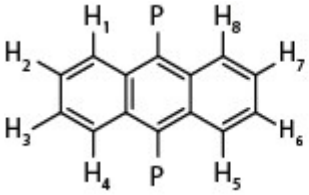
Experimental section



numbering scheme for **1–4**

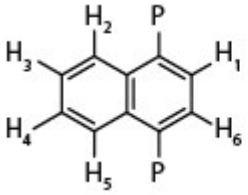
($AuC_2C_6H_5)_2$L1 (1). Recrystallization by gas-phase diffusion of pentane into a dichloromethane/acetone (1:2 v/v) solution at +5 C° gave yellow blocks crystals (93%). ESI MS (*m/z*): $[M–C_2Ph]^+$ 1041.14 (calculated 1041.14), $[M+Na]^+$ 1165.17 (calculated 1165.17). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K; *δ*): 36.3 (s). ^1H NMR ($CDCl_3$, 298 K; δ): 8.28–8.30 (m, 1,4,5,8-H $C_{14}H_8$, 4H), 7.65–7.70 (m, *ortho*-H Ph, 8H), 7.43–7.52 (m, *meta*+*para*-H Ph, ortho-H $C_2C_6H_5$, 16H), 7.17–7.26 (m, *meta*+*para*-H C_2 C_6H_5, 6H), 7.10–7.14 (m, 2,3,6,7-H $C_{14}H_8$, 4H). Anal. Calc. for $C_{54}H_{38}Au_2P_2$: C, 56.76; H, 3.35. Found: C, 56.70; H, 3.28.

($AuC_2C(CH_3)_2OH)_2$L1 (2). Recrystallization by gas-phase diffusion of diethyl ether into a dichloromethane /acetone (1:1 v/v) solution at +5 C° gave pale green blocks crystals (95%). ESI MS (*m/z*): $[M–C_2C(CH_3)_2OH]^+$ 1023.14 (calcd 1023.14), $[M+Na]^+$ 1129.18 calcd 1129.19), $[M+K]^+$ 1145.16 (calcd 1145.16). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K; *δ*): 36.4 (s). ^1H NMR ($CDCl_3$, 298 K; δ): 8.22–8.25 (m, 1,4,5,8-H $C_{14}H_8$, 4H), 7.60–7.65 (m, *ortho*-H Ph, 8H), 7.42–7.51 (m, *meta*+*para*-H Ph, 12H), 7.09–7.11 (m, 2,3,6,7-H $C_{14}H_8$, 4H), 1.96 (s, OH, 2H), 1.56 (s, Me, 12H). Anal. Calc. for $C_{48}H_{42}Au_2O_2P_2$: C, 52.09; H, 3.83. Found: C, 51.87; H, 3.74.

($AuC_2C_6H_{10}OH)_2$L1 (3). Recrystallization by gas-phase diffusion of pentane into a dichloromethane solution at +5 C° gave green needles (88%). ESI MS (*m/z*): $[M-C_2C_6H_{10}OH]^+$ 1063.18 (calcd 1063.18), $[M+Na]^+$ 1209.25 (calcd 1209.25), $[M+K]^+$ 1225.22 (calcd 1225.23). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K; *δ*): 36.3 (s). ^1H NMR ($CDCl_3$, 298 K; δ): 8.22–8.25 (m, 1,4,5,8-H $C_{14}H_8$, 4H), 7.60–7.65 (m, *ortho*-H Ph, 8H), 7.42–7.51 (m, *meta*+*para*-H Ph, 12H), 7.09–7.11 (m, 2,3,6,7-H $C_{14}H_8$, 4H), 3.0–0.5 (broad unresolved signals of Cy H atoms, 22H). Anal. Calc. for $C_{54}H_{50}Au_2O_2P_2$: C, 54.65; H, 4.25. Found: C, 54.73; H, 4.20.

($AuC_2C(C_6H_5)_2OH)_2$L1 (4). Recrystallization by gas-phase diffusion of pentane into an acetone solution at +5 C° give pale yellow microcrystalline material (78%). ESI MS (*m/z*): $[M–C_2C(C_6H_5)_2OH]^+$ 1147.18 (calcd 1147.19), $[M+Na]^+$ 1377.25 (calcd 1377.26), $[M+K]^+$ 1393.22 (calcd 1393.23). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K; *δ*): 36.4 (s). ^1H NMR ($CDCl_3$, 298 K; δ): 8.23–8.26 (m, 1,4,5,8-H $C_{14}H_8$, 4H), 7.68–7.70 (d, $^3J_{HH}$ 7.4 Hz, *ortho*-H $C_2C(C_6H_5)_2OH$, 8H), 7.61–7.66 (m, *ortho*-H Ph, 8H), 7.41–7.50 (m, *meta*+*para*-H Ph, 12H),

7.25–7.29 (m, *meta*-H $C_2C(C_6H_5)_2OH$, 8H), 7.17–7.21 (t, $^3J_{HH}$ 7.3 Hz, *para*-H $C_2C(C_6H_5)_2OH$, 4H), 7.09–7.11 (m, 2,3,6,7-H $C_{14}H_8$, 4H), 2.79 (s, OH, 2H). Anal. Calc. for $C_{68}H_{50}Au_2O_2P_2$: C, 60.27; H, 3.72. Found: C, 60.41; H, 3.81.



numbering scheme for **5–8**

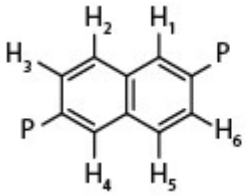
$(AuC_2C_6H_5)_2$L2 (5). Recrystallization by gas-phase diffusion of pentane into a dichloromethane solution at +5 C° gave colourless blocks crystals (72%). ESI MS (*m/z*): $[M+Na]^+$ 1115.14 (calcd 1115.15), $[M+K]^+$ 1131.16 (calcd 1131.13). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K; *δ*): 37.6 (s). ^1H NMR ($CDCl_3$, 298 K; δ): 8.47–8.49 (m, 2,5-H $C_{10}H_6$, 2H), 7.47–7.66 (m, *ortho*+*meta*+*para*-H Ph and *ortho*-H $C_2C_6H_5$ and 3,4-H $C_{10}H_6$, 26H), 7.18–7.26 (m, *meta*+*para*-H $C_2C_6H_5$, 6H), 6.85–6.89 (m, 1,6-H $C_{10}H_6$, 2H). Anal. Calc. for $C_{50}H_{36}Au_2P_2$: C, 54.96; H, 3.32. Found: C, 54.83; H, 3.40.

$(AuC_2C(CH_3)_2OH)_2$L2 (6). Recrystallization by gas-phase diffusion of dietyl ether into a dichloromethane solution at +5 C° gave colourless crystals (80%). ESI MS (*m/z*): $[M+Na]^+$ 1079.17 (calcd 1079.16). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K; *δ*): 36.6 (s). ^1H NMR ($CDCl_3$, 298 K; δ): 8.40–8.42 (m, 2,5-H $C_{10}H_6$, 2H), 7.45–7.61 (m, *ortho*+*meta*+*para*-H Ph and 3,4-H $C_{10}H_6$, 22H), 6.80–6.84 (m, 1,6-H $C_{10}H_6$, 2H), 1.95 (s, OH, 2H), 1.57 (s, Me, 12H). Anal. Calc. for $C_{44}H_{40}Au_2O_2P_2$: C, 50.01; H, 3.82. Found: C, 50.12; H, 3.78.

$(AuC_2C_6H_{10}OH)_2$L2 (7). Recrystallization by gas-phase diffusion of dietyl ether into a dichloromethane solution at +5 C° gave colourless crystals (76%). ESI MS (*m/z*): $[M+Na]^+$ 1159.24 (calcd 1159.23), $[2M+2Na]^{2+}$ 1159.24 (calcd 1159.23), $[M+K]^+$ 1175.21 (calcd 1159.21). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K; *δ*): 37.6 (s). ^1H NMR ($CDCl_3$, 298 K; δ): 8.41–8.44 (m, 2,5-H $C_{10}H_6$, 2H), 7.44–7.61 (m, *ortho*+*meta*+*para*-H Ph and 3,4-H $C_{10}H_6$, 22H), 6.80–6.84 (m, 1,6-H $C_{10}H_6$, 2H), 1.95 (s, OH, 2H), 1.25–1.90 (broad unresolved signals of Cy H atoms, 20H). Anal. Calc. for $C_{50}H_{50}Au_2O_2P_2$: C, 52.63; H, 4.43. Found: C, 52.50; H, 4.33.

$(AuC_2C(C_6H_5)_2OH)_2$L2 (8). Recrystallization by gas-phase diffusion of dietyl ether into a dichloromethane solution at +5 C° gave white microcrystalline material (82%). ESI MS (*m/z*): $[2M-2C_2C(Ph)_2OH]^{2+}$ 1097.67 (calcd 1097.67). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K; *δ*): 37.4 (s). ^1H NMR ($CDCl_3$, 298 K; δ): 8.43–8.46 (m, 2,5-H $C_{10}H_6$, 2H), 7.70 (d, $^3J_{HH}$ 8.6 Hz, *ortho*-H $C_2C(C_6H_5)_2OH$, 8H), 7.42–7.64 (m, *ortho*+*meta*+*para*-H Ph and 3,4-H $C_{10}H_6$, 22H), 7.28 (m, *meta*-H $C_2C(C_6H_5)_2OH$, 8H), 7.19 (t, $^3J_{HH}$ 7.2 Hz, *para*-H $C_2C(C_6H_5)_2OH$, 4H),

6.82–6.85 (m, 1,6-H $C_{10}H_6$, 2H), 2.79 (s, OH, 2H). Anal. Calc. for $C_{64}H_{48}Au_2O_2P_2$: C, 58.91; H, 3.71. Found: C, 59.01; H, 3.64.



numbering scheme for **9–12**

($AuC_2C_6H_5)_2$L3 (9). Recrystallization by gas-phase diffusion of pentane into a dichloromethane solution at +5 C° gave colourless blocks crystals (89%). ESI MS (*m/z*): $[M+Na]^+$ 1115.15 (calcd 1115.15). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K; *δ*): 43.0 (s). ^1H NMR ($CDCl_3$, 298 K; δ): 8.17 (d, $^3J_{HP}$ 14.4 Hz, 3,6-H $C_{10}H_6$, 2H), 7.89 (dd, $^3J_{HH}$ 8.5 Hz, $^4J_{HH}$ 1.7 Hz, 2,5-H $C_{10}H_6$, 2H, 2H), 7.44–7.64 (m, *ortho*+*meta*+*para*-H Ph and *ortho*-H $C_2C_6H_5$ and 1,4-H $C_{10}H_6$, 26H), 7.17–7.30 (m, *meta*+*para*-H $C_2C_6H_5$, 6H). Anal. Calc. for $C_{50}H_{36}Au_2P_2$: C, 54.96; H, 3.32. Found: C, 54.87; H, 3.42.

($AuC_2C(CH_3)_2OH)_2$L3 (10). Recrystallization by gas-phase diffusion of dietyl ether into a dichloromethane solution at +5 C° gave pale yellow crystals (83%). ESI MS (*m/z*): $[M-C_2C(CH_3)_2OH]^+$ 973.13 (calcd 973.13), $[M+Na]^+$ 1079.17 (calcd 1079.16). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K; *δ*): 43.0 (s). ^1H NMR ($CDCl_3$, 298 K; δ): 8.12 (d, $^3J_{HP}$ 14.4 Hz, 3,6-H $C_{10}H_6$, 2H), 7.86 (dd, $^3J_{HH}$ 8.5 Hz, $^4J_{HH}$ 1.7 Hz, 2,5-H $C_{10}H_6$, 2H), 7.34–7.63 (m, *ortho*+*meta*+*para*-H Ph and 1,4-H $C_{10}H_6$, 22H), 1.98 (s, OH, 2H), 1.60 (s, Me, 12H). Anal. Calc. for $C_{44}H_{40}Au_2O_2P_2$: C, 50.01; H, 3.82. Found: C, 49.95; H, 3.75.

($AuC_2C_6H_{10}OH)_2$L3 (11). Recrystallization by gas-phase diffusion of dietyl ether into a dichloromethane solution at +5 C° gave colourless crystals (95%). ESI MS (*m/z*): $[M+Na]^+$ 1159.24 (calcd 1159.24). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K; *δ*): 42.9 (s). ^1H NMR ($CDCl_3$, 298 K; δ): 8.12 (d, $^3J_{HP}$ 14.4 Hz, 3,6-H $C_{10}H_6$, 2H), 7.82–7.91 (m, 2,5-H $C_{10}H_6$, 2H), 7.46–7.58 (m, *ortho*+*meta*+*para*-H Ph and 1,4-H $C_{10}H_6$, 22H), 1.98 (s, OH, 2H), 1.26–1.96 (broad unresolved signals of Cy H atoms, 20H). Anal. Calc. for $C_{50}H_{50}Au_2O_2P_2$: C, 52.73; H, 4.43. Found: C, 52.71; H, 4.35.

($AuC_2C(C_6H_5)_2OH)_2$L3 (12). Recrystallization by gas-phase diffusion of dietyl ether into a dichloromethane solution at +5 C° gave white microcrystalline material (92%). ESI MS (*m/z*): $[M+Na]^+$ 1327.24 (calcd 1327.23). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K; *δ*): 42.4 (s). ^1H NMR ($CDCl_3$, 298 K; δ): 8.08 (d, $^3J_{HP}$ 14.0 Hz, 3,6-H $C_{10}H_6$, 2H), 7.86 (dd, $^3J_{HH}$ 8.4 Hz, $^4J_{HH}$ 1.8 Hz, 2,5-H $C_{10}H_6$, 2H), 7.70–7.75 (m, *ortho*-H $C_2C(C_6H_5)_2OH$, 8H), 7.43–7.59 (m, *ortho*+*meta*+*para*-H Ph and 1,4-H $C_{10}H_6$, 22H), 7.3 (dd, $^3J_{HH}$ 7.5 Hz, *meta*-H

$C_2C(C_6H_5)_2OH$, 8H), 7.2 (t, $^3J_{HH}$ 7.3 Hz, *para*-H $C_2C(C_6H_5)_2OH$, 4H), 2.81 (s, OH, 2H). Anal. Calc. for $C_{64}H_{48}Au_2O_2P_2$: C, 58.91; H, 3.71. Found: C, 58.88; H, 3.86.

$(AuC_2C_6H_5)_2$L4 (13). Recrystallization by gas-phase diffusion of diethyl ether into a dichloromethane/toluene (1:1 v/v) solution at room temperature gave yellow blocks crystals (77%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K; *δ*): 16.8 (s). ^1H NMR ($CDCl_3$, 298 K; δ): 8.44–8.46 (m, 1,4,5,8-H $C_{14}H_8$, 4H), 8.00–8.05 (m, *ortho*-H Ph, 8H), 7.67–7.69 (m, 2,3,6,7-H $C_{14}H_8$, 4H), 7.53–7.58 (m, *meta*+*para*-H Ph and *ortho*-H $C_2C_6H_5$, 16H), 7.26–7.28 (m, *meta*+*para*-H $C_2C_6H_5$, 6H). Anal. Calc. for $C_{58}H_{38}Au_2P_2$: C, 58.50; H, 3.22. Found: C, 58.21; H, 3.40.

$(AuC_2C_6H_4CF_3)_2$L4 (14). Recrystallization by gas-phase diffusion of diethyl ether into a dichloromethane solution at room temperature gave yellow microcrystalline material (63%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K; *δ*): 16.6 (s). ^1H NMR ($CDCl_3$, 298 K; δ): 8.44–8.46 (m, 1,4,5,8-H $C_{14}H_8$, 4H), 7.99–8.04 (m, *ortho*-H Ph, 8H), 7.66–7.69 (m, 2,3,6,7-H $C_{14}H_8$, 4H), 7.51–7.61 (m, *meta*+*para*-H Ph and *meta*+*ortho*-H $C_2C_6H_4CF_3$, 20H). Anal. Calc. for $C_{60}H_{36}Au_2F_6P_2$: C, 54.31; H, 2.73. Found: C, 54.70; H, 3.01.

$(AuC_2C_6H_4OMe)_2$L4 (15). Recrystallization by gas-phase diffusion of pentane into a dichloromethane/toluene (2:1 v/v) solution at +5 C° gave yellow microcrystalline material (68%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K; *δ*): 16.9 (s). ^1H NMR ($CDCl_3$, 298 K; δ): 8.43–8.46 (m, 1,4,5,8-H $C_{14}H_8$, 4H), 7.99–8.05 (m, *ortho*-H Ph, 8H), 7.66–7.69 (m, 2,3,6,7-H $C_{14}H_8$, 4H), 7.56–7.58 (m, *meta*+*para*-H Ph, 12H), 7.47–7.49 (d, $^3J_{HH}$ 8.7 Hz, *meta*-H $C_2C_6H_4OMe$, 4H), 6.81 (d, $^3J_{HH}$ 8.7 Hz, *ortho*-H $C_2C_6H_4OMe$, 4H), 3.80 (s, Me, 6H). Anal. Calc. for $C_{60}H_{42}Au_2O_2P_2$: C, 57.61; H, 3.38. Found: C, 57.63; H, 3.48.

$(AuC_2C_6H_4NMe_2)_2$L4 (16). Recrystallization by gas-phase diffusion of diethyl ether into a dichloromethane solution at room temperature gave brown microcrystalline material Yield: (81%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K; *δ*): 17.1 (s). ^1H NMR ($CDCl_3$, 298 K; δ): 8.43–8.46 (m, 1,4,5,8-H $C_{14}H_8$, 4H), 7.99–8.05 (m, *ortho*-H Ph, 8H), 7.66–7.68 (m, 2,3,6,7-H $C_{14}H_8$, 4H), 7.53–7.57 (m, *meta*+*para*-H Ph, 12H), 7.44 (d, $^3J_{HH}$ 8.8 Hz, *meta*-H $C_2C_6H_4NMe_2$, 4H), 6.63 (d, $^3J_{HH}$ 8.8 Hz, *ortho*-H $C_2C_6H_4NMe_2$, 4H), 2.96 (s, Me, 12H). Anal. Calc. for $C_{62}H_{48}Au_2N_2P_2$: C, 58.32; H, 3.79. Found: C, 57.97; H, 3.95.

$(AuC_2C_6H_5)_2$L5 (17). Recrystallization by gas-phase diffusion of diethyl ether into a dichloromethane/toluene (4:1 v/v) solution at +5 C° gave colourless needles (91%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K; *δ*): 16.7 (s). ^1H NMR ($CDCl_3$, 298 K; δ): 8.23–8.27 (m, 2,5-H $C_{10}H_6$, 2H), 7.92–7.97 (m, *ortho*-H Ph, 8H), 7.84 (s, 1,6-H $C_{10}H_6$, 2H), 7.68–7.71 (m, 3,4-H $C_{10}H_6$,

2H), 7.52–7.55 (m, *meta*+*para*-H Ph and *ortho*-H $C_2C_6H_5$, 16H), 7.18–7.29 (m, *meta*+*para*-H $C_2C_6H_5$, 6H). Anal. Calc. for $C_{54}H_{36}Au_2P_2$: C, 56.86; H, 3.18. Found: C, 56.36; H, 3.30.

$(AuC_2C_6H_4CF_3)_2$L5 (18). Recrystallization by gas-phase diffusion of pentane into a dichloromethane/hexane (5:1 v/v) solution at +5 C° gave white microcrystalline material (74%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K; *δ*): 16.4 (s). ^1H NMR ($CDCl_3$, 298 K; δ): 8.25–8.27 (m, 2,5-H $C_{10}H_6$, 2H), 7.91–7.97 (m, *ortho*-H Ph, 8H), 7.85 (s, 1,6-H $C_{10}H_6$, 2H), 7.69–7.71 (m, 3,4-H $C_{10}H_6$, 2H) 7.51–7.60 (m, *meta*+*para*-H Ph and *meta*+*ortho*-H $C_2C_6H_4CF_3$, 20H). Anal. Calc. for $C_{56}H_{34}Au_2F_6P_2$: C, 52.68; H, 2.68. Found: C, 52.31; H, 2.90.

$(AuC_2C_6H_4OMe)_2$L5 (19). Recrystallization by gas-phase diffusion of diethyl ether into a dichloromethane solution at +5 C° gave colourless blocks crystals (86%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K; *δ*): 16.8 (s). ^1H NMR ($CDCl_3$, 298 K; δ): 8.25–8.27 (m, 2,5-H $C_{10}H_6$, 2H), 7.91–7.97 (m, *ortho*-H Ph, 8H), 7.84 (s, 1,6-H $C_{10}H_6$, 2H), 7.68–7.70 (m, 3,4-H $C_{10}H_6$, 2H), 7.51–7.60 (m, *meta*+*para*-H Ph, 12H), 7.46–7.48 (d, $^3J_{HH}$ 8.9 Hz, *ortho*-H $C_2C_6H_4OMe$, 4H), 6.80–6.82 (d, $^3J_{HH}$ 8.9 Hz, *meta*-H $C_2C_6H_4OMe$, 4H), (s, Me, 6H). Anal. Calc. for $C_{56}H_{40}Au_2O_2P_2$: C, 56.01; H, 3.36. Found: C, 55.87; H, 3.42.

$(AuC_2C_6H_5)_2$L6 (20). Recrystallization by gas-phase diffusion of diethyl ether into a dichloromethane solution at +5 C° gave colourless crystals (77%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K; *δ*): 16.6 (s). ^1H NMR ($CDCl_3$, 298 K; δ): 8.16 (br s, 1,4-H $C_{10}H_6$, 2H), 7.86–7.93 (m, *ortho*-H Ph and 3,6-H $C_{10}H_6$, 10H), 7.65 (d, $^3J_{HH}$ 8.5 Hz, 2,5-H $C_{10}H_6$, 2H), 7.51–7.61 (m, *meta*+*para*-H Ph and *meta*+*ortho*-H $C_2C_6H_5$, 20H), 7.22–7.29 (m, *para*-H $C_2C_6H_5$, 2H). Anal. Calc. for $C_{54}H_{36}Au_2P_2$: C, 56.86; H, 3.18. Found: C, 56.74; H, 3.33.

$(AuC_2C_6H_4CF_3)_2$L6 (21). Recrystallization by gas-phase diffusion of pentane into a dichloromethane/hexane (5:1 v/v) solution at +5 C° gave white microcrystalline material (68%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K; *δ*): 16.4 (s). ^1H NMR ($CDCl_3$, 298 K; δ): 8.16 (br s, 1,4-H $C_{10}H_6$, 2H), 7.87–7.93 (m, *ortho*-H Ph and 3,6-H $C_{10}H_6$, 10 H), 7.66 (d, $^3J_{HH}$ 9.4 Hz, 2,5-H $C_{10}H_6$, 2H), 7.51–7.61 (m, *meta*+*para*-H Ph and *meta*+*ortho*-H $C_2C_6H_4CF_3$, 20H). Anal. Calc. for $C_{56}H_{34}Au_2F_6P_2$: C, 52.31; H, 2.68. Found: C, 52.21; H, 2.87.

$(AuC_2C_6H_4OMe)_2$L6 (22). Recrystallization by gas-phase diffusion of diethyl ether into a dichloromethane solution at +5 C° gave white microcrystalline material (83%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K; *δ*): 16.7 (s). ^1H NMR ($CDCl_3$, 298 K; δ): 8.15 (br s, 1,4-H $C_{10}H_6$, 2H), 7.86–7.92 (m, *ortho*-H Ph and 3,6-H $C_{10}H_6$, 10H), 7.65 (d, $^3J_{HH}$ 8.7 Hz, 2,5-H $C_{10}H_6$, 2H), 7.49–7.53 (m, *meta*+*para*-H Ph, 12H), 7.47 (d, $^3J_{HH}$ 8.7 Hz, *ortho*-H $C_2C_6H_4OMe$, 4H), 6.81

(d, $^3J_{HH}$ 8.7 Hz, *meta*-H $C_2C_6H_4OMe$, 4H), 3.80 (s, Me, 6H). Anal. Calc. for $C_{56}H_{40}Au_2O_2P_2$: C, 56.01; H, 3.36. Found: C, 55.99; H, 3.46.

X-ray diffraction measurements. The crystals of **1**–**3**, **7**, **9**, **12**, **13** and **19** were immersed in cryo oil and measured at a temperature of 100 K, 120 K (**12**) or 150 K (**13** and **19**). The diffraction data were collected with Bruker SMART APEX II, Agilent Technologies Xcalibur and Supernova Atlas diffractometers using Mo*Kα* (λ = 0.71073 Å) or Cu*Kα* (λ = 1.54184 Å) radiation. The structures were solved by direct methods using the *SHELXS*-97 program[1] incorporated in the *OLEX2* program package.[2] A semi-empirical absorption correction (*SADABS*[3] or *CrysAlisPro*[4]) was applied to the data for **1**, **3**, **7**, **9**, **12**, **13** and **19**. Analytical numeric absorption correction for **2** was applied in *CrysAlisPro*[4] program complex using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid.[5]

The crystallization solvent in the crystal of **13** was heavily disordered and could not be resolved unambiguously. The contribution of the missing solvent to the calculated structure factors was taken into account by using a *SQUEEZE* routine of *PLATON*.[6] The missing solvent was not taken into account in the unit cell content.

All the carbon-bound H atoms were positioned geometrically and constrained to ride on their parent atoms, with C–H = 0.93–0.96 Å, and U_{iso} = 1.2–1.5U_{eq} (parent atom). Positions of hydrogen atoms of the OH groups were localized from difference Fourier maps and kept fixed during refinement. Crystallographic data and refinement parameters for all structures are given in Table S1 (CCDC numbers are 993387, 993389, 993388, 1054718, 1054719, 1054720, 1937321 and 1937322 for **1**–**3**, **7**, **9**, **12**, **13** and **19**, respectively).

Table S1. Crystallographic data for **1**–**3**, **7**, **9**, **12**, **13** and **19**.

Compound	**1**	**2**	**3**	**7**	**9**	**12**	**13**	**19**
CCDC	993387	993389	993388	1054718	1054719	1054720	1937321	1937322
Formula	$C_{108}H_{76}Au_4P_4$, $(CH_2Cl_2)_{1.9}$	$C_{48}H_{42}Au_2O_2P$, $(CH_2Cl_2)_{0.18}$	$C_{54}H_{50}Au_2O_2P$, CH_2Cl_2	$C_{50}H_{48}Au_2O_2P$, $(CH_2Cl_2)_4$	$C_{50}H_{36}Au_2P_2$, CH_2Cl_2	$C_{64}H_{48}Au_2O_2P$, $(CH_2Cl_2)_4$	$C_{116}H_{76}Au_4P_4$	$C_{56}H_{40}Au_2O_2P_2$, CH_2Cl_2
Formula Mass	2447.64	1121.97	1271.74	1476.46	1177.58	1644.60	2381.51	1285.68
T (K)	100(2)	100(2)	100(2)	100(2)	100(2)	120(2)	150(2)	150(2)
λ (Å)	0.71073	1.54184	1.54184	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2/n$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	14.6199(3)	9.0271(2)	9.3433(5)	14.9682(8)	21.2923(9)	9.1677(3)	13.2298(5)	15.9763(14)
b (Å)	16.5507(2)	15.4167(3)	15.2120(9)	9.1406(4)	10.4445(2)	13.2137(4)	14.7956(6)	16.2982(14)
c (Å)	20.7234(6)	33.6004(7)	35.4426(17)	20.6675(8)	21.9593(8)	14.0242(4)	16.7821(6)	20.1413(17)
α (°)	90	90	90	90	90	102.5430(10)	66.1570(10)	90
β (°)	101.121(2)	90.243(2)	105.2850(10)	97.371(5)	118.544(5)	98.0120(10)	83.7050(10)	112.807(2)
γ (°)	90	90	90	90	90	95.7660(10)	64.1230(10)	90
V (Å^3)	4920.27(19)	4676.04(18)	4859.3(5)	2804.3(2)	4289.9(3)	1627.06(9)	2694.45(18)	4834.5(7)
Size (mm^3)	0.32x0.27x 0.19	0.42x0.23x 0.08	0.29x0.09x 0.07	0.21x0.17x 0.09	0.24x0.16x 0.09	0.20x0.12x 0.09	0.49 x 0.39 x 0.29	0.42 x 0.16 x 0.11
μ (mm^{-1})	6.160	12.726	13.140	5.703	7.066	4.925	5.531	4834.5(7)
F(000)	2360	2166	2480	1440	2264	804	1148	2488
Z	2	4	4	2	4	1	1	4

θ range, (°)	3.065–28.809	4.881–67.475	3.180–67.488	2.740–27.500	3.509– 36.553	2.59–36.52	2.516–25.999	2.436 – 30.059
Index ranges	-16<=h<=18, -21<=k<=20, -26<=l<=12	-10<=h<=10, -18<=k<=13, -40<=l<=34	-11<=h<=10, -18<=k<=18, -42<=l<=42	-19<=h<=18, -11<=k<=11, -24<=l<=26	-29<=h<=27, -13<=k<=14, -30<=l<=30	-12<=h<=12, -18<=k<=18, -19<=l<=19	-16<=h<=16, -18<=k<=18, -20<=l<=20	-22<=h<=21, -22<=k<=22, -28<=l<=26
ρ_{calc} (Mg/m^3)	1.652	1.594	1.738	1.749	1.823	1.678	1.468	1.766
Total ref.	26402	38843	41740	20807	14471	94475	47531	84585
Unique ref.	10893	8344	8435	6316	6165	9467	10539	14010
Unique $\lvert F_o\rvert \geq 4\sigma_F$	8762	7408	7781	5544	5523	9066	9586	10117
R_{int}	0.0307	0.0540	0.0331	0.0483	0.0436	0.0237	0.0228	0.0549
R_σ	0.0469	0.0373	0.0240	0.0451	0.0539	0.0112	0.0184	0.0552
Completeness to θ= 25.242°	99.9%	95.4%	91.7%	99.8%	96.7%	98.3%	99.3%	99.8%
R_1 ($\lvert F_o\rvert \geq 4\sigma_F$)	0.0387	0.0603	0.0280	0.0299	0.0315	0.0163	0.0311	0.0315
wR_2 ($\lvert F_o\rvert \geq 4\sigma_F$)	0.0911	0.1625	0.0690	0.0694	0.0671	0.0396	0.0765	0.0498
R_1 all data	0.0555	0.0656	0.0308	0.0373	0.0362	0.0177	0.0350	0.0617
wR_2 all data	0.0994	0.0656	0.0707	0.0742	0.0705	0.0401	0.0786	0.0560
GOF	1.058	1.063	1.026	1.065	1.059	1.063	1.056	1.001
ρ_{min}, ρ_{min}, e/Å^3	−1.881, 2.424	−3.112, 2.880	−1.853, 3.618	−1.183, 1.030	−2.002, 1.870	−0.778, 1.084	-1.043, 1.577	-0.953, 0.986

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2)+(aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$; $s = \{\Sigma[w(F_o^2 - F_c^2)]/(n - p)\}^{1/2}$ where n is the number of reflections and p is the number of refinement parameters; Refinement method - Full-matrix least-squares on F^2.

Table S2. Selected bond lengths and angles for complexes **1**–**3**, **7**, **9**, **12**, **13** and **19**.

	Au–Au, Å	Au–P, Å	Au–C, Å	C≡C, Å	P–Au–C, º
1	3.0917(4)	2.2783(14)	2.007(6)	1.136(9)	169.2(2)
		2.2737(15)	2.046(7)	1.187(9)	170.1(2)
2	-	2.2778(15)	1.999(7)	1.197(12)	176.8(2)
3	-	2.2880(8)	2.013(4)	1.194(6)	175.2(1)
		2.2782(9)	2.013(4)	1.187(6)	177.7(1)
7	-	2.2791(8)	2.011(4)	1.196(5)	176.5(1)
9	3.2118(3)	2.2785(9)	2.011(4)	1.183(5)	172.5(1)
12	-	2.2703(4)	2.005(2)	1.202(2)	176.31(5)
13	3.0326(3)	2.2611(14)	2.008(6)	1.155(8)	171.6(2)
		2.2697(14)	2.005(6)	1.189(8)	176.1(2)
19	3.0673(3)	2.2715(9)	2.024(3)	1.184(4)	176.8(1)
		2.2745(9)	2.024(3)	1.172(5)	172.2(2)

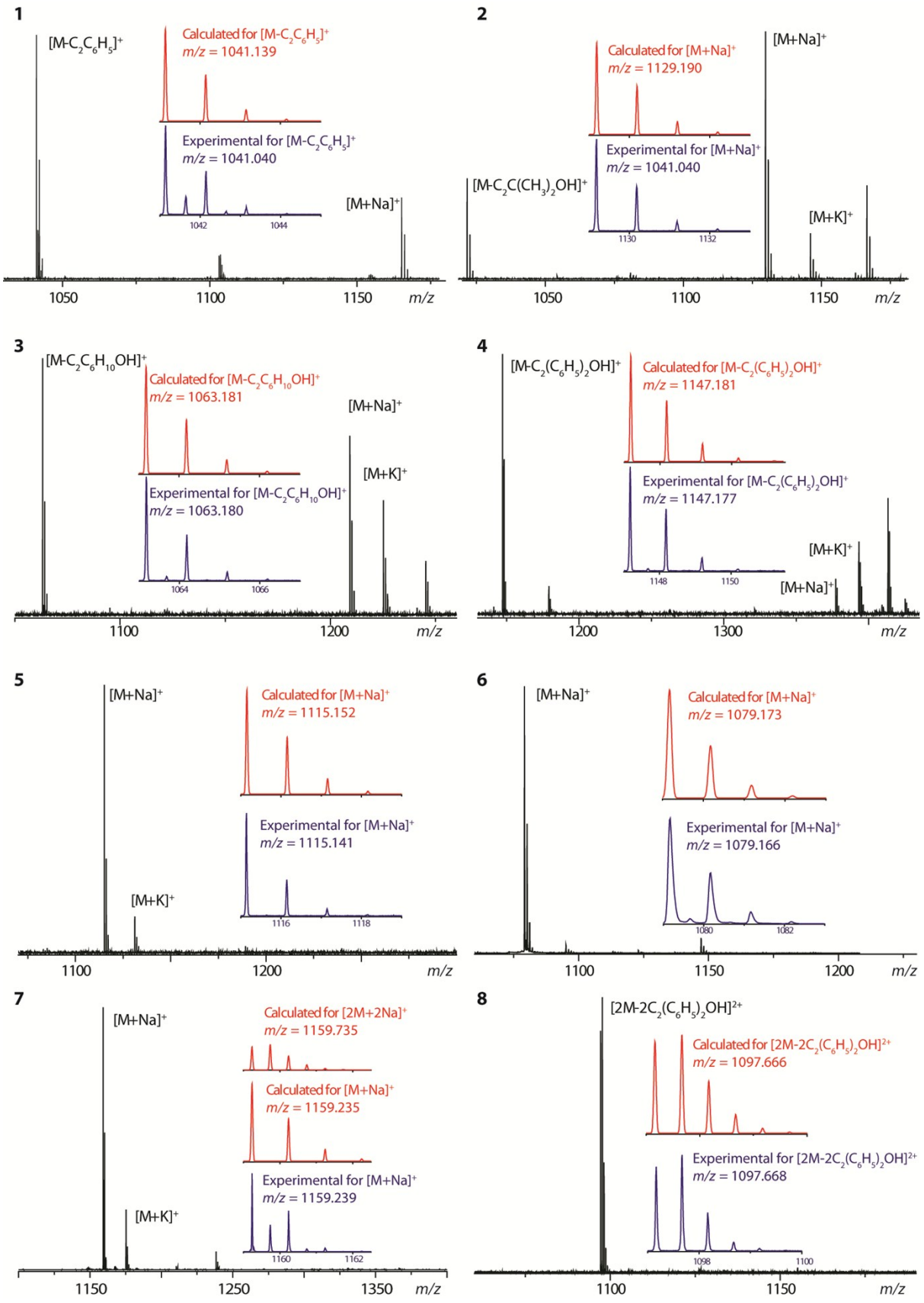


Figure S1. ESI MS of complexes **1**–**12**.

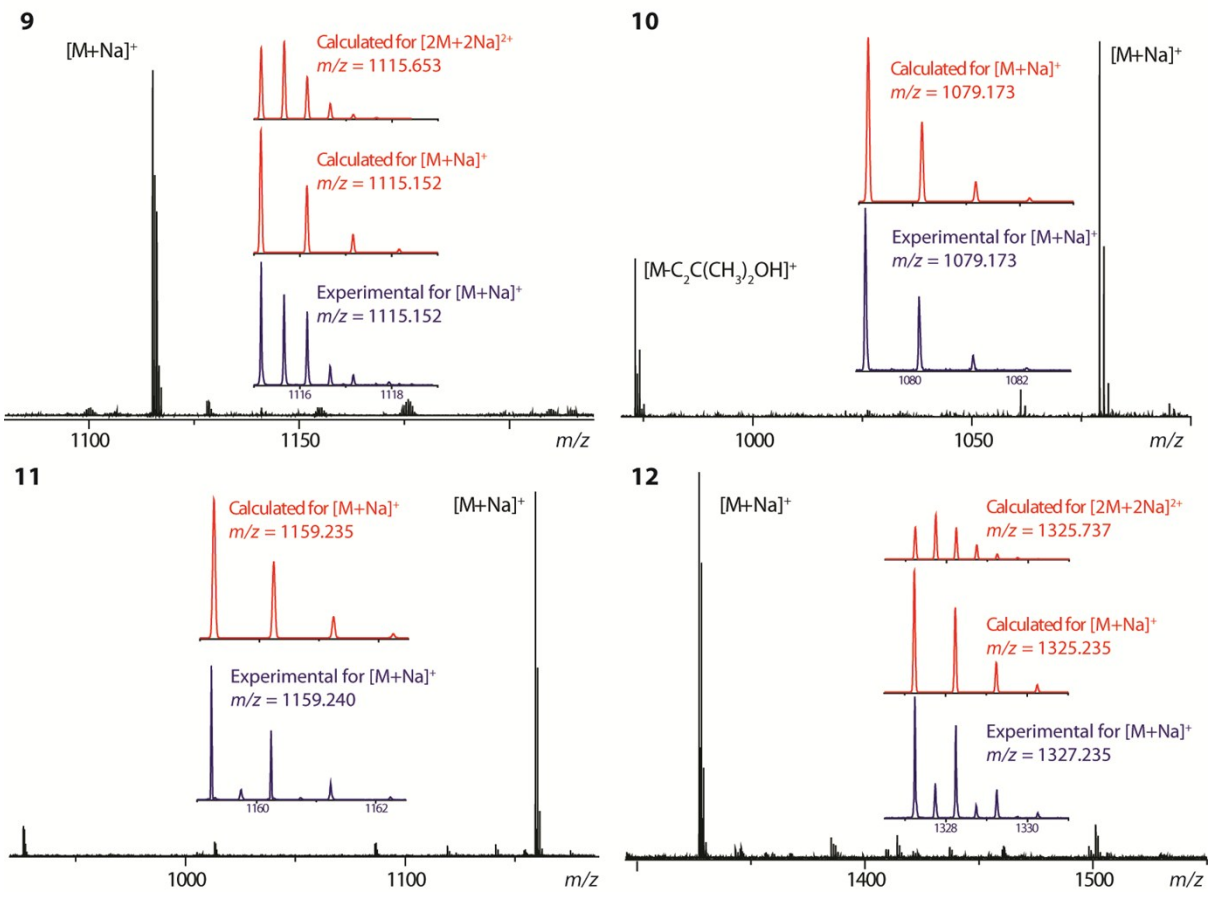


Figure S1. Continued.

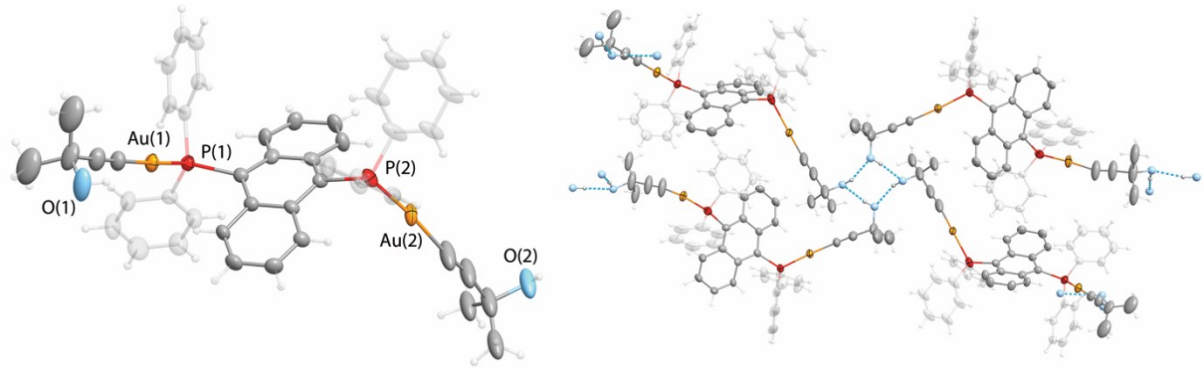


Figure S2. Molecular view of complex **2** (thermal ellipsoids are shown at 50% probability). Right view shows packing with intermolecular O–H···O hydrogen bonding.

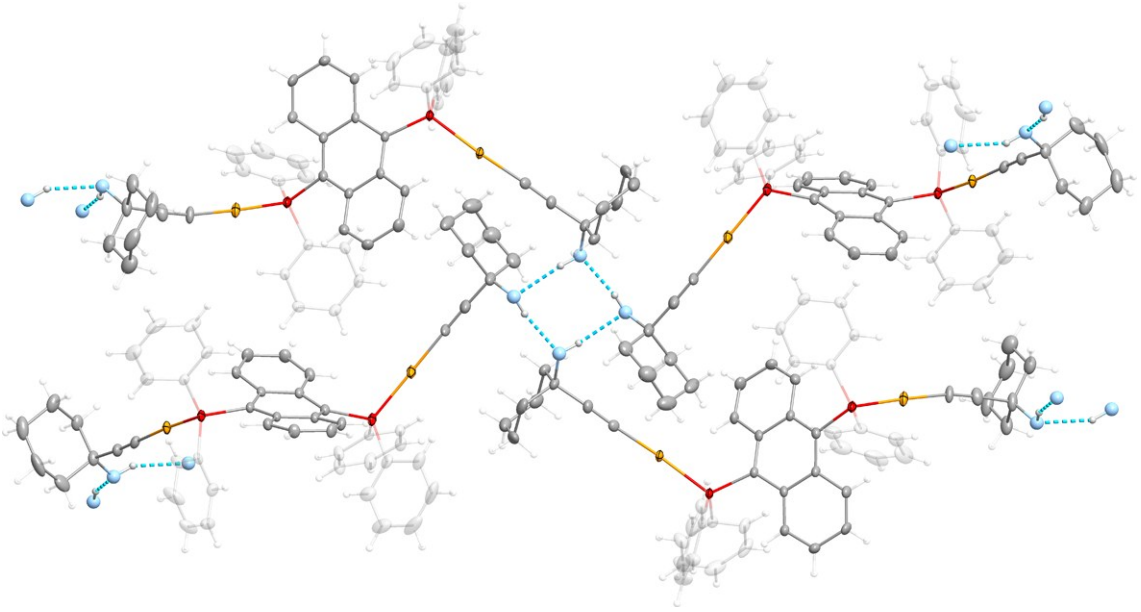


Figure S3. Packing of complex **3** showing intermolecular O–H···O hydrogen bonding.

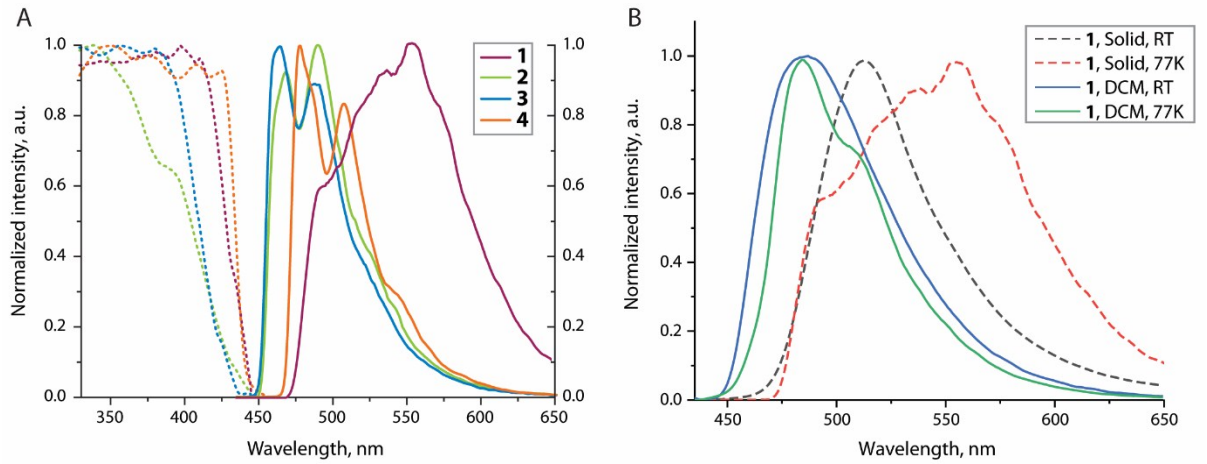


Figure S4. (A) normalized solid-state excitation and emission spectra of **1–4** at 77 K (λ_{ex} = 415 nm); (B) the emission spectra of **1** in the solid-state and in solution at 77 K and at room temperature.

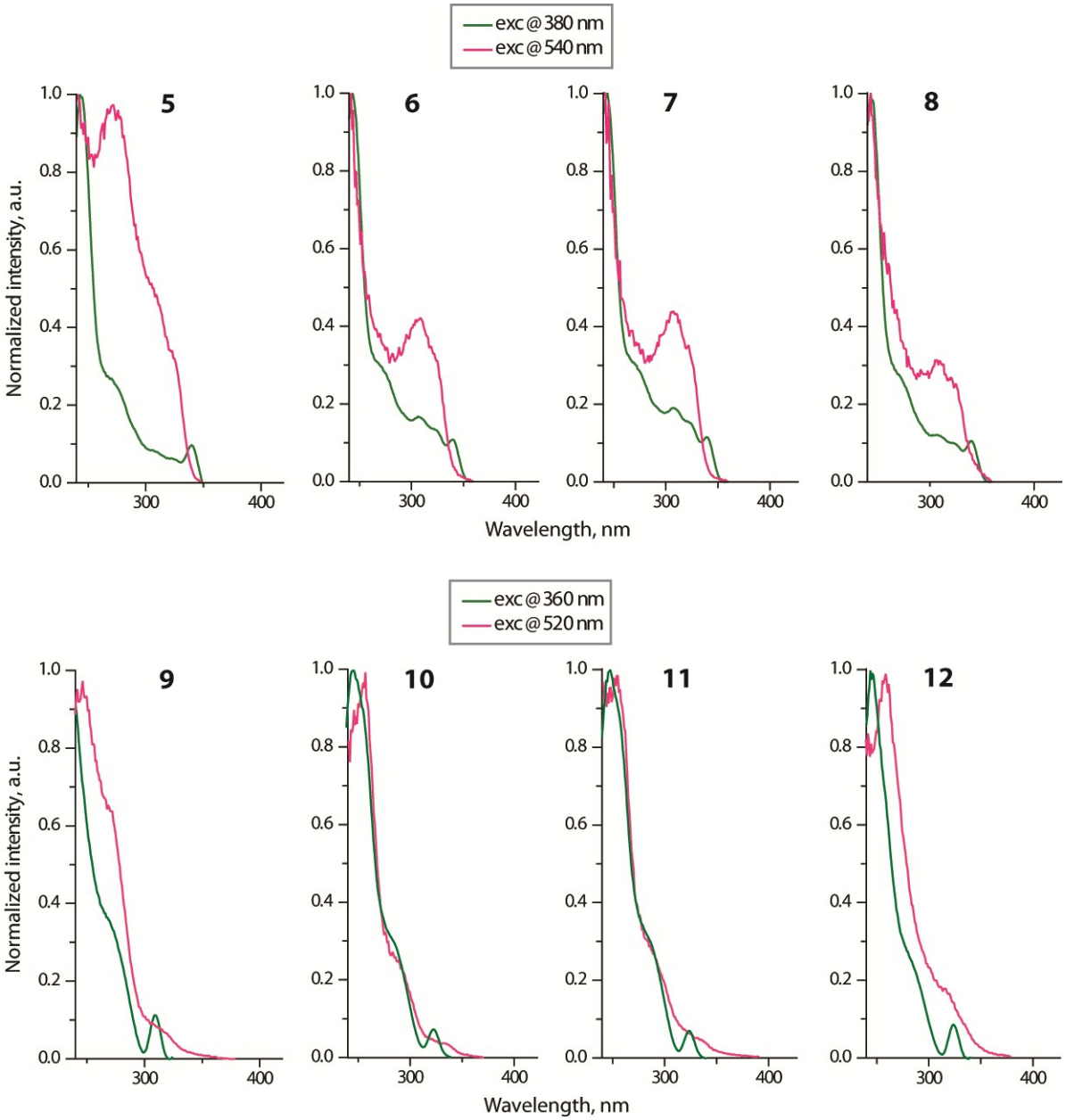


Figure S5. Normalized excitation spectra of **5–12** in degassed CH_2Cl_2 (298 K).

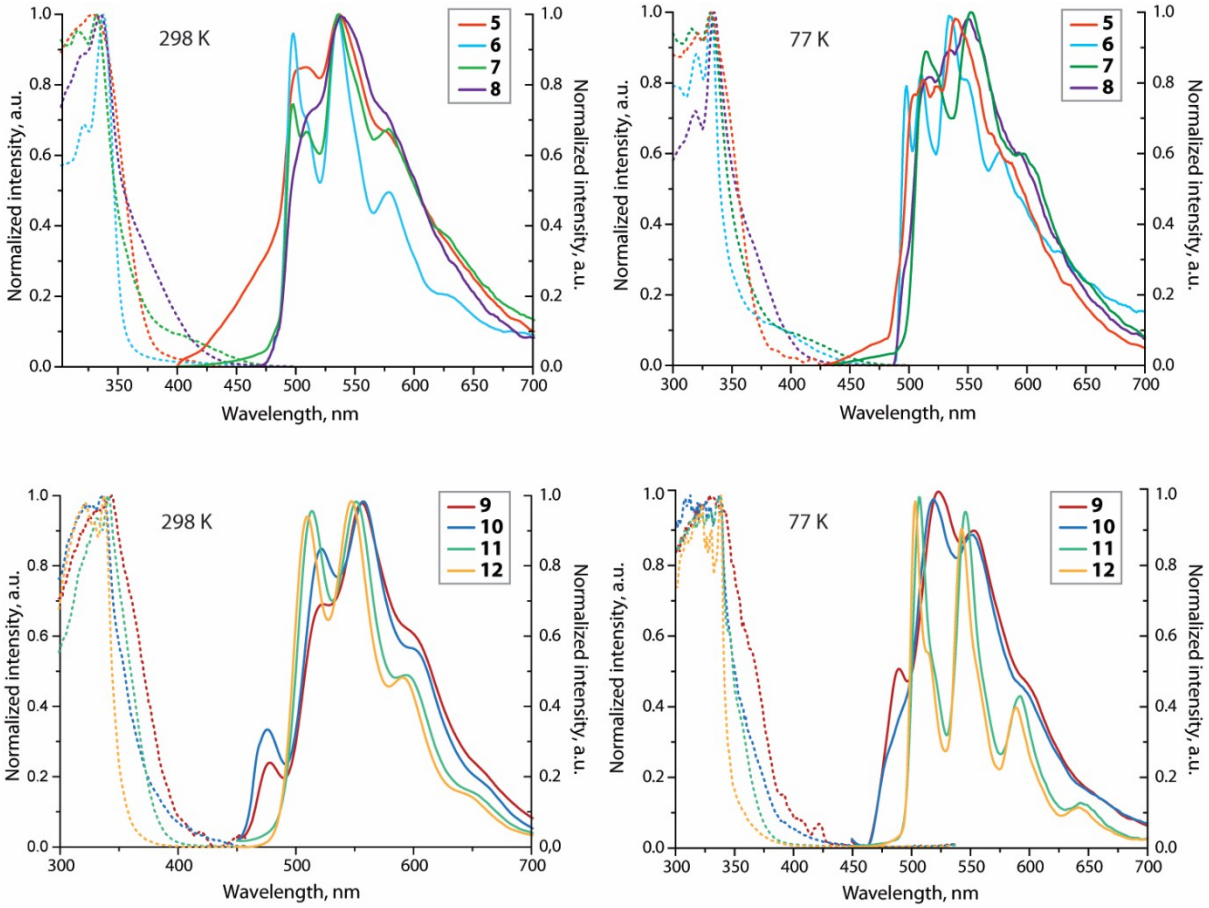


Figure S6. Normalized solid-state excitation and emission spectra of **5–8** (top) and **9–12** (bottom) at 298 K and 77 K (λ_{ex} = 330 nm).

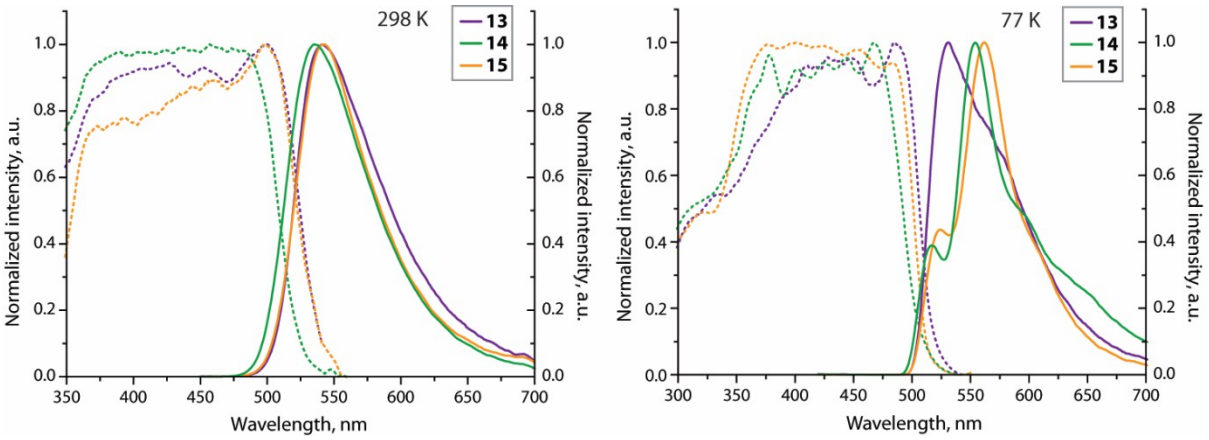


Figure S7. Normalized solid-state excitation and emission spectra of **13–15** at 298 K and 77 K (λ_{ex} = 350 nm).

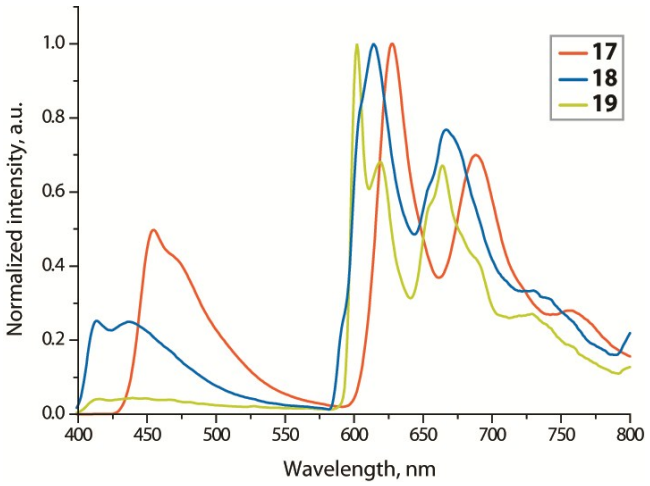


Figure S8. Normalized solid-state emission spectra of **17–19** at 77 K (λ_{ex} = 330 nm).

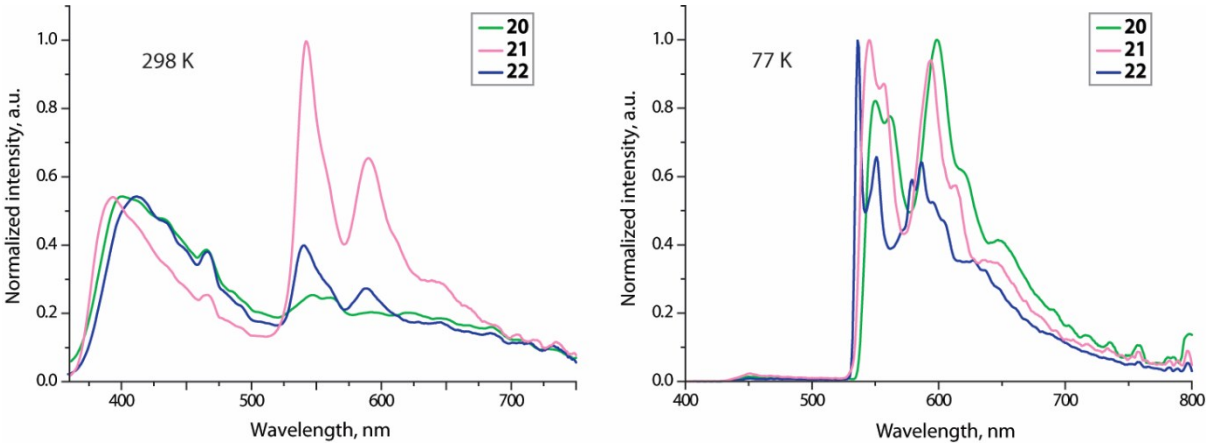


Figure S9. Normalized solid-state excitation and emission spectra of **20–22** at 298 K (under an Ar atmosphere) and 77 K (λ_{ex} = 330 nm).

Table S3. Calculated Commission Internationale de l'Eclairage (CIE) coordinates for complexes **17**–**22** in solid state on air or under argon atmosphere at 298 K.

Sample	CIE coordinates (x, y) under air/argon atmosphere
17	(0.37, 0.21)/(0.46, 0.23)
18	(0.26, 16)/(0.45, 0.25)
19	(0.54, 0.31)/(0.59, 0.31)
20	(0.27, 0.25)/(0.28, 0.25)
21	(0.32, 0.32)/(0.37, 0.40)
22	(0.23, 0.19)/(0.29, 0.28)

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