Supplementary Information (SI) for Journal of Materials Chemistry C.
This journal is © The Royal Society of Chemistry 2025

Supporting Information for

Self-Assembling and Ambipolar Charge Transport in Columnar Phases of Polynuclear Gold Isocyano-Triphenylene Complexes

Estela de Domingo,[a] Gregorio García,[a] Emiliano Tritto,[a] Bertrand Donnio,[b] Asmita Shah,[c] Dharmendra Pratap Singh,*[c] and Silverio Coco,*[a]*

[a] IU CINQUIMA/Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47071 Valladolid, Castilla y León, Spain. [b] Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), UMR 7504 (CNRS-Université de Strasbourg), F-67034 Strasbourg Cedex 2 (France). [c] Unité de Dynamique et Structure des Matériaux Moléculaires (UDSMM), Université du Littoral Côte d'Opale (ULCO), Calais cedex, France.

* e-mail addresses: silverio.coco@uva.es, bertrand.donnio@ipcms.unistra.fr, dharmendra.singh@univ-littoral.fr

Table of Contents

Experimental Section

General Considerations. General procedures are as reported before. Elemental analyses were performed by the "Servicio de análisis elemental, CACTI, Universidad de Vigo". IR spectra were recorded on a Perkin-Elmer Frontier spectrometer coupled to a Pike GladiATR-210 accessory. NMR spectra were recorded on Bruker AV-400 or Varian 500 instruments in $CDCl_3$. UV/Vis absorption spectra were obtained by means of a Shimadzu UV-2550 spectrophotometer, in dichloromethane (~$1x10^{-5}$ M). Luminescence spectra were recorded with a Perkin-Elmer LS-55 spectrometer in CH_2Cl_2. Photoluminescence quantum yield (QY) was measured with a FLS980 fluorescence spectrometer (Edinburgh Instruments) equipped with an integrating sphere. Fluorescence decays in dichloromethane, at room temperature. Lifetimes were obtained with the Time Correlated Single Photon Counting (TCSPC) and MCP-PMT counter module (TCC2) of the FLS980 spectrometer. Fluorescence decays were analyzed with the method of non-linear least squares iterative deconvolution ant the quality of the fits was judged by the values of the reduced Chi-square (c2) and the autocorrelation function of the residuals using the FAST (Advanced Fluorescence Lifetime Analysis Software) program provided by the equipment. Reconvolution Fit Analysis was used to fit a measured sample decay (red line in Figures) taking into account the IRF Instrument Response Function (black line in Figures). IRF was determined by using Ludox (a scatterer) instead of the sample.

Microscopy studies were carried out on a Leica DMRB microscope equipped with a Mettler FP82HT hot stage and a Mettler FP90 central processor, at a heating rate of 10 °C min^{-1}. DSC was performed using a DSC Q20 from TA Instruments with samples (2−5 mg) sealed in aluminum pans and a scanning rate of 10 °C/min under a nitrogen atmosphere.

MALDI-TOF MS was performed using a Bruker Daltonics autoflex speed instrument equipped with nitrogen laser (340 nm). Positive-ion mode spectra were recorded using the reflective mode. The accelerating voltage was 19 kV. The analytical sample was obtained by mixing the dichloromethane solution of the sample (1 mg/mL) and dichloromethane solution of the matrix (DCTB, 10 mg/mL) in a 1/5 (vol/vol) ratio. The prepared solution of the sample and the matrix (0.5 μL) was loaded on the MALDI plate and allowed to dry at 23ºC before the plate was inserted into the vacuum chamber of the MALDI instrument.

TEM observations were performed on a JEOL 1011 (110 kV) electron microscope. At least 200 particles were used to determine the mean diameter of the Au NP.

The S/WAXS patterns were obtained by transmission diffraction with a Guinier experimental set-up. A linear focalized monochromatic Cu-Kα_1 beam (λ = 1.5405 Å) was obtained using a sealed-tube generator (900 W) equipped with a bent quartz monochromator. In all cases, the crude powder was filled in thin Lindemann capillaries of 1 mm diameter and 10 μm wall thickness in air (corrections for air were made), and then heated to produce the mesophase. An initial set of diffraction patterns was recorded with a curved Inel CPS 120 counter gas-filled detector linked to a data acquisition computer; periodicities up to 70 Å can be measured, and the sample temperature controlled to within ± 0.01 ºC from 20 to 200 ºC. Alternatively, patterns were also recorded on an image plate; periodicities up to 120 Å can be measured (scanned by STORM 820 from Molecular Dynamics with 50 μm resolution). In each case, exposure times were varied from 1 to 24 h.

Electrochemical studies employed cyclic voltammetry using a potentiostat EG&G model 273. The three-electrode system was equipped with a platinum (3 mm diameter) working electrode, a saturated calomel reference electrode (SCE), and a Pt wire counter electrode. The electro-chemical potentials were calibrated relative to SCE using ferrocene as an internal standard (Fc/Fc$^+$) at +0.46 V vs. SCE). Tetra-n-butylammonium hexafluorophosphate (0.1 M) in CH_2Cl_2 was used as a supporting electrolyte and the solutions of the complexes were in the order 10^{-3} M. All scans were done at 100 mV s^{-1}.

Synthesis. Literature methods were used for the synthesis of 4-bromo-1-(dodecyloxy)-2-methoxybenzene,[1] 3-(dodecyloxy)-4-methoxyphenylboronic acid,[2] 1,2-bis(dodecyloxy)benzene, 4-(6-bromohexyloxy)nitrobenzene,[3] 2,6,10-trihydroxy-3,7,11-tris(dodecyloxy))triphenylene (**2**),[4] [AuCl(tht)] (tht = tetrahydrothiophene),[5] and $[Au(C\equiv C-C_6H_5)]_n$.[6]

Only examples are described, as the syntheses were similar for the rest of the complexes. Yields, IR, and analytical data are given for all the complexes.

Synthesis of the diisocyano-triphenylene ligand (7)

3,4'-Bis(dodecyloxy)-3',4-dimethoxybiphenyl. To a solution of 4-bromo-1-(dodecyloxy)-2-methoxybenzene (0.233 g, 0.63 mmol) and 3-(dodecyloxy)-4-methoxyphenylboronic acid (0.226 g, 0.67 mmol) in 30 mL of toluene, 3M NaOH (10 mL) and solid $[Pd(PPh_3)_4]$ (0.031 mmol, 5% mol) were added under nitrogen at room temperature. The mixture was stirred at 95 ºC for 20 h. The solvent was removed under vacuum and the and the residue was extracted with dichloromethane (3 x 30 mL). The dry product was purified by column chromatography (Silica gel, dichloromethane/hexane 1:3 v/v as eluent) and isolated as a white solid (0.32 g, 88 % yield). ^1H NMR ($CDCl_3$): δ 7.06 (m, 4H, ArH), 6.92 (d, 2H, *J* = 8.1 Hz, ArH), 4.07 (t, 2H, *J* = 6.9 Hz, OCH_2), 4.04 (t, 2H, *J* = 6.9 Hz, OCH_2), 3.93 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 1.87 (m, 4H, OCH_2CH_2), 1.46 (m, 4H, $OCH_2CH_2CH_2$), 1.36-1.26 (m, 32H, CH_2), 0.88 (m, 6H, CH_3).

2,6-Dimethoxy-3,7,10,ll-tetrakis(dodecyloxy)triphenylene. To a stirred mixture of $FeCl_3$ (12 (.41 g, 76.5 mmol) in 60 mL of dry CH_2Cl_2, 3,4'-Bis(dodecyloxy)-3',4-dimethoxybifenyl (3.57 g, 6.1 mmol) and 1,2-bis(dodecyloxy)benzene (8.18 g, 18.3 mmol) were added under N_2. After stirring for 1,5 h, the mixture was poured onto methanol (120 mL). The resulting solid was filtered off, washed with cold MeOH and purified by column chromatography (silica gel, hexane-toluene 1:4 v/v as eluent). The product was isolated as a white solid (3.99 g, 64 % yield). ^{1}H NMR ($CDCl_3$): δ 7.83 (m, 6H-TriPh), 4.25 (t, 4H, *J* = 6.8 Hz, O*CH₂*), 4.23 (t, 4H, *J* = 6.6 Hz, O*CH₂*), 4.10 (s, 6H, O*CH₃*), 1.96 (m, 8H, $OCH_2\mathit{CH_2}$), 1.56 (m, 8H, $OCH_2CH_2\mathit{CH_2}$), 1.43-1.27 (m, 64H, $\mathit{CH_2}$), 0.88 (t, 12H, *J* = 6.8 Hz*,* $\mathit{CH_3}$).

2,6-Dihydroxy-3,7,10,ll-tetrakis(dodecyloxy))triphenylene (1). To an ice-cooled solution of diphenylphosphine (2.67 g, 14.3 mmol) in 60 mL of dry THF under N_2, n-BuLi (2.5 M in hexane, 7.8 mL, 19.4 mmol) was added over 10 min with stirring. After stirring for 10 min at room temperature, 2,6-dimethoxy-3,7,10,ll-tetrakis(dodecyloxy)triphenylene (3.99 g, 3.89 mmol) was added. The solution was stirred at 57 °C for 4 h and at room temperature for 16 h. The mixture was poured onto dilute sulfuric acid and extracted with ethyl acetate (3 x 50 mL). The solvent was removed in vacuo and the residue purified by column chromatography (silica gel, hexane-toluene 1:5 v/v as eluent) to give a white solid (3.23 g, 83 % yield). ^{1}H NMR ($CDCl_3$): δ 7.93 (s, 2H-TriPh), 7.80 (m, 4H-TriPh), 5.89 (s, 2H, OH), 4.30-4.19 (m, 8H, $O\mathit{CH_2}$), 1.94 (m, 8H, $OCH_2\mathit{CH_2}$), 1.56 (m, 8H, $OCH_2CH_2\mathit{CH_2}$), 1.44-1.27 (m, 64H, $\mathit{CH_2}$), 0.88 (t, 12H, *J* = 6.8 Hz, $\mathit{CH_3}$).

2,6-Bis(6-(4-nitrophenoxy)hexyloxy)-3,7,10,11-tetrakis(dodecyloxy))triphenylene (3). To a solution of 2,6-dihydroxy-3,7,10,ll-tetrakis(dodecyloxy))triphenylene (2.97 g, 2.98 mmol) and 4-(6-bromohexyloxy)nitrobenzene (14.40 g, 47.7 mmol) in dry 2-butanone (90 mL), under nitrogen, was added K_2CO_3 (4.94 g, 35.7 mmol). The mixture was heated at reflux for 16 h. Then water (90 mL) was added, and the mixture was extracted with dichloromethane (2 × 50 mL). The combined organic layers were dried over $MgSO_4$, and the solvent was evaporated under vacuum. The crude product was purified by column chromatography (silica gel, hexane/dichloromethane 3:1 v/v as eluent) to give a yellow solid (3.84 g, 90 % yield). ^{1}H RMN ($CDCl_3$): δ 8.17 (d, 4H, $O_2N\text{-}C_6H_4$-, AA' part of AA′XX′ spin system, $N_{A,X} = J_{A,X} + J_{A,X'}$ = 8.8 Hz, $J_{A,A'} \approx J_{X,X'}$), 7.83 (s, 6H, ArH-TriPh), 6.91 (d, 4H, $O_2N\text{-}C_6H_4$-, XX' part of AA′XX′ spin system,, $J_{A,X} + J_{A,X'}$ = 8.8 Hz, $J_{A,A'} \approx$

$J_{X,X'}$), 4.24 (m, 12H, O*CH₂*), 4.07 (t, 4H, J = 6.4 Hz, O*CH₂*), 1.94 (m, 16H, OCH_2*CH₂*), 1.62 (m, 16H, OCH_2CH_2*CH₂*), 1.41-1.25 (m, 64H, *CH₂*), 0.88 (m, 12H, *CH₃*).

2,6-Bis(6-(4-(formylamino)phenoxy)hexyloxy-3,7,10,11-tetrakis(dodecyloxy))triphenylene (5). To a solution of 2,6-bis(6-(4-nitrophenoxy)hexyloxy)-3,7,10,11-tetrakis(dodecyloxy))triphenylene (3.84 g, 2.67 mmol) in toluene (50 mL) was added powder tin (4.44g, 37.4 mmol) and formic acid (75 mL, 98%). The mixture was refluxed for 3 h. After reaching room temperature, the toluene layer was separated and washed with water (2 x 50 mL). The organic solution was dried over $MgSO_4$, and the solvent was evaporated under vacuum to give the product as a yellow solid (3.10 g, 81 %. yield). IR: ν(N-H): 3310 cm^{-1}, ν(C=O): 1659 cm^{-1}. ^{1}H NMR ($CDCl_3$). The spectrum shows the resonances corresponding to the two conformational isomers, which arise from slow rotation of the -CHO group around the C-N bond at room temperature: δ 8.48 (d, 1H, J = 11.4 Hz, C*H*O), 8.29 (s, 1H, C*H*O), 7.83 (s, 6H, ArH-TriPh), 7.39 (d, 2H, ArH-isocyanide, AA' part of AA'XX' spin system, $N_{A,X} = J_{A,X} + J_{A,X'} = 9.0$ Hz, $J_{AA'} \approx J_{XX}$), 7.76 (broad, 1H, NH), 7.04 (broad, 1H, NH), 6.98 (d, 2H, ArH-isocyanide, AA' part of AA'XX' spin system, $N_{A,X} = J_{A,X} + J_{A,X'} = 9.0$ Hz, $J_{AA'} \approx J_{XX'}$), 6.85 (m, 4H, ArH-isocyanide, overlapped XX' parts of AA'XX' spin systems), 4.22 (m, 12H, OCH_2), 3.96 (t, 4H, J = 6.5 Hz, OCH_2), 1.92 (m, 16H, OCH_2*CH₂*), 1.68-1.25 (m, 80H, CH_2), 0.88 (m, 12H, CH_3).

2,6-Bis(6-(4-isocyanophenoxy)hexyloxy-3,7,10,11-tetrakis(dodecyloxy))triphenylene (7). To a solution of 2,6-bis(6-(4-(formylamino)phenoxy)hexyloxy-3,7,10,11-tetrakis(dodecyloxy))triphenylene (3.10 g, 2.16 mmol) and triethylamine (1.20 mL, 8.64 mmol) in dry dichloromethane (40 mL), under nitrogen atmosphere, was added dropwise a solution of bistrichloromethyl carbonate (triphosgene; 0.43 g, 1.44 mmol) in dry dichloromethane (10 mL). The mixture was stirred at room temperature for 1 h and the solvent was removed. The resulting product was purified by column chromatography (silica gel, dichloromethane/hexane 1:3 v/v as eluent) giving a pale yellow solid (2.35 g, 78 % yield). IR (cm^{-1}): ν(C≡N): 2121. ^{1}H NMR ($CDCl_3$):

δ 7.84 (s, 6H, ArH-TriPh), 7.27 (d, 4H, ArH-isocyanide, AA’ part of two AA´XX´ spin systems, $N_{A,X}= J_{A,X} + J_{A,X'} = 9.0$ Hz, $J_{AA'} \approx J_{XX'}$), 6.84 (d, 4H, ArH-isocyanide, XX’ part of two AA´XX´ spin systems, $N_{A,X}= J_{A,X} + J_{A,X'} = 9.0$ Hz, $J_{AA'} \approx J_{XX'}$), 4.22 (m, 12H, OCH_2), 3.98 (t, 4H, $J = 6.6$ Hz, OCH_2), 1.92 (m, 16H, $OCH_2\mathit{CH_2}$), 1.68-1.25 (m, 80H, CH_2), 0.88 (m, 12H, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, Me_4Si,): δ (*C*N not observed), 162.53, 159.41 (O-C_{Ph}), 149.10, 149.04, 148.94, 148.90, 148.85 (O-C_{TriPh}), 127.70 (H-C_{Ph}), 123.77, 123.65, 123.63, 123.59, 123.51, 119.32 (C_{TriPh}), 114.98 (N-C_{Ph}), 107.54, 107.52, 105.43, 107.37, 107.21 (H-C_{TriPh}), 69.84, 69.73, 69.70, 69.59, 69.54, 69.46, 68.24 (*O-*CH_2), 31.93, 29.73, 29.71, 29.68, 29.55, 29.53, 29.49, 29,47, 29,41, 29.38, 29.09, 26.21, 25.97, 25.84, 22.69 (-CH_2-), 14.11 (-CH_3). Anal. Calcd. (%) for $C_{92}H_{138}N_2O_8$: C, 78.92; H, 9.94; N, 2.00. Found: C, 78.76; H, 10.19; N, 2.12. MALDI-TOF MS: *m/z* 1399.0475 $[M]^+$ (calcd. 1399.0448 for $C_{92}H_{138}N_2O_8$).

Synthesis of the triisocyano-triphenylene ligand (8)

2,6,10-Tris(6-(4-nitrophenoxy)hexyloxy)-3,7,11-tris(dodecyloxy))triphenylene (4). To a solution of 2,6,10-trihydroxy-3,7,11-tris(dodecyloxy))triphenylene (**2**) (0.397 g, 0.48 mmol) and 4-(6-bromohexyloxy)nitrobenzene (3.47 g, 11.5 mmol) in dry 2-butanone (90 mL), under nitrogen, was added K_2CO_3 (1.84 g, 13.3 mmol). The mixture was heated at reflux for 16 h. Then water (90 mL) was added, and the mixture was extracted with dichloromethane (2 × 50 mL). The combined organic layers were dried over $MgSO_4$, and the solvent was evaporated under vacuum. The crude product was purified by column chromatography (silica gel, hexane/dichloromethane 2:1 v/v as eluent) to give a yellow solid (0.634 g, 89 % yield). ^1H RMN ($CDCl_3$): δ 8.16 (d, 6H, O_2N-C_6H_4-, AA´ part of AA´XX´ spin system, $N_{A,X} = J_{A,X} + J_{A,X'} = 9.2$ Hz, $J_{A,A'} \approx J_{X,X'}$), 7.84 (s, 3H, ArH-TriPh), 7.83 (s, 3H, ArH-TriPh), 6.91 (d, 6H, O_2N-C_6H_4-, XX´ part of AA´XX´ spin system, $J_{A,X} + J_{A,X'} = 9.2$ Hz, $J_{A,A'} \approx J_{X,X'}$), 4.26 (t, 6H, $J = 6.3$ Hz, OCH_2), 4.21 (t, 6H, $J = 6.6$ Hz, OCH_2), 4.07 (t, 6H, $J = 6.4$ Hz, OCH_2), 2.03-1.20 (m, 84H, CH_2), 0.87 (t, 9H, $J = 7.0$ Hz, CH_3).

2,6,10-Tris(6-(4-(formylamino)phenoxy)hexyloxy-3,7,11-tris(dodecyloxy))triphenylene (6). To a solution of 2,6,10-tris(6-(4-nitrophenoxy)hexyloxy)-3,7,11-tris(dodecyloxy))triphenylene (0.634 g, 0.43 mmol) in toluene (20 mL) was added powder tin (1.11g, 9.39 mmol) and formic acid (45 mL, 98%). The mixture was refluxed for 3 h. After reaching room temperature, the toluene layer was separated and washed with water (2 x 50 mL). The organic solution was dried over $MgSO_4$, and the solvent was evaporated under vacuum to give the product as a yellow solid (0.554 g, 88 % yield). IR: ν(N-H): 3310 cm^{-1}, ν(C=O): 1659 cm^{-1}. ^1H NMR ($CDCl_3$). The spectrum shows the resonances corresponding to the two conformational isomers, which arise from slow rotation of the -CHO group around the C-N bond at room temperature: δ 8.47 (d, 1.5H, J = 11.6 Hz, CHO), 8.31 (s, 1.5H, CHO), 7.84 (s, 3H, ArH-TriPh), 7.83 (s, 3H, ArH-TriPh), 7.40 (d, 3H, ArH-isocyanide, AA' part of AA'XX' spin system, $N_{A,X} = J_{A,X} + J_{A,X'} = 9.0$ Hz, $J_{AA'} \approx J_{XX}$), 7.70 (broad, 1.5 H, NH), 7.04 (broad, 1.5 H, NH), 6.98 (d, 3H, ArH-iisocyanide, AA' part of AA'XX' spin system, $N_{A,X} = J_{A,X} + J_{A,X'} = 9.0$ Hz, $J_{AA'} \approx J_{XX'}$), 6.85 (m, 6H, ArH-isocyanide, overlapped XX' parts of AA'XX' spin systems), 4.23 (m, 12H, OCH_2), 3.96 (t, 6H, J = 6.5 Hz, OCH_2), 2.04-1.18 (m, 84H, CH_2), 0.87 (t, 9H, J = 7.0 Hz, CH_3).

2,6,10-Tris(6-(4-isocyanophenoxy)hexyloxy-3,7,11-tris(dodecyloxy))triphenylene (8). To a solution of 2,6,10-tris(6-(4-(formylamino)phenoxy)hexyloxy-3,7,11-tris(dodecyloxy))triphenylene (0.295 g, 0.20 mmol) and triethylamine (0.12 mL, 1.19 mmol) in dry dichloromethane (25 mL), under nitrogen atmosphere, was added dropwise a solution of bistrichloromethyl carbonate (triphosgene; 0.059 g, 0.20 mmol) in dry dichloromethane (5 mL). The mixture was stirred at 38 °C for 1.5 h and the solvent was removed. The resulting product was purified by column chromatography (silica gel, dichloromethane/hexane 1:5 v/v as eluent) giving a pale yellow solid (0.138 g, 49 % yield). IR (cm^{-1}): ν(C≡N): 2122. ^1H NMR ($CDCl_3$):): δ 7.84 (s, 3H, ArH-TriPh), 7.83 (s, 3H, ArH-TriPh), 7.27 (d, 6H, ArH-isocyanide, AA´part of AA´XX´spin systems, $N_{A,X} = J_{A,X} + J_{A,X'} = 9.0$ Hz, $J_{AA'} \approx J_{XX'}$), 6.84 (d, 6H, ArH-isocyanide, XX´part of AA´XX´spin systems), 4.25 (t, 6H, *J* = 6.4 Hz, OCH$_2$), 4.21 (t, 6H, *J* = 6.6 Hz, OCH$_2$), 3.98 (t, 6H, *J* = 6.5 Hz, OCH$_2$), 2.04-1.18 (m, 84H, CH$_2$), 0.87 (t, 9H, *J* = 7.0 Hz, CH$_3$). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$, Me$_4$Si,): δ (*C*N not observed), 162.53, 159.40 (O-C_{Ph}), 149.02, 148.93 (O-C_{TriPh}), 127.70 (H-C_{Ph}), 123.69, 123.59 (C_{TriPh}), 119.32 (N-C_{Ph}), 114.98 (H-C_{Ph}), 107.46, 107.35 (H-C_{TriPh}), 69.69, 69.50, 68.24 (*O-CH$_2$*), 31.92, 29.72, 29.67, 29.53, 29.49, 29.40, 29.37, 29.09, 26.21, 25.97, 25.84, 22.68 (-CH$_2$-), 14.11 (-*CH$_3$*). Anal. Calcd. (%) for $C_{93}H_{129}N_3O_9$: C, 77.95; H, 9.07; N, 2.93. Encontrado: C, 78.04; H, 9.23; N, 2.78. MALDI-TOF MS: *m/z* 1431.9785 $[M]^+$ (calcd. 1431.9785 for $C_{93}H_{129}N_3O_9$).

Synthesis of isocyano-triphenylene gold complexes (9-12)

$[(AuCl)_2((CN)_2{-}TriPh)]$ (9). To a solution of [AuCl(tht)] (0.035 g, 0.11 mmol) in 30 mL of dichloromethane, (CN)$_2$−TriPh (0.075 g, 0.054 mmol) was added. After stirring for 30 min. the solvent was reduced to 10 mL under reduced pressure and acetone (20 mL) was added. The mixture was cooled at -20 ºC to afford the product as a white solid (0.084 g, 84 % yield). IR (CH$_2$Cl$_2$/cm^{-1}): ν(C≡N): 2223; ν(Au-Cl): 351. ^{1}H NMR (CDCl$_3$): (CDCl$_3$): δ 7.79 (m, 6H, ArH-TriPh), 7.31 (d, 2H, ArH-isocyanide, AA′ part of AA′XX′ spin system, $N_{A,X} = J_{A,X} + J_{A,X'} = 8.9$ Hz, $J_{A,A'} \approx J_{X,X'}$), 7.28 (d, 2H, ArH-isocyanide, XX′ part of AA’XX’ spin system, $N_{A,X} = J_{A,X} + J_{A,X'} = 8.9$ Hz, $J_{A,A'} \approx J_{X,X'}$), 6.87 (d, 2H, ArH-isocyanide, AA′ part of AA′XX′ spin system, $N_{A,X} = J_{A,X} + J_{A,X'} = 8.9$ Hz, $J_{A,A'} \approx J_{X,X'}$), 6.84 (d, 2H, ArH-isocyanide, XX′ part of AA′XX′ spin system, $N_{A,X} = J_{A,X} + J_{A,X'} = 8.9$ Hz, $J_{A,A'} \approx J_{X,X'}$), 4.21 (m, 12H, OCH$_2$), 4.01 (t, 4H, *J* = 6.6 Hz, OCH$_2$), 1.68-1.25 (m, 80H, CH$_2$), 0.88 (m, 12H, CH$_3$). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$, Me$_4$Si,): δ (*C*N not observed), 161.21 (O-C_{Ph}), 149.15, 149.07, 148.90, 148.81, 148.77, 140.48 (O-C_{TriPh}), 128.41, 128.39 (H-C_{Ph}), 123.74, 123.64, 123.60, 123.51, 123.41 (C_{TriPh}), 116.32 (N-C_{Ph}), 115.55, 115.51 (H-C_{Ph}), 107.54, 107.42, 107.37, 107.34, 107.22, 107.06 (H-C_{TriPh}), 69.87, 69.74, 69.53, 69.32, 69.17, 68.45, 68.40 (*O-CH$_2$*), 31.92, 29.73, 29.71, 29.68, 29.56, 29.53, 29.51, 29.47, 29.38, 29.33, 29.31, 28.91, 26.23, 26.21, 25.72, 25.68, 25.55, 25.50, 22.69 (-CH$_2$-), 14.12 (-*CH$_3$*). Anal. calcd (%) for

$C_{92}H_{138}Au_2Cl_2N_2O_8$: C, 59.25; H, 7.46; N, 1.50. Found: C, 59.15; H, 7.59; N, 1.61. MALDI-TOF MS: *m/z* 1862.9212 [M]$^+$ (calcd. 1862.9156 for $C_{92}H_{138}Au_2Cl_2N_2O_8$).

[(Au(C≡C-Ph))$_2$((CN)$_2$−TriPh)] (10). (CN)$_2$−TriPh (0.074 g, 0.053 mmol) was added to [Au(C≡C−C_6H_5)]$_n$ (0.031 g, 0.11 mmol) suspended in tetrahydrofurane (30 mL). After stirring for 30 min, the solvent was eliminated under reduced pressure and the resulting residue extracted in dichloromethane (20 mL). The dichloromethane solution was concentrated on a rotary evaporator until 10 mL and acetone (20 mL) was added to obtain a white solid (0.077 g, 73 % yield). IR (cm^{-1}): ν(C≡N): 2207, the ν(C≡C) absorption is not observed as reported for similar complexes.[6] ^{1}H NMR ($CDCl_3$): δ 7.82 (m, 6H, ArH-TriPh), 7.47 (d, 4H, *J* = 7.0 Hz, ArH- phenylacetylide), 7.33 (m, 4H, ArH-isocyanide, AA′ part of two AA′XX′ spin systems, 7.21 (m. 6H, ArH-phenylacetylide), 6.86 (m, 4H, ArH-isocyanide, XX′ part of two AA′XX′ spin systems, , 4.23 (m, 12H, OCH_2), 4.00 (t, 4H, *J* = 6.6 Hz, OCH_2), 1.99-1.20 (m, 80H, CH_2), 0.87 (m, 12H, CH_3). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, Me_4Si,): δ (*C*N and C≡C not observed), 161.08, 155.42 (O-*C_{Ph})*, 149.14, 149.07, 148.89, 148.83, 148.76 (O-*C_{TriPh}*), 132.45, 128.4, 127.92, 126.92 (H-*C_{Ph})*, 124.66, 124.64, 123.76, 123.65, 123.61, 123.53, 123.42, 122.13, 122.10 (*C_{TriPh}*), 116.42 (N-*C_{Ph})*, 115.49, 115.45 (H-*C_{Ph})*, 107.53, 107.45, 107.37, 105.34, 107.26, 107.08, 103.89 (H-*C_{TriPh}*), 69.88, 69.74, 69.55, 69.37, 69.23, 68.42, 68.38 (*O-CH_2*), 31.93, 29.73, 29.71, 29.68, 29.63, 29.57, 29.54, 29.51, 29.48, 29.38, 29.34, 28.93, 26.23, 26.21, 25.77, 25.60, 25.55, 22.69 (-CH_2-), 14.13 (*-CH_3*). Anal. calcd (%) for $C_{108}H_{148}Au_2N_2O_8$: C, 64.98; H, 7.47; N, 1.40. Found: C, 64.71; H, 7.57; N, 1.54. MALDI-TOF MS: *m/z* 1894.0145 [M - C≡C-Ph]$^+$ (calcd. 1894.0170 for $C_{100}H_{143}Au_2N_2O_8$).

[(AuCl)$_3$((CN)$_3$−TriPh)] (11). To a solution of [AuCl(tht)] (0.058 g, 0.18 mmol) in 30 mL of dichloromethane, (CN)$_3$−TriPh (0.086 g, 0.06 mmol) was added. After stirring for 30 min. the solvent was reduced to 10 mL under reduced pressure and acetone (20 mL) was added. The mixture was cooled at -20 ºC to afford the product as a white solid (0.097 g, 77 % yield). IR (cm^{-1}): ν(C≡N): 2221; ν(Au-Cl): 349. ^{1}H NMR ($CDCl_3$): ($CDCl_3$): δ 7.80 (s, 3H, ArH-TriPh), 7.79 (s, 3H, ArH-

TriPh), 7.29 (d, 6H, ArH-isocyanide, AA´part of AA´XX´spin systems, $N_{A,X}= J_{A,X} + J_{A,X'} = 9.0$ Hz, $J_{AA'} \approx J_{XX'}$), 6.86 (d, 6H, ArH-isocyanide, XX´part of AA´XX´spin systems),, 4.26 (t, 6H, $J = 6.4$ Hz, OCH_2), 4.23 (t, 6H, $J = 6.5$ Hz, OCH_2), 4.02 (t, 6H, $J = 6.5$ Hz, OCH_2), 2.04-120 (m, 84H, CH_2) 0.87 (t, 9H, $J = 7.0$ Hz, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, Me_4Si,): δ (*C*N not observed), 161.19 (O-C_{Ph}), 148.99, 148.91, 140.44 (O-C_{TriPh}), 128.39 (H-C_{Ph}), 123.56, 123.51 (C_{TriPh}), 116.29 (N-C_{Ph}), 115.53 (H-C_{Ph}), 107.27 (H-C_{TriPh}), 69.69, 69.20, 68.39 (*O-*CH_2), 31.92, 29.73, 29.72, 29.67, 29.55, 29.51, 29.37, 29.31, 28.89, 26.23, 25.65, 25.47, 22.69 (-CH_2-), 14.14 (-CH_3). Anal. Calcd. (%) for $C_{93}H_{129}Au_3Cl_3N_3O_9$: C, 52.43; H, 6.10; N, 1.97. Found: C, 52.56; H, 5.96; N, 1.97. MALDI-TOF MS: *m/z* 2127.7727 $[M]^+$ (calcd. 2127.7786 for $C_{93}H_{129}Au_3Cl_3N_3O_9$).

[(Au(C≡C-Ph))$_3$((CN)$_3$−TriPh)] (12). (CN)$_3$−TriPh (0.064 g, 0.045 mmol) was added to $[Au(C{\equiv}C{-}C_6H_5)]_n$ (0.040 g, 0.14 mmol) suspended in tetrahydrofurane (30 mL). After stirring for 30 min, the solvent was eliminated under reduced pressure and the resulting residue extracted in dichloromethane (20 mL). The dichloromethane solution was concentrated on a rotary evaporator until 10 mL and acetone (20 mL) was added to obtain a white solid (0.072 g, 69 % yield). IR (cm^{-1}): ν(C≡N): 2210, the ν(C≡C) absorption is not observed as reported for related complexes.[6] ^1H NMR ($CDCl_3$): δ 7.81 (m, 6H, ArH-TriPh), 7.47 (d, 6H, $J = 7.0$ Hz, ArH- phenylacetylide), 7.30 (d, 6H, ArH-isocyanide, AA´ part of AA´XX´ spin systems, $N_{A,X}= J_{A,X} + J_{A,X'} = 9.0$ Hz, $J_{AA'} \approx J_{XX'}$), 7.23 (m. 9H, ArH- phenylacetylide), 6.85 (d, 6H, ArH-isocyanide, XX´ part of two AA´XX´ spin systems), 4.27 (t, 6H, $J = 6.5$ Hz, OCH_2), 4.23 (t, 6H, $J = 6.5$ Hz, OCH_2), 3.99 (t, 6H, $J = 6.5$ Hz, OCH_2), 1.99-1.20 (m, 84H, CH_2), 0.87 (t, 9H, $J = 7.0$ Hz, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, Me_4Si,): δ (*C*N and C≡C not observed), 161.06, 155.43 (O-C_{Ph}), 149.09, 149.07. 148.97, 148.92, 148.89, 148.85 (O-C_{TriPh}), 132.46, 128.45, 128.42, 128.40, 128.37, 127.96, 126.94 (H-C_{Ph}), 124.72, 124,67, 123.67, 123.63, 123.52, 123.47, 122.20 (C_{TriPh}), 116.32 (N-C_{Ph}), 115.51, 115.47, 115.41, (H-C_{Ph}), 107.50, 105.34, 107.12, 103.91 (H-C_{TriPh}), 69.69, 69.64, 69.61, 69.43, 68.40, 68.32 (*O-*CH_2), 31.93, 29.74, 29.73, 29.69, 29.57, 29.53, 29.52, 29.40, 29.38, 29.33, 28.93, 28.91, 28.89, 26.25, 26.24, 25.79, 25.72, 25.63, 25.56, 25.44, 22.70 (-CH_2-), 14.15 (-CH_3). Anal. calcd (%) for $C_{117}H_{144}Au_3N_3O_9$: C, 60.38; H, 6.24; N, 1.81. Encontrado: C, 60.18; H, 6.30; N, 1.95. MALDI-TOF MS: *m/z* 2325.9948 $[M]^+$ (calcd. 2325.9894 for $C_{117}H_{144}Au_3N_3O_9$).

IR spectra

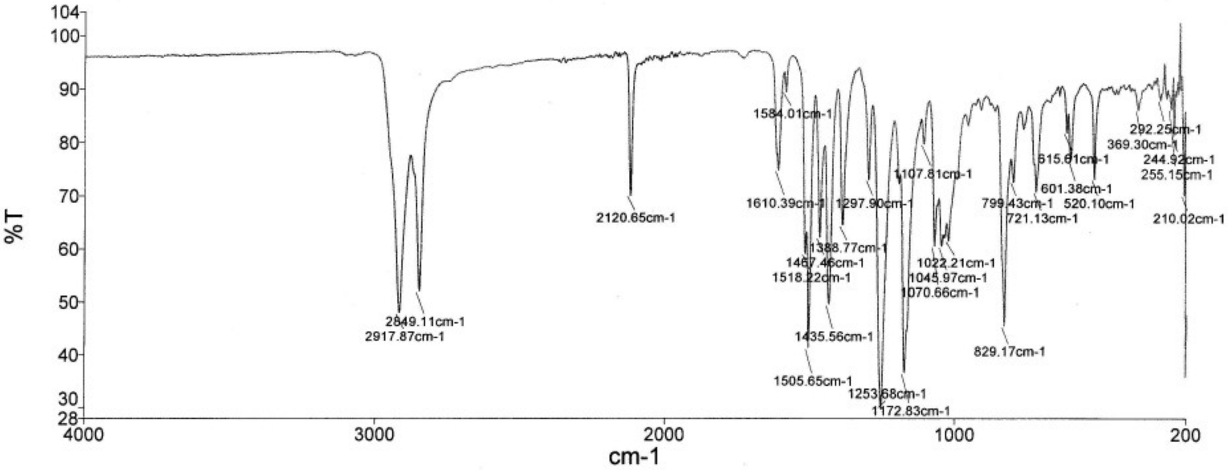


Figure S1: IR spectrum of (CN)$_2$−TriPh (**7**).

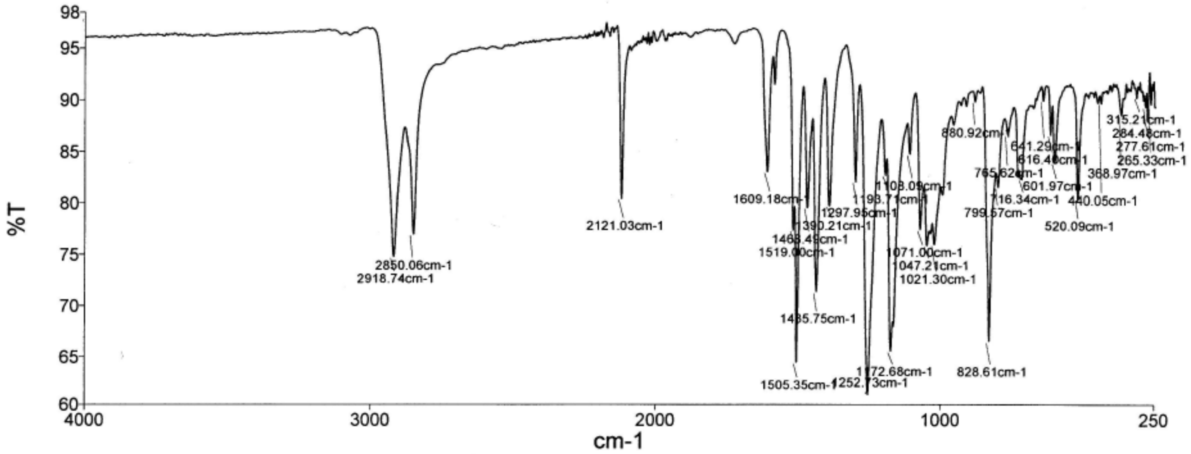


Figure S2: IR spectrum of (CN)$_3$−TriPh **(8).**

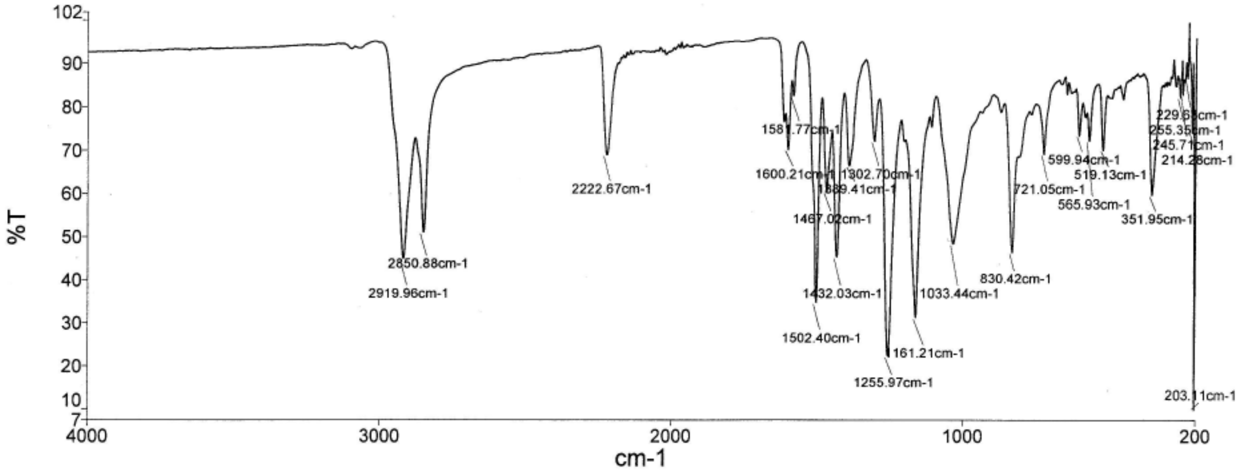


Figure S3: IR spectrum of [(AuCl)$_2$((CN)$_2$−TriPh)] **(9).**

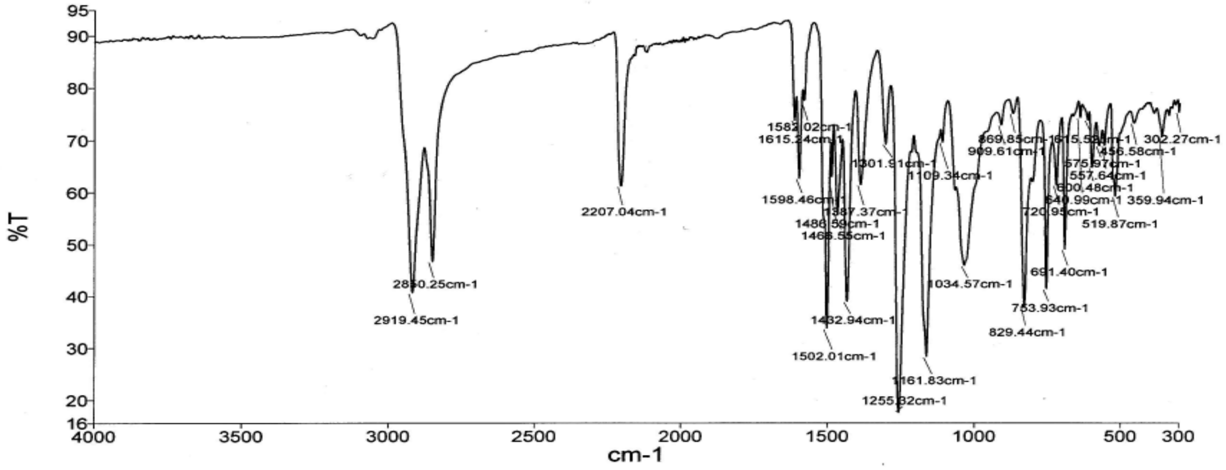


Figure S4: IR spectrum of [(Au(C≡C-Ph))$_2$((CN)$_3$−TriPh)] **(10).**

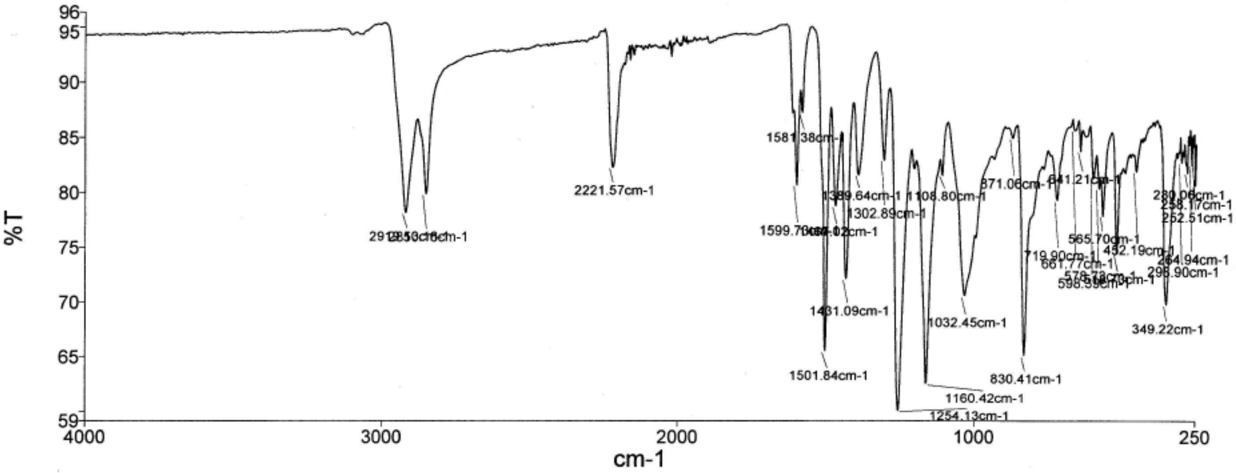


Figure S6: IR spectrum of [(AuCl)$_3$((CN)$_3$−TriPh)] **(11).**

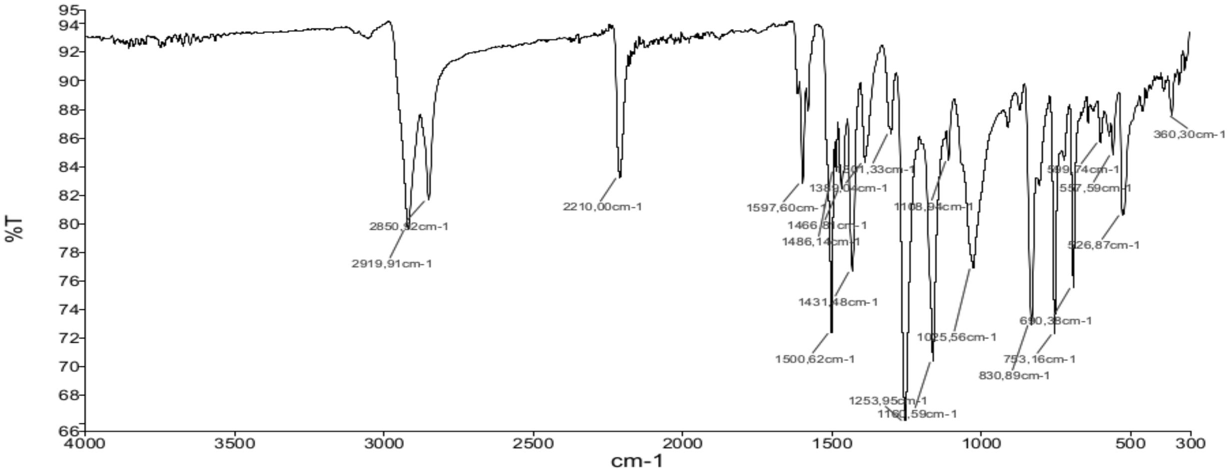


Figure S7: IR spectrum of [(Au(C≡C-Ph))$_3$((CN)$_3$−TriPh)] (**12**).

^{1}H RMN spectra [Varian 500 (499.72 MHz)].

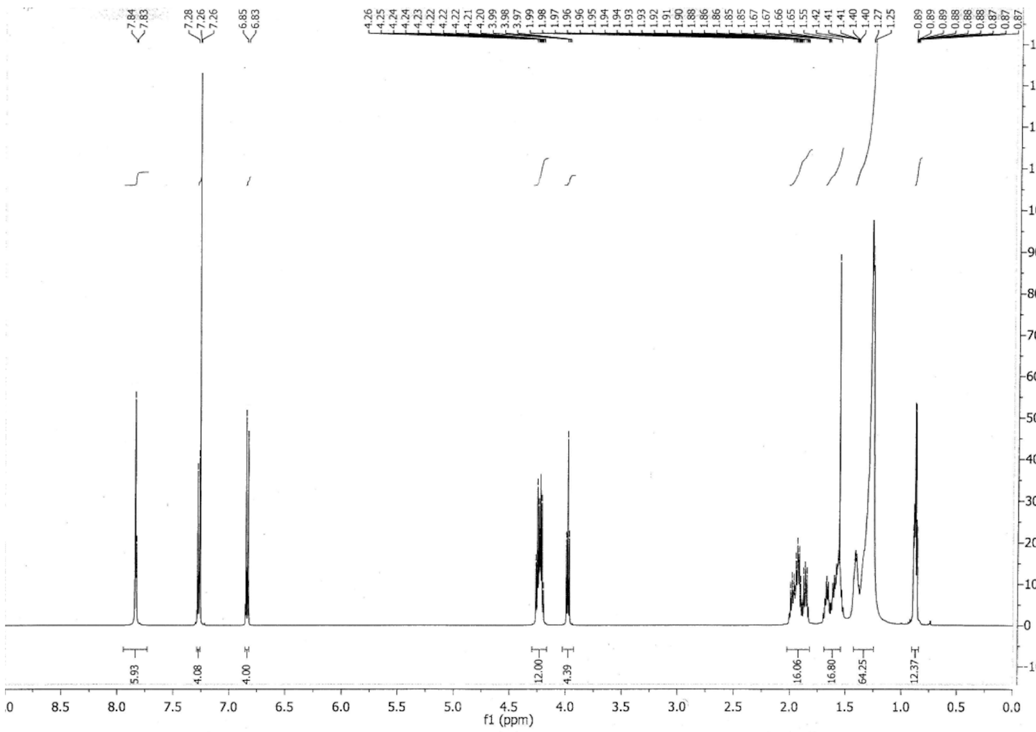


Figure S8: ^{1}H NMR spectrum of $(CN)_2$−TriPh (**7**).

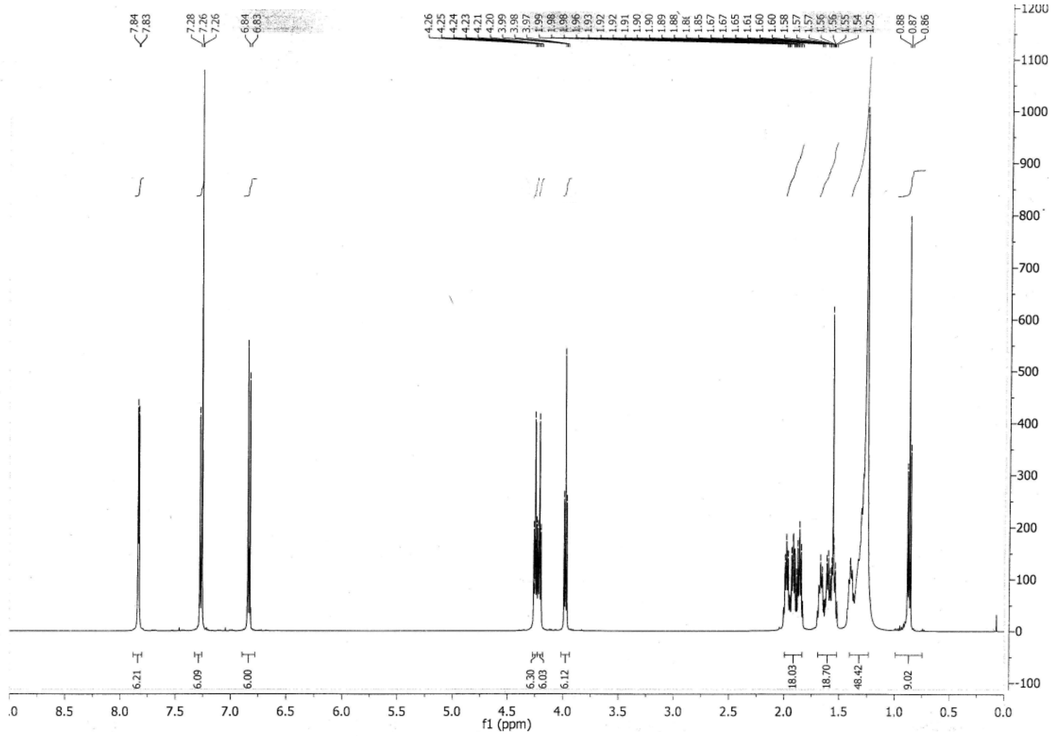


Figure S9: ^{1}H NMR spectrum of $(CN)_3$−TriPh **(8)**.

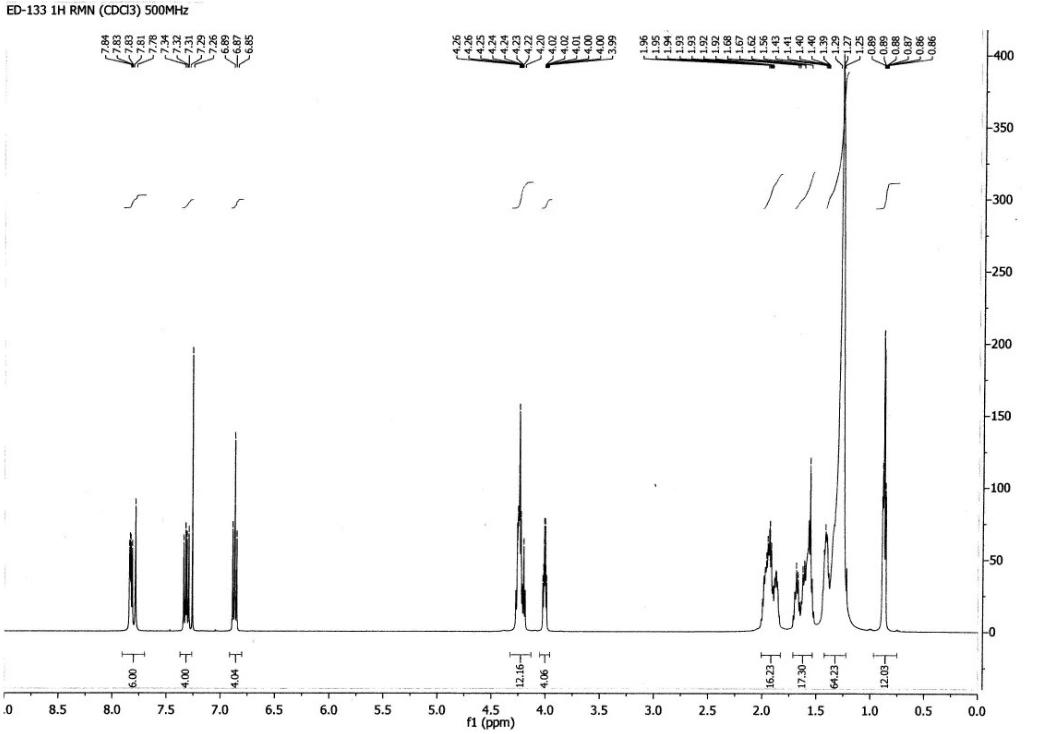


Figure S10: ^{1}H NMR spectrum of [(AuCl)$_2$((CN)$_2$−TriPh)] **(9).**

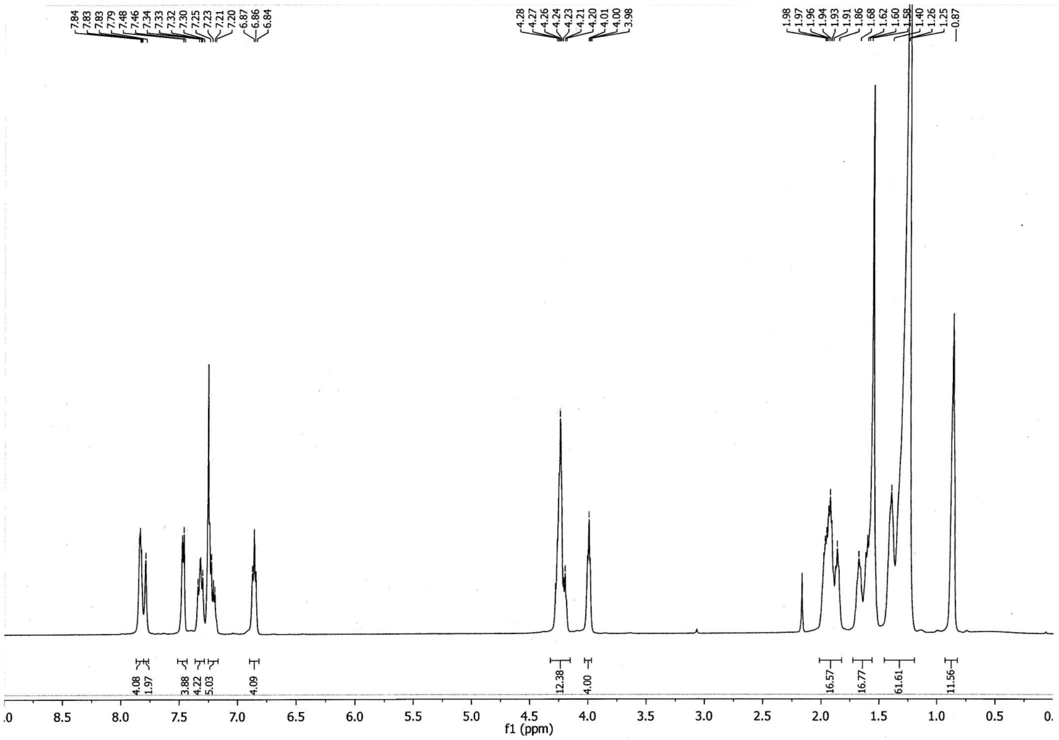


Figure S11: ^{1}H NMR spectrum of [(Au(C≡C-Ph))$_2$((CN)$_2$−TriPh)] **(10).**

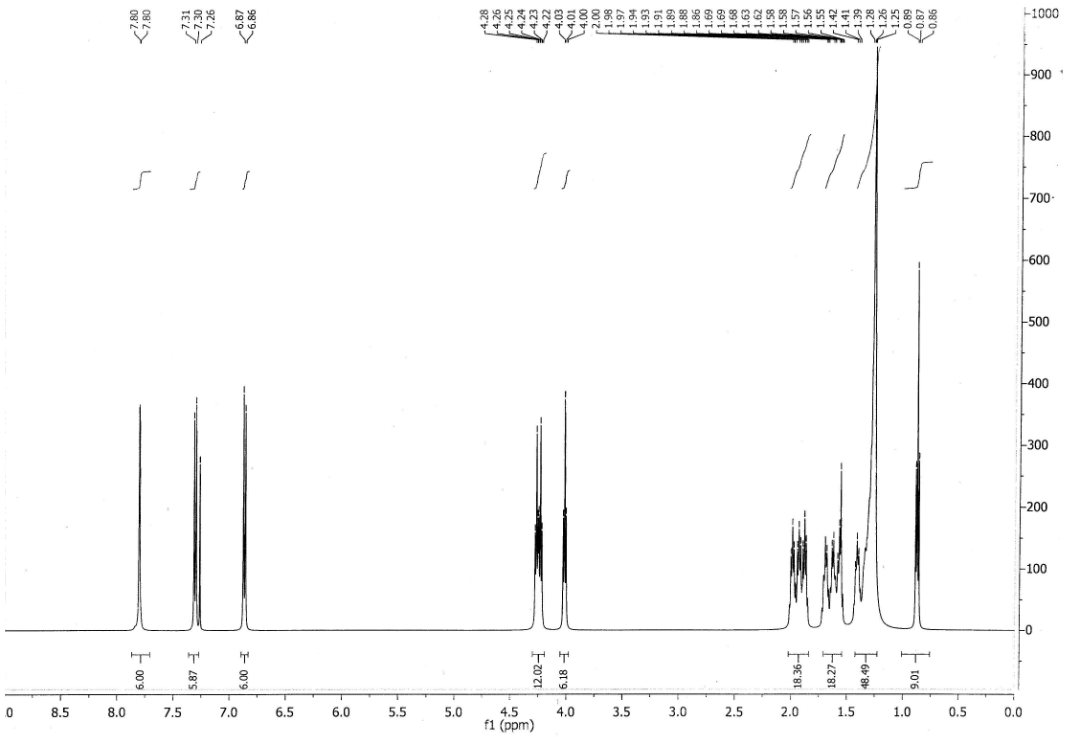


Figure S12: ^{1}H NMR spectrum of [(AuCl)$_3$((CN)$_3$−TriPh)] **(11).**

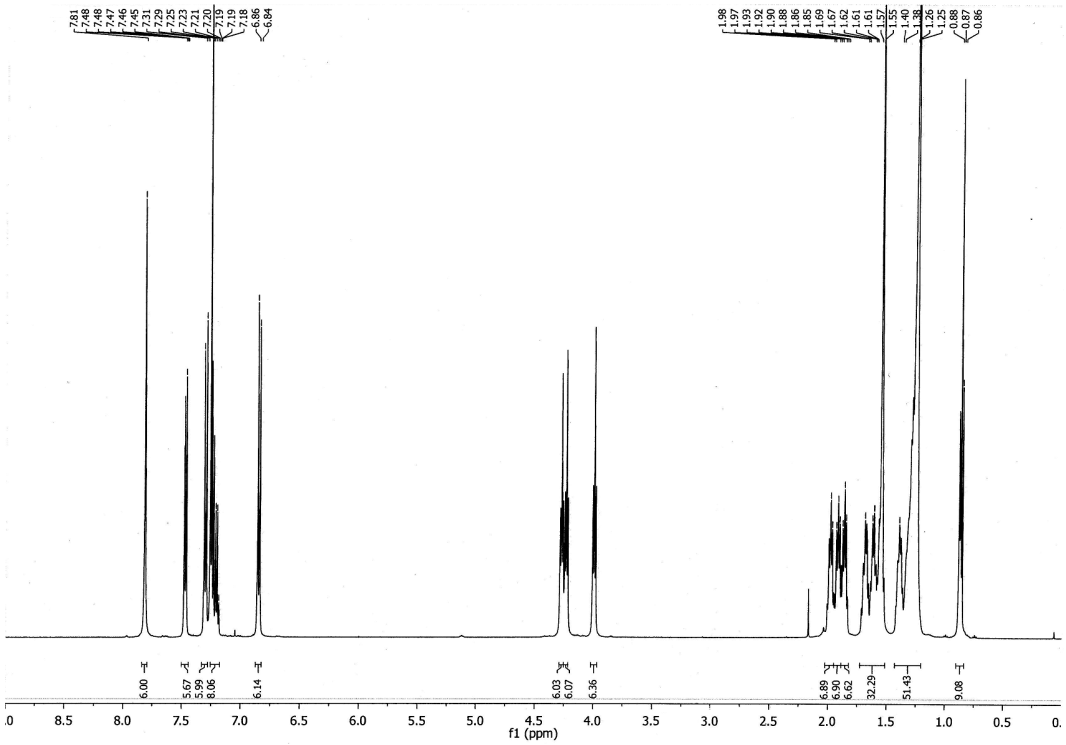


Figure S13: ^{1}H NMR spectrum of [(Au(C≡C-Ph))$_3$((CN)$_3$−TriPh)] **(12).**

^{13}C{^{1}H} NMR spectra (Varian 500 (126 MHz MHz) in CDCl$_3$

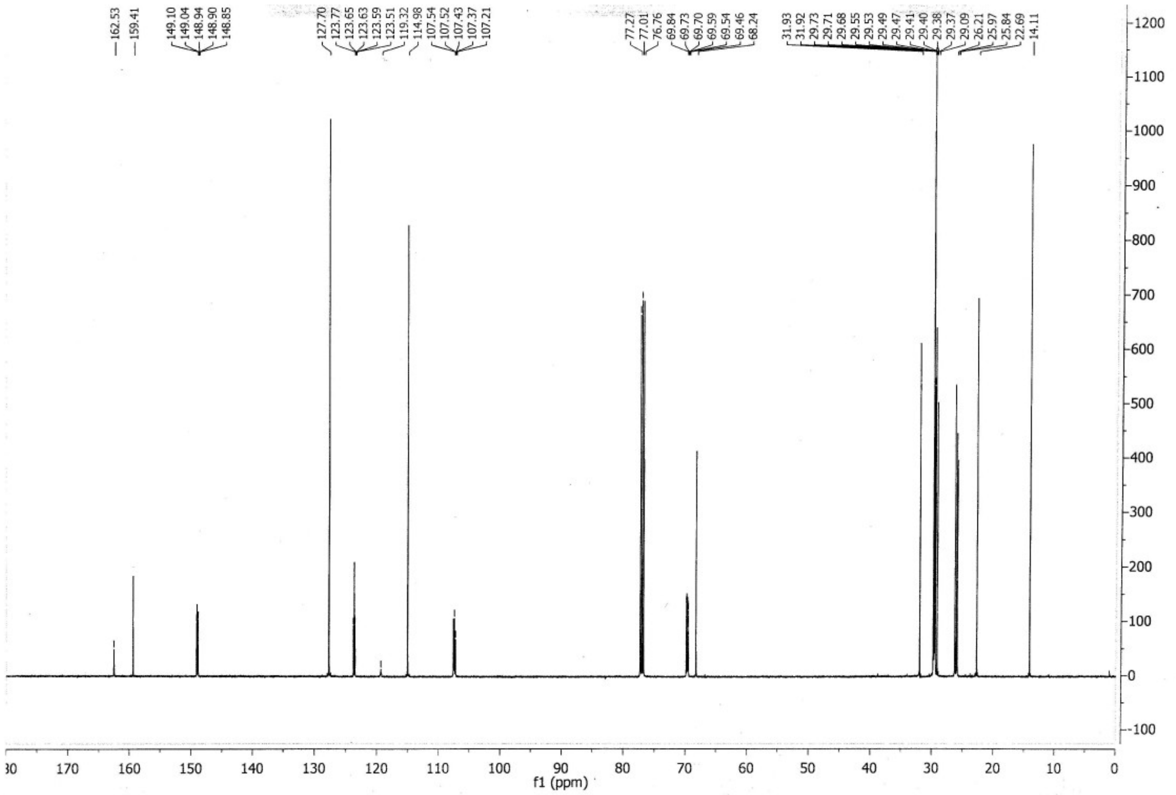


Figure S14: ^{13}C{^{1}H} NMR spectrum of (CN)$_2$−TriPh (**7**).

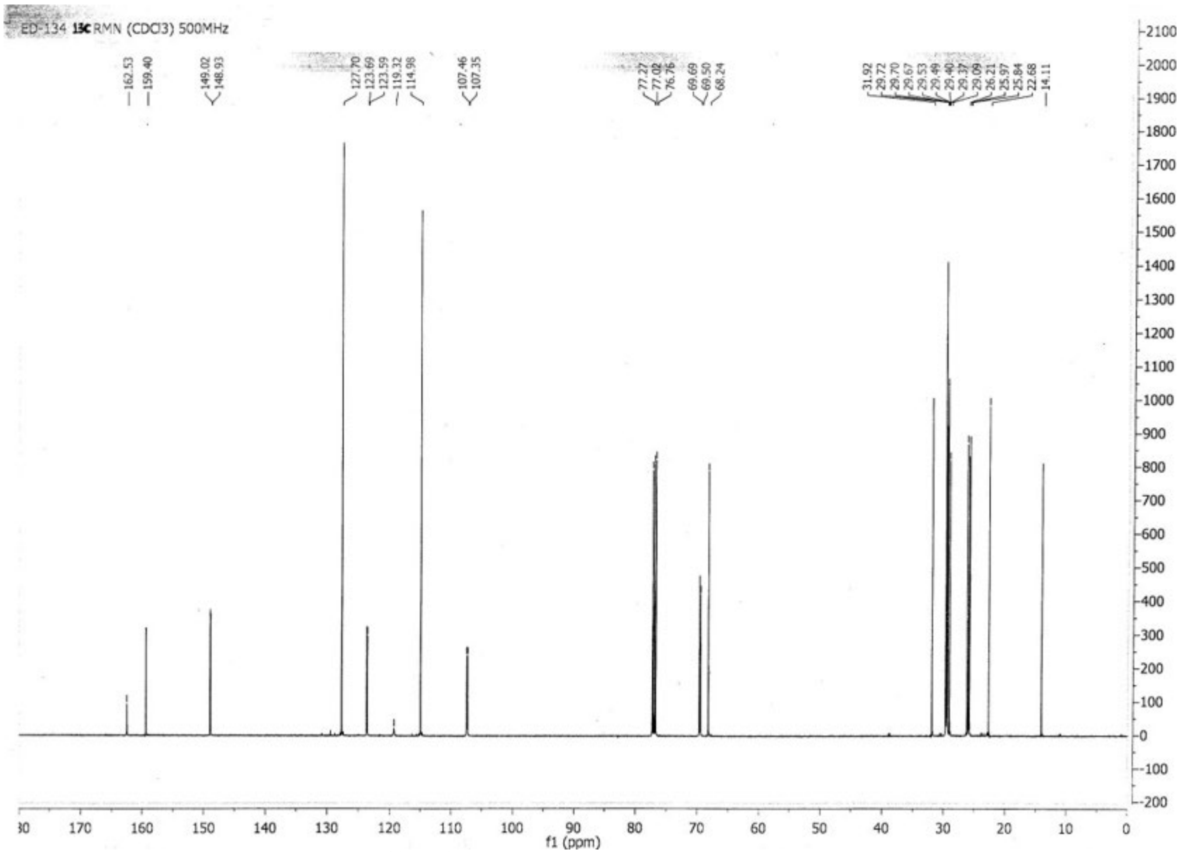


Figure S15: ^{13}C{^{1}H} NMR spectrum of (CN)$_2$−TriPh (**8**).

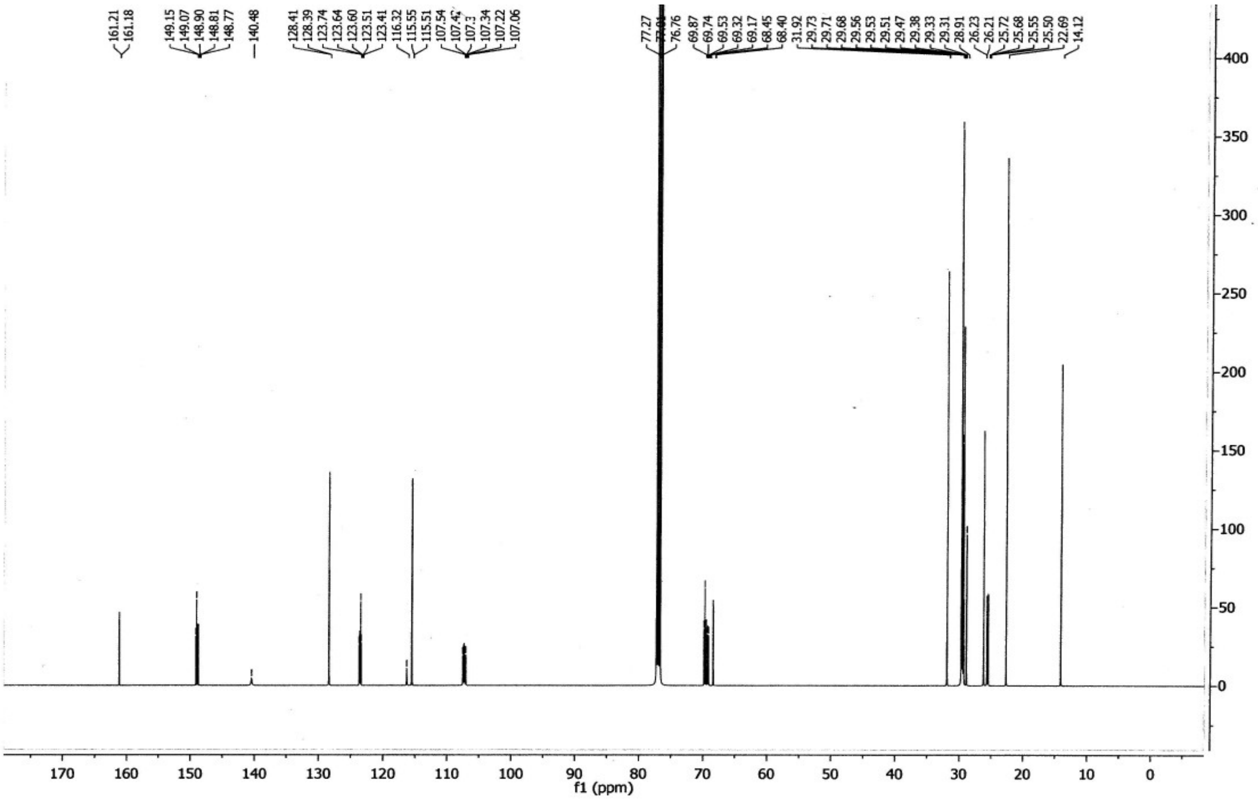


Figure S16: $^{13}C\{^1H\}$ NMR spectrum of [$(AuCl)_2((CN)_2$−TriPh)] **(9).**

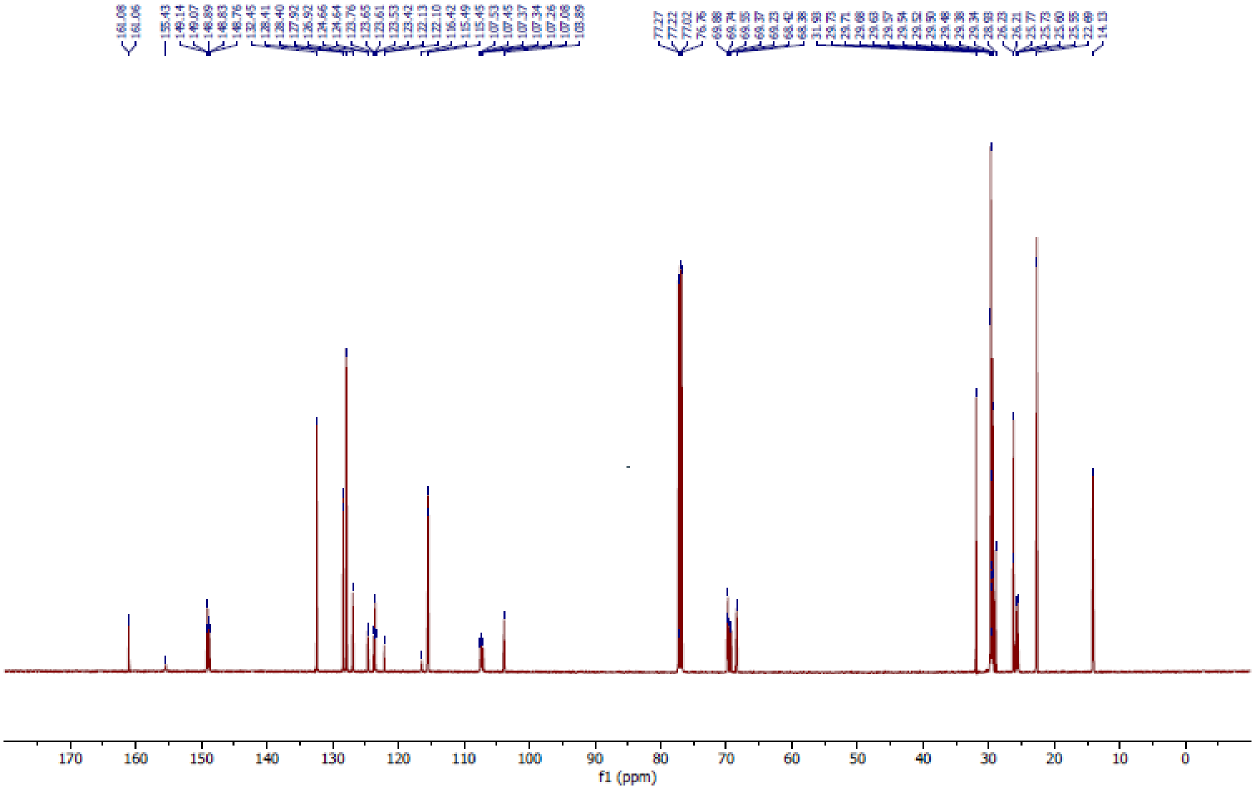


Figure S17: $^{13}C\{^1H\}$ NMR spectrum of [$(Au(C{\equiv}C\text{-}Ph))_2((CN)_2$−TriPh)] **(10).**

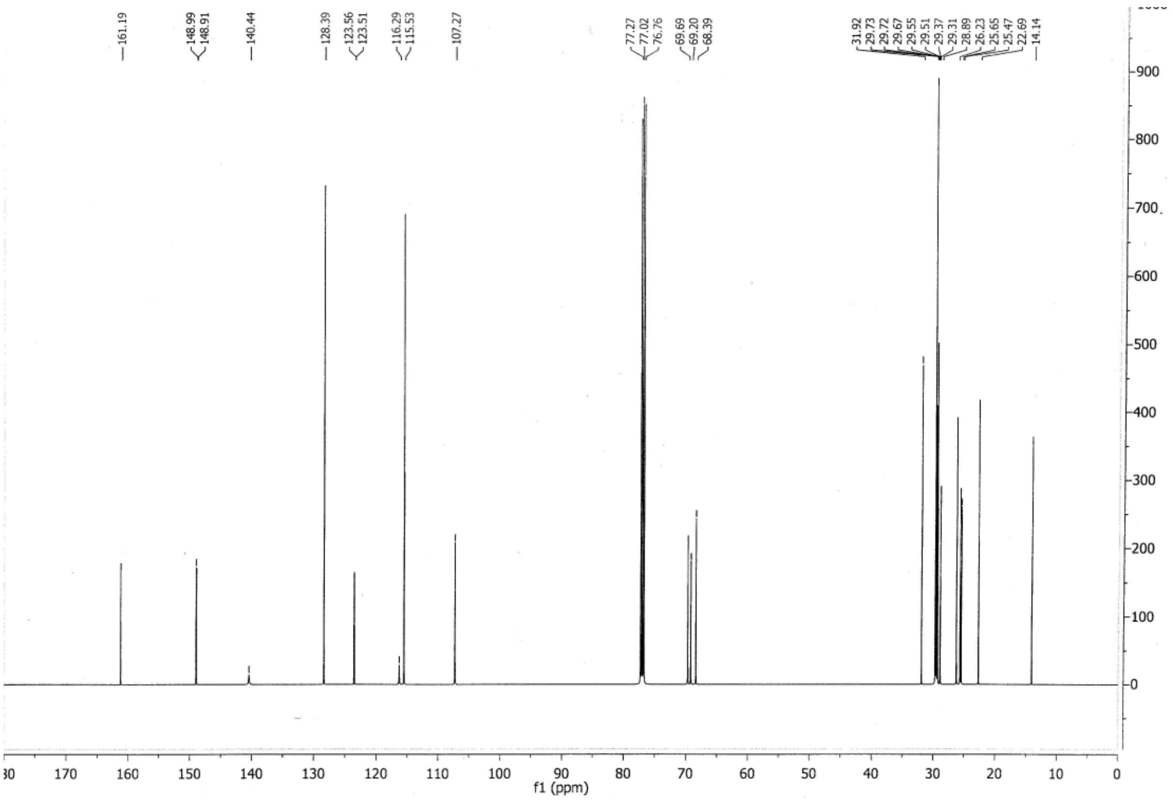


Figure S18: $^{13}C\{^{1}H\}$ NMR spectrum of $[(AuCl)_3((CN)_3{-}TriPh)]$ **(11).**

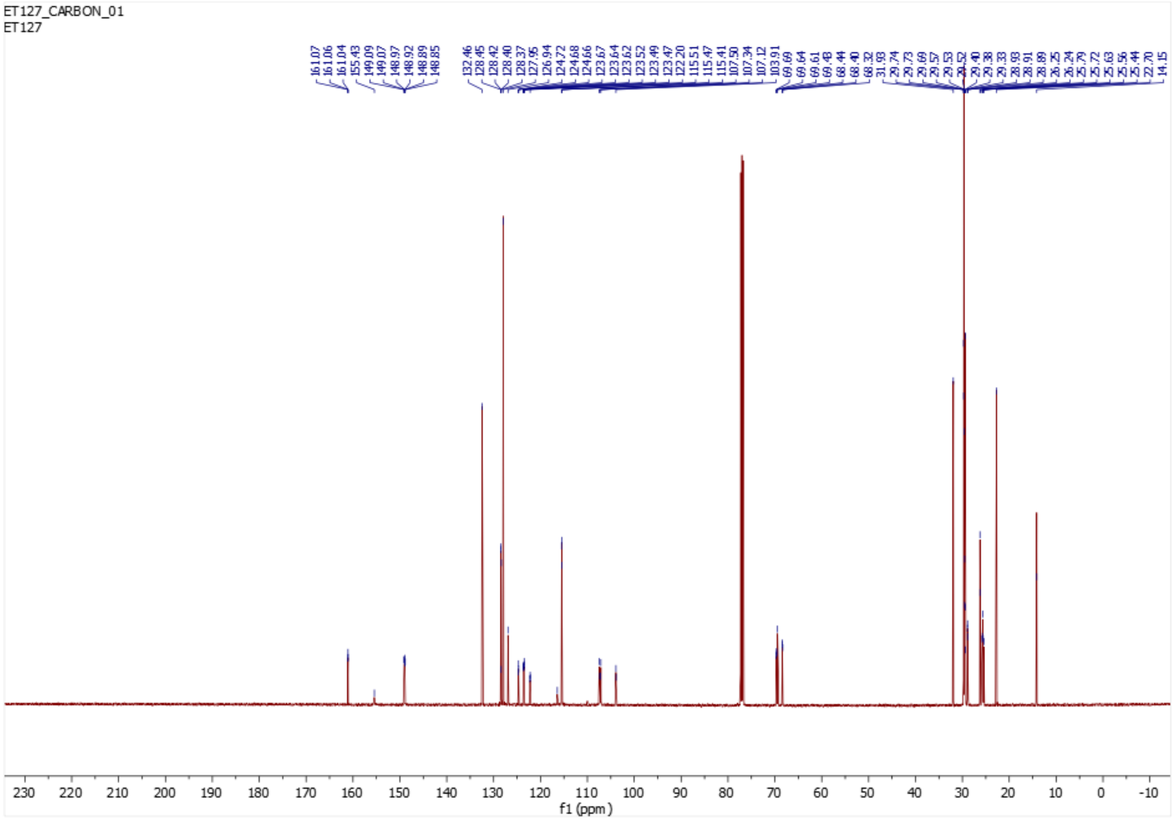
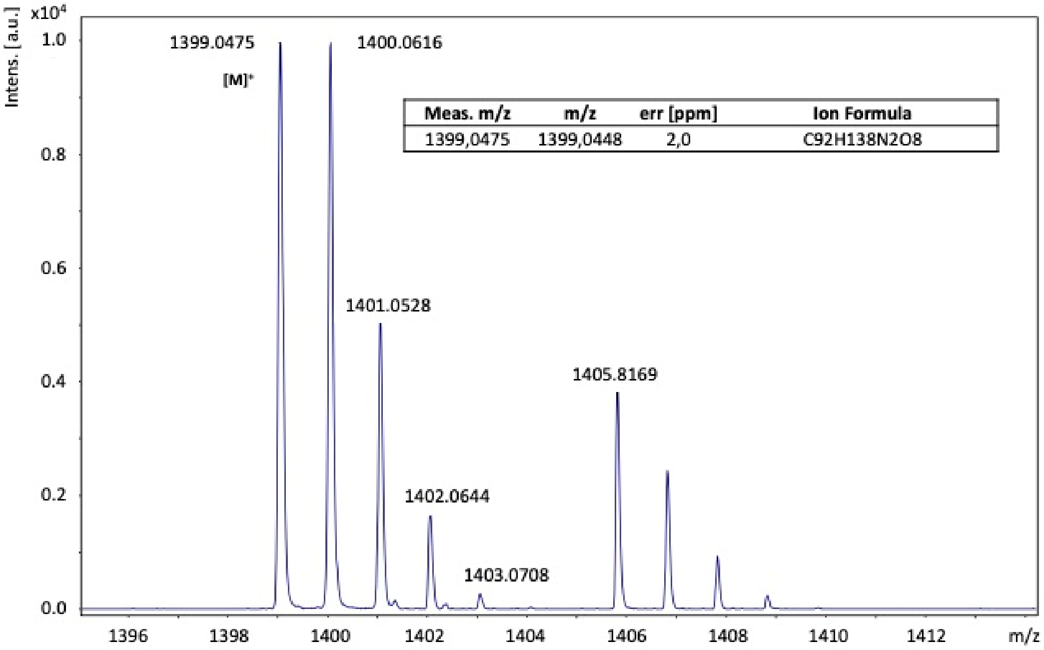


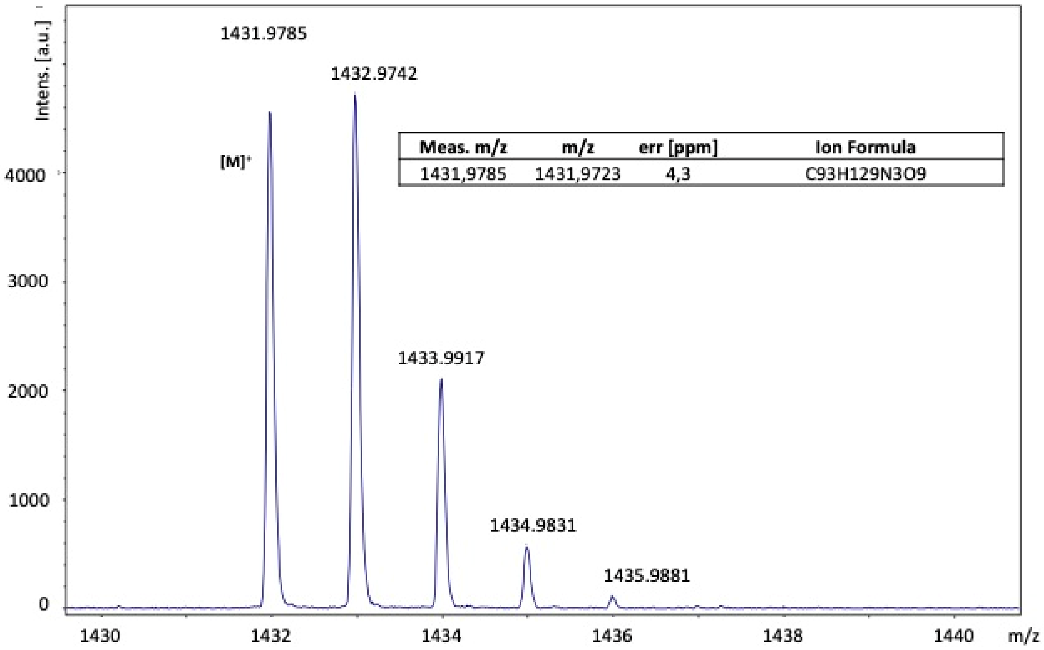
Figure S19: $^{13}C\{^{1}H\}$ NMR spectrum of $[(Au(C{\equiv}C\text{-}Ph))_3((CN)_3{-}TriPh)]$ **(12)**.

MALDI-TOF MS



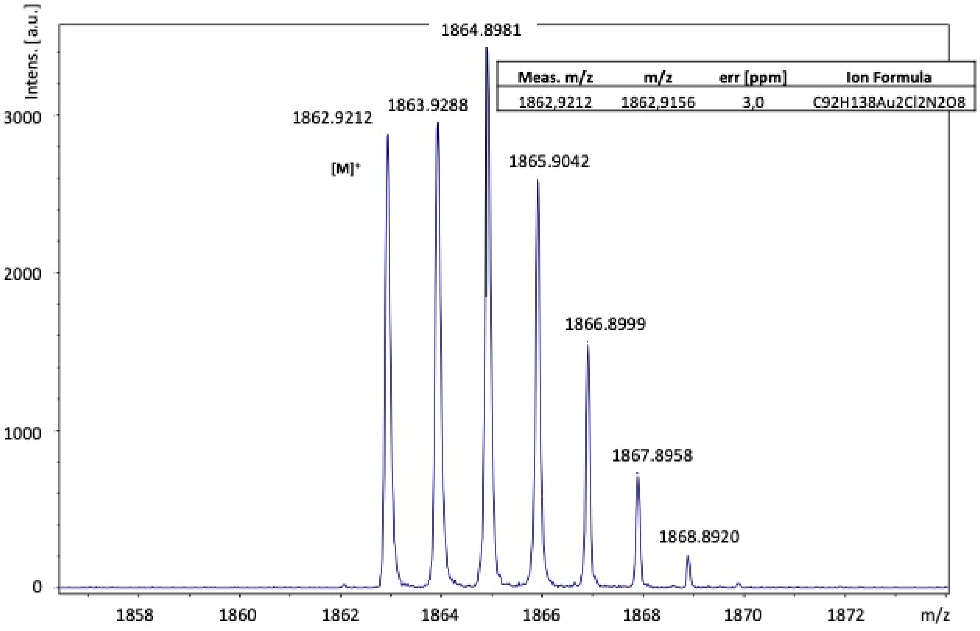
Meas. m/z	m/z	err [ppm]	Ion Formula
1399,0475	1399,0448	2,0	C92H138N2O8

Figure S20: MALDI-TOF mass spectrum of (CN)$_2$−TriPh (**7**).



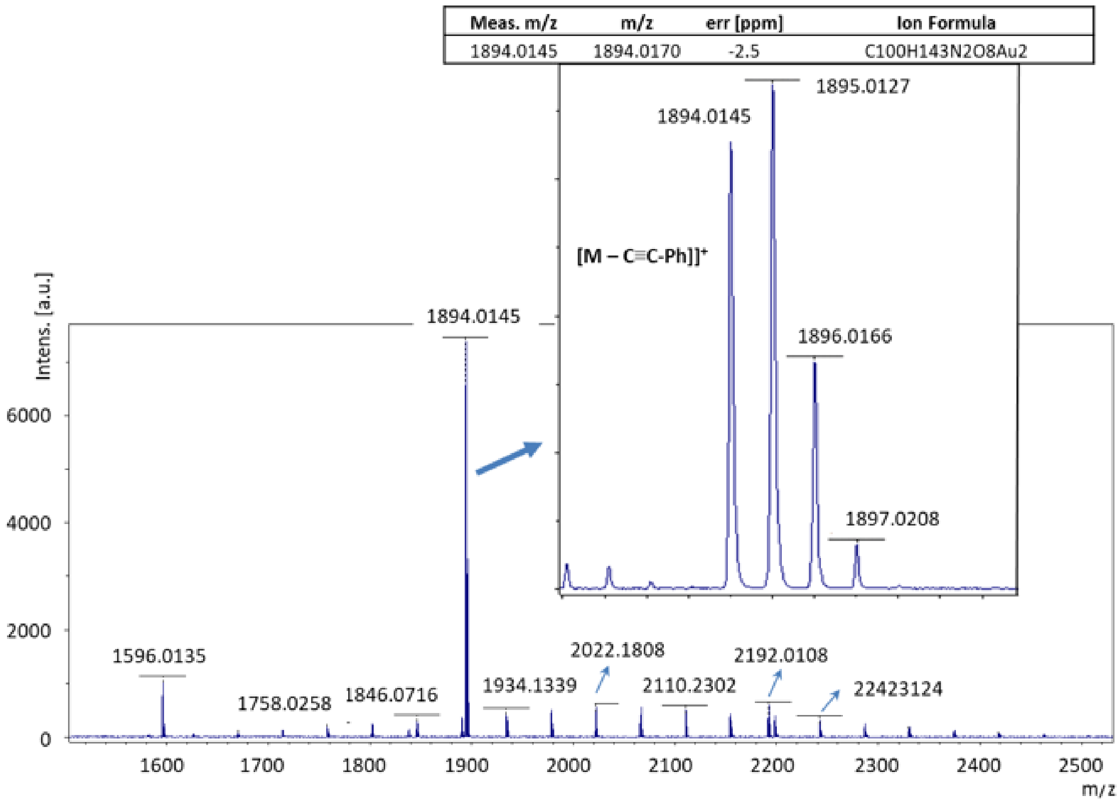
Meas. m/z	m/z	err [ppm]	Ion Formula
1431,9785	1431,9723	4,3	C93H129N3O9

Figure S21: MALDI-TOF mass spectrum of (CN)$_3$−TriPh (**8**).



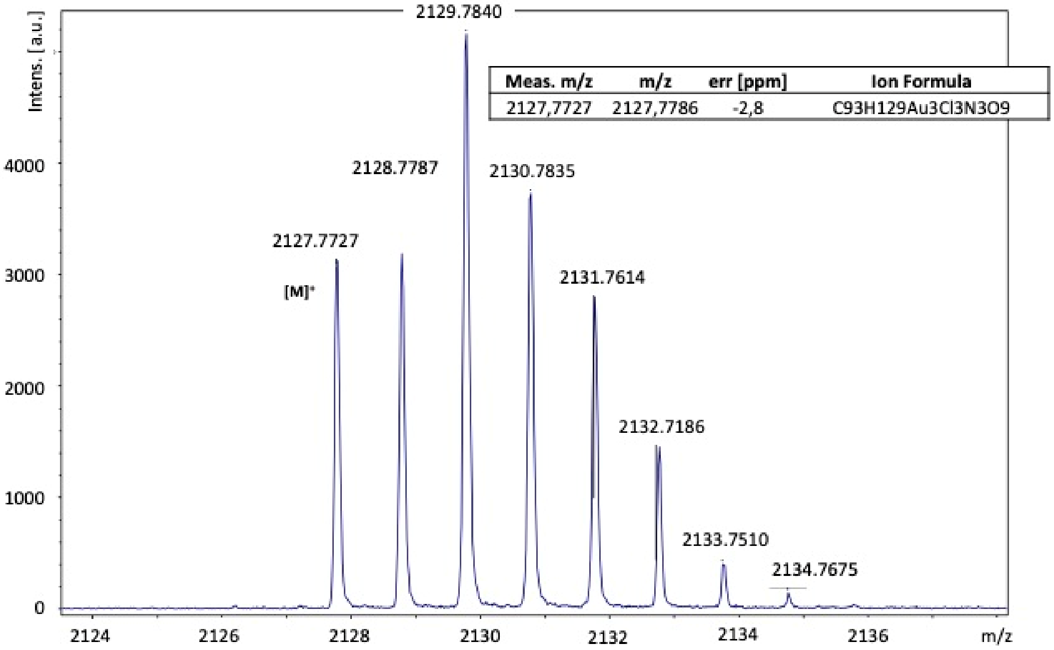
Meas. m/z	m/z	err [ppm]	Ion Formula
1862,9212	1862,9156	3,0	C92H138Au2Cl2N2O8

Figure S22: MALDI-TOF mass spectrum of [$(AuCl)_2((CN)_2$−TriPh)] **(9)**.



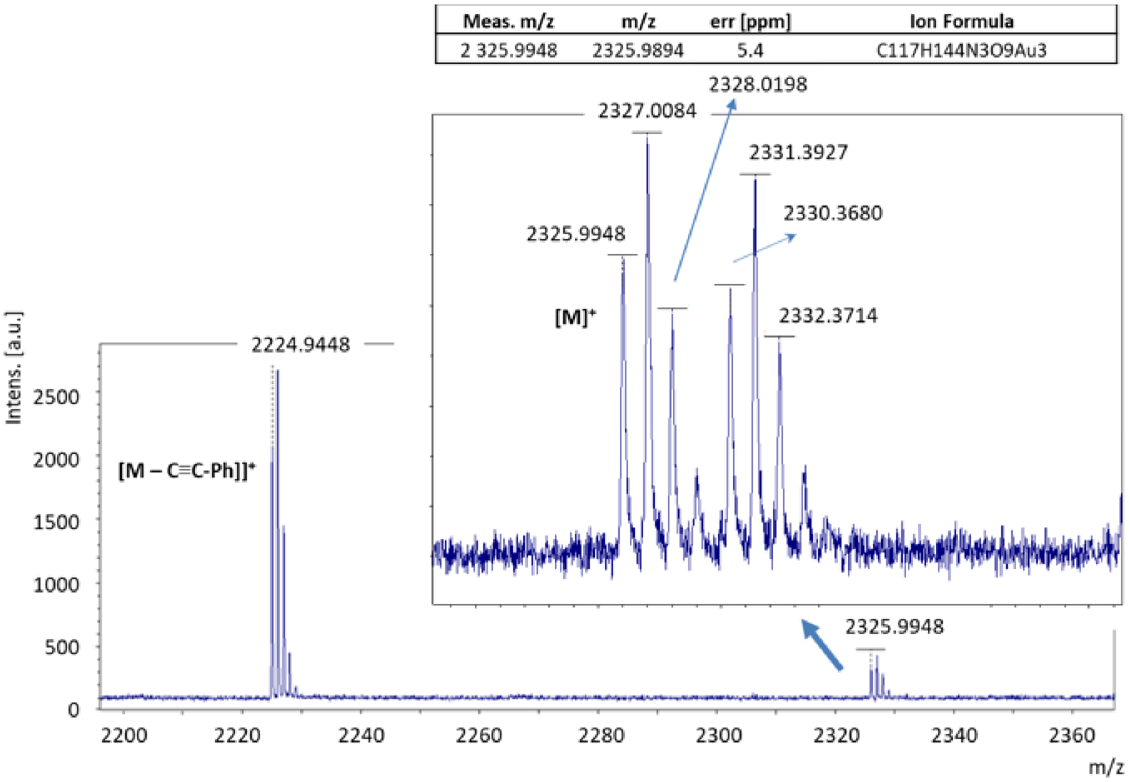
Meas. m/z	m/z	err [ppm]	Ion Formula
1894.0145	1894.0170	-2.5	C100H143N2O8Au2

Figure S23: The MALDI-TOF mass spectrum of [$(AuC{\equiv}C\text{-}Ph)_2((CN)_2$−TriPh)] **10.**



Meas. m/z	m/z	err [ppm]	Ion Formula
2127,7727	2127,7786	-2,8	C93H129Au3Cl3N3O9

Figure S24: MALDI-TOF mass spectrum of [(AuCl)$_3$((CN)$_3$-TriPh)] **(11).**



Meas. m/z	m/z	err [ppm]	Ion Formula
2 325.9948	2325.9894	5.4	C117H144N3O9Au3

Figure S25: MALDI-TOF mass spectrum of [(AuC≡C-Ph)$_3$((CN)$_3$−TriPh)] **(12).**

UV-Visible and luminescence data

Table S1. UV-Visible and luminescence data for the free isocyanides, and for the organometallic complexes, in dichloromethane solution at 298 K (10^{-5} M).

Compd.	λ (nm) ($\varepsilon/10^3$ (M^{-1} cm^{-1}))	λ_{ex} (nm)	λ_{em} (nm)	τ* (ns)	QY* (%)
$(CN)_2$-TriPh (**7**)	346 (1.9), 307 (18.2), 279 (78.6), 272 (56.6), 252 (45.8)	275	385	8.22	11.24
$(CN)_3$-TriPh **(8)**	345 (2.7), 307 (21.9), 279 (95.2), 271 (64.6), 251 (68.3)	275	385	8.23	10.65
$[(AuCl)_2(CN)_2$-TriPh] (**9**)	346 (3.4), 307 (24.7), 280 (143.4), 271 (117.4), 262 (90.3)	279	385	3.82	3.92
$[(AuCC$-$Ph)_2(CN)_2$-TriPh] **(10)**	346 (4.2), 302 (81.9), 280 (182.4), 272 (144.5)	321	385	4.10	4.38
$[(AuCl)_3(CN)_3$-TriPh] **(11)**	346 (5.9), 308 (36.3), 279 (187.3), 271 (161.7), 261 (124.5)	309	385	2.95	3.37
$[(AuCC$-$Ph)_3(CN)_3$-TriPh] **(12)**	345 (3.1), 302 (103.6), 280 (213.0), 272 (172.9)	322	385	3.19	2.72

* Lifetime τ (± 0.03). Absolute Quantum Yields φ using an integrating sphere (± 3%)

DSC scans: a) first heating, b) first cooling, c) second heating

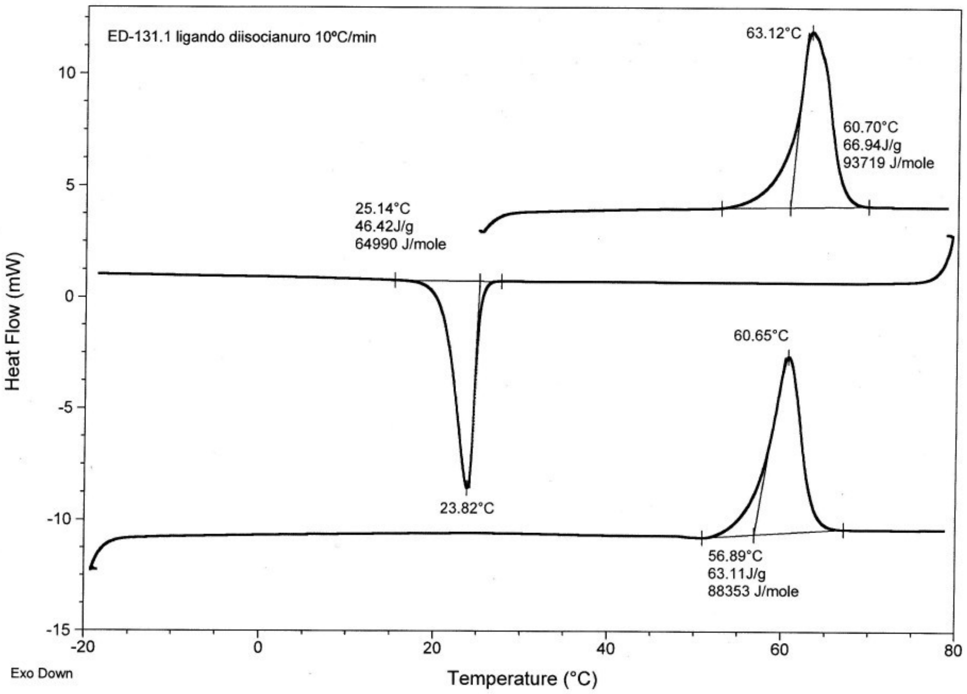


Figure S26: DSC scans of $(CN)_2$−TriPh **(7).**

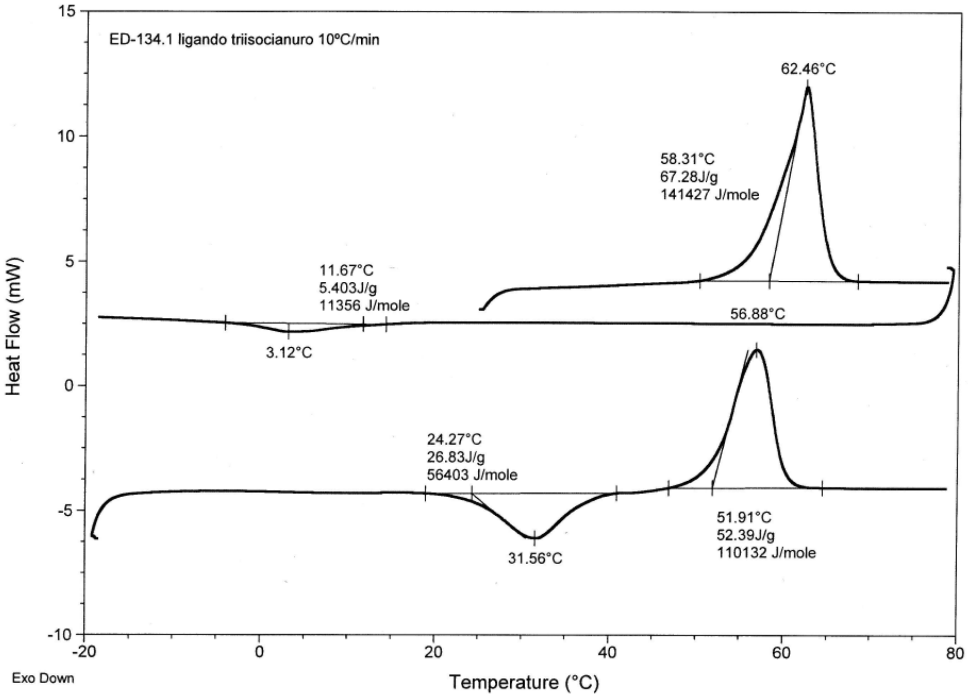


Figure S27: DSC scans of $(CN)_3$−TriPh (**8**).

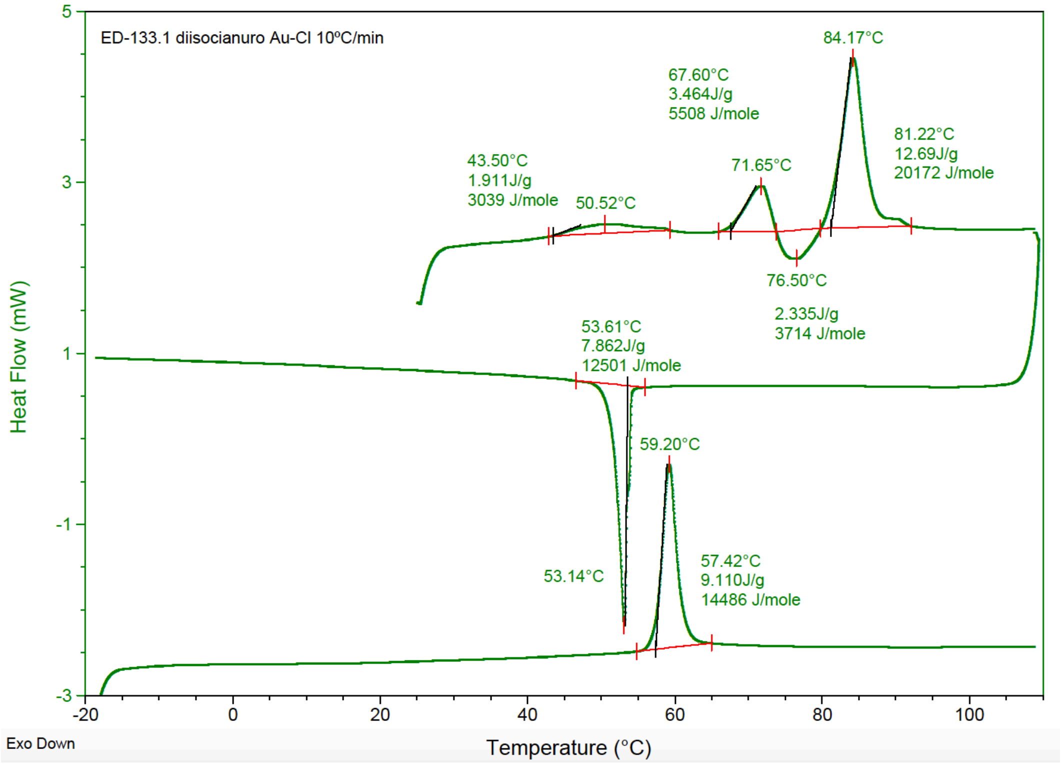


Figure S28: DSC scans of [$(AuCl)_2(CN)_2$-TriPh] **(9).**

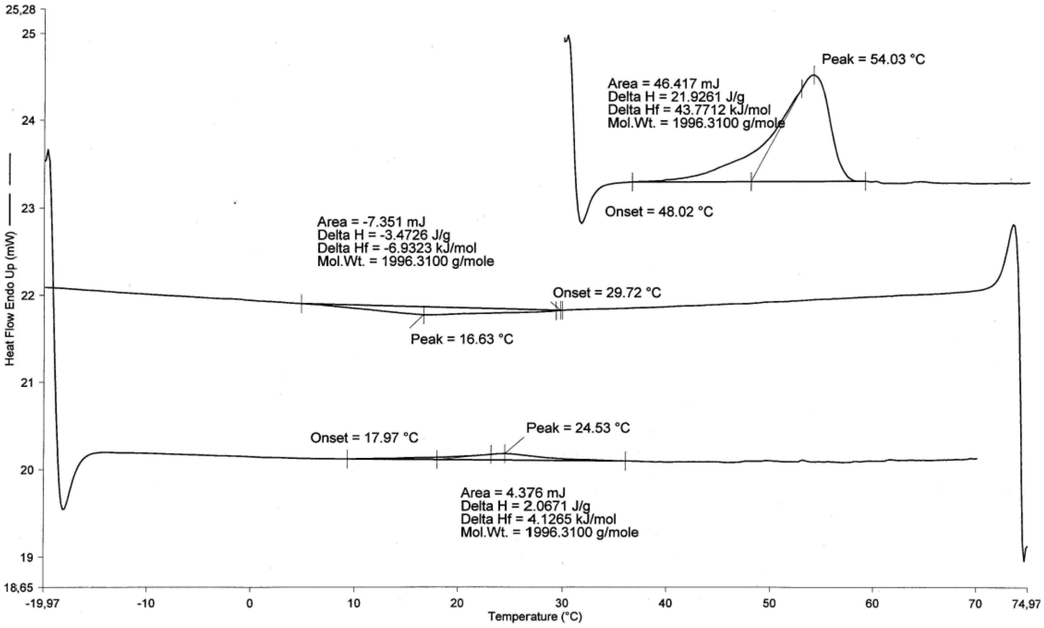


Figure S29: DSC scans of [$(AuCC-Ph)_2(CN)_2$-TriPh)] **(10).**

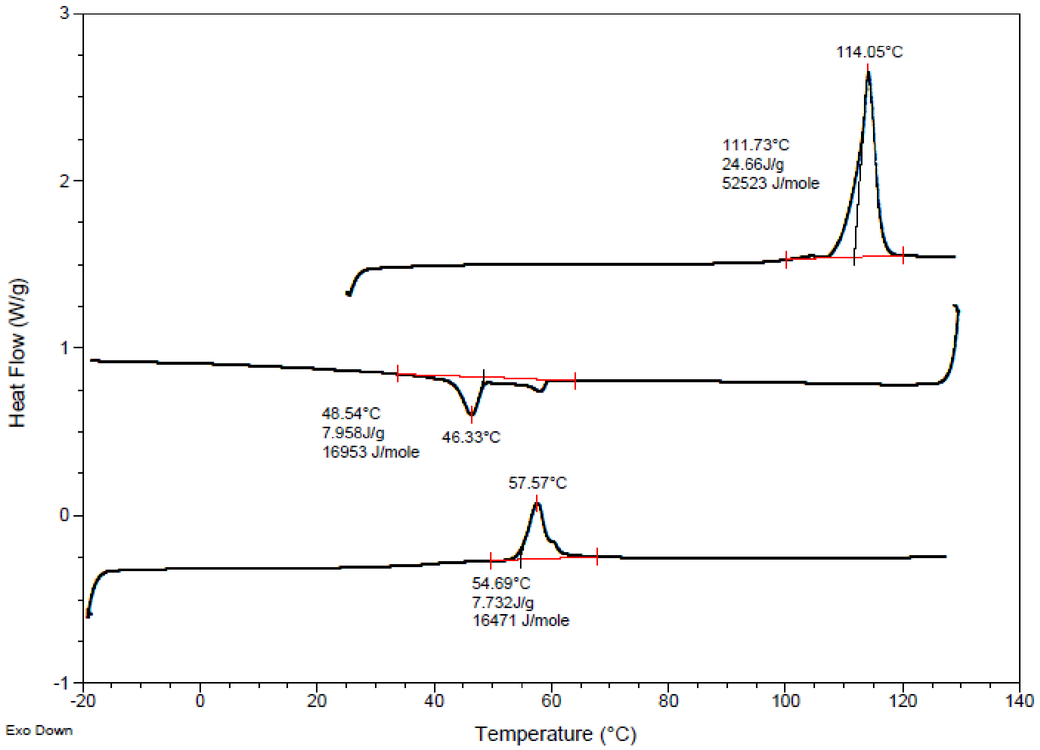


Figure S30: DSC scans of [$(AuCl)_3(CN)_3$-TriPh] **(11).**

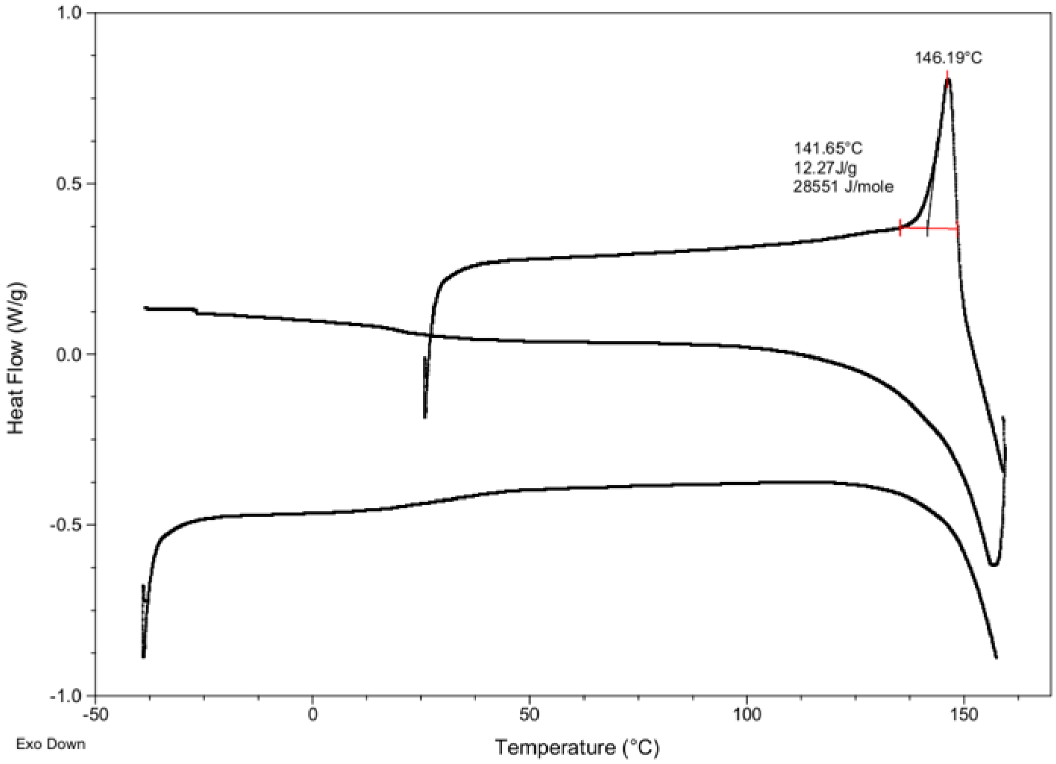
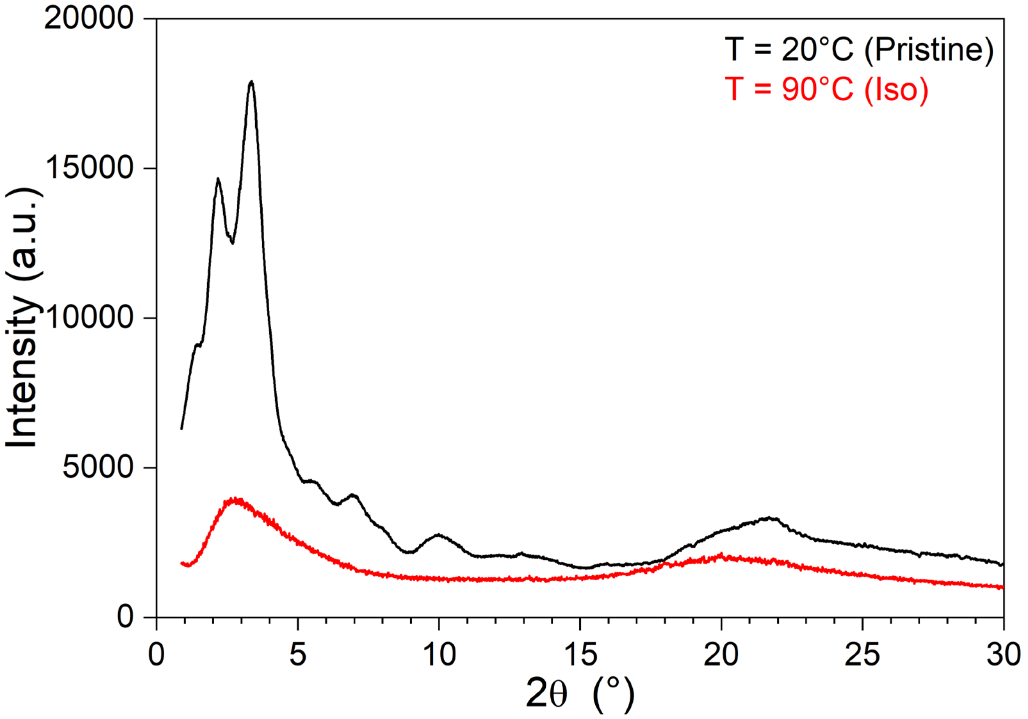
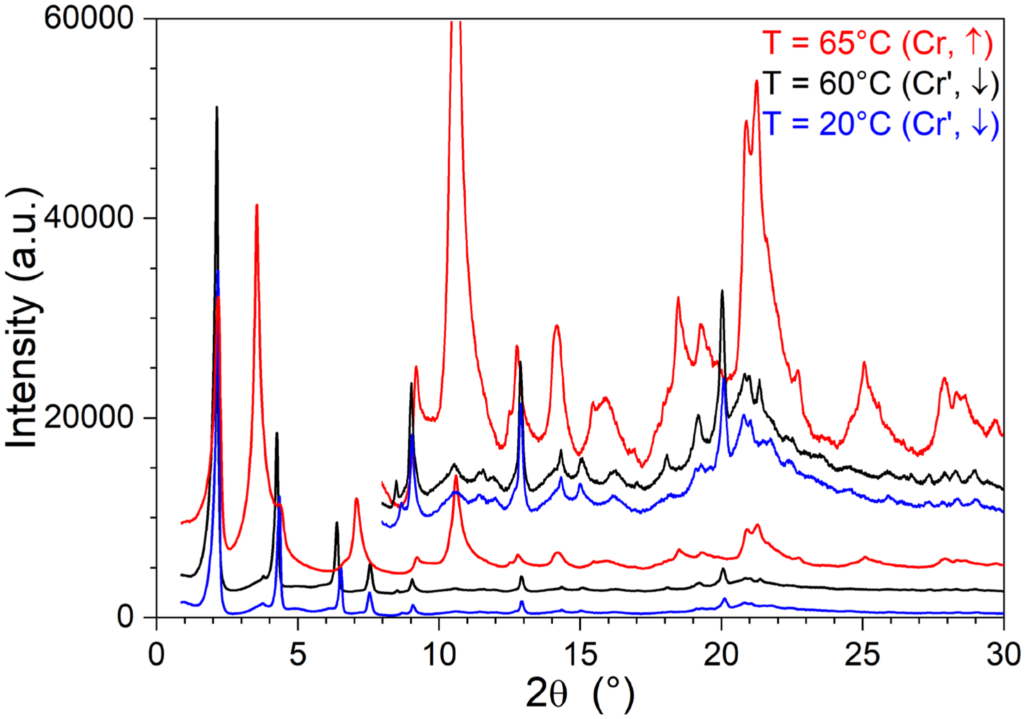


Figure S31: DSC scans of [$(AuCC\text{-}Ph)_3(CN)_3$-TriPh] **(12).**

S/WAX



T = 20°C (Pristine)
T = 90°C (Iso)
Intensity (a.u.)
2θ (°)
0
5000
10000
15000
20000
0
5
10
15
20
25
30



T = 65°C (Cr, ↑)
T = 60°C (Cr', ↓)
T = 20°C (Cr', ↓)
Intensity (a.u.)
2θ (°)
0
20000
40000
60000
0
5
10
15
20
25
30

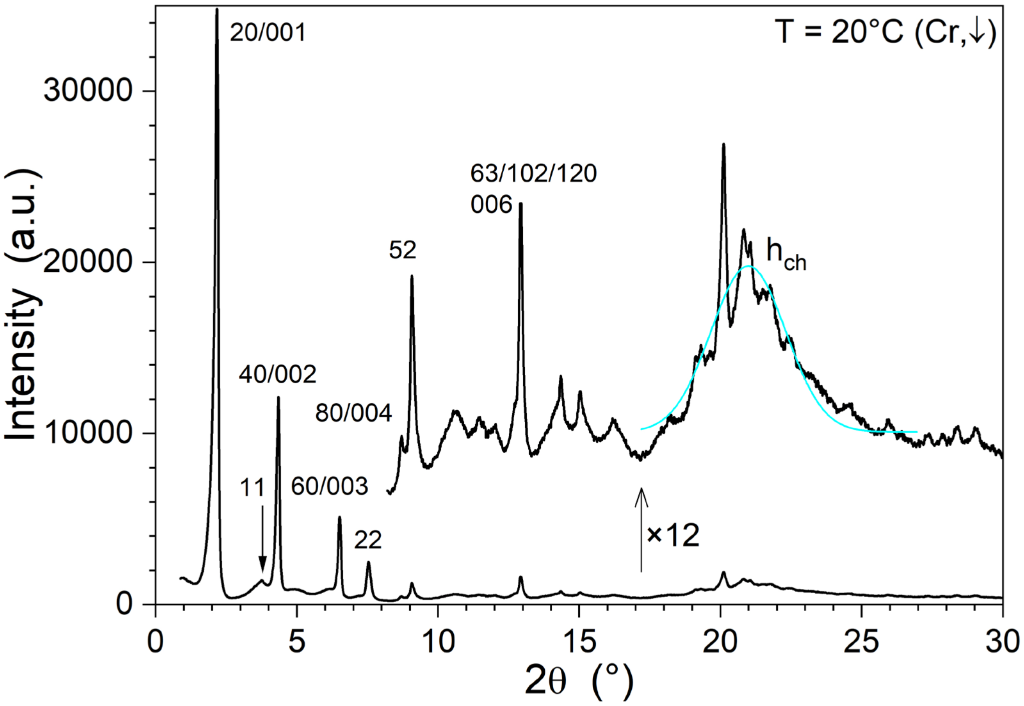


Figure S32: S/WAXS patterns of $[(AuCl)_2(CN)_2\text{-TriPh}]$ (**9**), recorded at different temperatures. Top: SWAXS patterns of pristine state and isotropic liquid; middle: SWAXs patterns recorded at 65°C on heating, and at 60 and 20°C on cooling from the isotropic liquid.; bottom: pre-indexation of the SWAXS pattern at 20°C on cooling.

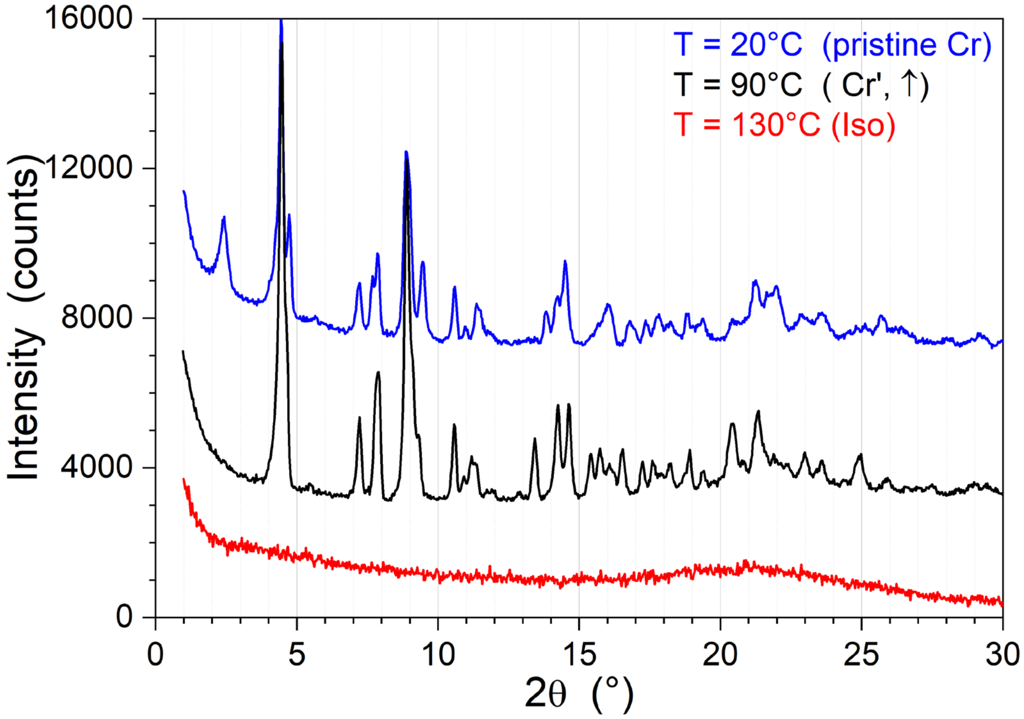


Figure S33: S/WAXS patterns of $[(AuCl)_3(CN)_3\text{-TriPh}]$ (**11**), recorded at different temperatures, from pristine state, at 90°C and in the isotropic liquid.

Table S2. Mesophases indexation[a] at T = 20°C (measured after cooling from the isotropic liquid).

Cpd	$2\theta_{meas.}$	$d_{meas.}$	I	*hk*	00*l*	$d_{calc.}$
(**9**)	2.174	40.61	VS (sh)	20	001	-
	3.762	23.47	M (sh)	11	x	-
	4.348	20.30	S (sh)	40	002	20.30
	6.523	13.54	W (sh)	60	003	13.54
	7.536	11.72	W (sh)	22	x	11.74
	8.648	10.22	VW (sh)	80	004	10.15
	9.137	9.67	M (sh)	52	x	9.78
	12.911	6.85	M (sh)	63/102/120	006	7.00/6.77
	20.10	4.41	-	-	-	-
	20.98	4.23	-	-	"h_{ch}"	-
(**11**)	2.368	37.28	VS (sh)	20	001	-
	4.736	18.64	S (sh)	40	002	18.64
	5.795	15.24	S (sh)	11	x	-
	7.152	12.35	W (sh)	60	003	12.42
	7.474	11.82	M (sh)	41	x	11.95
	9.526	9.28	M (sh)	80	004	9.32
	11.878	7.44	M (sh)	100/32	005/x	7.46/7.43
	21.58	4.11	VS (br)	-	h_{ch}	-

[a] $2\theta_{meas.}$: experimentally measured diffraction angle for each reflection (°); $d_{meas.}$ and $d_{calc.}$: experimentally measured and theoretically calculated d-spacing (Å); Intensity and shape of the reflection: VS, S, M, W, VW stand for very strong, strong, medium, weak, very weak; sh and br stand for sharp and broad peak, respectively; *hk* (columnar) and 00*l* (lamellar) Miller indexations; h_{ch}: average distance between molten chains.

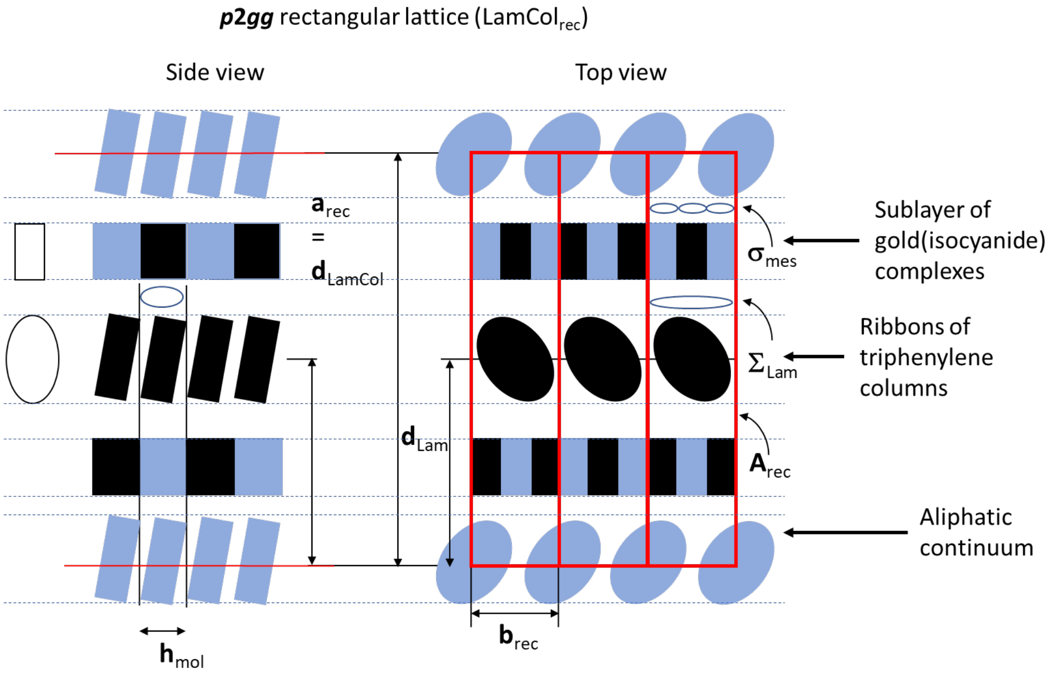


Figure S34: Side and top views of the Lam$_{Colrec}$ *p*2*gg* lattice of **11**.

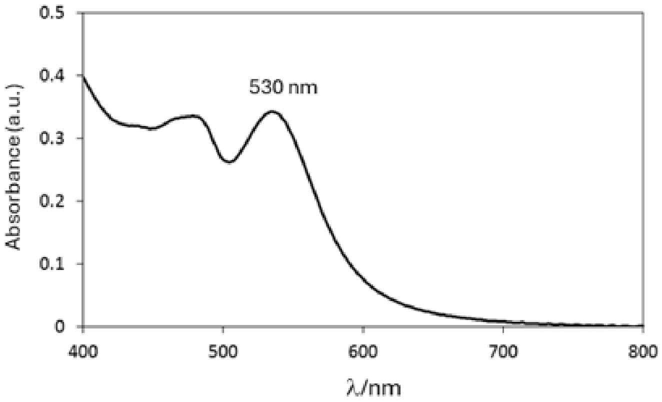


Figure S35: UV-Vis spectrum of gold nanoparticles obtained by thermal decomposition of [(Au(C≡C-Ph)$_3$((CN)$_3$-TriPh)] **(12)**.

Electrochemical parameters and mobility measurements

Table S3. Electrochemical parameters (HOMO and LUMO energy levels)

Compound	$E_{1/2}^{ox}$ (V)/eV[a]	E_{HOMO}/eV[b]	E_{LUMO}/eV[c]	Optical gap (E_g)/ eV[d]
$(CN)_2$-TriPh **(7)**	0.89	-5.22	-1.76	3.46
$(CN)_3$-TriPh **(8)**	0.92	-5.29	-1.84	3.45
$[(AuCl)_2(CN)_2$-TriPh] **(9)**	0.90	-5.24	-1.78	3.46
$[(AuCl)_3(CN)_3$-TriPh] **(11)**	0.90	-5.26	-1.83	3.43

[a] V vs. calomel electrode with a platinum work electrode in dichloromethane. [b] E_{HOMO} (eV) = -[$E_{1/2}$ox(V)- $E_{1/2}$ox fc (V)] - 4.8(eV) ($E_{1/2}$ox fc is the averaged oxidation potential of the system ferrocene/ferrocinium (Fc) versus the calomel electrode).[7] [c] LUMO potential were calculated from the optical gap observed in the absorption spectra and the HOMO potentials obtained with CV.[7] [d] Optical gap calculated from $E_g = 1242/\lambda_{onset}$ where λ_{onset} is the onset of the band of the absorption spectra that appears at highest wavelength.

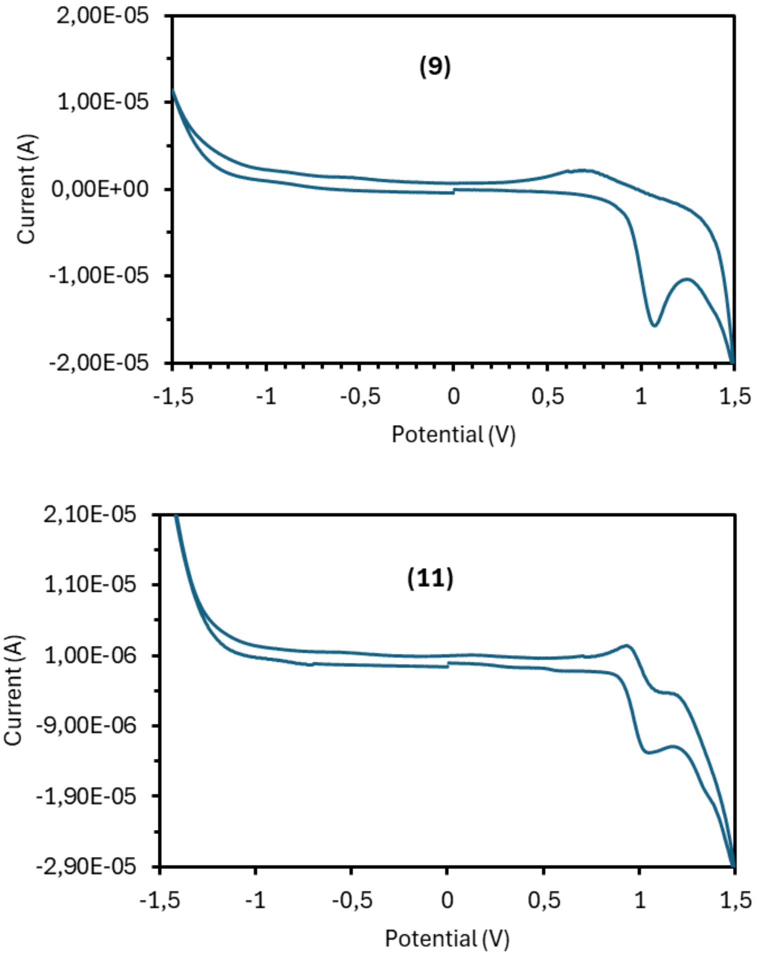


Figure S36. Cyclic voltammograms for **9** and **11**.

Mobility measurements

The charge carrier mobility measurements were carried out with the help of time-of-flight technique in which **9** and **11** compounds were filled in a 20 μm homeotropically anchored ITO-coated glass cells. Due to the π-π stacking of disc-like shape, both complexes preferably adopt homeotropic orientation, i.e. columnar axis remains perpendicular to substrate.[8- 14] The compounds **9** and **11** were irradiated via a Nd:YAG pulse laser with an excitation wavelength of 355 nm. A suitable bias voltage (150 – 220 V) was applied to observe the transient photocurrent curves for the electrons and holes. After estimating the transit time at different temperatures, the electron and hole mobilities were determined by using an equation: $\mu_{e,h}(T) = d^2/V.\tau$, where, d is the thickness of cell, V is the applied positive/negative bias voltage and τ is the transit time for charge carriers at a particular temperature. The required voltage to observe a good photocurrent signal in the compounds **9** and **11** has been estimated to be 180 – 220V and 150 – 200V, respectively which is in good agreement with their optical bandgaps. The compound **11** requires lower voltage as it has lower optical bandgap as compared to compound **9**.

Quantum Chemical Calculations

Quantum Chemical calculations were carried out using GFN2-xTB tight-binding method as implemented in the xTB package. The GFN2-xTB was designed to accurately describe molecular structure and non-covalent interactions for large systems like those reported herein with a reduced computational cost.[15] In addition, this method has demonstrated its effectiveness to study non-covalent interactions with various contexts, such as biochemical systems,[15,16] transition metal complexes[17] and supramolecular materials,[18,19] including liquid crystals.[20,21,22]

To find the preferred orientation between molecules, the evolution of the total energy of a dimer was calculated at 5º intervals between 0º and 180º when one molecule is rotated respect to another molecule (See Figure 29) with the inter-disc distance kept at the experimental value: 5.27 Å and 4.66 Å for the di(chloro-gold) and tri(chloro-gold) complexes, respectively.

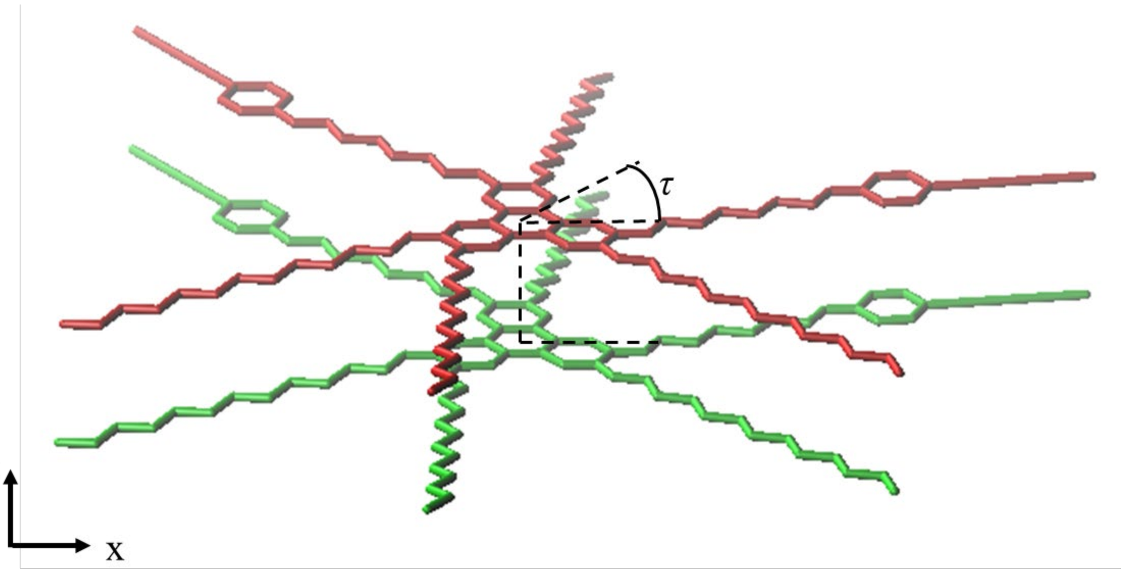


Figure S37: Representation of two stacked molecules of di(chloro-gold) complex **9** (molecules 1 and 2 are highlighted in different colours) showing the azimuthal angle and *z*-direction.

References

---

[1] T. García, L. Larios-López, R. J. Rodríguez-González, G. Martínez-Ponce, C. Solano and D. Navarro-Rodríguez, *Polymer*, 2012, **53**, 2049−-2061

[2] J. J. Conde and W. Mendelson, *Tetrahedron Lett.*, 2000, **41**, 811−814.

---

[3] E. Tritto, R. Chico, G. Sanz-Enguita, C. L. Folcia, J. Ortega, S. Coco and P. Espinet, *Inorg. Chem.,* 2014, **53**, 3449−3455.

[4] H.-M. Chen, K.-Q. Zhao, L. Wang, P. Hu and B.-Q. Wang, *Soft Mater.* 2011, **9**, 359–381,

[5] R. Usón, A. Laguna and J. Vicente, *J. Organomet. Chem.,* 1977, **131**, 471−475.

[6] P. Alejos, S. Coco and P. Espinet, *New J. Chem.*, 1995, **19**, 799−805.

[7] M. M. Ahmida and S. H. Eichhorn, *ECS Trans.,* 2010, **25**, 1−10.

[8] S. Dhingra, S. P. Gupta, A. Shah, D. P. Singh and S. K. Pal, *Chem. Comm.*, 2024, **60**, 2922−2925.

[9] M. Gupta, A. Krishna KM, S. Sony, S. Dhingra, A. Shah and D. P. Singh, *Chemm. Comm.*, 2023, **59**, 10652−10655.

[10] M. Vadivel, S. Singh, D. P. Singh, V.A. Raghunathan, and S. Kumar, *J. Phys. Chem. B*, 2021, **125**, 10364−10372.

[11] A. Shah, D. P. Singh, B. Duponchel, F. Krasisnski, A. Daoudi, S. Kumar and R. Douali, *J. Mol. Liq.*, 2021, **342**, 117353.

[12] A. Shah, B. Duponchel, A. Gowda, S. Kumar, C. Legrand, R. Douali, and D. P. Singh, *New J. Chem.*, 2020, **44**, 14872−14878.

[13] P. Mahesh, A. Shah, K. Swamynathan, D. P. Singh, R. Douali, and S. Kumar, *J. Mater. Chem. C*, 2020, **8**, 9252−-9261.

[14] I. Bala, W.-Y. Yang, S. P. Gupta, J. De, R. A. K. Yadav, D. P. Singh, D. K. Dubey, J.-H. Jou, R. Douali and S. K. Pal, *J. Mater. Chem. C*, 2019, **7**, 5724−5738.

[15] C. Bannwarth, S. Ehlert, S. Grimme, *J. Chem. Theory Comput.*, 2019, **15**, 1652−1671.

[16] A. S. Christensen, T. Kubař, Q. Cui and M. Elstner, *Chem. Rev.*, 2016, **116**, 5301−5337.

[17] M. Bursch, H. Neugebauer, S. Grimme, *Angew. Chem. Int. Ed.*, 2019, **58**, 11078−11087.

[18] E. E. Greciano, J. Calbo, J. Buendía, J. Cerdá, J. Aragó, E. Ortí and L. Sánchez, *J. Am. Chem. Soc.*, 2019, **141**, 7463−7472.

[19] M. A. Martínez, A. Doncel-Giménez, J. Cerdá, J. Calbo, R. Rodríguez, J. Aragó, J. Crassous, E. Ortí and L. Sánchez, *J. Am. Chem. Soc.*, 2021, **143**, 13281−13291.

[20] E. Castellanos, R. M. Gomila, R. Manha, G. Fernández, A. Frontera and B. Soberats, *J. Mater. Chem. C*, 2023, **11**, 10884−10892.

[21] L. Rubert, M. F. Islam, A. B. Greytak, R. Prakash, M. D. Smith, R. M. Gomila, A. Frontera, L. S. Shimizu and B. Soberats, *Angew. Chem. Int. Ed.*, 2023, **62**, e202312223.

[22] E. de Domingo, G. García, C. L. Folcia, J. Ortega, J. Etxebarria and S. Coco, *Cryst. Growth Des.*, 2023, **23**, 6812-−6821.