Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

Aurophilicity in Action: Stepwise Formation of Dinuclear Au(I) Macrocycles with Rigid 1,8-Dialkynylanthracenes

Philipp Niermeier,[a] Lucas Wickemeyer,[a] Beate Neumann,[a] Hans-Georg Stammler,[a] Lukas Goett-Zink,[b] Tilman Kottke,[b]* and Norbert W. Mitzel[a]*

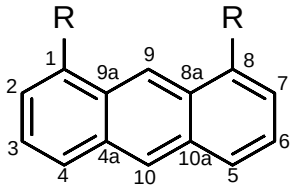
[a] Universität Bielefeld, Fakultät für Chemie, Lehrstuhl für Anorganische Chemie und Strukturchemie
Centre for Molecular Materials CM_2, Universitätsstraße 25, D-33615 Bielefeld
E-Mail: mitzel@uni-bielefeld.de; Fax: +49 521 106 6026; Tel: +49 521 106 6128.

[b] Physikalische und Biophysikalische Chemie, Fakultät für Chemie, Universität Bielefeld,
Universitätsstraße 25, 33615 Bielefeld, Germany; E-mail: tilman.kottke@uni-bielefeld.de

Table of Contents

Experimental

General: 1,8-Diethynylanthracene (**1**),[S1,S2] was synthesised according to literature protocols. Chloroauric acid ($HAuCl_4$) was prepared by dissolving elemental gold in *aqua regia*. Tri-*para*-tolylphosphane, (purchased from ACROS ORGANICS) and tri-*n*-butylphosphane (from ABCR) were used without further purification. All metalation reactions of **1** were carried out under an anhydrous, inert atmosphere of nitrogen or argon using standard Schlenk techniques in dry solvents (THF dried over K, EtOH dried over Na, *n*-hexane over $LiAlH_4$, all distilled before use). Column chromatography was performed on silica gel 60 (0.04–0.063 mm). NMR spectra were recorded on a Bruker *Avance III 500*, a Bruker *Avance III 500 HD* and a Bruker *Avance* 600 at 298 K. The chemical shifts (δ) were measured in ppm with respect to the solvent ($CDCl_3$: ^{1}H NMR δ = 7.26 ppm, ^{13}C NMR δ = 77.16 ppm) or referenced externally (^{31}P: 85 % H_3PO_4). Elemental analyses were performed by Mikroanalytisches Labor Kolbe (Oberhausen). The numbering scheme for NMR assignments of the anthracenes (Scheme S1) is based on IUPAC guidelines.



Scheme S1. Numbering scheme for NMR spectroscopic assignments.

Chloro(tri-*para*-tolylphosphane)gold(I): A suspension of tri-*para*-tolylphosphane (2.76 g, 9.07 mmol) in ethanol (45 mL) was added to a solution of chloroauric acid ($HAuCl_4$, 1.51 g, 4.44 mmol) in ethanol (66 mL) at 0 °C. After stirring for 1 h at 0 °C and precipitation of a white solid the mixture is allowed to warm to ambient temperature and stirred for 30 min. The solid was isolated by filtration and washed with a mixture of cold water and ethanol (1:1, 40 mL), affording *p*-Tol_3PAuCl as a colorless solid (1.04 g). In order to increase the yield, the combined filtrates were concentrated under reduced pressure, leaving a suspension of approx. 20 mL. Filtration and washing the residue with a mixture of cold water and ethanol (1:1, 10 mL) afforded a second fraction of *p*-Tol_3PAuCl (0.59 g). The filtrate was extracted with dichloromethane (3 × 10 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. Washing the residue with ethanol (10 mL) afforded a third fraction of *p*-Tol_3PAuCl (0.17 g). Total yield: 1.80 g (75%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36 – 7.43 (m, 6H, H_{meta}), 7.23 – 7.27 (m, 6H, H_{ortho}), 2.40 (s, 9H, CH_3) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 142.6 (d, $^4J_{P,C}$ = 2.5 Hz, *C*CH_3), 134.2 (d, $^3J_{P,C}$ = 14.0 Hz, C_{meta}), 130.0 (d, $^2J_{P,C}$ = 12.3 Hz, C_{ortho}), 125.9 (d, $^1J_{P,C}$ = 64.5 Hz, P*C*), 21.6 (d, $^5J_{P,C}$ = 1.3 Hz, *C*H_3) ppm. ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ = 31.2 (s) ppm.

Chloro(tri-*n*-butylphosphane)gold(I): A solution of tri-*n*-butylphosphane (0.4 mL, 1.6 mmol) in ethanol (8 mL) was added to a solution of chloroauric acid ($HAuCl_4$, 0.25 g, 0.74 mmol) in ethanol (11 mL) at 0 °C. After stirring for 1 h at 0 °C and for 30 min at ambient temperature the solvent was evaporated under reduced pressure. Column chromatography [∅ = 3 cm, *l* = 12.5 cm, eluent: *n*-hexane/ethyl acetate (7:3)] afforded *n*-Bu_3PAuCl as a colorless oil. R_f = 0.5. Yield: 0.25 g (78%). ^{1}H NMR (500 MHz,

$CDCl_3$): δ = 1.73 – 1.82 (m, 6H, PCH_2), 1.51 – 1.61 (m, 6H, PCH_2CH_2), 1.46 (h, $^3J_{H,H}$ = 7.3 Hz, 6H, CH_2CH_3), 0.94 (t, $^3J_{H,H}$ = 7.2 Hz, 9H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 27.5 (PCH_2CH_2), 25.8 (d, $^1J_{P,C}$ = 36.2 Hz, PCH_2), 24.2 (d, $^3J_{P,C}$ = 15.0 Hz, CH_2CH_3), 13.8 (CH_3) ppm. $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ = 22.1 (s) ppm.

[*p*-Tol$_3$PAu(I)]$_2$-9,10-anthracenyldiacetylide (2): A freshly prepared solution of NaOEt (0.043 M, 25 mL, 1.08 mmol) was added to a solution of 1,8-diethynylanthracene (**1**; 60 mg, 0.27 mmol) and *p*-Tol$_3$PAuCl (315 mg, 0.59 mmol) in THF (24 mL). The mixture was stirred overnight under exclusion of light at ambient temperature. After removing the solvent under reduced pressure the residue was dissolved in dichloromethane (10 mL). *n*-Hexane (22 mL) was added and a solid precipitated. The suspension was filtered. The filtrate was stored overnight under exclusion of light, slowly growing crystals. Removing the supernatant solution via syringe afforded **2** as a yellow crystalline solid (191 mg). In order to increase the yield, the removed solution was evaporated under reduced pressure. Washing the residue with *n*-hexane (5 mL) afforded a second fraction of **2** (122 mg). Total yield: 313 mg (96%). ^1H NMR (500 MHz, $CDCl_3$): δ = 9.89 (s, 1H, *H*9), 8.34 (s, 1H, *H*10), 7.84 (d, $^3J_{H,H}$ = 8.7 Hz, 2H, *H*4/*H*5), 7.70 (dd, $^3J_{H,H}$ = 6.9 Hz, $^4J_{H,H}$ = 0.7 Hz, 2H, *H*2/*H*7), 7.38 – 7.44 (m, 12H, H_{meta}), 7.35 (dd, $^3J_{H,H}$ = 8.4, 7.0 Hz, 2H, *H*3/*H*6), 7.04 – 7.09 (m, 12H, H_{ortho}), 2.24 (s, 18H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 141.6 (d, $J_{P,C}$ = 2.3 Hz, CCH_3), 134.4 (d, $J_{P,C}$ = 14.2 Hz, C_{meta}), 132.3, 131.7, 131.5 (*C*2/*C*7), 129.8 (d, $J_{P,C}$ = 11.6 Hz, C_{ortho}), 127.4 (d, $J_{P,C}$ = 57.3 Hz, PC_{ipso}), 127.2 (*C*4/*C*5), 126.9 (*C*10), 126.0 (*C*9), 125.1 (*C*3/*C*6), 124.0 (d, $J_{P,C}$ = 2.9 Hz), 102.5 (d, $J_{P,C}$ = 26.9 Hz, *C*≡CP), 21.5 (CH_3) ppm. No signal observed for C≡*C*P. $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ = 40.2 (s) ppm. Elemental analysis calcd (%) for $C_{60}H_{50}P_2Au_2$: C 58.74, H 4.11, P 5.05; found: C 58.64, H 4.19, P 4.99.

[*n*-Bu$_3$PAu(I)]$_2$-1,8-anthracenyldiacetylide (3): A freshly prepared solution of NaOEt (0.087 M, 8 mL, 0.7 mmol) was added to a solution of 1,8-diethynylanthracene (**1**; 71 mg, 0.31 mmol) and *p*-Tol$_3$PAuCl (300 mg, 0.69 mmol) in THF (12 mL). The mixture was stirred overnight under exclusion of light at ambient temperature. The solvent was removed under reduced pressure. The residue was suspended in ethanol (3 mL). The suspension was filtered and washed with following degassed solvents: ethanol (1 mL), water (2 × 5 mL) and *n*-hexane (2 × 3 mL). **3** was afforded as a yellow solid, contaminated with approx. 10% of the dimeric species **5**. Yield: 300 mg [≈ 85% (**2**) and ≈ 9% (**5**)]. ^1H NMR (500 MHz, $CDCl_3$): δ = 10.02 (s, 1H, *H*9), 8.26 (s, 1H, *H*10), 7.73 (d, $^3J_{H,H}$ = 8.5 Hz, 2H, *H*4/*H*5), 7.48 (d, $^3J_{H,H}$ = 6.6 Hz, 2H, *H*2/*H*7), 7.28 (dd, $^3J_{H,H}$ = 8.3, 6.9 Hz, 2H, *H*3/*H*6), 1.42 – 1.65 (m, 24H, PCH_2CH_2), 1.30 (h, $^3J_{H,H}$ = 7.3 Hz, 12H, CH_2CH_3), 0.59 (t, $^3J_{H,H}$ = 7.1 Hz, 18H, CH_3) ppm. $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ = 29.6 (s) ppm. Due to fast dimerisation, a $^{13}C\{^1H\}$ NMR spectrum could not be recorded. Elemental analysis calcd (%) for $C_{84}H_{124}P_4Au_4$: C 49.32, H 6.11, P 6.06; found: C 47.06, H 5.82, P 5.76. Too low value for carbon is due to contamination by an access of *n*-Bu$_3$PAuCl.

Macrocyle 4: Single crystals of the "dimeric" compound **4** were obtained from a saturated toluene solution of monomer **2**, by slow evaporation of the solvent. **4** was solely characterised in the crystalline state by X-ray diffraction analysis.

Macrocyle 5: A solution of monomer **3** (10 mg) in $CDCl_3$ (0.5 mL, degassed) was stored in a PTFE-seated NMR tube, until the signal intensities of **3** in the ^1H and 31P NMR spectra are not further decreasing (≈ 5 h; ratio of **5**/**3** approx. 90:10). Using even less concentrated solutions the "dimeric species" **5** can

be obtained in almost quantitative yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.65 (s, 2H, *H*9), 8.33 (s, 2H, *H*10), 7.83 (d, $^{3}J_{H,H}$ = 8.4 Hz, 4H, *H*4/*H*5), 7.78 (d, $^{3}J_{H,H}$ = 6.9 Hz, 4H, *H*2/*H*7), 7.33 (dd, $^{3}J_{H,H}$ = 8.2, 7.1 Hz, 4H, *H*3/*H*6), 1.74 – 1.83 (m, 24H, PCH_2), 1.57 – 1.67 (m, 24H, PCH_2CH_2), 1.48 (h, $^{3}J_{H,H}$ = 7.1 Hz, 24H, CH_2CH_3), 0.97 (t, $^{3}J_{H,H}$ = 7.2 Hz, 36H, CH_3) ppm. $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ = 132.3 (*C*2/*C*7), 132.0, 131.7, 127.2 (*C*4/*C*5), 127.0 (*C*10), 125.6 (*C*9), 125.0 (*C*3/*C*6), 124.0, 102.7 (d, $J_{P,C}$ = 25.7 Hz, *C*≡CP), 27.2 (PCH_2CH_2), 25.6 (d, $^{1}J_{P,C}$ = 32.1 Hz, PCH_2), 24.6 (d, $^{3}J_{P,C}$ = 14.3 Hz, CH_2CH_3), 13.9 (CH_3) ppm. No signal observed for C≡*C*P. $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$): δ = 28.3 (s) ppm.

Dimerisation of 3 followed by time-resolved ^{31}P NMR spectroscopy: A solution of monomer **3** (24 mg) in $CDCl_3$ (0.5 mL, degassed) was stored in a PTFE-seated NMR tube and frozen in liquid nitrogen after filling. Directly after thawing the sample was placed in the NMR spectrometer and the dimerisation was followed by time-resolved ^{31}P NMR spectroscopy (298 K, 242 MHz). The ratio of **5**/**3** as a function of the reaction time is given in Table S1.

Table S1: Ratio of monomer **3** and dimer **5**, determined by time resolved ^{31}P NMR spectroscopy.

reaction progress / min	**3**	**5**
0	91	9
5	80	20
10	74	26
15	70	30
20	64	36
25	60	40
30	56	44
35	52	48
40	49	51
45	46	54
50	44	56
55	41	59
60	39	61
70	35	65
80	31	69
90	28	72
100	26	74
110	24	76
120	22	78
140	20	80
160	18	82
180	17	83
210	16	84
240	15	85
300	14	86

Photophysical properties

The absorption and emission spectra of **3**/**5** were recorded using a solution of **3** (1.3 mg; starting with approx. 10% of **5**) in CH_2Cl_2 (10 mL, degassed) directly after preparation as well as after storage overnight in the spectrometer or in the glove box.

Absorption spectroscopy on 3/5: UV/VIS absorption spectra were recorded with a spectral resolution of 2.0 nm at 20°C in a Thermo Evolution 300 UV-Visible spectrophotometer using Hellma Analytics QS absorption cells (1 x 1 cm path length), sealed with with a greased stopper.

Fluorescence spectroscopy on 3/5: Fluorescence emission spectra were recorded with a spectral resolution of 2.5 nm at 20°C in a Jasco FP8300 spectrometer (Jasco, Gross-Umstadt, Germany) using Hellma Analytics QS fluorescence cells (1 x 1 cm path length), sealed with a greased stopper.

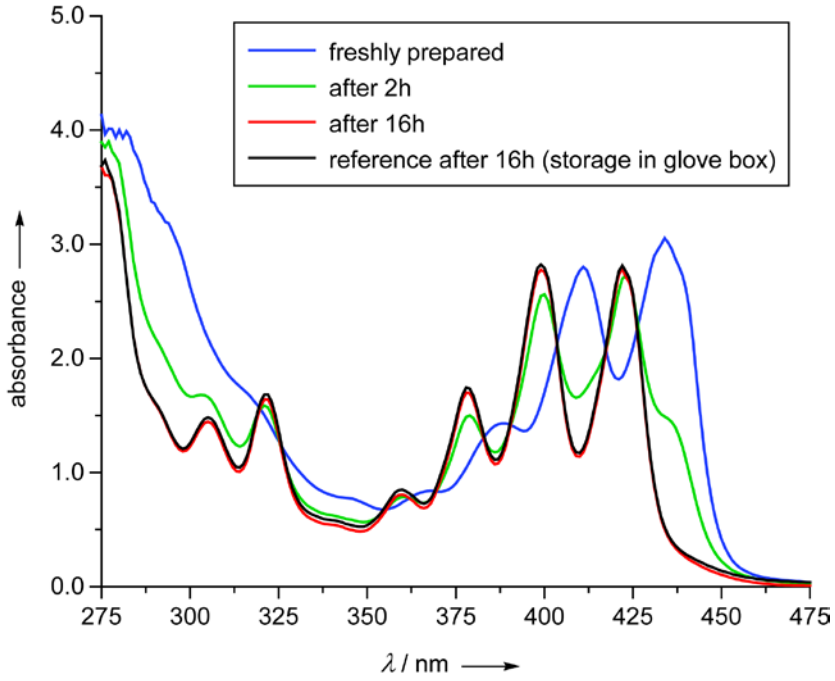


Figure S1: UV/VIS absorption spectra of **3**/**5** mixtures (0.13 mg mL^{-1}) in CH_2Cl_2 recorded directly after preparation (blue line), after 2h (green line) and after 16h [storing the solution in the spectrometer (red line) or in the glove box (black line)].

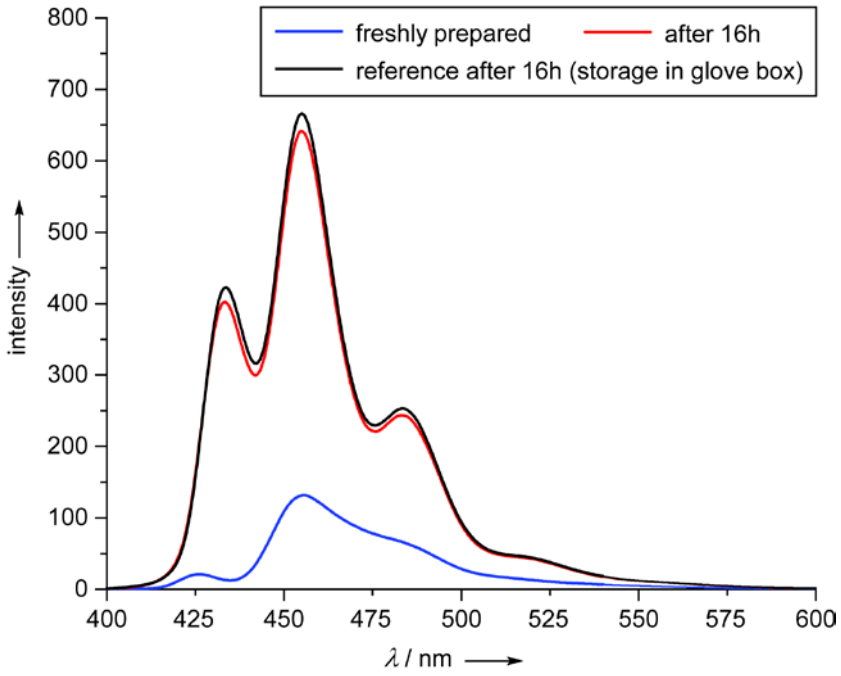


Figure S2: Emission spectra of **3**/**5** mixtures (0.13 mg mL^{-1}) in CH_2Cl_2 recorded directly after preparation (blue line; excitation at 376 nm) and after 16h [storing the solution in the spectrometer (red line) or in the glove box (black line); in both cases excitation at 368 nm]. The different excitation wavelengths correspond to the excitation maxima, respectively.

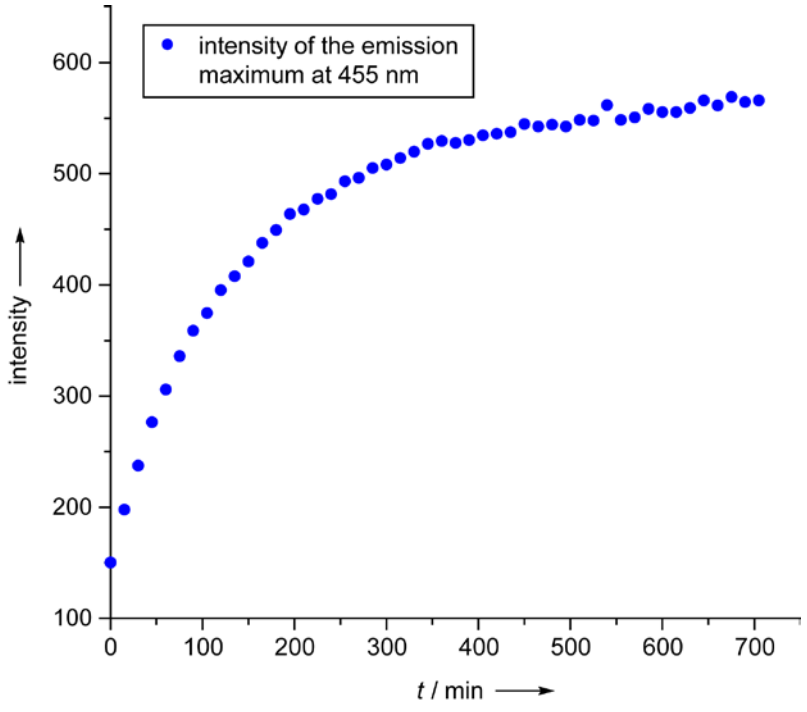


Figure S3: Intensity of the maximum at 455 nm in the emission spectra of **3**/**5** mixtures (0.13 mg mL^{-1}; excitation at 376 nm) in CH_2Cl_2 as a function of time.

Crystallographic data

Crystal Structure Determination: Suitable crystals of compounds **2**, **4** and **5** (all from toluene) were obtained by slow evaporation of saturated solutions, respectively. They were selected, coated with PARATONE-N oil, mounted on a glass fibre and transferred onto the goniometer of the diffractometer into a nitrogen gas cold stream solidifying the oil. Data collection was performed on a RIGAKU SUPERNOVA diffractometer. Using Olex2[S3] the structures were solved with the SHELXT structure solution program[S4] and refined with the SHELX refinement package[S5]. **4** contains one disordered p-*tol* ligand with ratio 85:15. The ADP's of these disordered atoms were constrained to be equal pair wisely. Crystal and refinement details, as well as CCDC numbers are provided in Table S2. CCDC 1878771–1878773 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via:

http://www.ccdc.cam.ac.uk/conts/retrieving.html.

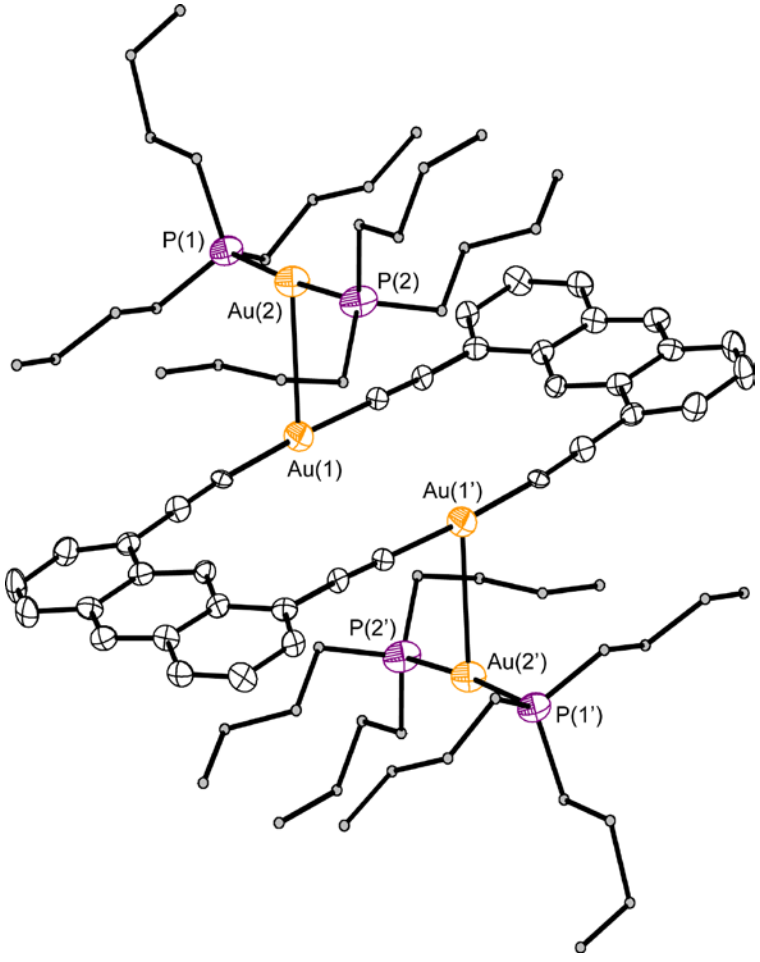


Figure S4: Molecular structure of macrocycle **5** in the crystalline state displaying the butyl groups.

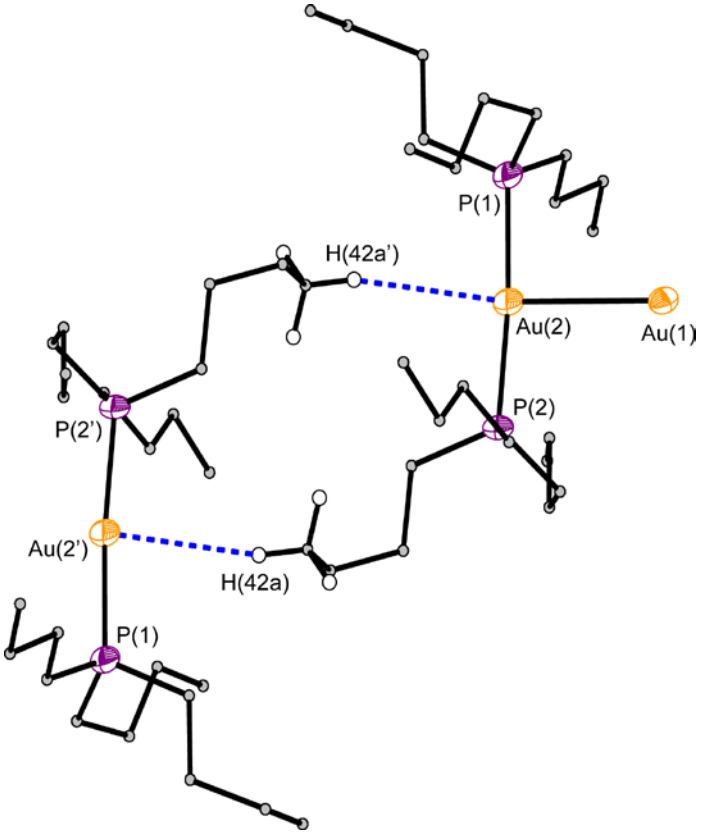


Figure S5: Excerpt of the crystal structure of macrocycle **5**. The coordination geometry at Au(2) can be considered square planar if the short intermolecular contact between Au(2) and H(42a') [blue dotted lines; 3.042(1) Å] is taken into account.

Table S2: Crystallographic data for compounds **2**, **4** and **5**.

	2	**4** · *toluene*	**5**
Empirical formula	$C_{60}H_{50}P_2Au_2$	$C_{85}H_{66}P_2Au_4$	$C_{84}H_{124}P_4Au_4$
M_r	1226.87	1937.18	2045.57
λ [Å]	1.54184	0.71073	1.54184
T [K]	100.0(1)	100.0(1)	100.0(1)
F(000)	2392	1844	1004
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a [Å]	15.6517(2)	14.2534(3)	11.2609(13)
b [Å]	12.1844(2)	13.3100(2)	14.3119(17)
c [Å]	26.4203(5)	18.9631(4)	14.3796(12)
α [°]	90	90	117.469(11)
β [°]	97.7936(14)	111.149(2)	97.066(10)
γ [°]	90	90	96.219
V [Å^3]	4991.99(15)	3355.24(13)	2004.4(4)
Z	4	2	1
$\rho_{calcd.}$ [g cm^{-3}]	1.632	1.917	1.695
μ [mm^{-1}]	11.778	8.812	14.506
θ_{max} [°]	72.35	30.1	72.104
Index ranges h	$-19 \le h \le 19$	$-20 \le h \le 20$	$-13 \le h \le 13$
Index ranges k	$-15 \le k \le 12$	$-18 \le k \le 18$	$-16 \le k \le 17$
Index ranges l	$-32 \le l \le 32$	$-26 \le l \le 26$	$-17 \le l \le 17$
Reflexes collected	84443	77564	13679
Independent reflexes	9736	9849	7736
R_{int}	0.0569	0.0479	0.0758
Observed reflexes, $I>2\sigma(I)$	9463	8202	5119
Parameters	582	443	421
R_1, $I>2\sigma(I)$	0.0365	0.0267	0.0648
wR_2, $I>2\sigma(I)$	0.0885	0.0570	0.1588
R_1 (all data)	0.0374	0.0392	0.1002
wR_2 (all data)	0.0889	0.0617	0.1823
GoF	0.961	1.026	1.014
ρ_{max}/ρ_{min} [e Å^{-3}]	2.74/−1.31	1.92/−0.93	3.63/–4.85
CCDC number	1878771	1878772	1878773

References

[S1] H. E. Katz, *J. Org. Chem*. **1989**, *54*, 2179–2183.

[S2] F. Vögtle, H. Kock, K. Rissanen, *Chem. Ber*. **1992**, *125*, 2129–2135.

[S3] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann*, J. Appl. Cryst.* **2009,** *42*, 339-341.

[S4] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2015,** *71*, 3-8.

[S5] G. M. Sheldrick, *Acta Crystallogr., Sect. C* **2015,** *71*, 3-8.