Cooperative Au(I)···Au(I) Interactions and Hydrogen Bonding as Origin of a Luminescent Adeninate Hydrogel Formed by Ultrathin Molecular Nanowires.

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Supporting Information

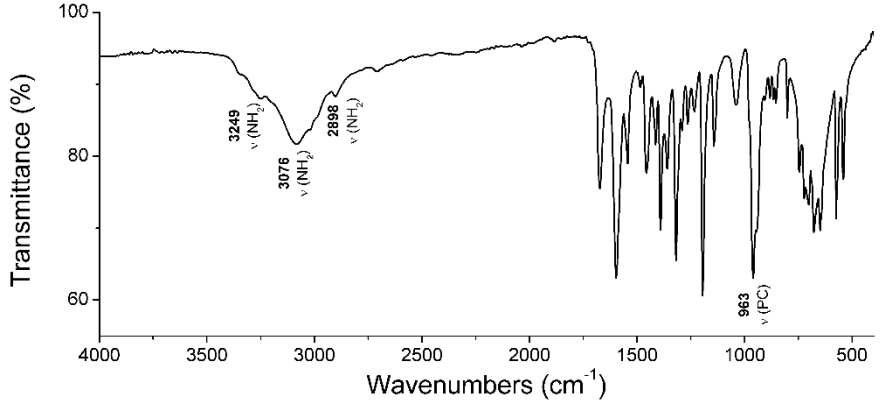


Fig. S1: UATR-IR spectrum of [Au(^{9}*N*-adeninate)(PMe_3)] (**1**).

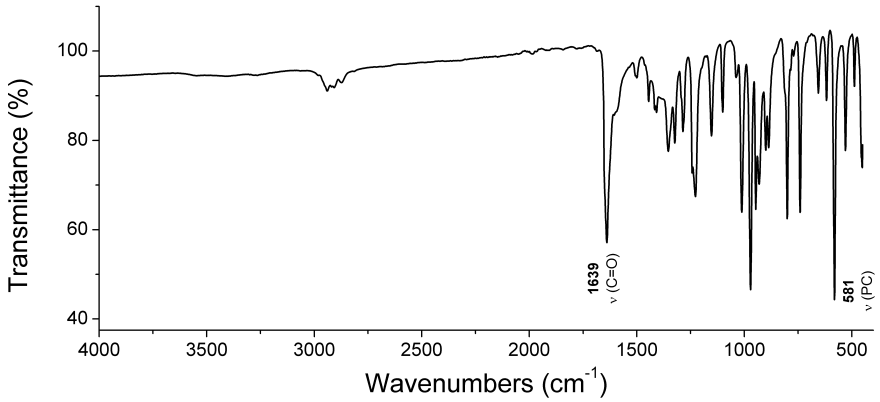


Fig. S2: UATR-IR spectrum of [Au(acac)(PTA)] (**2**).

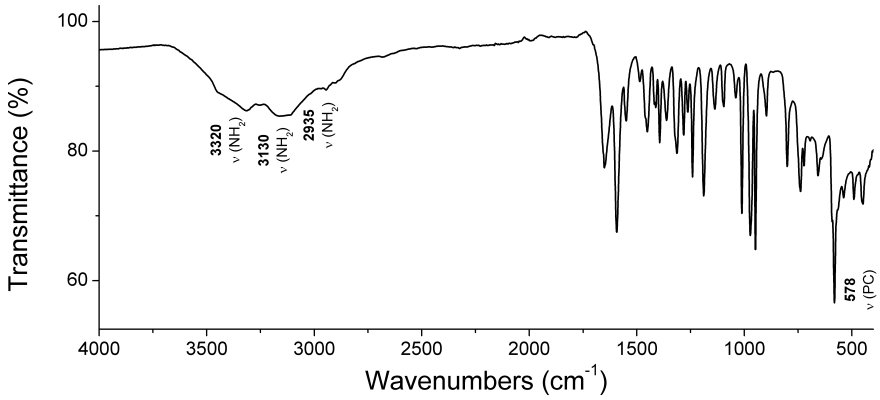


Fig. S3: UATR-IR spectrum of [Au(^{9}*N*-adeninate)(PTA)] (**3**).

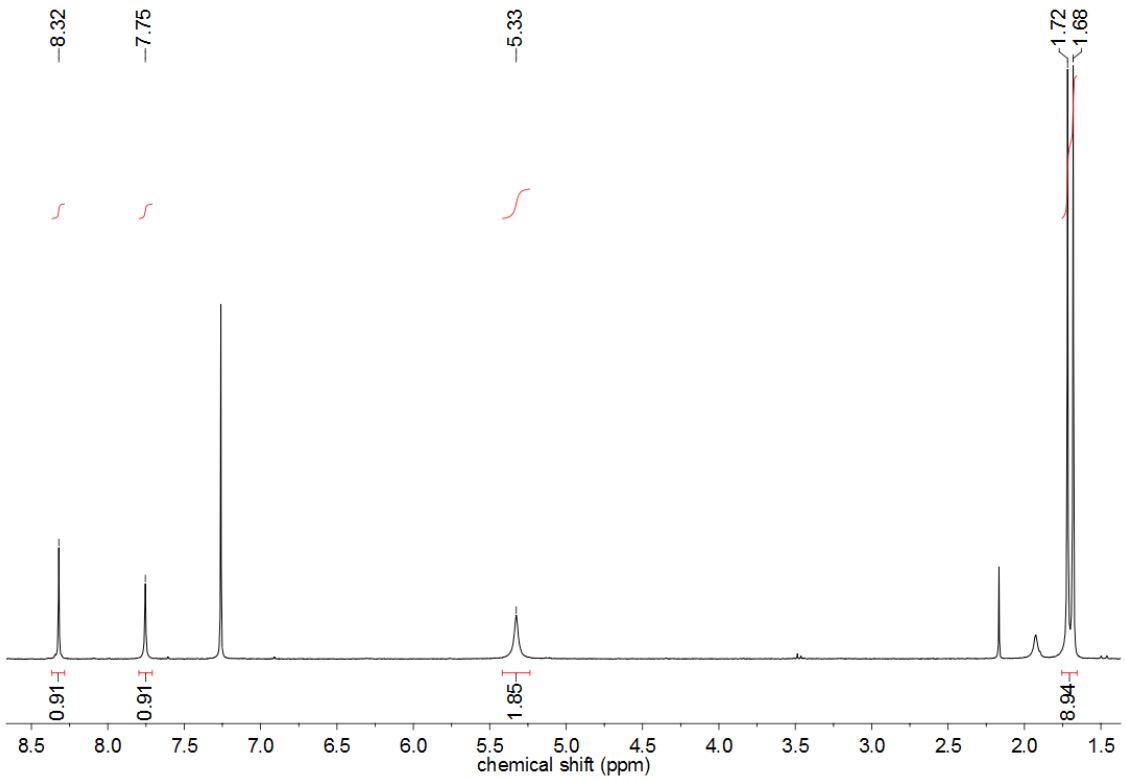


Fig. S4: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of [Au(^{9}*N*-adeninate)(PMe_3)] (**1**).

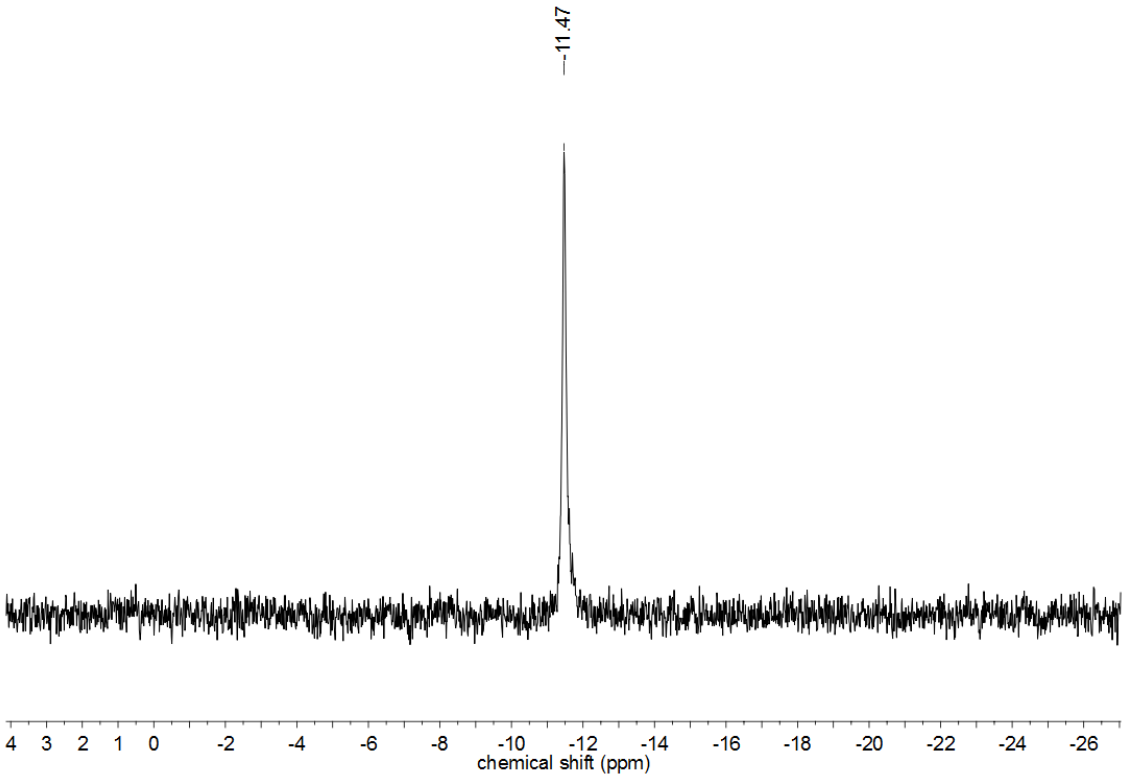


Fig. S5: ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) spectrum of [Au(^{9}*N*-adeninate)(PMe_3)] (**1**).

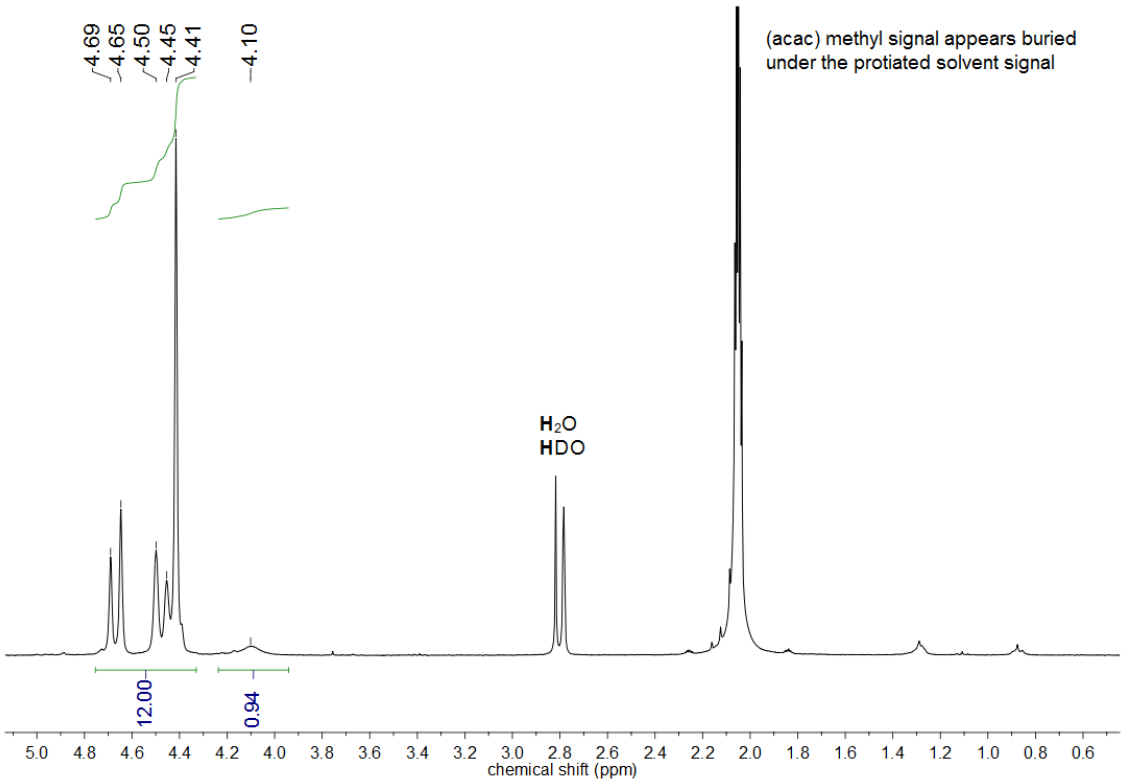


Fig. S6: ^{1}H NMR (300 MHz, d^{6}-acetone) spectrum of [Au(acac)(PTA)] (**2**).

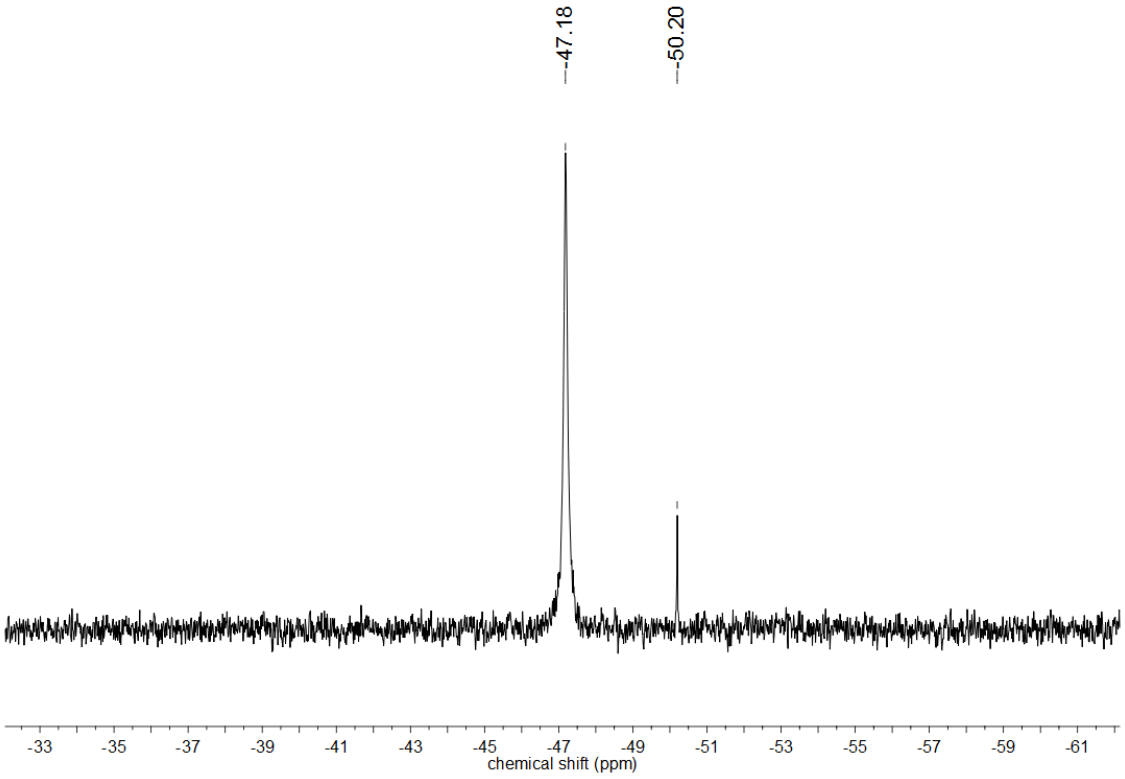


Fig. S7: ^{31}P{^{1}H} NMR (121 MHz, d^{6}-acetone) spectrum of [Au(acac)(PTA)] (**2**).

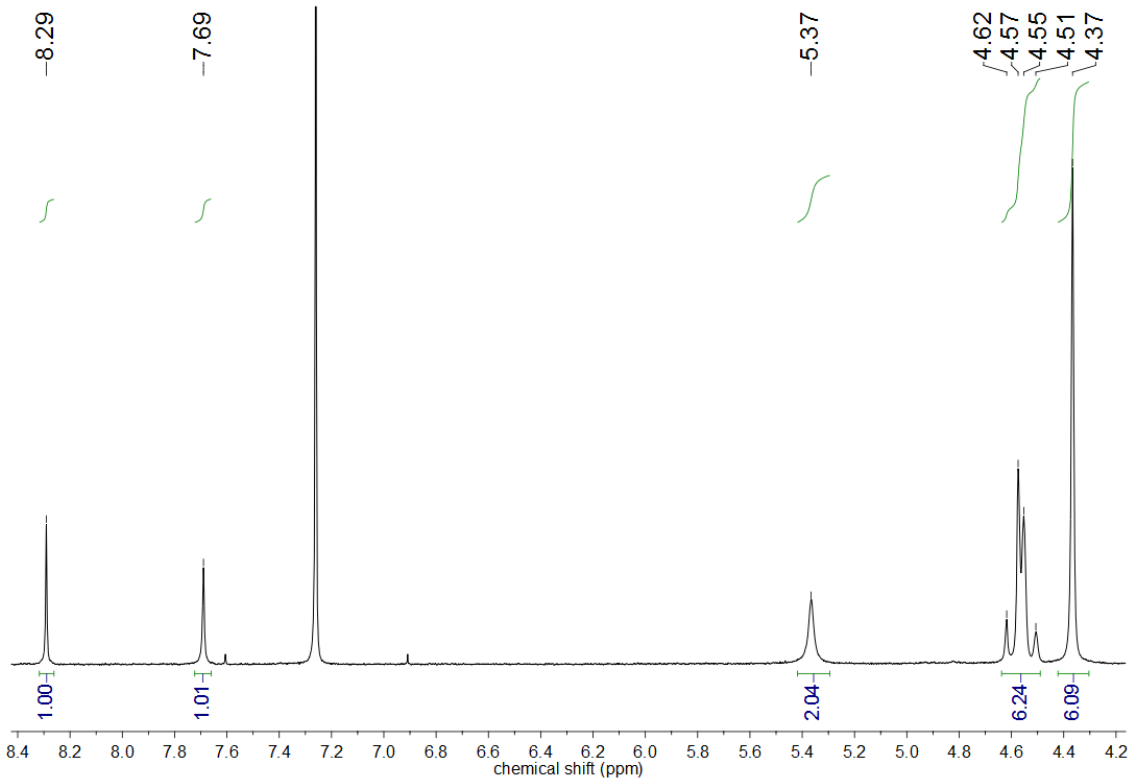


Fig. S8: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of [Au(^{9}*N*-adeninate)(PTA)] (**3**).

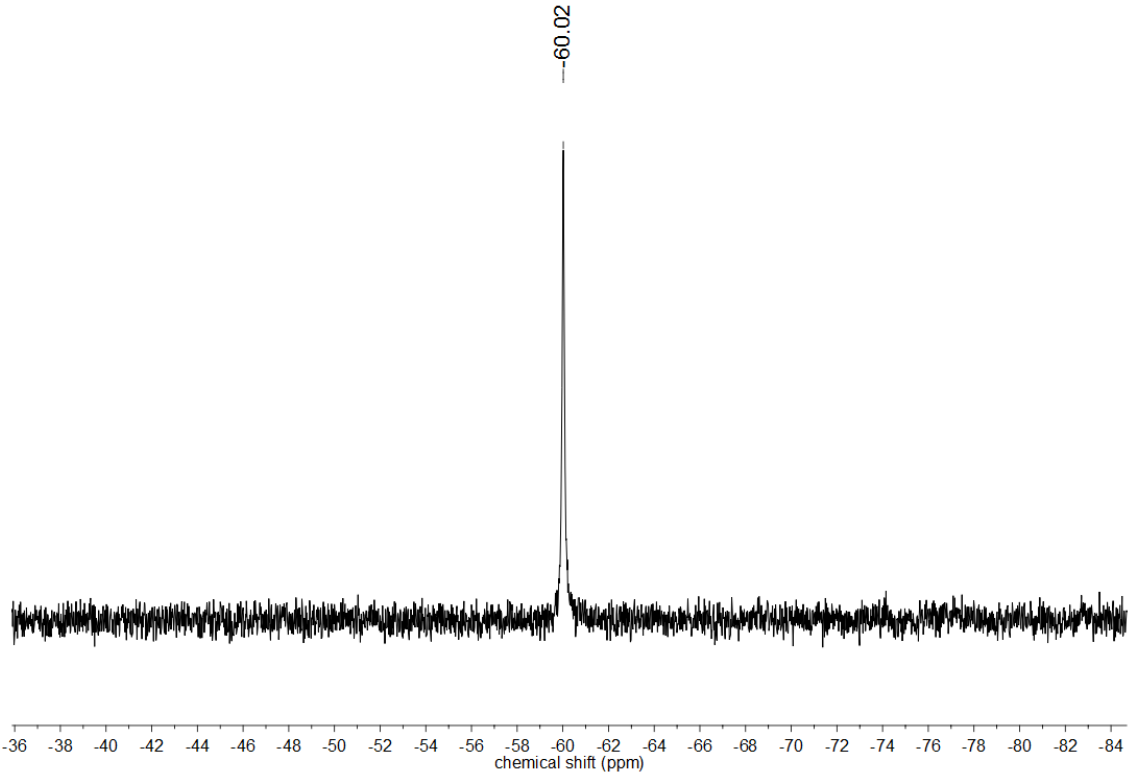


Fig. S9: ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) spectrum of [Au(^{9}*N*-adeninate)(PTA)] (**3**).

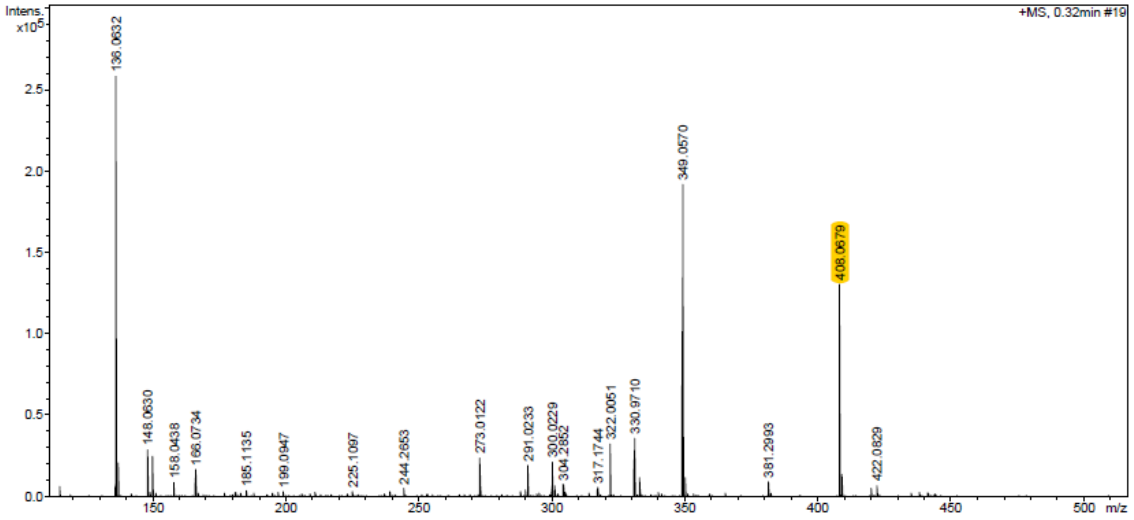


Fig. S10: ESI-(+) MS spectrum of [Au(^{9}*N*-adeninate)(PMe$_3$)] (**1**). The protonated molecular peak ([M+H]$^+$) appears highlighted in yellow.

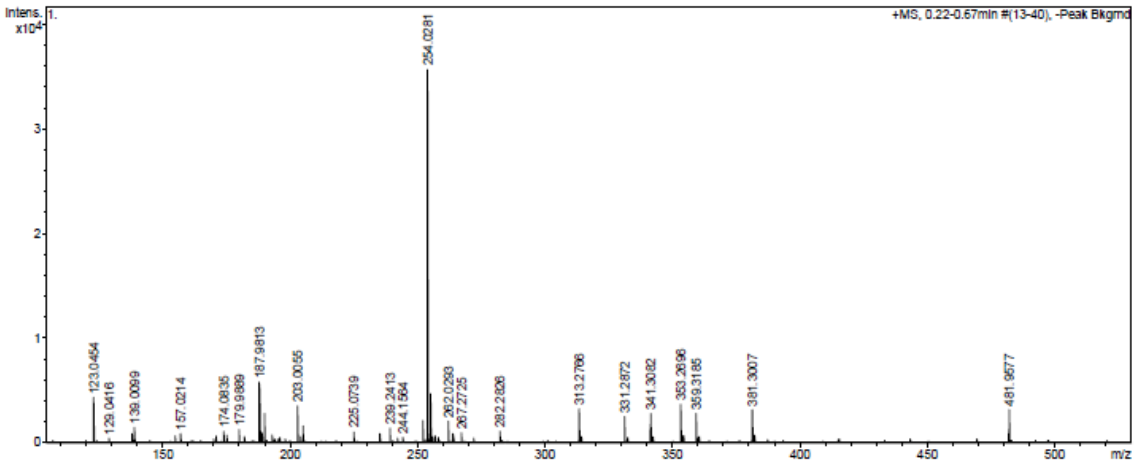


Fig. S11: ESI-(+) MS spectrum of [Au(acac)(PTA)] (**2**).

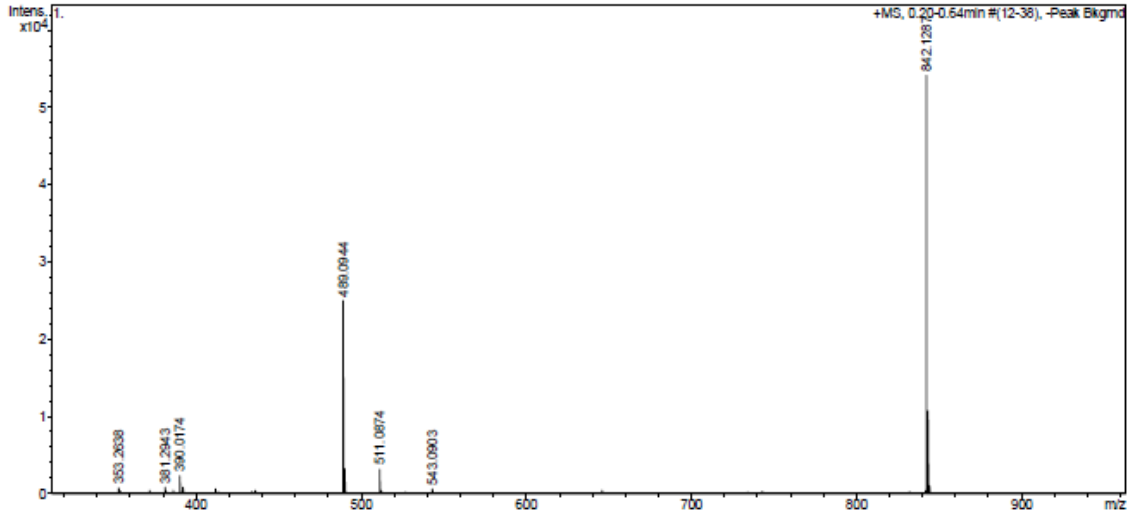


Fig. S12: ESI-(+) MS spectrum of [Au(^{9}*N*-adeninate)(PTA)] (**3**).

Table S1: Data collection and structure refinement details for **1** and **3**·3H_2O.

Parameter	Value(s) (for **1**)	Value(s) (for **3**·3H_2O)
Empirical formula	$C_8H_{13}AuN_5P$	$C_{11}H_{16}AuN_8P·3H_2O$
Formula mass	407.17 g mol^{-1}	542.30 g mol^{-1}
Crystal habit	Colourless needles	Colourless sheets
Temperature	173(2) K	173(2) K
Wavelength	0.71073 Å	0.71073 Å
Space group	$P\,2_12_12_1$	P -1
Crystal system	Orthorhombic	Triclinic
Unit cell dimensions	a = 8.0903(2) Å α = 90º b = 17.4585(8) Å β = 90º c = 17.8775(8) Å γ = 90º	a = 14.3956(7) Å α = 72.419(3)º b = 14.4748(7) Å β = 73.697(3)º c = 20.1034(6) Å γ = 77.656(2)º
Volume	2525.10(17) $Å^3$	3794.5(3) $Å^3$
Z	8	8
Density (calculated)	2.142 Mg m^{-3}	1.899 Mg m^{-3}
Absorption coefficient	11.757 mm^{-1}	7.865 mm^{-1}
F(000)	1520	2096
Crystal size	(0.1 · 0.1 · 0.05) mm^3	(0.125 · 0.1 · 0.05) mm^3
θ range ($2\theta_{max}$/º)	1.630 – 27.482	1.847 – 27.509
Index ranges	-10 <= h <= 10 -22 <= k <= 22 -23 <= l <= 23	-18 <= h <= 18 -18 <= k <= 18 -26 <= l <= 25
Total reflections	37784	62072
Independent reflections	5745 [R_{int} = 0.0727]	17307 [R_{int} = 0.0940]
Completeness to θ = 25.242º	99.5 %	99.5 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / Restrains / Parameters	5745 / 52 / 271	17307 / 432 / 868
Goodness-of-fit on F^2	1.047	1.032
Final R índices [$I > 2\sigma(I)$]	R1 = 0.0418, wR2 = 0.0973	R1 = 0.0703, wR2 = 0.1606
R índices (all data)	R1 = 0.0495, wR2 = 0.1015	R1 = 0.1212, wR2 = 0.1831
Largest diff. peak and hole (e/$Å^3$)	2.569, -3.859	2.904, -2.160

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

Au(1)-Au(2)	3.2081(6)
Au(1)-N(1)	2.048(10)
Au(1)-P(1)	2.233(3)
Au(2)-N(6)	2.043(10)
Au(2)-P(2)	2.231(3)
N(1)-Au(1)-P(1)	175.3(3)
N(6)-Au(2)-P(2)	173.4(3)

Table S3: Selected hydrogen bond lengths (in Å) and angles (in º) for **1**.

D-H···A	**d(D-H)**	**d(H···A)**	**d(D···A)**	***θ* (DHA)**
N(5)-H(5A)···N(2)#1	0.86	2.21	3.051(13)	165.4
N(5)-H(5B)···N(4)#2	0.86	2.12	2.913(14)	153.0
N(10)-H(10D)···N(7)#3	0.86	2.07	2.909(14)	166.5
N(10)-H(10E)···N(9)#4	0.86	2.25	3.083(14)	162.8

Symmetry transformations used to generate equivalent atoms:
#1 x+1/2,-y+5/2,-z+1; **#2** x-1/2,-y+5/2,-z+1; **#3** x+1/2,-y+5/2,-z+2; **#4** x-1/2,-y+5/2,-z+2.

Table S4: Selected bond lengths (in Å) and angles (in º) for **3**·3H_2O.

Au(1)-Au(2)	3.0942(7)
Au(3)-Au(4)	3.0969(7)
Au(1)-P(1)	2.224(3)
Au(2)-P(2)	2.225(3)
Au(3)-P(3)	2.227(3)
Au(4)-P(4)	2.225(3)
Au(1)-N(13)	2.050(9)
Au(2)-N(18)	2.049(10)
Au(3)-N(23)	2.049(10)
Au(4)-N(28)	2.055(10)
N(13)-Au(1)-P(1)	173.5(3)
N(18)-Au(2)-P(2)	176.6(3)
N(23)-Au(3)-P(3)	177.6(3)
N(28)-Au(4)-P(4)	172.8(3)

Table S5: Hydrogen bond lengths (in Å) and angles (in º) for **3**·3H_2O.

D-H···A	**d(D-H)**	**d(H···A)**	**d(D···A)**	***θ* (DHA)**
C(3)-H(3A)...N(31)	0.97	2.67	3.55(2)	150.6
C(5)-H(5B)...N(9)#1	0.97	2.52	3.220(19)	128.7
C(6)-H(6B)...N(32)#1	0.97	2.61	3.56(2)	166.7
C(8)-H(8A)...N(22)#2	0.97	2.49	3.430(18)	162.4
C(9)-H(9A)...O(15)#3	0.97	2.41	3.28(2)	148.7
C(9)-H(9B)...O(11)#4	0.97	2.48	3.43(2)	163.8

Table S5. (cont.)

D-H···A	d(D-H)	d(H···A)	d(D···A)	*θ* (DHA)
C(14)-H(14A)...O(10)	0.97	2.55	3.387(14)	144.9
C(15)-H(15A)...N(27)#5	0.97	2.64	3.49(2)	145.5
C(17)-H(17D)...O(5)	0.97	2.66	3.419(16)	135.9
C(19)-H(19B)...N(16)	0.97	2.46	3.40(2)	162.1
C(21)-H(21A)...O(10)	0.97	2.50	3.41(2)	156.8
C(22)-H(22C)...O(1)#6	0.97	2.57	3.463(18)	153.4
C(24)-H(24A)...N(4)#7	0.97	2.65	3.25(2)	120.1
N(17)-H(17A)...N(16)#7	0.86	2.29	3.087(15)	154.6
N(22)-H(22A)...O(1)#8	0.86	2.47	2.921(13)	113.5
C(35)-H(35)...N(14)	0.93	2.69	3.327(18)	126.2
N(27)-H(27B)...O(6)#4	0.87	2.55	3.18(2)	130.0
N(32)-H(32A)...N(31)#1	0.86	2.16	3.017(15)	178.5
N(32)-H(32B)...N(19)	0.86	2.68	3.197(17)	120.0
O(1)-H(1C)...O(4)	0.85	1.94	2.760	163.0
O(1)-H(1D)...N(7)#9	0.85	2.10	2.886(12)	153.1
O(2)-H(2C)...O(16)	0.85	2.10	2.873	151.8
O(2)-H(2D)...O(17)	0.85	2.26	2.721	114.2
O(3)-H(3C)...N(20)#10	0.85	2.28	2.824(13)	122.4
O(3)-H(3D)...O(7)#5	0.85	2.04	2.836(13)	155.8
O(4)-H(4C)...O(16)#9	0.85	2.33	3.105(9)	152.2
O(4)-H(4D)...N(30)#9	0.85	2.09	2.876(12)	153.1
O(5)-H(5C)...O(6)	0.85	2.44	2.895	113.9
O(5)-H(5D)...N(21)#1	0.85	2.14	2.945(14)	157.8
O(6)-H(6C)...O(5)	0.85	2.30	2.895	127.6
O(6)-H(6D)...N(10)#11	0.85	2.20	2.968(14)	151.0
O(7)-H(7D)...N(29)	0.85	2.11	2.811(12)	140.0
O(8)-H(8D)...N(5)#12	0.85	1.96	2.753(14)	154.9
O(9)-H(9C)...O(10)	0.85	1.94	2.772	164.6
O(9)-H(9D)...O(5)#9	0.85	2.15	2.934(8)	152.5
O(11)-H(11D)...N(19)#1	0.85	2.39	3.154(13)	149.2
O(11)-H(11D)...N(22)#1	0.85	2.40	2.893(16)	117.1
O(12)-H(12C)...N(2)#10	0.85	2.38	2.917(16)	121.9
O(13)-H(13C)...O(3)	0.85	1.99	2.792	157.3
O(13)-H(13D)...O(9)	0.85	2.42	3.061	132.8
O(14)-H(14D)...O(16)#9	0.85	2.40	3.135(13)	145.2
O(15)-H(15C)...N(6)#5	0.85	1.83	2.679(15)	179.6

Table S5. (cont.)

D-H···A	**d(D-H)**	**d(H···A)**	**d(D···A)**	***θ* (DHA)**
O(15)-H(15D)...O(14)	0.85	1.99	2.758	149.9
O(16)-H(16C)...O(12)#11	0.85	1.95	2.793(12)	172.4
O(16)-H(16D)...O(14)#9	0.85	2.49	3.135(10)	133.3
O(18)-H(18C)...O(8)#10	0.85	1.78	2.621	171.6
O(18)-H(18D)...O(11)#9	0.85	1.79	2.294(8)	115.8

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z; **#2** -x+1,-y,-z; **#3** x-1,y,z-1; **#4** x,y-1,z; **#5** -x+1,-y,-z+1; **#6** x-1,y,z; **#7** -x,-y,-z+1; **#8** x,y,z-1; **#9** -x+1,-y+1,-z+1; **#10** x,y,z+1; **#11** -x,-y+1,-z+1; **#12** x+1,y,z.

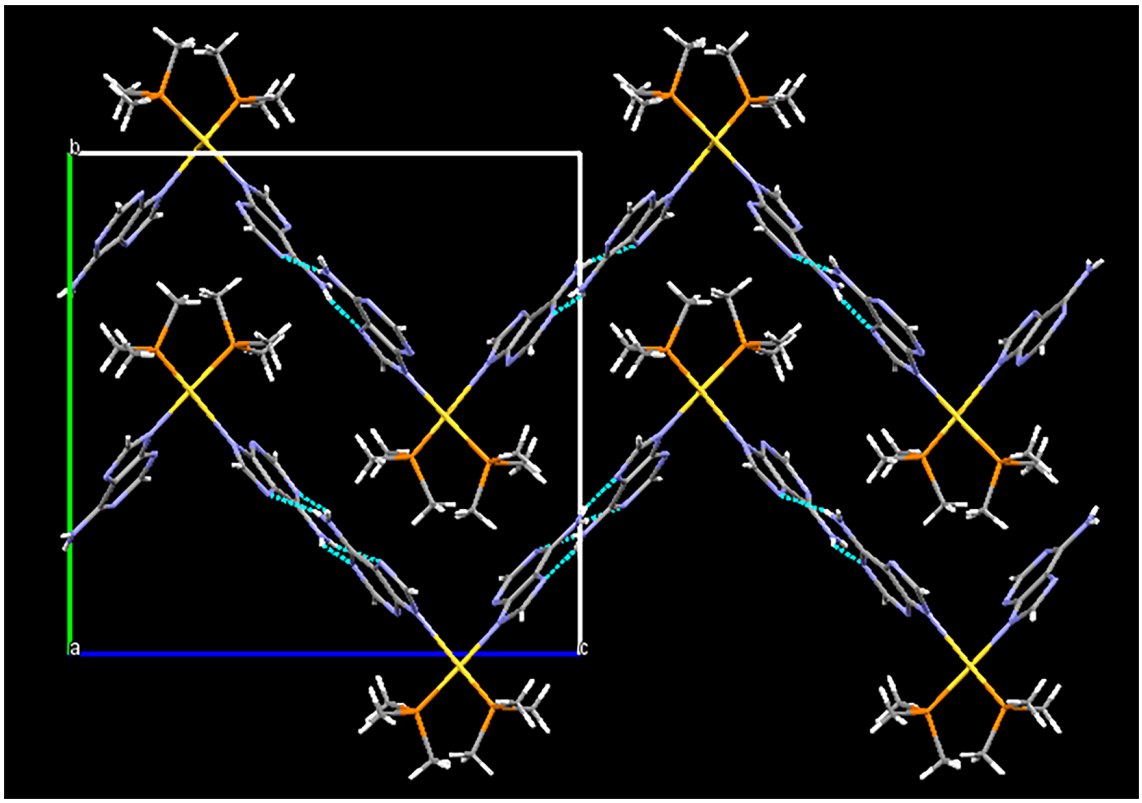


Fig. S13: Crystalline packing of **1** seen along *a* crystallographic axis. Blue dashes represent hydrogen bonding.

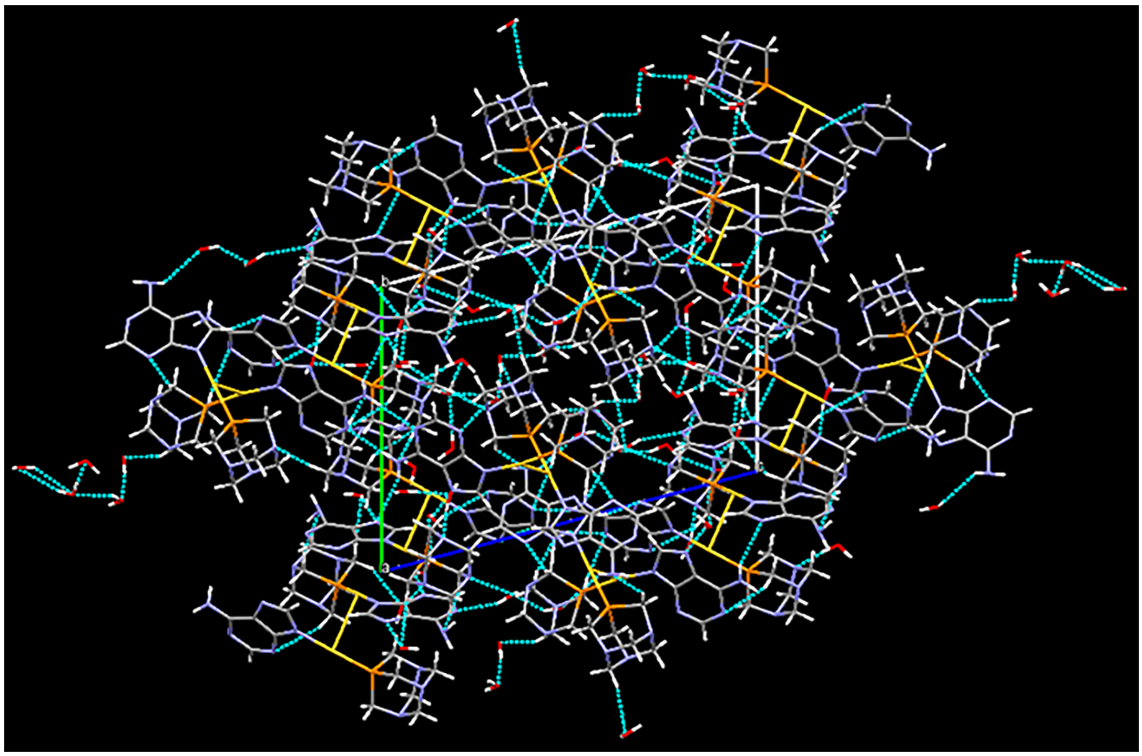


Fig. S14: Crystalline packing of **3**·3H_2O seen along *a* crystallographic axis. Blue dashes represent hydrogen bonding.

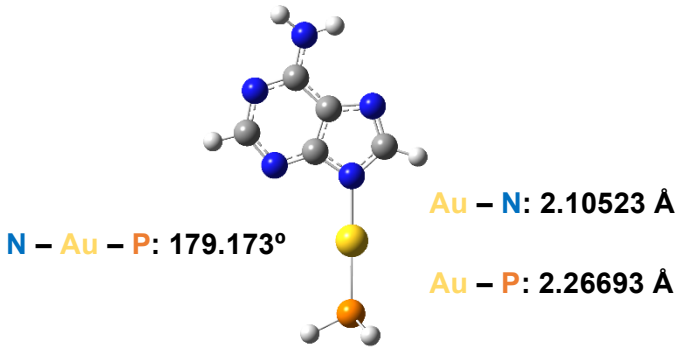


Fig. S15: Theoretical model [Au(^{9}*N*-adeninate)(PH_3)] showing selected bond lengths and angles.

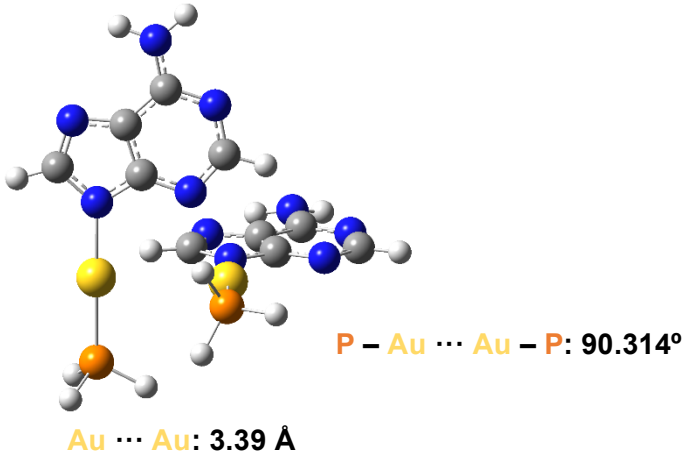


Fig. S16: Theoretical model **1a** (aurophilicity at equilibrium distance) showing selected bond lengths and angles.

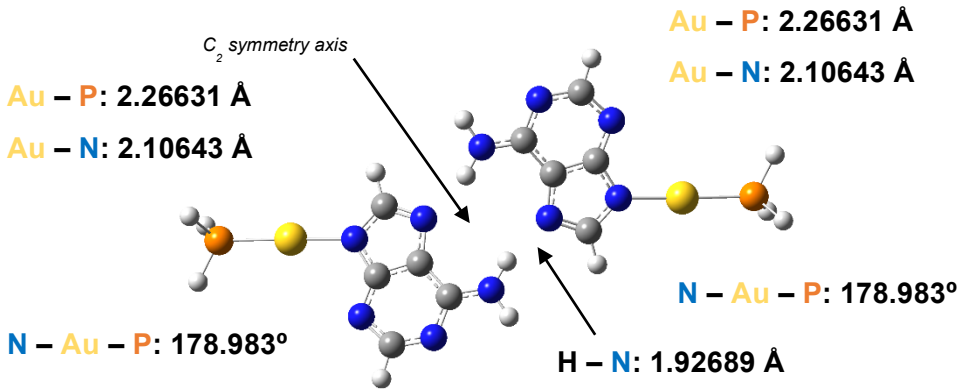


Fig. S17: Theoretical model **1b** (hydrogen bonding) showing selected bond lengths and angles.

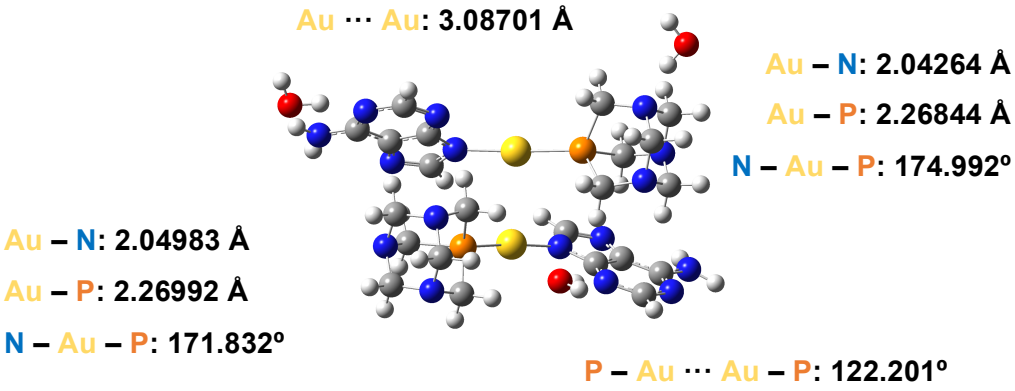


Fig. S18: Theoretical model **3a** showing selected bond lengths and angles.

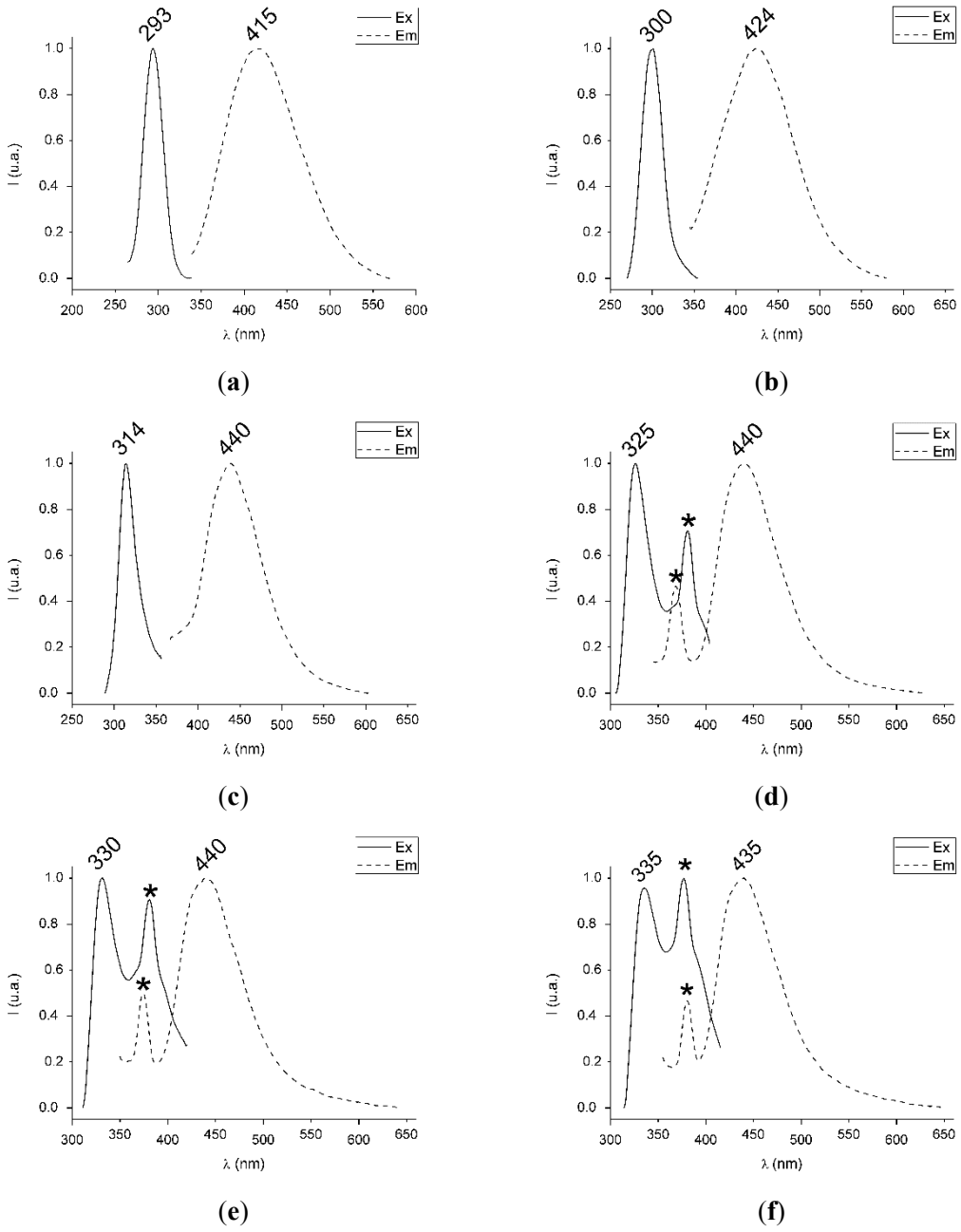
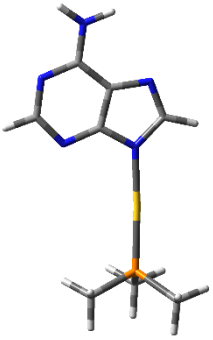
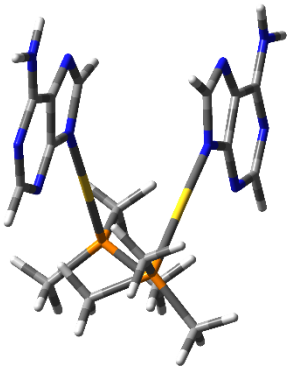


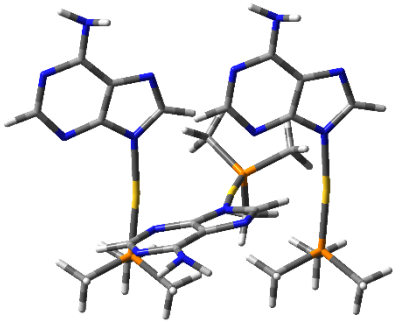
Fig. S19: Excitation and emission spectra of aqueous solutions of [Au(^{9}*N*-adeninate)(PMe_3)] at concentrations (a) 0.3 mM, (b) 0.5 mM, (c) 1.2 mM, (d) 5.0 mM, (e) 10.0 mM, (f) 15.0 mM. Maxima pointed with * correspond to instrumental artifacts.



Monomer (**1c**)



Dimer (**1d**)



Trimer (**1e**)

Fig. S20: Theoretical aggregation models **1c-1e** in aqueous solution.

Table S6: TD-DFT singlet-singlet excitations for models **1c-1e**.

Model	Excitation[a]	λ_{calc} (nm)	*f* (u.a.)	Contributions[b]
d	$S_0 \rightarrow S_1$	299.29	0.0103	HOMO→LUMO+1 (89)
	$S_0 \rightarrow S_4$	268.53	0.0698	HOMO-1→LUMO+1 (61)
				HOMO→LUMO (26)
	$S_0 \rightarrow S_5$	268.33	0.1109	HOMO→LUMO (41)
				HOMO-1→LUMO+1 (37)
e	$S_0 \rightarrow S_1$	331.57	0.0293	HOMO→LUMO (76)
f	$S_0 \rightarrow S_2$	374.50	0.0905	HOMO→LUMO+1 (96)
	$S_0 \rightarrow S_5$	355.24	0.0282	HOMO-1→LUMO+1 (47)
				HOMO-1→LUMO (35)

[a]Higher oscillator strength transitions among the first five singlet-singlet excitations are only included. [b]Only high value contributions are included ([coeff]^2·100).

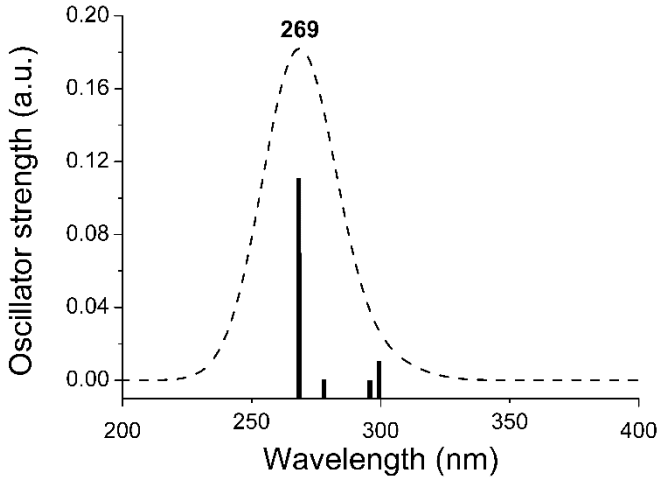


Fig. S21: Predicted TD-DFT absorption spectrum for model **1c**.

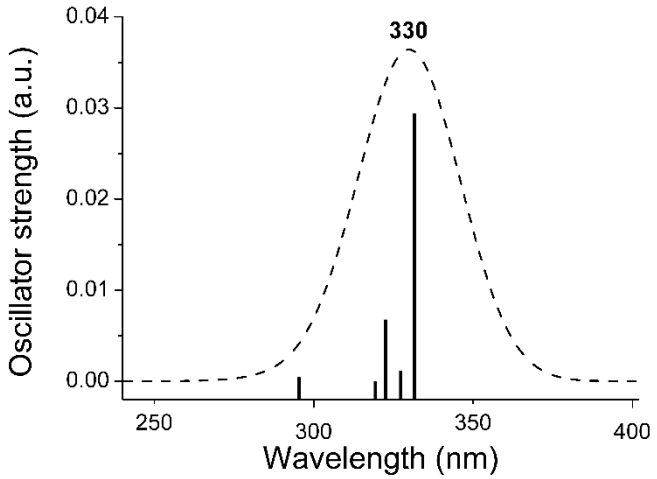


Fig. S22: Predicted TD-DFT absorption spectrum for model **1d**.

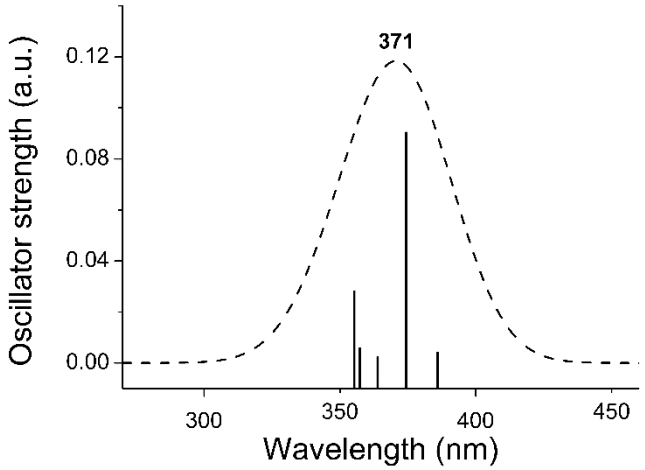


Fig. S23: Predicted TD-DFT absorption spectrum for model **1e**.

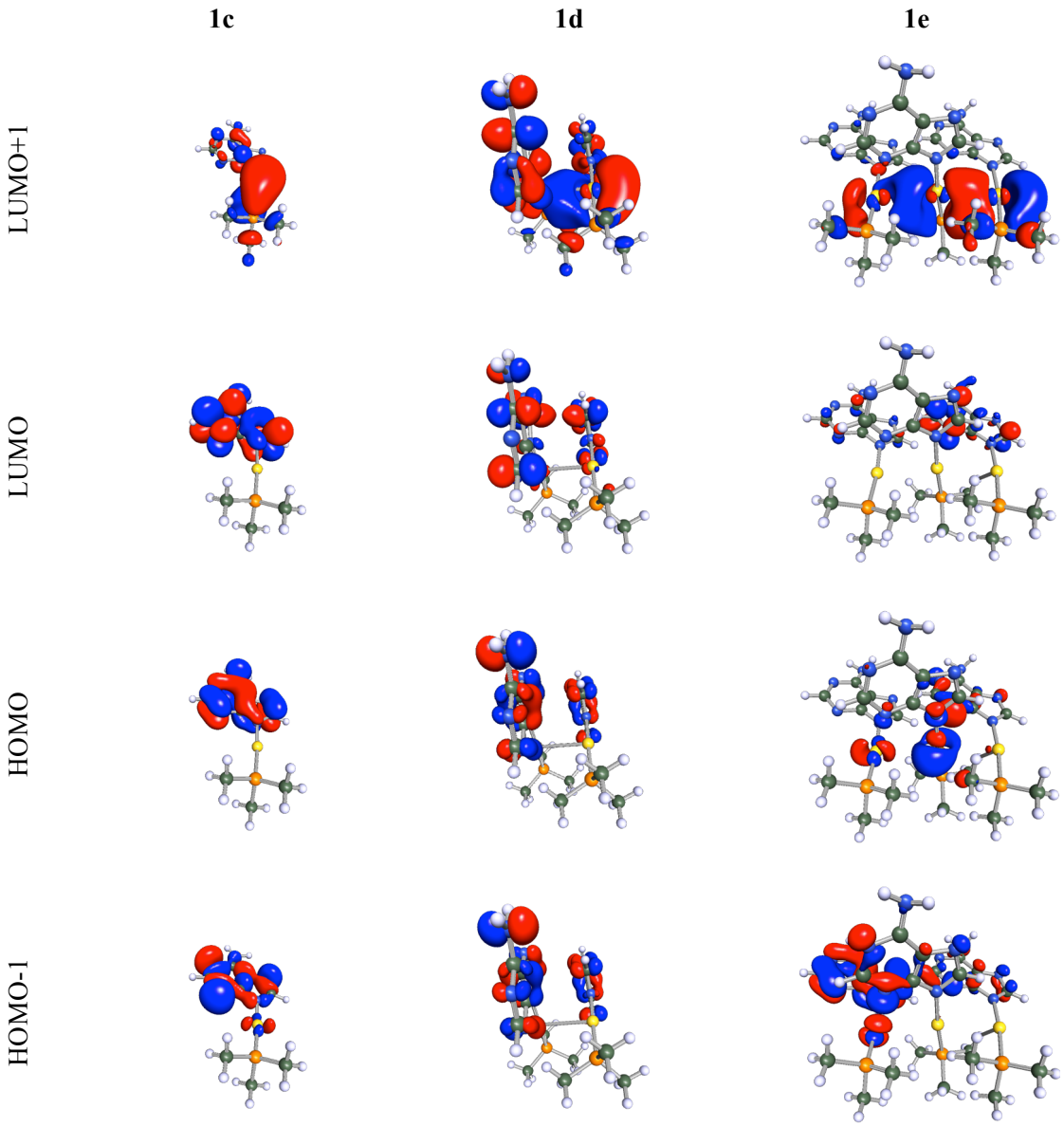
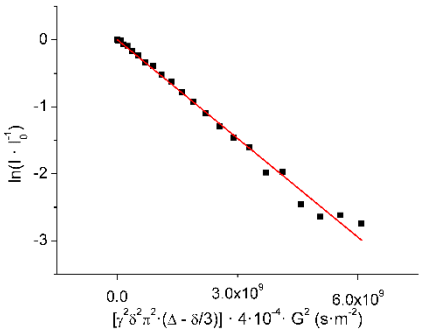
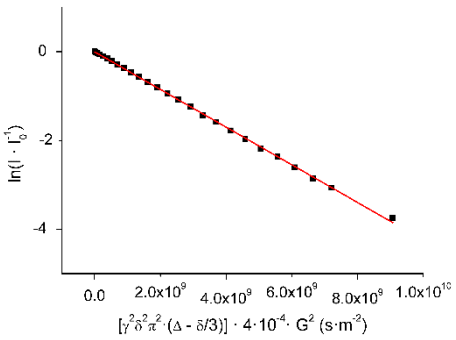


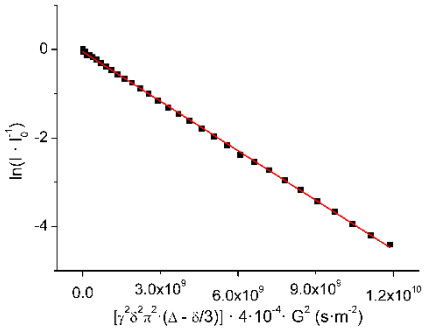
Fig. S24: Calculated molecular orbitals responsible of the most contributing transitions to the theoretical excitations.



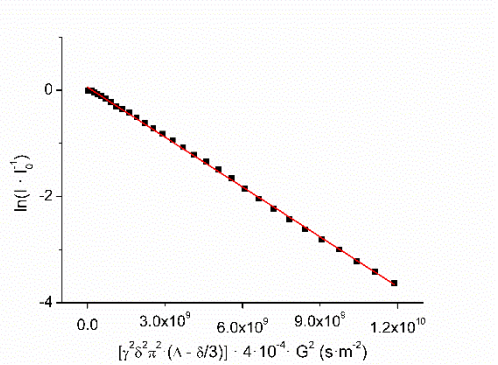
(a) 5.0 mM



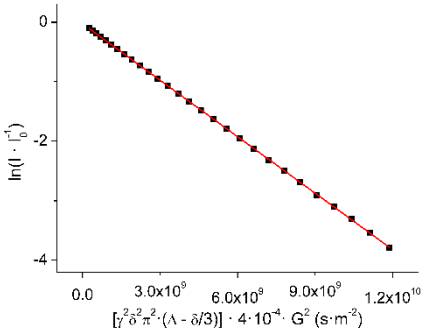
(b) 25.0 mM



(c) 50.0 mM



(d) 75.0 mM

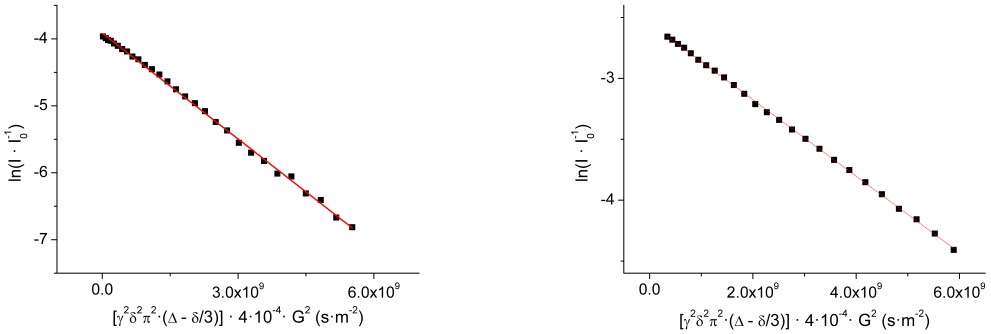


(e) 100.0 mM

Fig. S25: Plots of ^{1}H ln(I/I$_0$) (^{2}CH signal) *vs* arbitrary units proportional to the square of the gradient amplitude, in D_2O at different concentrations of **1**.

Table S7: Translational diffusion coefficient D_t, hydrodynamic radius r_H, hydrodynamic volume V_H and number of molecules of [Au(^{9}N-adeninate)(PMe_3)] at different concentrations in D_2O, retrieved from PSGE-NMR experiments.

Concentration (mM)	D_t (m·s^{-1})	r_H (Å)	V_H (Å^3)	Number of molecules (compared to $V_{X\text{-}ray}$ = 315.64 Å^3)
5.0	4.923E-10	5.25967	609.49	1.93
25.0	4.24186E-10	6.04763	926.50	2.94
50.0	3.72158E-10	7.16672	1541.88	4.85
75.0	3.12408E-10	8.31203	2405.53	7.62
100.0	2.8145E-10	9.60795	3715.19	11.77



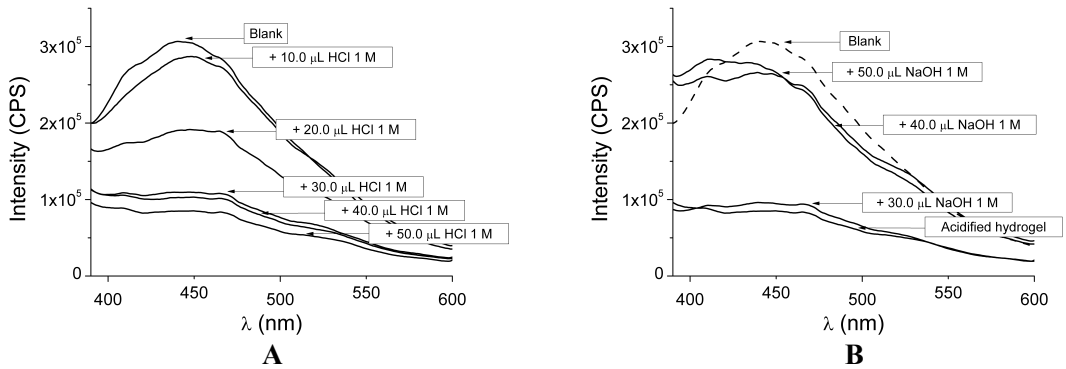
(a) 5.0 mM **(b)** 25.0 mM

Fig. S26: Plots of ^{1}H ln(I/I$_0$) (^{2}CH signal) *vs* arbitrary units proportional to the square of the gradient amplitude, in D_2O at different concentrations of **3**.

Table S8: Translational diffusion coefficient D_t, hydrodynamic radius r_H, hydrodynamic volume V_H and number of molecules of [Au(^{9}*N*-adeninate)(PTA)] at different concentrations in D_2O, retrieved from PSGE-NMR experiments.

Concentration (mM)	D_t (m·s^{-1})	r_H (Å)	V_H (Å^3)	Number of molecules (compared to $V_{X\text{-}ray}$ = 474.31 Å^3)
5.0	5.2675E-10	4.73391	444.37	0.94
25.0	3.1396E-10	7.51884	1780.50	3.75

Study of the luminescence of the hydrogel at different pH: Five consecutive 10.0 µL aliquots of 1 M aqueous HCl were added to a sample of the hydrogel of **1** in a quartz cuvette. The gel was mixed gently and luminescence (excitation at 365 nm) was recorded immediately after each addition. Then, five 10.0 µL aliquots of 1 M aqueous NaOH were added to the former acidified hydrogel, and luminescence was recorded again following the same procedure. Results are shown in Fig. S27.



A **B**

Fig. S27: Emission spectra (excitation at 365 nm) for complex **1** in the hydrogel form (A): after the addition of aqueous 1 M HCl; (B): recovery of the original luminescence by addition of aqueous 1 M NaOH to the former acidified hydrogel.

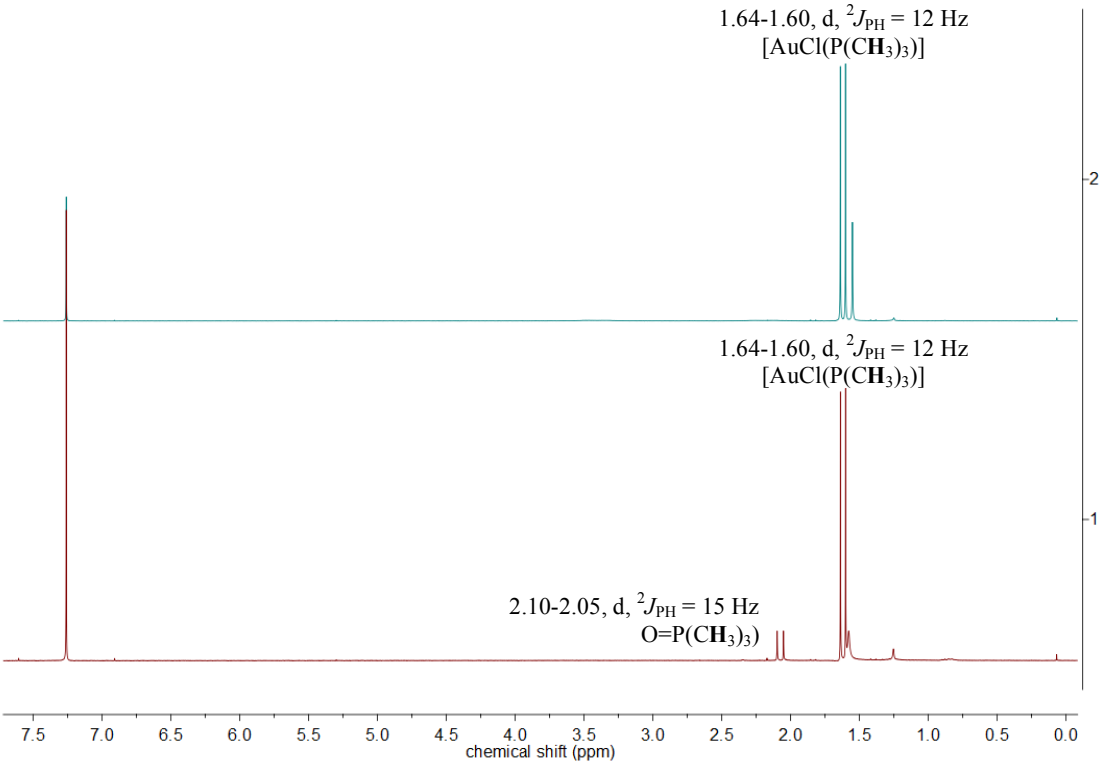


Fig. S28: ^{1}H NMR (300 MHz, $CDCl_3$) spectra of (1): the white precipitate formed by addition of HCl to the hydrogel of **1**, it is, [AuCl(PMe_3)] with traces of trimethylphosphine oxide; (2) pure [AuCl(PMe_3)].

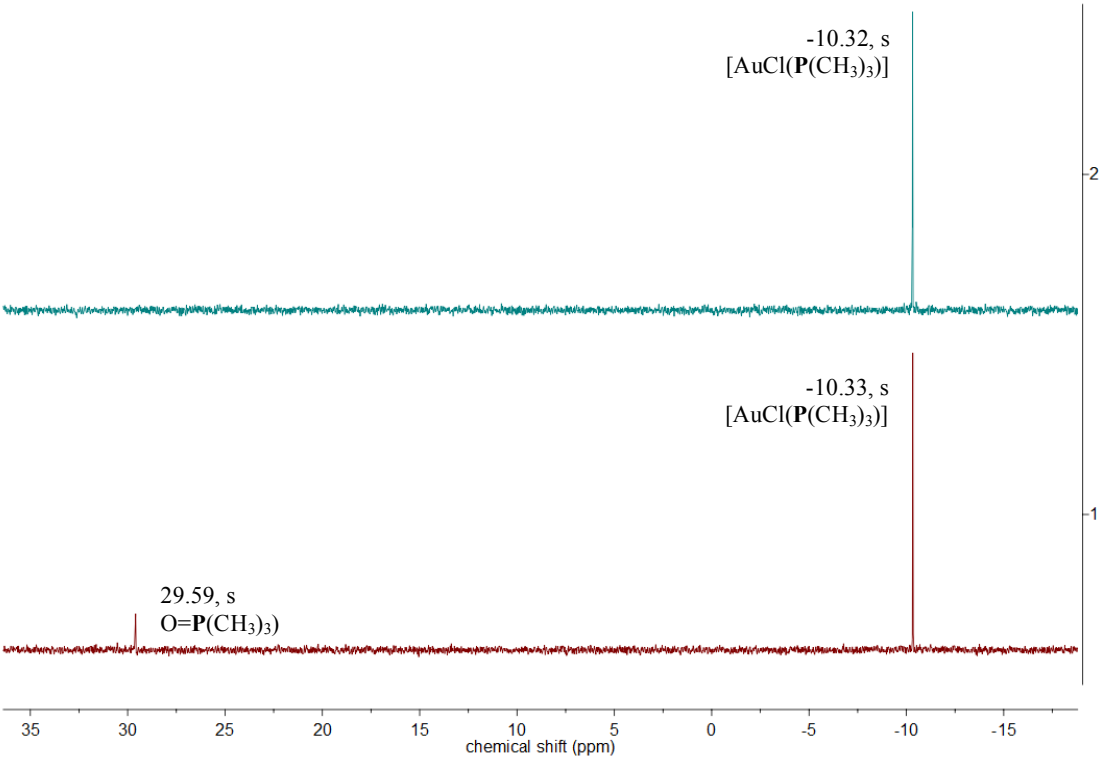


Fig. S29: $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$) spectra of (1): the white precipitate formed by addition of HCl to the hydrogel of **1**, it is, [AuCl(PMe_3)] with traces of trimethylphosphine oxide; (2) pure [AuCl(PMe_3)].

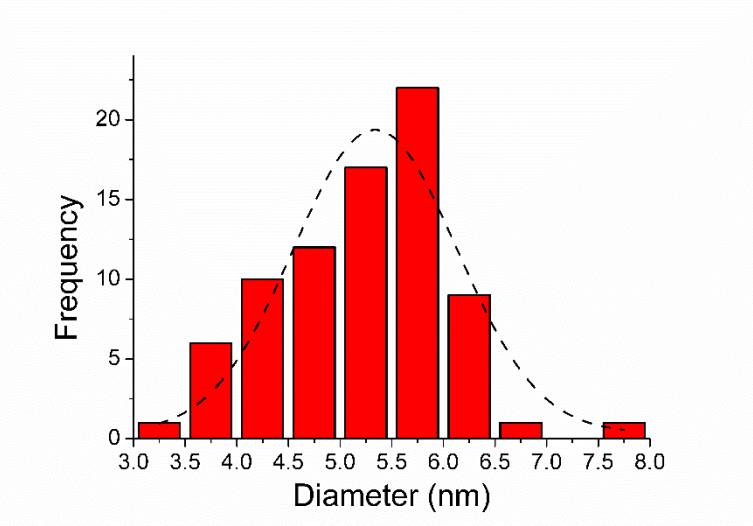


Fig. S30: Frequency histogram for the Au(I) UNWs diameter (Ø = 5.3 ± 1.9 nm).

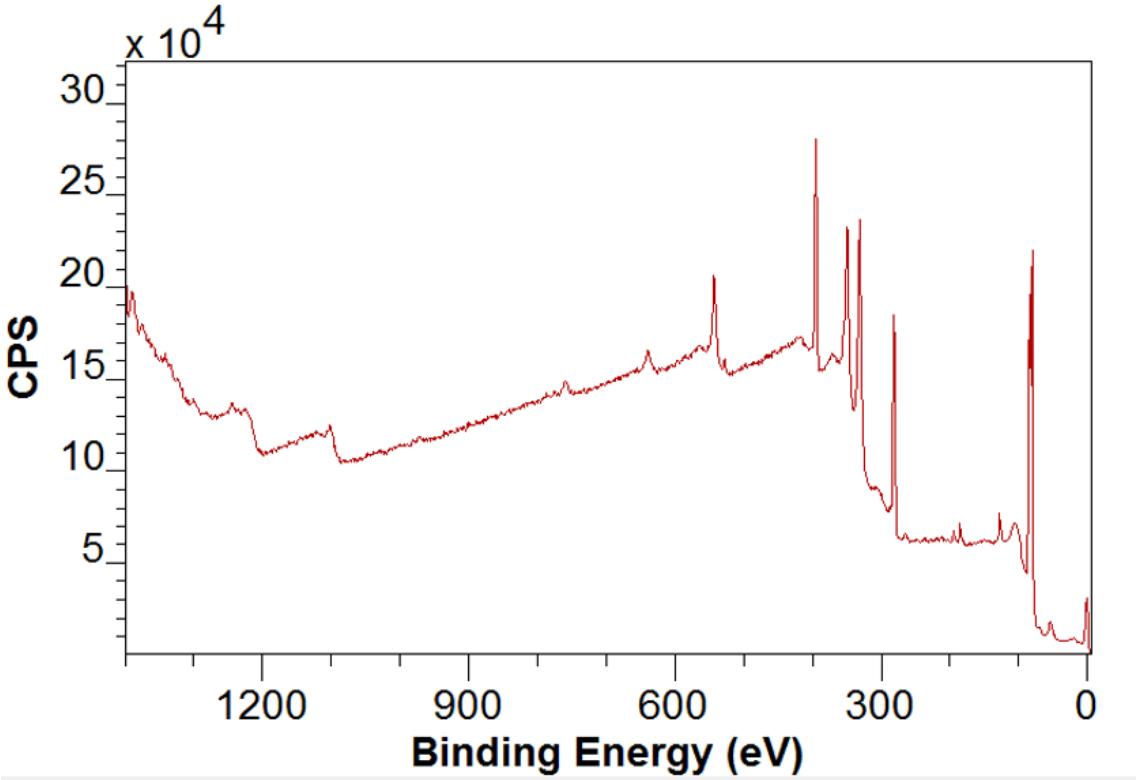


Fig. S31: XPS wide spectrum.

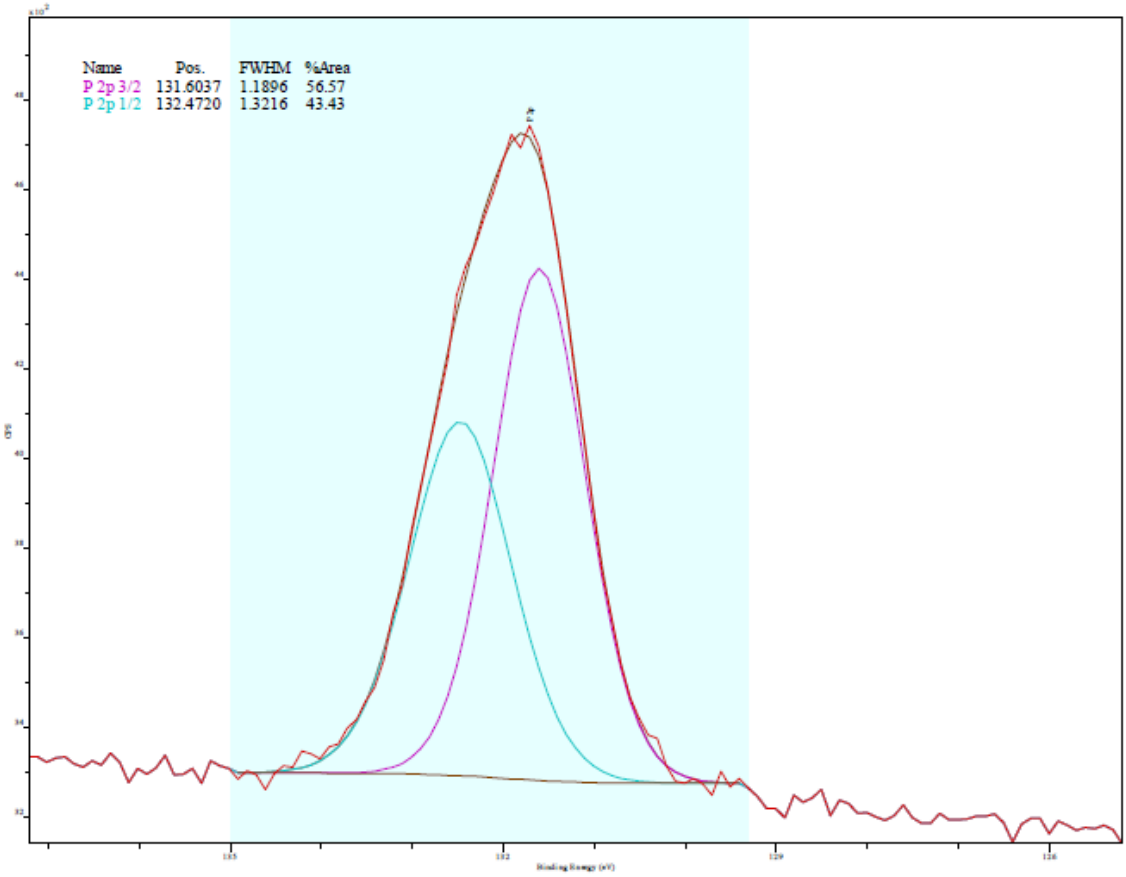


Fig. S32: XPS spectrum in the P 2p region.

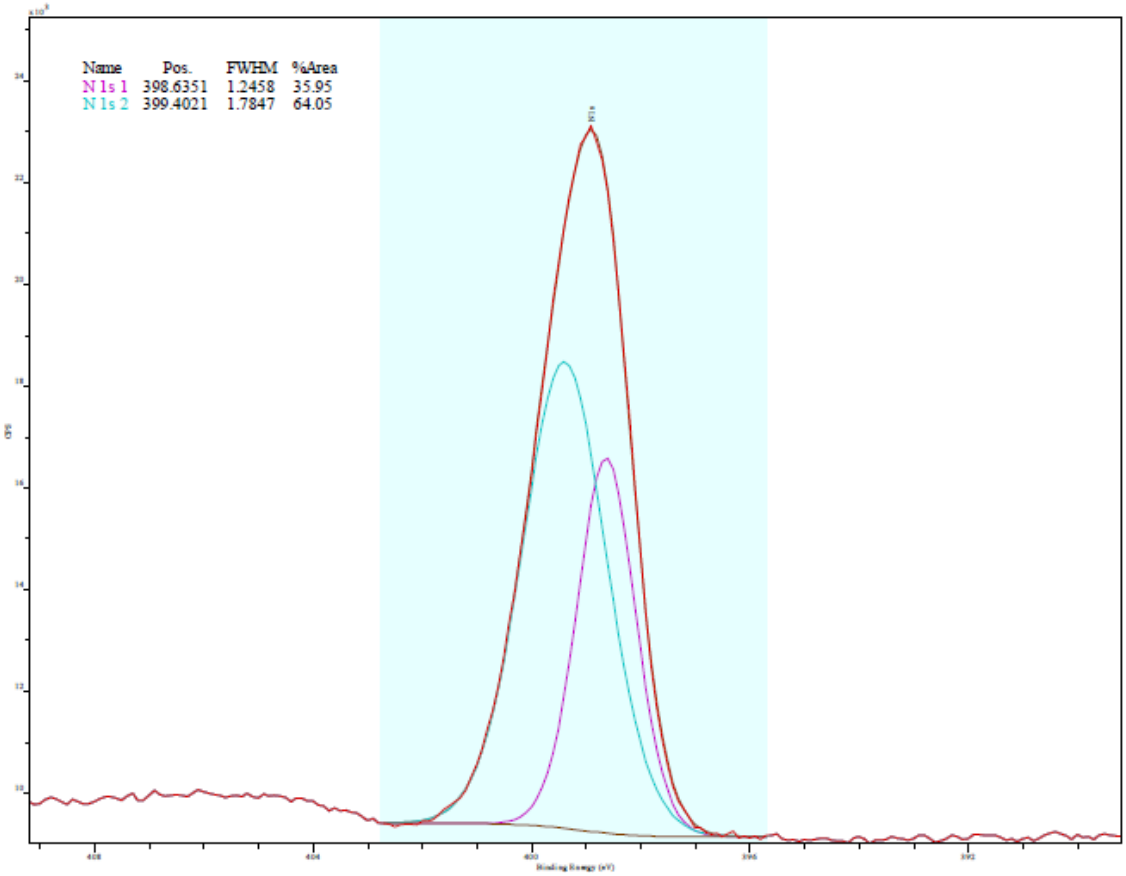


Fig. S33: XPS spectrum in the N 1s region.

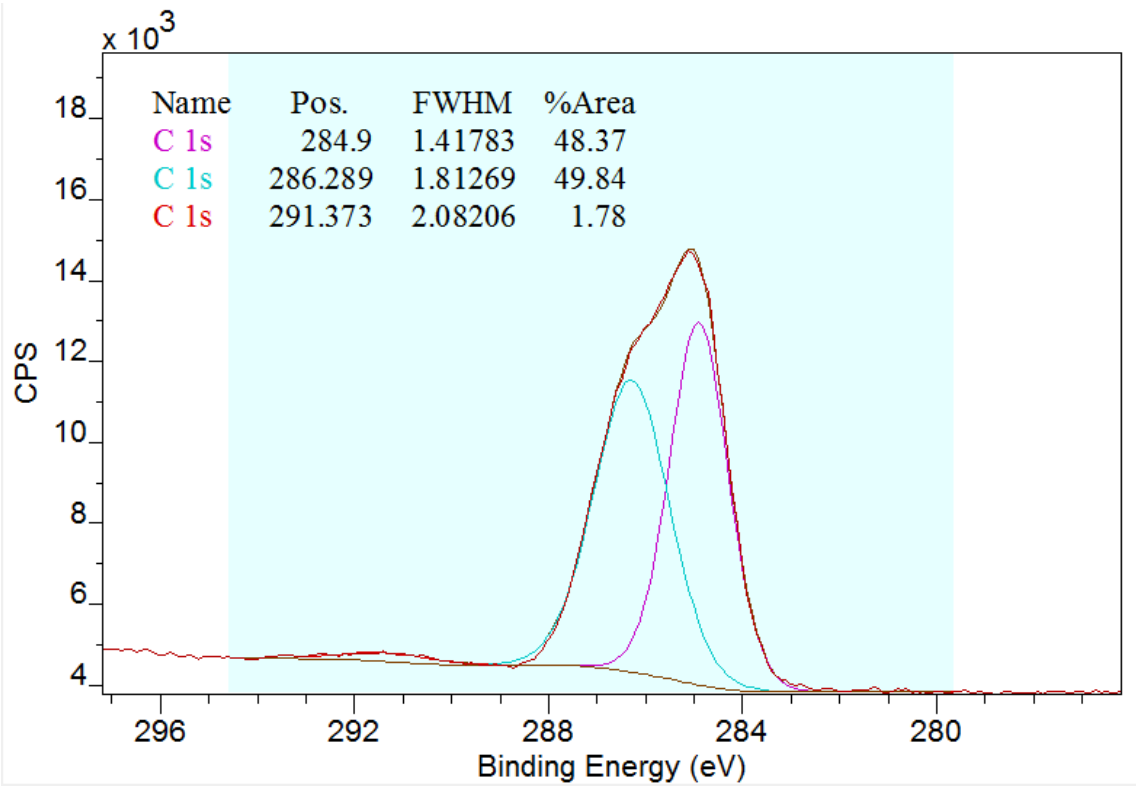


Fig. S34: XPS spectrum in the C 1s region.

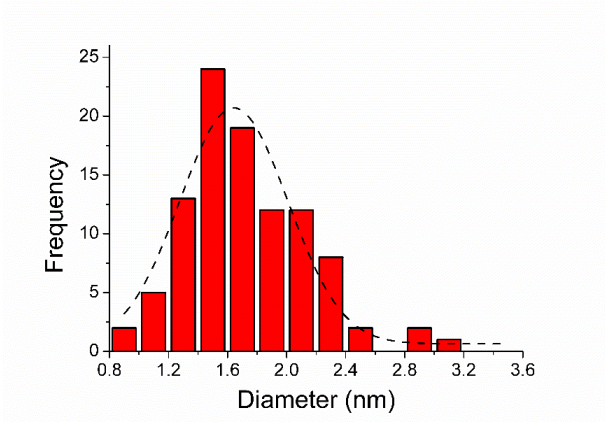


Fig. S35: Frequency histogram of the electronically produced Au UNPs.

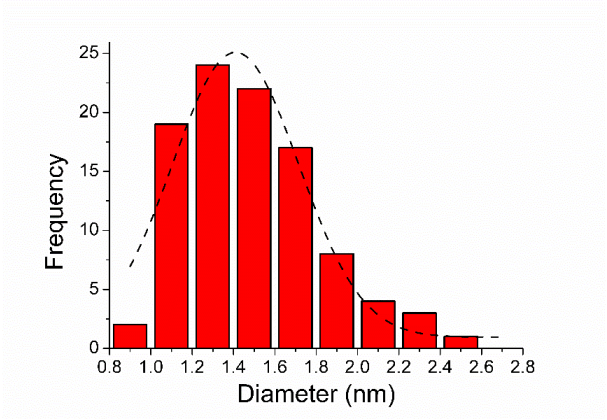


Fig. S36: Frequency histogram of the thermally produced Au UNPs.

Table S9: Geometry in *xyz* format for model [Au(^{9}*N*-adeninate)(PH_3)] fully optimized at the DFT/PBE1PBE level of theory.

Au	-1.43230800	-0.11889700	0.00054600
P	-3.60332800	0.53350000	-0.00055800
N	0.50563400	-0.67164500	0.00006500
N	2.41329800	-1.89378000	0.00015600
N	3.88227800	1.49319600	0.00637500
N	1.48391800	1.54889500	-0.00265400
C	1.10458900	-1.90394400	0.00399300
C	2.70961300	-0.55471400	-0.00769300
C	1.54570100	0.21406100	-0.00547300
C	3.91907500	0.15947100	-0.00635900
C	2.69000400	2.09485400	0.00429000
H	0.50474200	-2.81455600	0.01059200
H	2.72162800	3.19018800	0.01227500
N	5.11689600	-0.46169200	-0.04694300
H	5.93241700	0.09665500	0.16160500
H	5.13919200	-1.45137200	0.15262100
H	-4.43115600	0.14366000	1.09519400
H	-4.43502100	0.12507700	-1.08655000
H	-3.85760500	1.93753400	-0.01202400

Table S10: Geometry in *xyz* format for model **1a** (aurophilicity at equilibrium distance, 3.39 Å).

Au	-0.10483083	0.00554942	-0.00216650
P	-0.10483083	0.00554942	2.26475850
N	-0.07643683	0.00554942	-2.01719550
H	-0.77205783	-1.05758058	2.94483950
H	-0.67857683	1.12224142	2.94425550
H	1.16551217	-0.04879758	2.91234950
C	-1.08307083	0.05398142	-2.94545550
C	1.06989917	-0.04766158	-2.75836250
N	-0.69698783	0.03852342	-4.19587150
H	-2.12674883	0.10104542	-2.63305350
N	2.32865117	-0.11561558	-2.31504350
C	0.66929017	-0.02412758	-4.09427750
C	3.19712417	-0.16686958	-3.31298650
C	1.69991617	-0.07814858	-5.04703750
N	2.96427917	-0.15630758	-4.62797150
H	4.25339717	-0.22947658	-3.02805050
N	1.45220817	-0.02408958	-6.37292650
H	2.20988517	-0.27168658	-6.99336150
H	0.50179317	-0.17475558	-6.67919650
H	0.95558783	3.08918758	0.03631450
C	-0.09418017	3.40313758	0.02068550
N	-0.29097717	4.72404058	0.02018250
N	-0.99111017	2.42952958	0.00153950
C	-1.54565417	5.17779658	0.00506850
C	-2.23876017	2.90740258	-0.02321050
C	-2.60318417	4.25384458	-0.02329450
N	-1.76024417	6.50988858	0.04687450
N	-3.40575817	2.19817458	-0.06004350
N	-3.96699417	4.39312358	-0.06310650
H	-0.96932317	7.10976758	-0.13995850
H	-2.68784117	6.84283358	-0.17335250
Au	-3.48937017	0.18471658	-0.07211350
C	-4.38732017	3.15386058	-0.08290150
P	-3.55159417	-2.08132742	-0.08328950
H	-5.43975917	2.87039958	-0.11602750
H	-4.15524617	-2.73960442	-1.19694250
H	-4.22627217	-2.74782442	0.98371250
H	-2.29902217	-2.76375342	-0.04510650

Table S11: Geometry in *xyz* format for model **1b** fully optimized at the DFT/PBE1PBE level of theory.

Au	-6.04453900	0.31621300	-0.37207800
N	-4.10506400	0.01429000	0.08973900
N	-1.90871100	0.29218000	0.52017100
N	-4.27253000	-2.36903300	0.46638100
N	-2.17513500	-3.35538500	1.07801800
C	-3.03987400	0.86032500	0.18003800
C	-3.59875800	-1.21647200	0.40688300
C	-3.47989600	-3.37178700	0.81538500
C	-1.50920700	-2.19208900	1.00461700
C	-2.24157900	-1.03340400	0.66556400
Au	6.04453800	-0.31621600	-0.37207700
N	4.10506600	-0.01428600	0.08974200
N	1.90871000	-0.29217200	0.52016700
N	4.27253400	2.36903600	0.46638200
N	2.17513800	3.35539300	1.07801100
C	3.03987300	-0.86032000	0.18003800
C	3.59876000	1.21647600	0.40688300
C	3.47990000	3.37179200	0.81538200
C	1.50920800	2.19209700	1.00460800
C	2.24158000	1.03341100	0.66556000
H	-3.14570700	1.92680200	-0.01956900
H	-3.95874200	-4.35480900	0.89529000
H	3.14570600	-1.92679700	-0.01956800
H	3.95874700	4.35481400	0.89528700
N	0.20083300	2.18673700	1.27359800
H	-0.41511100	1.39805200	1.02919600
H	-0.21278600	3.09527500	1.43174100
N	-0.20083300	-2.18672500	1.27361200
H	0.21278700	-3.09526300	1.43175400
H	0.41511100	-1.39804200	1.02920500
P	8.23160300	-0.61654400	-0.88464000
H	8.56437500	-1.13038400	-2.17428000
H	9.06573000	0.54095800	-0.85974100
H	9.00728100	-1.49479400	-0.06921400
P	-8.23160500	0.61653300	-0.88463800
H	-8.56437700	1.13044800	-2.17424800
H	-9.06571200	-0.54098500	-0.85981700
H	-9.00730500	1.49471900	-0.06916400

Table S12: Geometry in *xyz* format for model **3a** fully optimized at the DFT-D3/PBE1PBE level of theory.

Au	0.07080100	-1.69646300	-0.51312800
Au	-0.03282600	1.36795500	-0.87120600
P	-1.85131000	-1.78614000	0.69102200
C	-2.00997500	-3.22281800	1.88107200
H	-1.11466400	-3.21202700	2.51981200
H	-2.00640000	-4.16236700	1.30823600
C	-2.15904300	-0.40678900	1.91775600
H	-2.24406700	0.55194400	1.38442500
H	-1.28444000	-0.35739300	2.58374600
C	-3.55718100	-1.88316200	-0.07251300
H	-3.60854900	-2.78342800	-0.70297900
H	-3.72735200	-1.01506700	-0.72291100
N	-3.23070300	-3.10938500	2.65502100
N	-3.36267200	-0.67257400	2.67889700
N	-4.55926900	-1.94316300	0.97290000
C	-3.25441200	-1.89558300	3.45940900
H	-4.12481600	-1.94987200	4.13010500
H	-2.34536700	-1.85355900	4.07701100
C	-4.54058600	-0.75997900	1.82376400
H	-4.61259900	0.14089300	1.20050000
H	-5.42954100	-0.79412400	2.47003700
C	-4.41521700	-3.12505100	1.80807300
H	-5.29913600	-3.19006700	2.45957400
H	-4.39422600	-4.02135800	1.17054200
P	1.99205400	1.69547900	0.09750200
C	2.41552200	0.68204700	1.61168700
H	2.42851600	-0.38135100	1.34142100
H	1.61875300	0.81731500	2.35752500
C	3.61551500	1.52829100	-0.82282400
H	3.61113500	2.22920500	-1.67059300
H	3.70519500	0.51435500	-1.23437300
C	2.30014200	3.38704300	0.83962600
H	1.49834800	3.60880200	1.56002000
H	2.25169100	4.14477700	0.04314600
N	4.72171400	1.81787700	0.06641400
N	3.69593200	1.09050700	2.15081400
N	3.59731800	3.43858000	1.49974100
C	4.77976300	0.89954100	1.19673300
H	5.73124700	1.06629400	1.72141200
H	4.76990700	-0.13477900	0.83009000
C	4.69512800	3.17813500	0.55951400
H	5.63680500	3.38345200	1.08746200
H	4.61667600	3.88022400	-0.28277500
C	3.69142200	2.46676700	2.59706800
H	2.85475100	2.63120500	3.29119100
H	4.62722900	2.66995300	3.13637600
N	1.93451100	-1.73287200	-1.36580600
C	2.38790200	-1.37511100	-2.60343600
H	1.69848600	-1.01330100	-3.36591600
N	3.68474100	-1.49878600	-2.79030100
C	4.12157700	-1.97960900	-1.58525000
C	3.05073700	-2.12879700	-0.70005700

N	3.15766900	-2.56027200	0.56955100
C	4.40955400	-2.84694500	0.90692300
H	4.55907300	-3.20638600	1.93068200
N	5.51065200	-2.74473900	0.16821000
C	5.39584000	-2.30981100	-1.09343900
N	6.50121200	-2.18035500	-1.83933000
H	7.37560000	-2.53045200	-1.47678500
H	6.40586900	-1.95633400	-2.81866800
N	-1.92567300	1.17461500	-1.61426600
C	-2.41549900	0.46369100	-2.67329100
H	-1.74430100	-0.07018300	-3.34573700
N	-3.72395200	0.47452800	-2.80336300
C	-4.12901000	1.25185800	-1.75099300
C	-3.03011400	1.68908000	-1.00828000
N	-3.08048100	2.43599500	0.10682700
C	-4.31973100	2.72889900	0.44969800
H	-4.44862400	3.33330300	1.35332300
N	-5.45699500	2.36576300	-0.15643600
C	-5.40101600	1.61774900	-1.27535300
N	-6.53520900	1.25096000	-1.87337300
H	-7.42600300	1.49912900	-1.44376700
H	-6.47905900	0.64793200	-2.67988500
O	4.48671800	5.78829200	2.69165100
H	4.04494200	5.00863300	2.24361900
H	3.80622100	6.48834700	2.76288500
O	1.12959600	-2.45523700	2.47772500
H	1.83944200	-2.55825300	1.76755200
H	1.60228900	-2.58874600	3.32365600
O	-8.12770500	2.38435000	0.16875400
H	-8.57325300	3.19368600	0.48720300
H	-7.12930400	2.53901700	0.25851100

Table S13: Geometry in *xyz* format for model **1c** fully optimized at the DFT-D3/PBE level of theory.

```
Au 1.337307 -0.290769 4.338821
 P 1.127181 -1.924738 5.883327
 N 1.420183 1.203951 2.958545
 N -0.936546 1.857111 3.134883
 N -1.505314 3.698496 1.662637
 N 2.083097 2.719123 1.372829
 C 0.311374 1.960003 2.633093
 C -1.767561 2.759389 2.595246
 C -0.251377 3.780528 1.170933
 C 0.740293 2.886529 1.654362
 C 2.518256 -2.073204 7.077945
 C 0.946764 -3.621712 5.195766
C -0.360172 -1.709160 6.942806
 C 2.434815 1.714532 2.168535
 H -2.812378 2.737115 2.961098
 H 2.326921 -2.886767 7.811878
 H 2.643201 -1.109816 7.616265
 H 3.457718 -2.286297 6.525069
 H 0.813938 -4.369696 6.008411
 H 1.849235 -3.876022 4.600374
 H 0.066430 -3.649090 4.519196
H -0.450170 -2.537649 7.679621
H -0.290665 -0.738442 7.477910
H -1.264789 -1.680751 6.298960
 H 3.452404 1.297679 2.217619
 N 0.026740 4.710942 0.215235
H -0.695539 5.386077 -0.035083
 H 0.990115 4.833338 -0.093843
```

Table S14: Geometry in *xyz* format for model **1d** fully optimized at the DFT-D3/PBE level of theory.

```
Au 0.714525 0.259568 4.972097
P 0.762620 -1.446588 6.466496
N 0.715130 1.816936 3.632679
N 1.045423 0.599877 1.516907
N 0.908823 2.047935 -0.424299
N 0.380635 3.911161 2.760271
C 0.811738 1.704694 2.262371
C 1.082267 0.868863 0.201783
C 0.662056 3.140591 0.331911
C 0.605390 3.007160 1.743519
C 2.143731 -2.627695 6.168582
C -0.749359 -2.480736 6.513427
C 0.988964 -0.897431 8.203202
C 0.454476 3.157178 3.854852
Au -2.216667 0.036633 4.046395
P -1.949644 -1.499159 2.398814
N -2.516197 1.460739 5.495430
N -2.667419 3.526006 6.481373
N -2.612195 1.430867 9.563395
N -2.461314 0.093813 7.544952
C -2.596983 2.833801 5.346683
C -2.628848 2.543263 7.448205
C -2.531562 1.258026 6.858787
C -2.665857 2.587383 8.866035
C -2.514878 0.279058 8.874012
C -2.230191 -0.809288 0.720732
C -0.287623 -2.265296 2.299881
C -3.122662 -2.913475 2.520514
H 1.277184 0.003892 -0.462538
H 2.133536 -3.446929 6.921391
H 3.112579 -2.087203 6.219256
H 2.042913 -3.061274 5.150511
H -0.637902 -3.303946 7.253784
H -0.943658 -2.907638 5.506542
H -1.591128 -1.800352 6.798963
H 1.034224 -1.773074 8.887771
H 1.924353 -0.305657 8.288610
H 0.126767 -0.254876 8.481498
H 0.308548 3.541771 4.875365
H -2.585219 3.294067 4.347322
H -2.470065 -0.639934 9.491090
H -3.251863 -0.378604 0.661430
H -2.110058 -1.599341 -0.053039
H -1.486864 -0.003828 0.541295
H 0.439911 -1.436137 2.108556
H -0.044064 -2.758725 3.264669
H -0.251911 -3.014123 1.477475
H -2.971370 -3.434582 3.490162
H -2.962541 -3.631906 1.686477
H -4.165981 -2.534121 2.491027
N 0.458523 4.338679 -0.279911
H 0.606716 4.407548 -1.286909
```

H 0.365365 5.176298 0.294188
N -2.740144 3.765966 9.541244
H -2.854265 3.746344 10.554651
H -2.865992 4.630379 9.015255

Table S15: Geometry in *xyz* format for model **1e** fully optimized at the DFT-D3/PBE level of theory.

```
Au 0.790474 0.226508 4.497019
P 0.976469 -0.750019 6.539332
N 0.774315 1.109053 2.641935
N -0.723533 3.010712 3.068783
N -1.217569 4.276655 1.066545
N 1.082640 1.425586 0.389332
C 0.043445 2.224248 2.285759
C -1.307791 4.005160 2.389791
C -0.444518 3.484848 0.293944
C 0.244765 2.401511 0.894328
C 2.593989 -1.603963 6.766837
C -0.259401 -2.053397 6.916642
C 0.897837 0.424183 7.946641
C 1.367292 0.692230 1.464217
Au -5.454883 -0.118258 4.634188
Au -2.319765 -0.077094 4.360422
P -5.862911 -1.955336 5.894325
P -2.325222 -1.255984 2.408640
N -5.155332 1.501034 3.414616
N -2.268673 1.046881 6.096053
N -1.892799 2.887583 7.411574
N -3.173697 0.576508 10.039012
N -3.118376 -0.467307 7.849630
N -5.597159 0.421607 1.253536
N -4.882637 1.773153 -0.627003
N -4.278041 3.468902 2.642481
C -1.823495 2.357013 6.188514
C -2.416261 1.863596 8.171721
C -2.653358 0.714121 7.374278
C -5.171127 1.438897 2.036150
C -2.703302 1.749281 9.556525
C -3.342895 -0.439273 9.174957
C -5.440946 0.692585 -0.053027
C -4.428137 2.772422 0.168339
C -4.614283 2.659684 1.574368
C -3.843302 -2.240655 2.097229
C -2.134102 -0.224498 0.906270
C -0.954369 -2.481718 2.305172
C -4.398191 -3.005095 6.232311
C -7.084742 -3.085357 5.105842
C -6.563410 -1.608576 7.555962
C -4.609488 2.738666 3.701470
H -1.969619 4.672857 2.963665
H 2.663874 -2.048205 7.784196
H 3.419548 -0.875606 6.622486
H 2.700104 -2.406089 6.006044
H 0.007302 -2.570064 7.864963
H -0.278602 -2.787797 6.083523
H -1.269902 -1.599028 7.019107
H 0.937945 -0.123965 8.913339
H 1.757316 1.123895 7.877667
H -0.038470 1.018391 7.895880
```

H 2.030252 -0.186399 1.446903
H -1.431358 2.865487 5.290208
H -3.716332 -1.382975 9.619421
H -5.793652 -0.088980 -0.754022
H -4.689334 -1.528490 1.933369
H -4.058794 -2.891362 2.970489
H -3.705463 -2.867543 1.188524
H -1.081870 0.110569 0.803187
H -2.424699 -0.808826 0.006709
H -2.787361 0.668222 0.986570
H 0.012547 -1.944543 2.412622
H -0.977660 -3.019821 1.332141
H -1.047677 -3.211833 3.137374
H -4.678295 -3.898852 6.832406
H -3.679856 -2.355726 6.787217
H -3.939051 -3.324144 5.272500
H -7.258818 -3.983808 5.737970
H -6.703189 -3.399709 4.111166
H -8.043318 -2.546302 4.951996
H -6.758760 -2.554739 8.107421
H -5.830845 -0.992368 8.118240
H -7.508735 -1.036386 7.448506
H -4.462394 3.063946 4.742114
N -3.802253 3.838521 -0.407565
H -3.542190 3.688992 -1.387092
H -3.110648 4.346795 0.172938
N -0.379600 3.723835 -1.050663
H -0.685862 4.640276 -1.383018
H 0.331123 3.220423 -1.584209
N -2.494307 2.783304 10.413911
H -2.799527 2.689268 11.382921
H -2.232188 3.692648 10.033071