Electronic Supplementary Material (ESI) for Dalton Transactions.


# Balancing ionic and H-bonding interactions for the formation of Au(I) hydrometallogels.

**D. Blasco, J. M. López-de-Luzuriaga,* M. Monge, M. E. Olmos and M. Rodríguez-Castillo**

# Electronic Supplementary Information

## EXPERIMENTAL SECTION

**General procedures.** [AuCl($PMe_3$)][1] and [Au($^9$*N*-adeninate)($PMe_3$)][2] were prepared according to previously published methods. Adenine (6-aminopurine, Sigma-Aldrich) and Ag($OCOCF_3$) (Sigma-Aldrich) were used as received. HPLC grade tetrahydrofuran (THF) was dried and degasified with a MBRAUN MB-SPS800 system prior to use.

**Physical measurements.** $^1$H (δ($SiMe_4$) = 0.0 ppm), $^{19}$F (δ($CCl_3F$) = 0.0 ppm) and $^{31}$P{$^1$H} (δ(85% $H_3PO_4$) = 0.0 ppm) NMR spectra were recorded at 298 K with a Bruker ARX 300 spectrometer. UATR-IR spectrum was recorded in the range 4000-400 $cm^{-1}$ with a Perkin-Elmer Two spectrophotometer equipped with a diamond crystal-UATR accessory. ESI-MS spectra were obtained with a Bruker MicroTOF-Q spectrometer with ESI ionisation source. CHNS elemental analysis was carried out with a Perkin-Elmer 240C microanalyser. UV-Vis absorption measurements were registered with a Hewlett-Packard 8453 diode array spectrophotometer in quartz cells (optical path = 1 cm). Steady-state solid luminescence measurements were carried out in a Jobin-Yvon Horiba Fluorolog 3-22 Tau-3 spectrofluorimeter. Lifetime measurements were recorded with a Datastation HUB–B with a nanoLED controller and DAS6 software. The nanoLED employed for lifetime measurements was one of 320 nm. The lifetime data were fitted with the Jobin-Yvon software package. $^1$H PGSE-NMR measurements were carried out with the double stimulated echo pulsed sequence (Double STE)[3] in a Bruker AVANCE 400, equipped with a BBI H-BB Z-GRD probe at 298 K without spinning, at different concentrations in $D_2O$. This instrument was also employed for recording NMR spectra at 220 K in $d^8$-THF.

**Microscopy.** For a direct observation of liquid samples in its original state, specimens were vitrified in liquid ethane and analysed in a STEM microscope at low temperature. The vitrification method is a very fast sample cooling that prevents the formation of crystalline ice. Moreover, the thin layer of amorphous ice formed during the vitrification process protects the material from electron beam damage. The vitrification process was performed in a FEI Vitrobot: a 3 µl drop of an aqueous suspension of the material was placed on a TEM quantifoil carbon grid, the excess of water was blotted away at the Vitrobot with filter paper, and finally the grid was freeze-plunged in liquid ethane. Samples were then transferred under liquid nitrogen atmosphere to a Gatan TEM cryo-holder equipped with a liquid nitrogen reservoir. That way samples were handled and observed at T = 100 K. STEM images were obtained in a Tecnai F30 (FEI) operated at 300 KV and coupled with a High Angle Annular Dark Field (HAADF) detector.

**Crystallography.** A suitable single crystal was mounted in inert oil on a MiteGen MicroMount and transferred to the cold nitrogen stream of a Nonius Kappa CCD area-detector diffractometer, equipped with an Oxford Instruments low-temperature controller system (Mo Kα = 0.71073 Å, graphite monochromator). Data was collected in $\omega$ and $\varphi$ scan mode. Absorption effects were treated by semiempirical corrections based on multiple scans.[4] The structure was solved by direct methods and refined on $F_0^2$ with SHELXL-97.[5] All non-hydrogen atoms were treated anisotropically, and all hydrogen atoms were included as riding bodies.

**Rheology.** Rheological measurements were carried out in a HAAKE RheoStress 1 rheometer with a cone-plate system (Ti; diameter, 35 mm; cone angle, 1 °), at a constant temperature of 25.0 ± 0.1 °C controlled with a cyclic water bath.

**Computational details.** Theoretical calculations were performed with the Gaussian 09 package program.[6] Model systems [Au(9*N*-adenine)($PMe_3$)]$^+$ (**1a**) and [Au(7*N*-adenine)($PMe_3$)]$^+$ (**1b**) were built from the X-ray structure of **1**, and were completely optimized at the DFT/PBE1PBE level of theory[7] with the third dispersion correction by Grimme (DFT-D3).[8] Model systems (**1c-1g**) were built from the optimized structure of **1a** and that of $(CF_3CO_2)^-$, modelling each interaction by keeping collinear the interacting atoms and, if necessary, disposing the interacting units orthogonally (**1e**, **1f**). For model **1g'** we have only evaluated the π-stacking by suppressing the C-H···O bonds through the substitution of the methyl groups of the phosphine by H atoms and the $CF_3CO_2^-$ by formiate ones. The interaction energy at the RHF and MP2 levels of theory was obtained according to *eqn. 1* and, for models **1c-1g**, at different values of distance $R$, which describes the interaction direction. The counterpoise (cp) correction by Boys and Bernardi for the basis set superposition error (BSSE)[9] on $\Delta E$ was thereby performed.

$$\Delta E = E_{AB}^{(AB)} - E_{A}^{(AB)} - E_{B}^{(AB)} = V(R) \qquad \textit{eqn. 1}$$

Calculation points were fitted using the four-parameter ($A, B, C, n$) *eqn. 2*, which had been previously used to derive the Herschbach-Laurie relation.[10]

$$\Delta E = V(R) = A \cdot \exp(-BR) - CR^{-n} \qquad \textit{eqn. 2}$$

For the calculation of electrostatic potential surfaces, the electronic density of models **1c**, **1d** and **1g** at their respective equilibrium distance $R$ was calculated at the MP2 level of theory.

The following basis set combinations were employed: for gold, the quasi-relativistical (QR) 19-valence electrons (VE) pseudopotential (PP) from Andrae[11] and the corresponding basis sets augmented with two *f* polarisation functions were used.[12] Carbon, nitrogen, oxygen, fluorine and phosphorus were treated by Stuttgart pseudopotentials,[13] including only the VE for each atom. For these atoms, the double-ζ basis set were used,[14] augmented by *d*-type polarisation functions.[15] For hydrogen, a double-ζ plus a *p*-type polarisation function was used.[14]

**Synthesis and Characterization.**

*Synthesis of [Au(9N-adenine)($PMe_3$)]$CF_3CO_2$ (**1**)*. An argon protected solution of [AuCl($PMe_3$)] (0.2000 g, 0.65 mmol) in 30 mL of dry THF is cooled to 0 ºC in a refrigerating bath. Then, Ag($OCOCF_3$) (0.1434 g, 0.65 mmol) is added to the solution, which is kept under stirring and protected from direct light for 2 hours. After that time, the reaction flask is taken from the bath and opened to air, and the white solid of AgCl is carefully removed by filtration over Celite. Solid adenine (0.0878 g, 0.65 mmol) is added to the transparent filtrate. After 1 hour of stirring, unreacted adenine is filtered over Celite, and the filtrate is concentrated *in vacuo* to a volume of *ca.* 2 mL. Addition of 20 mL of diethyl ether leads to the precipitation of **1** (0.2700 g, 0.52 mmol) as a white solid, which is retrieved from the solution by filtering. Yield: 80%. $^1$H NMR (300 MHz, $CDCl_3$): 8.23 (1H, s, $^2$CH), 8.06 (1H, s, $^8$CH), 1.78-1.75 (9H, d, $^2J_{PH}$ = 11 Hz, $P(CH_3)_3$). $^{19}$F (282 MHz, $CDCl_3$): -75.71 (s, $CF_3CO_2$). $^{31}$P{$^1$H} NMR (121 MHz, $CDCl_3$): -12.21 (s, $P(CH_3)_3$). UATR-IR (cm$^{-1}$): 3307 ($NH_2$), 3076 ($NH_2$), 2980 ($NH_2$), 1661 (C=O). ESI-MS *m/z*: (+) 408.1 ($M^+$, calcd.: 408.1); (-) 113.0 ($CF_3CO_2^-$, calcd.: 113.0). Anal. Calcd. for $C_{10}H_{14}AuF_3N_5O_2P$: C, 23.04; H, 2.71; N, 13.44. Found: C, 23.64; H, 2.79; N, 13.57.

*Preparation of the hydrogel of **1***. *Method A*: A weighted sample of **1** (0.030 g, 0.058 mmol) is dissolved in 2 mL of MilliQ water, rendering a transparent solution. The solution is transferred to a 10 mL Schlenk vessel, where is subjected to vacuum for six hours. After that time, a translucent, semisolid material has formed in the bottom of the vessel. *Method B*: A weighted sample of **1** is dissolved in an appropriate volume of MilliQ water to a concentration of 40 mg $mL^{-1}$. The transparent solution is then kept undisturbed for at least 24 h, forming the hydrogel.

*Determination of* $T_{gel}$. The melting temperature $T_{gel}$ was determined by test tube inversion method, by increasing the temperature of an oil bath by 2 $^{o}$C intervals and keeping the tube undisturbed for 30 min before checking. $T_{gel}$ was considered that for which the gel starts to flow.

## REFERENCES


1. K. Angermainer, E. Zeller and H. Schmidbaur, *J. Organomet. Chem.*, 1994, **472**, 371-376.
2. D. Blasco, J. M. López-de-Luzuriaga, M. Monge, M. E. Olmos, D. Pascual and M. Rodríguez-Castillo, *Inorg. Chem.*, 2018, **57**, 3805-3817.
3. A. A. Khrapitchev and P. T. Callaghan, *J. Magn. Reson.*, 2001, **152**, 259-268.
4. R. H. Blessing, *Acta Cryst.*, 1995, **A51**, 33-38.
5. G. M. Sheldrick, *SHELXL97, Program for Crystal Structure Refinement*; University of Göttingen: Germany, 1997.
6. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson et al, Gaussian 09, 2009.
7. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.
8. S. Grimme, *Wiley Interdiscip. Rev. Comput. Mol. Sci.*, 2011, **1**, 211-228.
9. S. F. Boys and F. Bernardi, *Mol. Phys.*, 1970, **19**, 553-566.
10. D. R. Herschbach and V. W. Laurie, *J. Chem. Phys.*, 1961, **35**, 458-464.
11. D. Andrae, U. Häussermann, M. Dolg, H. Stoll and H. T. Preuss, *Theor. Chim. Acta*, 1990, **77**, 123-141.
12. P. Pyykko, N. Runeberg and F. Mendizabal, *Chem. Eur. J.*, 1997, **3**, 1451-1457.
13. A. Bergner, M. Dolg, W. Küchle, H. Stoll and H. Preuss, *Mol. Phys.*, 1993, **80**, 1431-1441.
14. S. Huzinaga, *Gaussian Basis Sets for Molecular Orbital Calculations*, Elsevier: Amsterdam, 1984, p. 16.
15. S. Huzinaga, *J. Chem. Phys.*, 1965, **42**, 1293-1302.

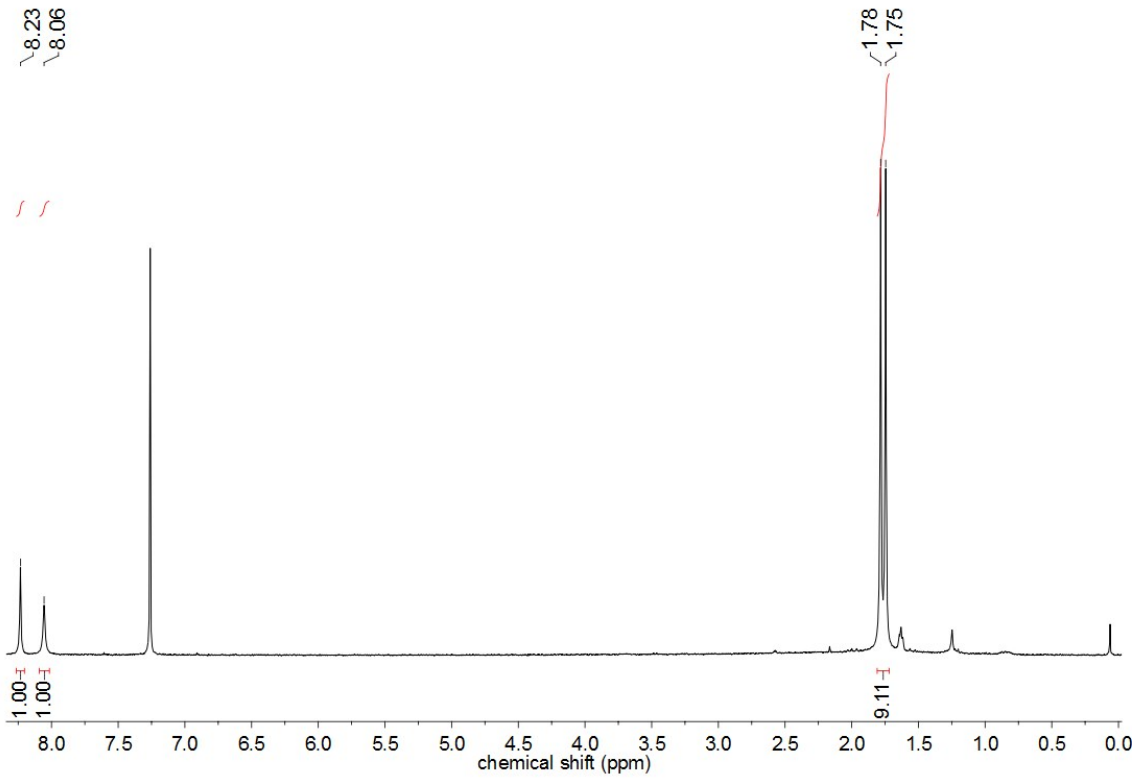


**Figure S1**: $^{1}$H NMR (300 MHz, $CDCl_3$) spectrum of [Au($^{9}$*N*-adenine)($PMe_3$)]$CF_3CO_2$ (**1**).

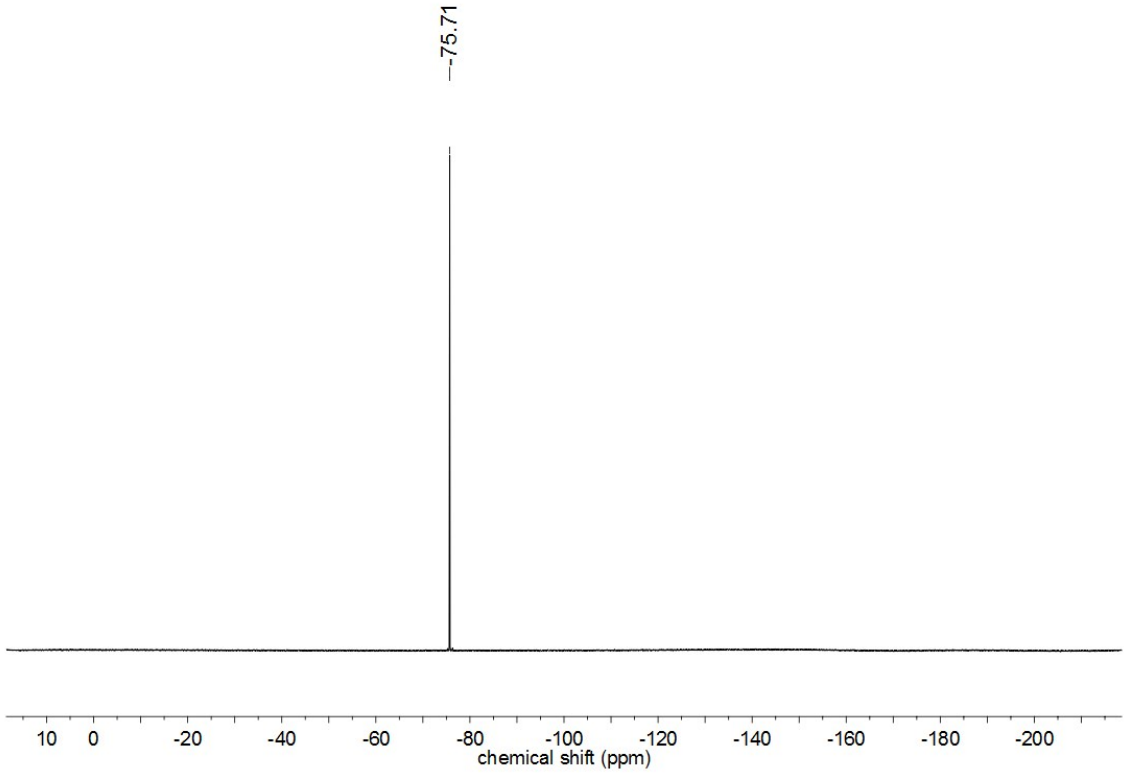


**Figure S2**: $^{19}$F NMR (282 MHz, $CDCl_3$) spectrum of [Au($^{9}$*N*-adenine)($PMe_3$)]$CF_3CO_2$ (**1**).

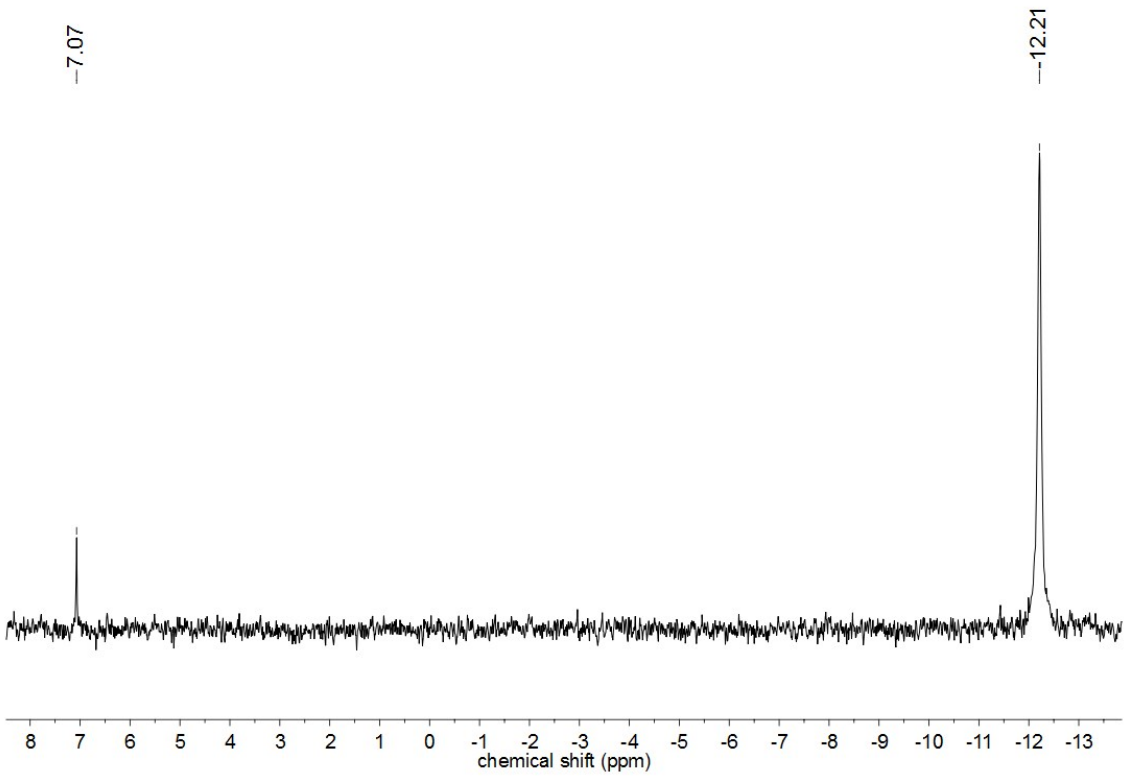


**Figure S3**: $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) spectrum of [Au(9*N*-adenine)($PMe_3$)]$CF_3CO_2$ (**1**).

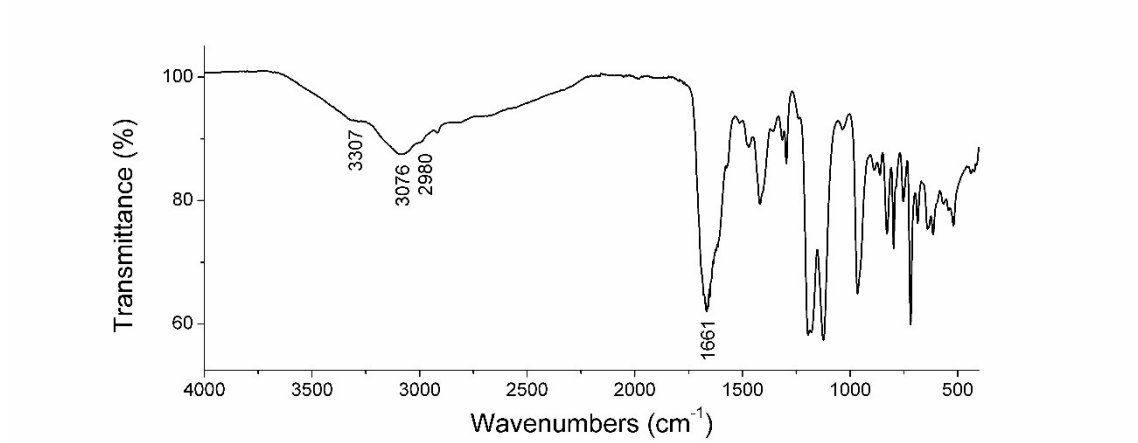


**Figure S4**: UATR-IR spectrum of [Au(9*N*-adenine)($PMe_3$)]$CF_3CO_2$ (**1**).

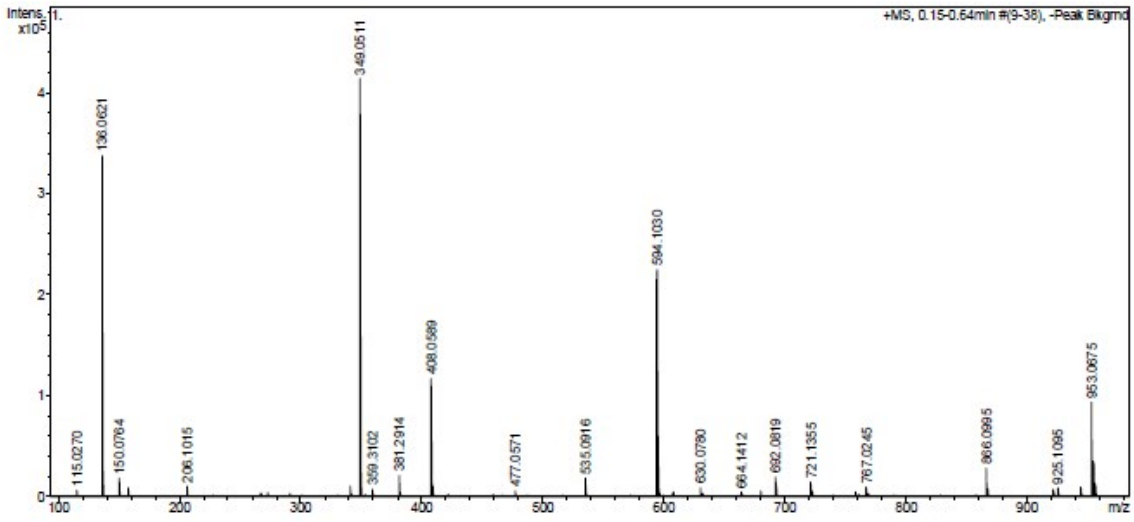


**Figure S5**: ESI-(+) MS spectrum of [Au($^9$*N*-adenine)($PMe_3$)]$CF_3CO_2$ (**1**).

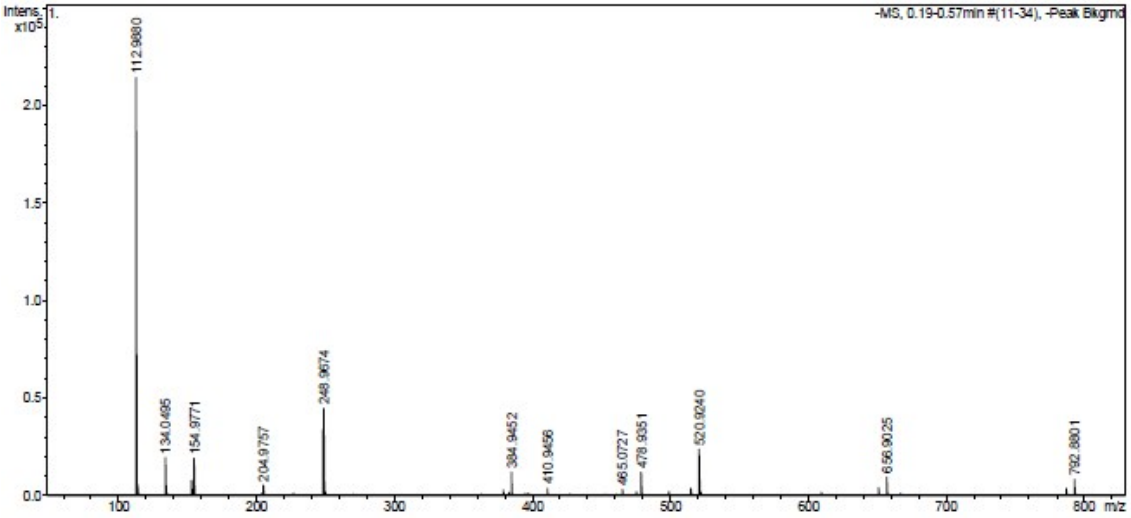


**Figure S6**: ESI-(-) MS spectrum of [Au($^9$*N*-adenine)($PMe_3$)]$CF_3CO_2$ (**1**).

**Table S1**: Data collection and structure refinement details for **1**.

| Parameter | Value(s) (for **1**) |
|---|---|
| Empirical formula | $C_{10}H_{14}AuF_3N_5O_2P$ |
| Formula mass | 521.20 |
| Crystal habit | Colorless prism |
| Temperature | 173(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Triclinic |
| Space group | *P* -1 |
| Unit cell dimensions | *a* = 7.1858(5) Å α = 103.280(3)º<br>*b* = 7.6550(7) Å β = 101.295(6)º<br>*c* = 15.5113(14) Å γ = 93.609(6)º |
| Volume | 809.11(12) Å$^3$ |
| *Z* | 2 |
| Density (calculated) | 2.139 Mg m$^{-3}$ |
| Absorption coefficient | 9.233 mm$^{-1}$ |
| *F*(000) | 492 |
| Crystal size | 0.225 x 0.06 x 0.05 mm$^3$ |
| $\theta$ range ($2\theta_{max}$/º) | 2.725 – 27.445 |
| Index ranges | -9 <= *h* <= 9<br>-9 <= *k* <= 9<br>-20 <= *l* <= 20 |
| Total reflections | 9758 |
| Independent reflections | 3528 [$R_{int}$ = 0.0.0470] |
| Completeness to $\theta$ = 25.242º | 96.5 % |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / Restrains / Parameters | 3528 / 62 / 199 |
| Goodness-of-fit on $F^2$ | 1.105 |
| Final *R* indexes [$I > 2\sigma(I)$] | R1 = 0.0510, wR2 = 0.1317 |
| *R* indexes (all data) | R1 = 0.0578, wR2 = 0.1371 |
| Largest diff. peak and hole (e/Å$^3$) | 2.212, -2.274 |

**Table S2:** Selected bond lengths (Å) and angles (º) for **1**.

| | |
|---|---|
| Au-N(1) | 2.068(7) |
| Au-P | 2.238(2) |
| N(1)-Au-P | 176.7(2) |

**Table S3:** Hydrogen bond lengths (Å) and angles (º) for **1**.

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| C(7)#1-H(7)#1...Au | 0.93 | 2.82 | 3.720(9) | 162.5 |
| C(1)-H(1A)...O(1)#2 | 0.96 | 2.59 | 3.427(18) | 146.0 |
| C(4)-H(4)...N(4)#1 | 0.93 | 2.30 | 3.224(11) | 170.7 |
| N(2)-H(2)...O(2)#3 | 0.86 | 1.88 | 2.711(11) | 160.7 |
| N(5)-H(5A)...O(1)#4 | 0.86 | 2.12 | 2.961(11) | 166.4 |
| N(5)-H(5B)...O(2)#3 | 0.86 | 2.32 | 3.142(12) | 159.1 |

Symmetry transformations used to generate equivalent atoms:

#1 x,y+1,z  #2 x+1,y+1,z  #3 -x+1,-y+1,-z+2  #4 -x+1,-y,-z+2

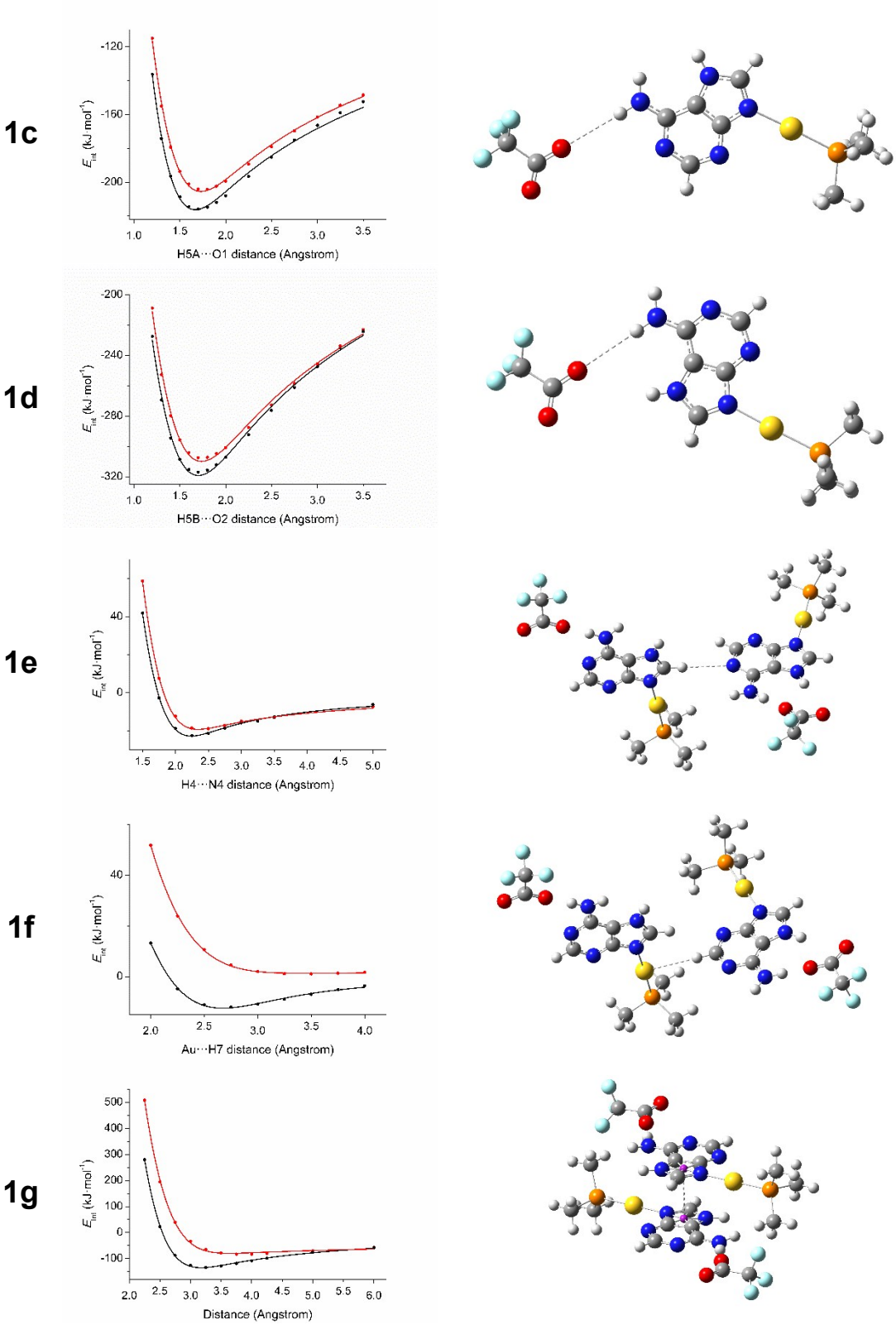


**Figure S7:** Interaction energy profiles of models **1c-1g'** for different values of interaction distance (see each graphic caption and associated figure), at RHF (red) and MP2 (black) levels of theory. Variable distance $R$ is depicted as a dashed bond.

**1g'**

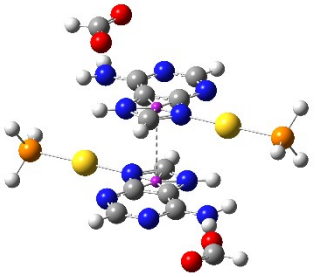

**Figure S7 (cont.):** Interaction energy profiles of models **1c-1g'** for different values of interaction distance (see each graphic caption and associated figure), at RHF (red) and MP2 (black) levels of theory. Variable distance $R$ is depicted as a dashed bond.

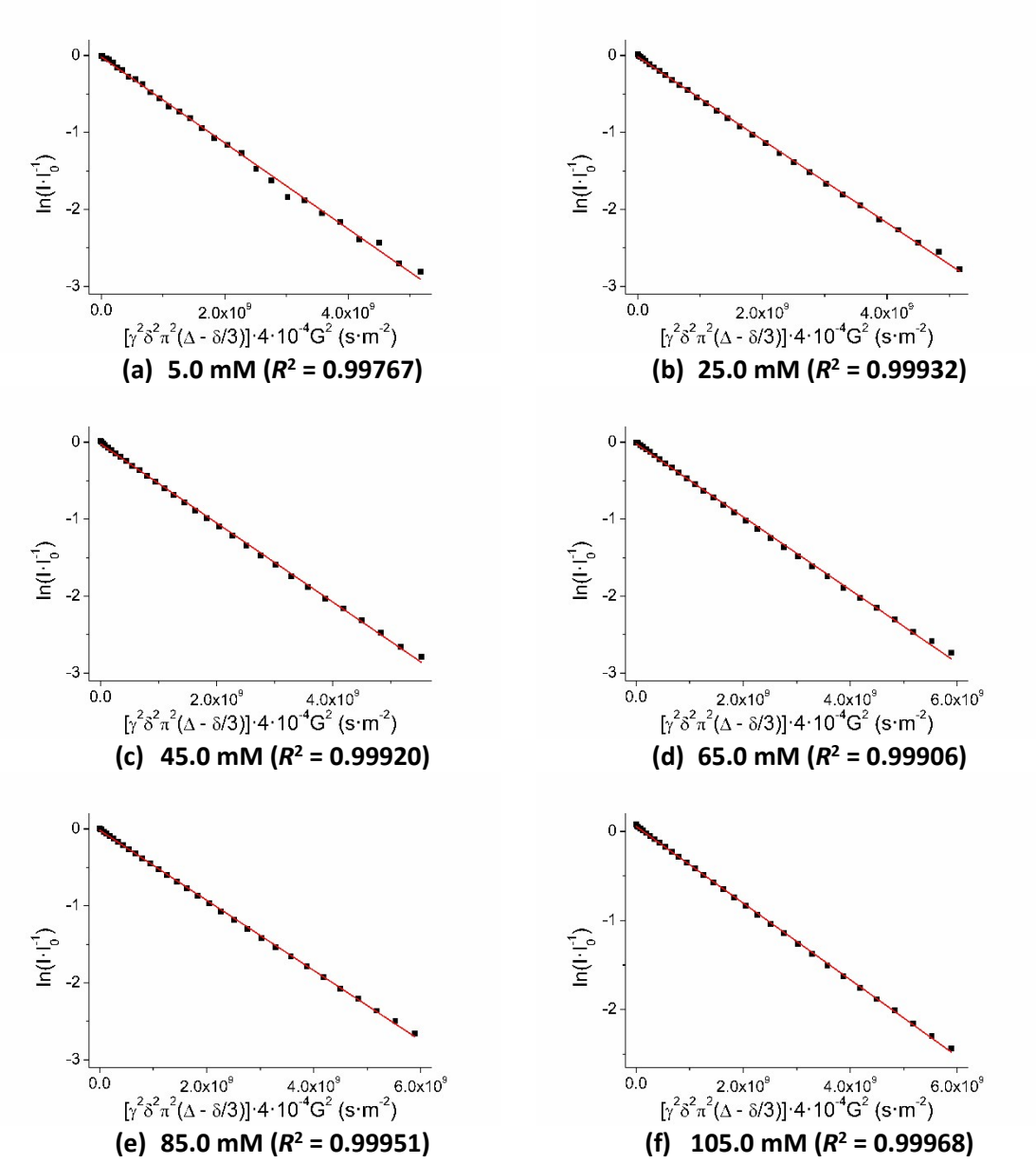


**Figure S8:** Plots of $\ln(I \cdot I_0^{-1})$ ($^1H$ $^2CH$ signal) versus arbitrary units proportional to the square of the gradient amplitude $G^2$, in $D_2O$ at different concentrations of **1**.


**Figure S9**: Photographs of solutions of **1** at different concentrations to illustrate its real aspect. In the second photograph the tubes had been inverted to identify the gel formation. Below 40 mg $mL^{-1}$, transparent solutions are obtained; at 40 mg $mL^{-1}$, a translucent gel is formed; at higher concentrations (45 and 50 mg $mL^{-1}$), turbidity starts to appear.

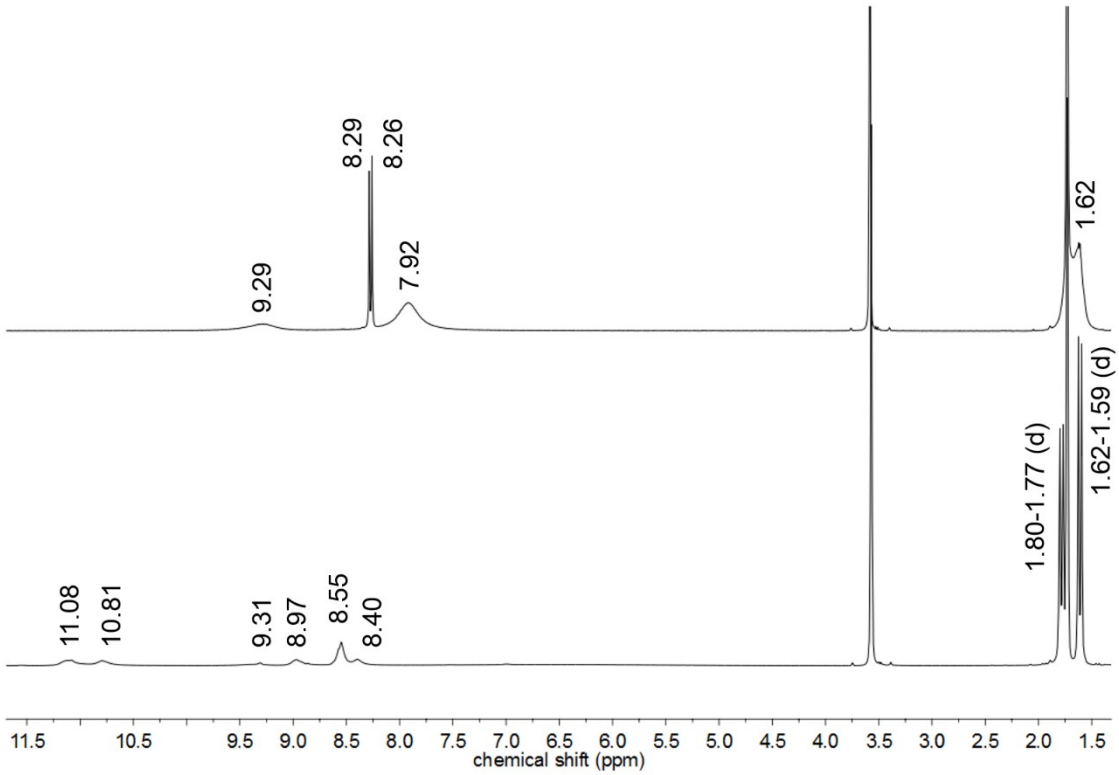


**Figure S10:** $^{1}$H NMR (400 MHz, $d^{8}$-THF) spectra of the equimolecular mixture of [Au($^{9}N$-adeninate)($PMe_3$)] and $CF_3CO_2H$ at (top) 298 K and (bottom) 220 K.

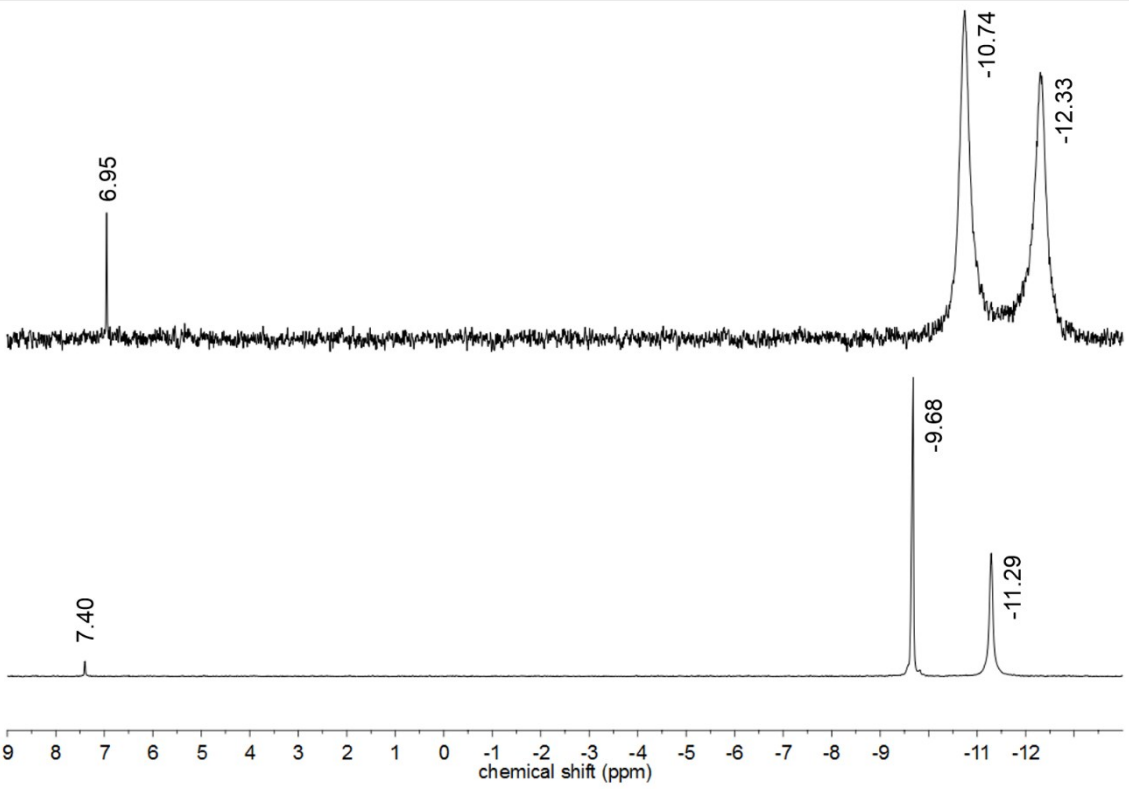


**Figure S11:** $^{31}P\{^{1}H\}$ NMR (162 MHz, $d^{8}$-THF) spectra of the equimolecular mixture of [Au($^{9}N$-adeninate)($PMe_3$)] and $CF_3CO_2H$ at (top) 298 K and (bottom) 220 K.

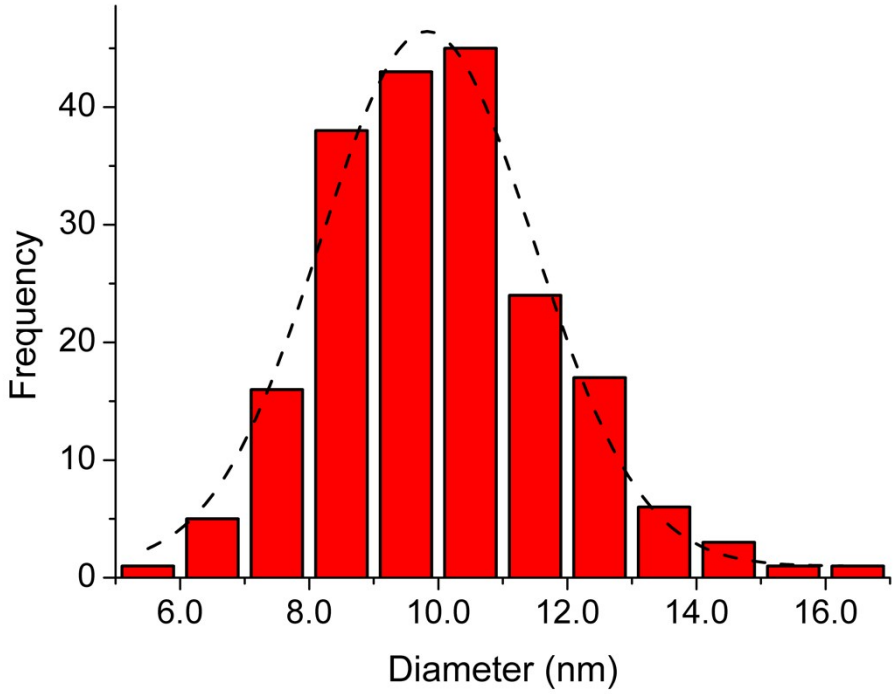


**Figure S12:** Frequency histogram for the [Au($^9$*N*-adenine)($PMe_3$)]($CF_3CO_2$) nanowires diameter. (9.82 $\pm$ 1.65 nm, $R^2$ = 0.97)

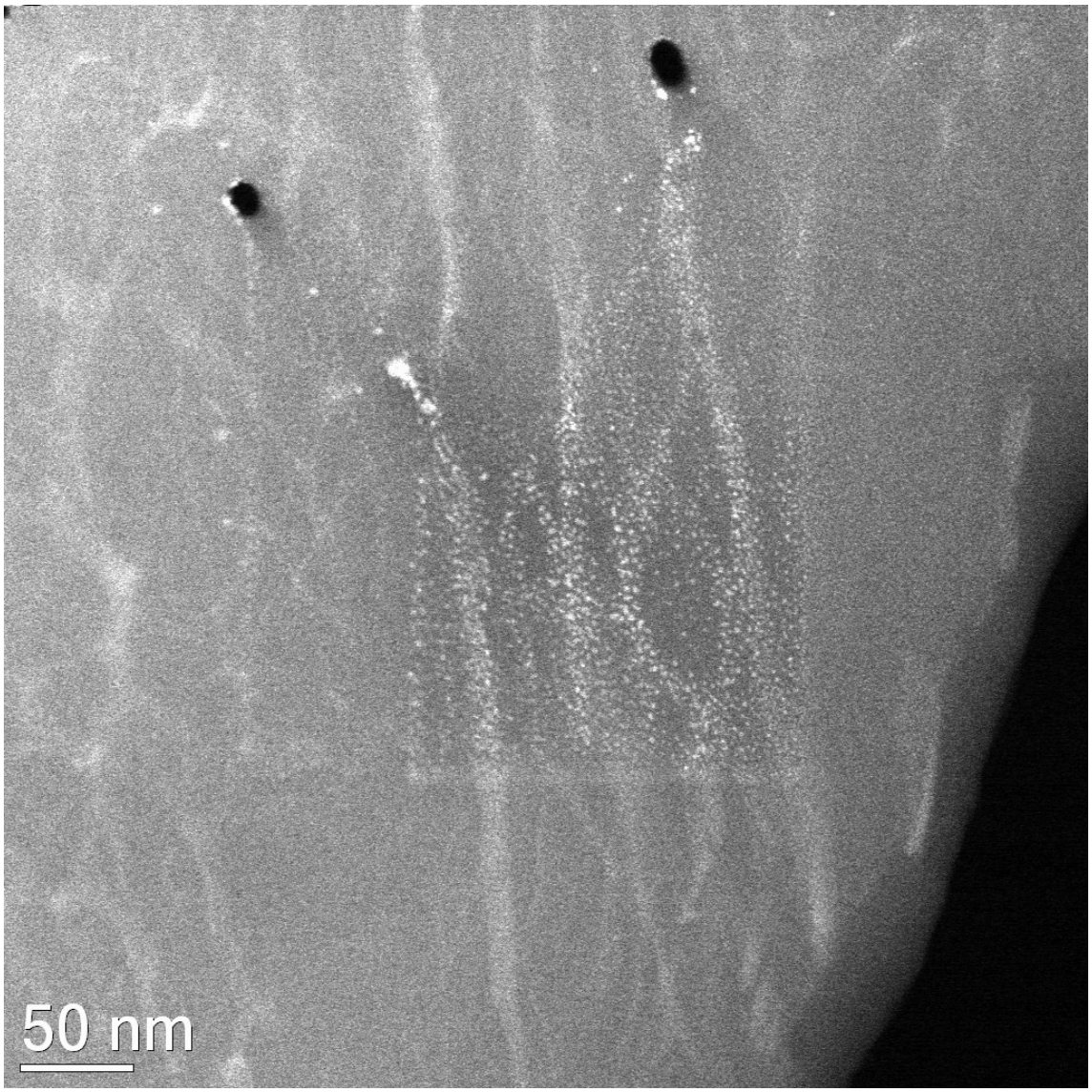


**Figure S13:** Cryo-STEM micrograph of a neat hydrogel sample demonstrating the reductive ability of the electron scanning beam. $Au^0$ nanoparticles (seen as white dots in the centre of the image) form by the *in situ* reduction of [Au($^9$*N*-adenine)($PMe_3$)]($CF_3CO_2$), and remain deposited along the former nanofibre.

**Table S4:** Cartesian coordinates of the optimized structure of **1a** (PBE/DFT-D3).

| | | | |
|---|---|---|---|
| Au | 0.90320800 | -0.28256300 | 0.00243000 |
| P | 3.10323700 | 0.32332100 | -0.00139800 |
| C | 4.07647000 | -0.44129600 | -1.35102700 |
| C | 3.98848200 | -0.10743000 | 1.54279200 |
| C | 3.32415000 | 2.12992300 | -0.20110900 |
| N | -1.11701200 | -0.77996200 | 0.00216500 |
| N | -3.06389500 | -1.80521400 | -0.00654900 |
| N | -1.90780100 | 1.49510700 | 0.00229600 |
| N | -4.28815400 | 1.68317900 | -0.00364300 |
| N | -5.75286500 | -0.07796500 | -0.01879500 |
| C | -1.73087700 | -1.94722200 | -0.00556400 |
| C | -3.34176100 | -0.45167000 | -0.00087700 |
| C | -2.10389600 | 0.18468600 | 0.00322100 |
| C | -4.48961700 | 0.36791500 | 0.00046800 |
| C | -3.04921300 | 2.16921600 | -0.00490800 |
| H | 4.04489000 | -1.53409900 | -1.24840200 |
| H | 3.63697400 | -0.16092300 | -2.31754000 |
| H | 5.11900700 | -0.09545900 | -1.30387000 |
| H | 3.95739000 | -1.19521100 | 1.68937600 |
| H | 5.03360400 | 0.22831400 | 1.48075500 |
| H | 3.49289800 | 0.38120000 | 2.39222300 |
| H | 2.80932100 | 2.64975300 | 0.61780100 |
| H | 2.88061300 | 2.44568400 | -1.15476100 |
| H | 4.39437100 | 2.38106300 | -0.18679600 |
| H | -3.72044700 | -2.57554400 | -0.02830700 |
| H | -5.99242800 | -1.04464100 | 0.13386700 |
| H | -6.48573900 | 0.61710200 | 0.04924700 |
| H | -1.23570000 | -2.91535900 | -0.01150300 |
| H | -2.97103900 | 3.26004100 | -0.00936600 |

**Table S5:** Cartesian coordinates of the optimized structure of **1b** (PBE/DFT-D3).

| | | | |
|---|---|---|---|
| N | 4.75731900 | -0.29034700 | -0.09056800 |
| N | 3.77935000 | 1.89069400 | -0.03436800 |
| N | 1.52487300 | 2.31680000 | 0.07687700 |
| C | 1.74633400 | -2.04274000 | 0.03796500 |
| C | 2.35268200 | 0.03206100 | 0.02485300 |
| C | 3.51474600 | -0.73095600 | -0.02991800 |
| C | 2.53278600 | 1.43059500 | 0.03314100 |
| C | 4.79901700 | 1.03711400 | -0.09588100 |
| H | 0.60251800 | 2.02435100 | 0.36920600 |
| H | 1.78320300 | 3.28902700 | 0.19362900 |
| H | 1.14999200 | -2.95139400 | 0.05475600 |
| H | 5.79297900 | 1.48995600 | -0.15176900 |
| N | 3.08805400 | -2.03874800 | -0.01521000 |
| H | 3.69328100 | -2.85256400 | -0.04343700 |
| N | 1.25969100 | -0.81592700 | 0.06280600 |
| Au | -0.74775500 | -0.29542700 | 0.02789300 |
| P | -2.96369900 | 0.27597100 | -0.04021400 |
| C | -3.55153400 | 1.11661700 | 1.47608300 |
| H | -2.98185000 | 2.04335000 | 1.62578600 |
| H | -4.62062400 | 1.35402000 | 1.37901800 |
| H | -3.39602800 | 0.45820500 | 2.34107400 |
| C | -3.36956600 | 1.40457700 | -1.42318600 |
| H | -4.44417400 | 1.63651000 | -1.41234700 |
| H | -2.79159600 | 2.33269000 | -1.32091300 |
| H | -3.10451000 | 0.92327800 | -2.37400300 |
| C | -4.05754400 | -1.17670200 | -0.25209600 |
| H | -3.91344700 | -1.86708900 | 0.58962900 |
| H | -5.10666100 | -0.84981400 | -0.28615800 |
| H | -3.80147000 | -1.69204800 | -1.18736500 |

**Table S6:** Cartesian coordinates of the optimized structure of $CF_3CO_2^-$ (PBE/DFT-D3).

| | | | |
|---|---|---|---|
| C | -0.51472000 | 0.00000700 | -0.01004500 |
| F | -1.06431900 | -1.06751300 | -0.60402000 |
| F | -0.98481900 | -0.00022100 | 1.25441800 |
| F | -1.06433300 | 1.06772900 | -0.60363700 |
| C | 1.05131700 | 0.00000500 | -0.02613200 |
| O | 1.55011800 | 1.14081000 | -0.01273700 |
| O | 1.55008900 | -1.14081300 | -0.01273600 |

**Table S7:** Cartesian coordinates of the optimized structure of [Au($^9$*N*-adenine)($PH_3$)]$^+$, employed in the building of model **1g'** (PBE/DFT-D3).

| | | | |
|---|---|---|---|
| Au | -1.45534700 | -0.12482300 | 0.00015900 |
| N | 0.51492000 | -0.73919000 | -0.00018700 |
| N | 2.40502900 | -1.85957500 | -0.00156500 |
| N | 1.41084200 | 1.49307900 | -0.00016900 |
| N | 3.79634900 | 1.56820000 | -0.00077500 |
| N | 5.17712800 | -0.25669100 | -0.00380000 |
| C | 1.06864200 | -1.93819300 | -0.00182700 |
| C | 2.75121800 | -0.52083400 | -0.00009400 |
| C | 1.54791100 | 0.17663200 | 0.00036200 |
| C | 3.93761700 | 0.24440500 | 0.00071200 |
| C | 2.58347600 | 2.11356800 | -0.00176200 |
| H | 3.02237900 | -2.66244200 | -0.00685000 |
| H | 5.37685500 | -1.24292200 | 0.03761600 |
| H | 5.94603800 | 0.40130200 | 0.01500200 |
| H | 0.52566300 | -2.88040600 | -0.00348500 |
| H | 2.55668100 | 3.20676900 | -0.00321300 |
| P | -3.61783800 | 0.58522400 | 0.00050800 |
| H | -4.42055600 | 0.19180100 | -1.10806700 |
| H | -4.42501600 | 0.17743000 | 1.10061800 |
| H | -3.80514400 | 1.99692700 | 0.00931800 |

**Table S8:** Cartesian coordinates of the optimized structure of $HCO_2^-$, employed in the building of model **1g'** (PBE/DFT-D3).

| | | | |
|---|---|---|---|
| O | -1.13833900 | -0.21054700 | 0.00000000 |
| O | 1.13833800 | -0.21055400 | 0.00000000 |
| C | 0.00000000 | 0.31859800 | 0.00000000 |
| H | 0.00000300 | 1.45722000 | 0.00000000 |

**Table S9:** Cartesian coordinates of model **1c** ($R$ = 3.00000 Å).

| | | | |
|---|---|---|---|
| Au | 1.08307687 | -0.45378288 | -0.15993816 |
| P | 3.28235784 | 0.15213971 | -0.21702338 |
| C | 4.22568167 | -0.62273390 | -1.58195235 |
| C | 4.20160670 | -0.26676023 | 1.31046877 |
| C | 3.49842725 | 1.95717089 | -0.43536776 |
| N | -0.93655204 | -0.95124793 | -0.11174823 |
| N | -2.88293890 | -1.97661230 | -0.06959243 |
| N | -1.72761779 | 1.32372484 | -0.11152283 |
| N | -4.10755960 | 1.51165339 | -0.06628311 |
| N | -5.57188161 | -0.24961194 | -0.03559799 |
| C | -1.55019529 | -2.11855678 | -0.09698697 |
| C | -3.16089297 | -0.62307529 | -0.06812318 |
| C | -1.92337208 | 0.01334158 | -0.09625018 |
| C | -4.30860915 | 0.19645141 | -0.04766968 |
| C | -2.86905026 | 1.99771469 | -0.09864678 |
| H | 4.19660479 | -1.71472171 | -1.47030680 |
| H | 3.76487232 | -0.34977437 | -2.54062903 |
| H | 5.26893438 | -0.27650599 | -1.56049470 |
| H | 4.17398827 | -1.35339015 | 1.46601214 |
| H | 5.24503240 | 0.06854038 | 1.22278227 |
| H | 3.72481685 | 0.22832941 | 2.16688776 |
| H | 3.00171603 | 2.48322557 | 0.39072555 |
| H | 3.03385480 | 2.26561554 | -1.38136805 |
| H | 4.56865094 | 2.20845458 | -0.44663342 |
| H | -3.53965130 | -2.74711164 | -0.07094592 |
| H | -5.81144461 | -1.21628794 | 0.11706401 |
| H | -6.30475561 | 0.44545506 | 0.03244401 |
| H | -1.05506932 | -3.08669164 | -0.10647155 |
| H | -2.79122061 | 3.08847678 | -0.11316696 |
| C | -10.82032892 | 2.75040333 | 0.34144771 |
| F | -10.93554120 | 1.60069614 | -0.33631614 |
| F | -11.20697554 | 2.47329651 | 1.60381692 |
| F | -11.76160462 | 3.56166261 | -0.15886680 |
| C | -9.37796800 | 3.36012867 | 0.31776936 |
| O | -9.35922484 | 4.60066606 | 0.42328515 |
| O | -8.47655628 | 2.50521835 | 0.23407987 |

**Table S10:** Cartesian coordinates of model **1d** ($R$ = 3.00000 Å).

| | | | |
|---|---|---|---|
| Au | 1.35387349 | -1.18091965 | -0.33803548 |
| P | 3.62359379 | -0.95878673 | -0.41718345 |
| C | 4.42155493 | -1.99283256 | -1.70066593 |
| C | 4.46151421 | -1.39553409 | 1.15153227 |
| C | 4.13940447 | 0.75968930 | -0.78225510 |
| N | -0.72054553 | -1.32734688 | -0.27447866 |
| N | -2.81141691 | -2.00509004 | -0.17204767 |
| N | -1.11835828 | 1.03978395 | -0.47378461 |
| N | -3.43288453 | 1.62668593 | -0.47484411 |
| N | -5.17212654 | 0.14440077 | -0.31640167 |
| C | -1.52147198 | -2.36997872 | -0.17045192 |
| C | -2.85813260 | -0.62887568 | -0.28682898 |
| C | -1.53135480 | -0.21331442 | -0.35198292 |
| C | -3.85190576 | 0.37002223 | -0.34938019 |
| C | -2.13038613 | 1.89403381 | -0.53168966 |
| H | 4.20967287 | -3.05119735 | -1.49888002 |
| H | 4.01182737 | -1.72829362 | -2.68456410 |
| H | 5.50816119 | -1.82561369 | -1.69474182 |
| H | 4.25202904 | -2.44518302 | 1.39663263 |
| H | 5.54630828 | -1.24827004 | 1.04961204 |
| H | 4.07579139 | -0.75725689 | 1.95758185 |
| H | 3.73920184 | 1.42916434 | -0.00925656 |
| H | 3.73194316 | 1.06078222 | -1.75652434 |
| H | 5.23661113 | 0.82637454 | -0.80068820 |
| H | -3.58818949 | -2.65209016 | -0.11766524 |
| H | -5.57040746 | -0.75217501 | -0.08687434 |
| H | -5.77778372 | 0.95559201 | -0.31585685 |
| H | -1.19596157 | -3.40465877 | -0.09296026 |
| H | -1.87051794 | 2.95121149 | -0.63596867 |
| C | -8.81429594 | -4.54599348 | 0.85270057 |
| F | -9.37559921 | -3.37132711 | 1.16823486 |
| F | -9.27264875 | -4.85359472 | -0.37821535 |
| F | -9.36314417 | -5.44391851 | 1.68152650 |
| C | -7.24850199 | -4.52975716 | 0.88020324 |
| O | -6.74294679 | -5.63632334 | 1.14542601 |
| O | -6.75629583 | -3.42174495 | 0.59654726 |

**Table S11:** Cartesian coordinates of model **1e** ($R$ = 3.00000 Å).

| | | | |
|---|---|---|---|
| Au | 0.91798382 | 0.32594641 | 0.00418249 |
| P | 3.11801082 | 0.93182541 | 0.00036649 |
| C | 4.09123882 | 0.16723141 | -1.34927951 |
| C | 4.00325082 | 0.50102841 | 1.54454649 |
| C | 3.33895282 | 2.73842941 | -0.19929751 |
| N | -1.10223618 | -0.17145859 | 0.00392649 |
| N | -3.04911918 | -1.19670959 | -0.00478251 |
| N | -1.89302418 | 2.10360941 | 0.00405249 |
| N | -4.29469222 | 2.34998469 | -0.00183144 |
| N | -5.73797416 | 0.53072138 | -0.02644955 |
| C | -1.71610218 | -1.33871859 | -0.00379951 |
| C | -3.32698618 | 0.15683341 | 0.00088449 |
| C | -2.08912018 | 0.79318841 | 0.00498049 |
| C | -4.47484118 | 0.97642141 | 0.00223049 |
| C | -3.03443518 | 2.77772041 | -0.00315151 |
| H | 4.05966482 | -0.92557359 | -1.24666651 |
| H | 3.65173682 | 0.44761141 | -2.31578751 |
| H | 5.13377482 | 0.51307241 | -1.30212551 |
| H | 3.97214082 | -0.58675559 | 1.69110849 |
| H | 5.04837882 | 0.83675641 | 1.48251549 |
| H | 3.50767582 | 0.98964741 | 2.39398849 |
| H | 2.82413782 | 3.25824741 | 0.61962849 |
| H | 2.89541982 | 3.05422641 | -1.15293951 |
| H | 4.40917982 | 2.98954441 | -0.18498051 |
| H | -3.70567218 | -1.96703959 | -0.02653251 |
| H | -5.97828738 | -0.43699525 | 0.11822648 |
| H | -6.47118516 | 1.22531343 | 0.04278127 |
| H | -1.22092418 | -2.30685559 | -0.00973351 |
| H | -2.95626018 | 3.86854541 | -0.00761251 |
| Au | -6.52535415 | 6.11292291 | -3.10465700 |
| P | -6.31462164 | 5.70405684 | -5.33975053 |
| C | -6.90816603 | 4.04721785 | -5.84562668 |
| C | -4.59091527 | 5.81161183 | -5.94884499 |
| C | -7.26457390 | 6.89557611 | -6.35482275 |
| N | -6.74910393 | 6.53151118 | -1.07896687 |
| N | -6.72195739 | 6.51340926 | 1.12114774 |
| N | -7.96778975 | 8.58289499 | -1.40746250 |
| N | -8.59088024 | 9.66484133 | 0.62788352 |
| N | -8.12445708 | 8.89043000 | 2.73263302 |
| C | -6.35823280 | 5.87828148 | -0.00198136 |
| C | -7.39916464 | 7.66055960 | 0.75405473 |
| C | -7.41055623 | 7.65947462 | -0.63775911 |
| C | -8.02988547 | 8.74146810 | 1.40453569 |
| C | -8.53779031 | 9.54572419 | -0.69657861 |
| H | -6.32636629 | 3.27685795 | -5.32236403 |
| H | -7.96636237 | 3.94280363 | -5.57134431 |
| H | -6.79308082 | 3.92329724 | -6.93195532 |
| H | -3.97349865 | 5.06729919 | -5.42873184 |
| H | -4.56455986 | 5.62330406 | -7.03175738 |
| H | -4.19460700 | 6.81380163 | -5.73801288 |
| H | -6.91311082 | 7.91366732 | -6.14069889 |
| H | -8.32882417 | 6.82637749 | -6.09316411 |
| H | -7.12816436 | 6.67158386 | -7.42246945 |
| H | -6.53450642 | 6.17325018 | 2.05607936 |
| H | -7.60385960 | 8.32418960 | 3.38340728 |

| | | | |
|---|---|---|---|
| H | -8.54804647 | 9.74606418 | 3.06925091 |
| H | -5.80924508 | 4.93958014 | -0.01301519 |
| H | -9.02382261 | 10.34615596 | -1.26147860 |
| C | -8.20579175 | -3.47293339 | 0.74344028 |
| F | -8.62413673 | -4.68240681 | 0.34768046 |
| F | -8.53775746 | -3.37766025 | 2.04750377 |
| F | -8.98596995 | -2.59233354 | 0.10287641 |
| C | -6.67231275 | -3.23176403 | 0.53605133 |
| O | -6.37532712 | -2.03583345 | 0.35725675 |
| O | -5.98868982 | -4.26914333 | 0.61925309 |
| C | -9.56430896 | 12.44324572 | 5.57161397 |
| F | -9.47570699 | 11.31560334 | 6.28927452 |
| F | -8.42260234 | 13.12122244 | 5.80975965 |
| F | -10.54075104 | 13.16048043 | 6.14309574 |
| C | -9.76557568 | 12.20542608 | 4.03679666 |
| O | -10.38298880 | 13.12416995 | 3.46659611 |
| O | -9.24457351 | 11.15302184 | 3.62276680 |

**Table S12:** Cartesian coordinates of model **1f** ($R$ = 3.00000 Å).

| | | | |
|---|---|---|---|
| Au | 1.07672438 | -2.23657233 | -0.21990364 |
| P | 3.34644468 | -2.01443941 | -0.29905161 |
| C | 4.14440582 | -3.04848524 | -1.58253409 |
| C | 4.18436510 | -2.45118677 | 1.26966411 |
| C | 3.86225536 | -0.29596338 | -0.66412326 |
| N | -0.99769464 | -2.38299956 | -0.15634682 |
| N | -3.08856602 | -3.06074272 | -0.05391583 |
| N | -1.39550739 | -0.01586873 | -0.35565277 |
| N | -3.71003364 | 0.57103325 | -0.35671227 |
| N | -5.44927565 | -0.91125191 | -0.19826983 |
| C | -1.79862109 | -3.42563140 | -0.05232008 |
| C | -3.13528171 | -1.68452836 | -0.16869714 |
| C | -1.80850391 | -1.26896710 | -0.23385108 |
| C | -4.12905487 | -0.68563045 | -0.23124835 |
| C | -2.40753524 | 0.83838113 | -0.41355782 |
| H | 3.93252376 | -4.10685003 | -1.38074818 |
| H | 3.73467826 | -2.78394630 | -2.56643226 |
| H | 5.23101208 | -2.88126637 | -1.57660998 |
| H | 3.97487993 | -3.50083570 | 1.51476447 |
| H | 5.26915917 | -2.30392272 | 1.16774388 |
| H | 3.79864228 | -1.81290957 | 2.07571369 |
| H | 3.46205273 | 0.37351166 | 0.10887528 |
| H | 3.45479405 | 0.00512954 | -1.63839250 |
| H | 4.95946202 | -0.22927814 | -0.68255636 |
| H | -3.86533860 | -3.70774284 | 0.00046660 |
| H | -5.84755657 | -1.80782769 | 0.03125750 |
| H | -6.05493283 | -0.10006067 | -0.19772501 |
| H | -1.47311068 | -4.46031145 | 0.02517158 |
| H | -2.14766705 | 1.89555881 | -0.51783683 |
| C | -8.56358636 | -4.41337610 | 0.66663007 |
| F | -9.12488963 | -3.23870973 | 0.98216436 |
| F | -9.02193917 | -4.72097734 | -0.56428585 |
| F | -9.11243459 | -5.31130113 | 1.49545600 |
| C | -6.99779241 | -4.39713978 | 0.69413274 |
| O | -6.49223721 | -5.50370596 | 0.95935551 |
| O | -6.50558625 | -3.28912757 | 0.41047676 |
| Au | -1.43480861 | 4.79555990 | -0.80389020 |
| P | -1.48409262 | 4.63430724 | -3.07958929 |
| C | -3.04130894 | 3.92841173 | -3.73541617 |
| C | -0.14652646 | 3.59345859 | -3.77333187 |
| C | -1.30414422 | 6.26435069 | -3.89388331 |
| N | -1.38043515 | 4.99855434 | 1.26602078 |
| N | -1.45472115 | 4.69577453 | 3.44417986 |
| N | -0.82300869 | 7.34166948 | 1.24669730 |
| N | -0.59643616 | 8.29170359 | 3.42559310 |
| N | -0.87546538 | 7.15867344 | 5.39679107 |
| C | -1.59184153 | 4.13066378 | 2.23630899 |
| C | -1.13313901 | 6.02569365 | 3.25124683 |
| C | -1.09067730 | 6.20431674 | 1.87154892 |
| C | -0.86162420 | 7.15092525 | 4.05711800 |
| C | -0.59189611 | 8.33343934 | 2.09538788 |
| H | -3.17605576 | 2.91333462 | -3.33891983 |
| H | -3.88537970 | 4.55238127 | -3.41274036 |
| H | -3.00427929 | 3.89449055 | -4.83368233 |
| H | -0.23745723 | 2.57265279 | -3.37911340 |

| | | | |
|---|---|---|---|
| H | -0.21812447 | 3.57471207 | -4.87031633 |
| H | 0.82574992 | 4.00637365 | -3.47320590 |
| H | -0.35324158 | 6.71920168 | -3.58601896 |
| H | -2.12769915 | 6.91909741 | -3.57932610 |
| H | -1.32184285 | 6.14220549 | -4.98631934 |
| H | -1.59021107 | 4.20886455 | 4.32139329 |
| H | -0.69487076 | 7.98582531 | 5.94301811 |
| H | -1.28777687 | 6.35700899 | 5.85742702 |
| H | -1.84754054 | 3.08318860 | 2.09510502 |
| H | -0.36582584 | 9.30879146 | 1.65537571 |
| C | -0.24847060 | 10.17001713 | 9.07607743 |
| F | -1.10976547 | 9.22164387 | 9.46751532 |
| F | 0.95430652 | 9.79643436 | 9.55942299 |
| F | -0.58922601 | 11.27212626 | 9.75703072 |
| C | -0.19045042 | 10.37435527 | 7.52442982 |
| O | 0.12388272 | 11.53042439 | 7.18514121 |
| O | -0.43194683 | 9.33926442 | 6.87582742 |

**Table S13:** Cartesian coordinates of model **1g** ($R$ = 3.00000 Å).

| | | | |
|---|---|---|---|
| Au | 3.32224341 | -0.23646370 | -3.09215821 |
| P | 5.37012792 | 0.76677546 | -3.00898441 |
| C | 6.52093983 | 0.20373273 | -4.31739370 |
| C | 6.25806673 | 0.49858173 | -1.42994524 |
| C | 5.25987304 | 2.58415190 | -3.20259370 |
| N | 1.43094650 | -1.09974293 | -3.17240569 |
| N | -0.29011048 | -2.46807175 | -3.25731816 |
| N | 0.23255273 | 0.98925310 | -3.20753589 |
| N | -2.13924940 | 0.73282246 | -3.30894989 |
| N | -3.25014592 | -1.26920650 | -3.37983768 |
| C | 1.04501568 | -2.36050425 | -3.20280574 |
| C | -0.81419628 | -1.18955729 | -3.26492758 |
| C | 0.28301957 | -0.33478887 | -3.21235516 |
| C | -2.09328105 | -0.59699225 | -3.31079260 |
| C | -1.01288555 | 1.44011084 | -3.26145256 |
| H | 6.68854911 | -0.87656339 | -4.21436458 |
| H | 6.07568193 | 0.40341520 | -5.30115457 |
| H | 7.47854942 | 0.73656097 | -4.22914200 |
| H | 6.42348349 | -0.57694599 | -1.28298086 |
| H | 7.22440910 | 1.02260948 | -1.45068057 |
| H | 5.64722414 | 0.88189687 | -0.60179270 |
| H | 4.62555640 | 2.99473642 | -2.40575716 |
| H | 4.80357503 | 2.81778407 | -4.17372209 |
| H | 6.26352764 | 3.02925028 | -3.14590118 |
| H | -0.79101568 | -3.34662154 | -3.30407812 |
| H | -3.31470547 | -2.26602966 | -3.24817805 |
| H | -4.10209663 | -0.72301673 | -3.35321309 |
| H | 1.71099916 | -3.22001177 | -3.18739075 |
| H | -1.13826577 | 2.52652723 | -3.26452708 |
| C | -7.85367695 | -0.01945773 | -3.34624943 |
| F | -7.71257129 | -1.15862860 | -4.03678780 |
| F | -8.25699337 | -0.38529647 | -2.11200565 |
| F | -8.89757986 | 0.61226306 | -3.89910722 |
| C | -6.55086784 | 0.84690246 | -3.27668571 |
| O | -6.76920151 | 2.06745979 | -3.16272027 |
| O | -5.50299555 | 0.17510641 | -3.30943312 |
| Au | -2.73214506 | -2.73372160 | -0.32217832 |
| P | -4.78020553 | -3.73714692 | -0.39849096 |
| C | -5.83818819 | -3.15047477 | -1.77319402 |
| C | -5.77536317 | -3.49636699 | 1.11986809 |
| C | -4.65560879 | -5.55088482 | -0.61604170 |
| N | -0.84040580 | -1.87020002 | -0.25624110 |
| N | 0.88148408 | -0.50153169 | -0.19781762 |
| N | 0.35895258 | -3.95890907 | -0.24528063 |
| N | 2.73191831 | -3.70203203 | -0.17794122 |
| N | 3.84371240 | -1.69967457 | -0.13653350 |
| C | -0.45414378 | -0.60931077 | -0.23764390 |
| C | 1.40570085 | -1.78000060 | -0.19172767 |
| C | 0.30805015 | -2.63496064 | -0.23022144 |
| C | 2.68529396 | -2.37236676 | -0.15950023 |
| C | 1.60544112 | -4.40942946 | -0.22091082 |
| H | -6.01324486 | -2.07207270 | -1.66295931 |

| | | | |
|---|---|---|---|
| H | -5.32585146 | -3.33301373 | -2.72718760 |
| H | -6.79924957 | -3.68425100 | -1.76076914 |
| H | -5.95126673 | -2.42350895 | 1.27399357 |
| H | -6.73760778 | -4.01941640 | 1.02313521 |
| H | -5.22297710 | -3.89456951 | 1.98137850 |
| H | -4.07762155 | -5.97581282 | 0.21537437 |
| H | -4.13310887 | -5.76759713 | -1.55727059 |
| H | -5.66048217 | -5.99636274 | -0.63673134 |
| H | 1.38383316 | 0.37743104 | -0.19433195 |
| H | 3.89834581 | -0.70536513 | 0.01683708 |
| H | 4.69215091 | -2.24671701 | -0.06071256 |
| H | -1.12017683 | 0.25015671 | -0.25314907 |
| H | 1.73146376 | -5.49569121 | -0.23447309 |
| C | 8.43474587 | -2.95235018 | 0.19318410 |
| F | 8.34095132 | -1.80109575 | -0.48525541 |
| F | 8.75152484 | -2.60856640 | 1.45861826 |
| F | 9.51479594 | -3.57479165 | -0.29723882 |
| C | 7.13082696 | -3.81908703 | 0.15722041 |
| O | 7.34157946 | -5.04158488 | 0.26445989 |
| O | 6.08727457 | -3.14624222 | 0.06396306 |
| X | 0.34684247 | -1.45945319 | -3.21896581 |
| X | 0.24407337 | -1.51032189 | -0.22115813 |

**Table S14:** Cartesian coordinates of model **1g'** ($R$ = 3.15909 Å).

| | | | |
|---|---|---|---|
| Au | 3.27883043 | -0.13840545 | 1.58151395 |
| N | 1.36716853 | 0.59353795 | 1.31844238 |
| N | -0.45163466 | 1.69890067 | 0.69555507 |
| N | 0.36524304 | -0.91695543 | 2.89966222 |
| N | -1.99259913 | -0.63196665 | 3.13556235 |
| N | -3.25907777 | 0.90252590 | 2.00500875 |
| C | 0.88389715 | 1.55151231 | 0.54840808 |
| C | -0.85090813 | 0.75256276 | 1.64024221 |
| C | 0.29962117 | 0.06918326 | 2.01929573 |
| C | -2.06182903 | 0.36079938 | 2.25124629 |
| C | -0.82481817 | -1.20603598 | 3.40982531 |
| H | -1.01917440 | 2.37278940 | 0.19603830 |
| H | -3.39768318 | 1.68239204 | 1.38303200 |
| H | -4.04963029 | 0.54183073 | 2.52410084 |
| H | 1.46917313 | 2.16444891 | -0.13302793 |
| H | -0.85635194 | -2.01319046 | 4.14692488 |
| P | 5.37510589 | -0.96801181 | 1.89443031 |
| H | 6.01751387 | -1.52995987 | 0.75442910 |
| H | 6.36220665 | -0.05343317 | 2.36053359 |
| H | 5.48670061 | -2.02503323 | 2.84222715 |
| O | -5.34977332 | -0.05136871 | 3.37779993 |
| O | -6.38296436 | -1.40258965 | 4.89106674 |
| C | -6.33021133 | -0.49870048 | 4.02157451 |
| H | -7.32830870 | -0.00749140 | 3.77872612 |
| X | 0.26578943 | 0.90620006 | 1.26614369 |
| Au | -3.27883043 | 0.13840545 | -1.58151395 |
| N | -1.36716853 | -0.59353795 | -1.31844238 |
| N | 0.45163466 | -1.69890067 | -0.69555507 |
| N | -0.36524304 | 0.91695543 | -2.89966222 |
| N | 1.99259913 | 0.63196665 | -3.13556235 |
| N | 3.25907777 | -0.90252590 | -2.00500875 |
| C | -0.88389715 | -1.55151231 | -0.54840808 |
| C | 0.85090813 | -0.75256276 | -1.64024221 |
| C | -0.29962117 | -0.06918326 | -2.01929573 |
| C | 2.06182903 | -0.36079938 | -2.25124629 |
| C | 0.82481817 | 1.20603598 | -3.40982531 |
| H | 1.01917440 | -2.37278940 | -0.19603830 |
| H | 3.39768318 | -1.68239204 | -1.38303200 |
| H | 4.04963029 | -0.54183073 | -2.52410084 |
| H | -1.46917313 | -2.16444891 | 0.13302793 |
| H | 0.85635194 | 2.01319046 | -4.14692488 |
| P | -5.37510589 | 0.96801181 | -1.89443031 |
| H | -6.36220665 | 0.05343317 | -2.36053359 |
| H | -6.01751387 | 1.52995987 | -0.75442910 |
| H | -5.48670061 | 2.02503323 | -2.84222715 |
| O | 5.34977332 | 0.05136871 | -3.37779993 |
| O | 6.38296436 | 1.40258965 | -4.89106674 |
| C | 6.33021133 | 0.49870048 | -4.02157451 |
| H | 7.32830870 | 0.00749140 | -3.77872612 |
| X | -0.26578943 | -0.90620006 | -1.26614369 |