Supplementary Information (SI) for Nanoscale.

Sulfur functionalized diamondoid phosphines enable building nanocomposites interfacing sp^3-carbon and gold nanolayer

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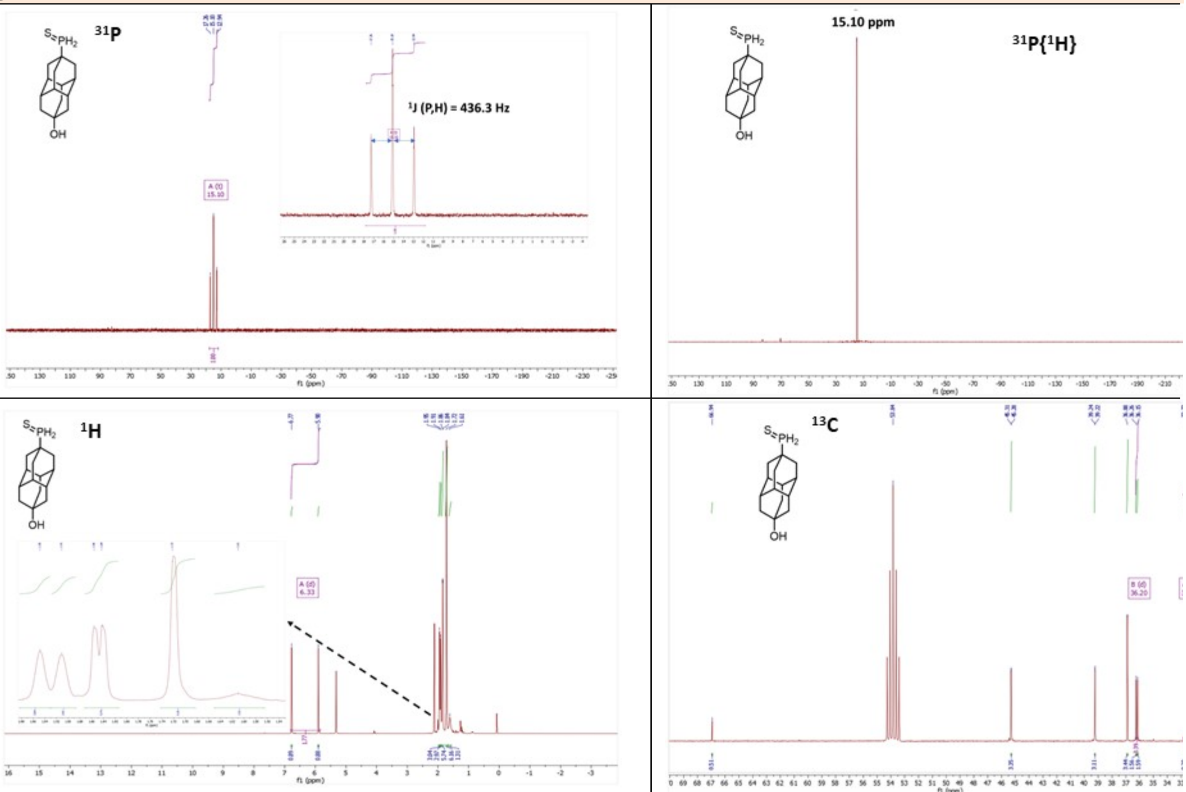
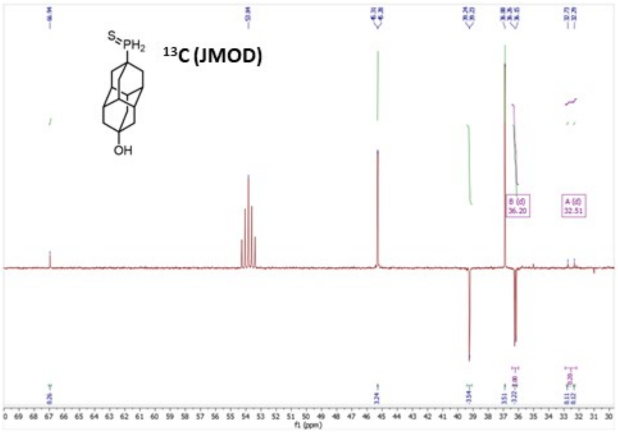
CONTENT

NMR characterization of difunctionalized diamantanes 2,3 and 4

Figure S1a. ^{31}P, ^{1}H and ^{13}C NMR of **2**





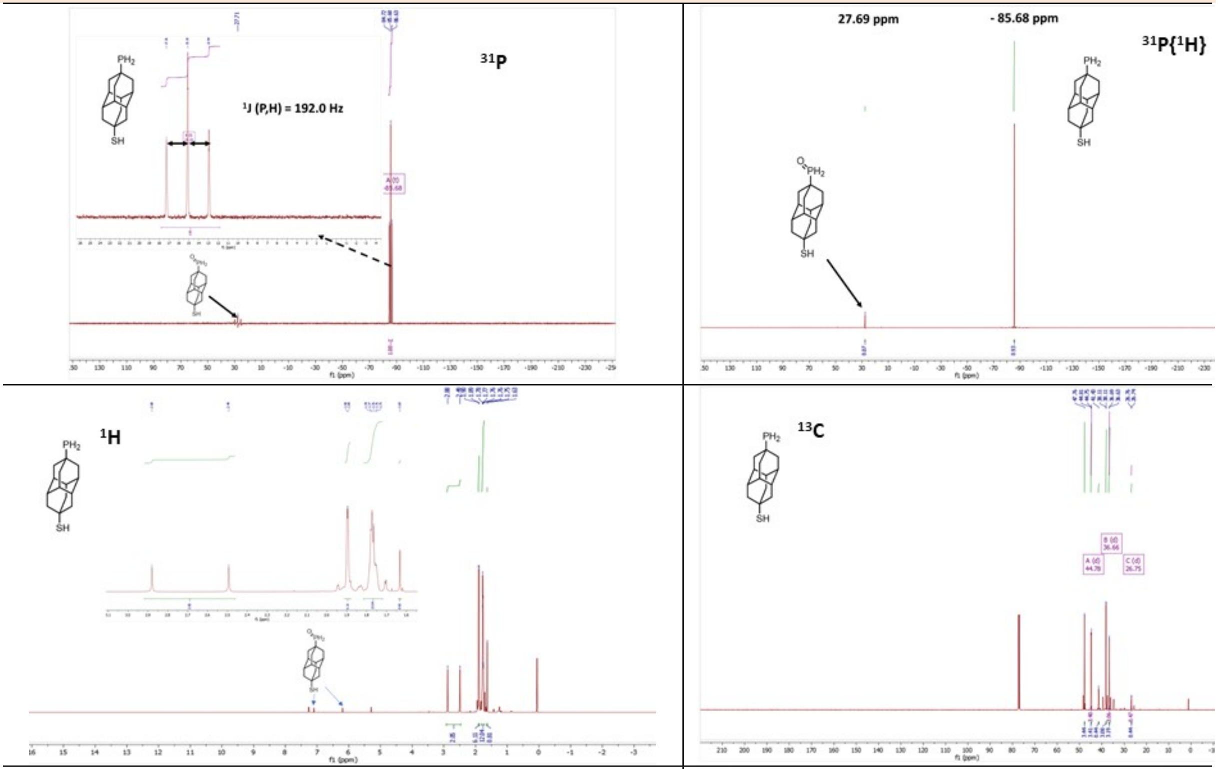
^{1}H NMR (500 MHz, 298 K, CD_2Cl_2) δ = 6.33 (d, ^{1}J(P,H) = 435.0 Hz, 2H, S=PH), 1.98 – 1.93 (m, 3H, CH, H-2,6,12), 1.92 – 1.88 (m, 3H, CH, H-1,7,11), 1.87 – 1.81 (m, 6H, CH_2, H-3,5,13), 1.74 – 1.68 (m, 6H, CH_2, H-8,10,14), 1.61 (s, 1H, O-H) ppm.

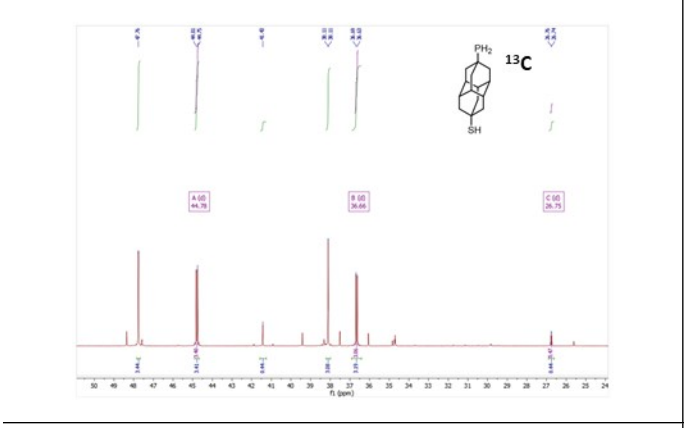
^{13}C NMR (125.7 MHz, 298K, CD_2Cl_2) δ = 66.94 (s, 1C, C_q, C-9), 45.32 – 45.26 (m, 3C, CH_2, C-8,10,14), 39.27 – 39.20 (m, 3C, CH, C-1,7,11), 36.93 – 36.83 (m, 3C, CH_2, C-3,5,13), 36.20 (d, ^{3}J(C,P) = 13.8 Hz, 3C, CH, C-2,6,12), 32.51 (d, ^{1}J(C,P) = 55.3 Hz, 1C, C-4).

^{31}P NMR (202 MHz, 298 K, CD_2Cl_2) δ = 15.10 (t, ^{1}J(P-H) = 436.3 Hz, S=PH) ppm.

NMR characterization of 9-phosphinodiamantane-4-thiol, 3

Figure S1b. ^{31}P, ^{1}H and ^{13}C NMR of **3**





^{1}H NMR (500 MHz, 298 K, Chloroform-d): δ = 2.69 (d, ^{1}J = 192.0 Hz, 2H, PH), 1.91 – 1.88 (m, 6H, CH, H-1,2,6,7,11,12), 1.80 – 1.73 (m, 12H, CH_2, H-3,5,8,10,13,14), 1.63 (s, 1H, SH) ppm.

^{13}C NMR (127 MHz, 298 K, Chloroform-d) δ = 47.76 (s, 3C, CH_2, C-8,10,14), 44.78 (d, ^{2}J(C,P) = 8.6 Hz, 3C, CH_2, C-3,5,13), 41.43 (s, 1C, C-9), 38.11 (m, 3C, CH, C-1,7,11), 36.66 (d, ^{3}J(C,P) = 8.2 Hz, 3C, CH, C-2,6,12), 26.75 (d, ^{1}J(C,P) = 3.1 Hz, 1C, C-4) ppm.

^{31}P NMR (202 MHz, 298 K, CDCl3): δ = -85.68 (t, ^{1}J(P-H) = 192.0 Hz, PH_2) ppm.

Synthesis of (9-thioacetyldiamant-4-yl)phosphoryl dichloride (3) from (9-hydroxydiamant-4-yl) phosphoryl dichloride (1a) via 1b:

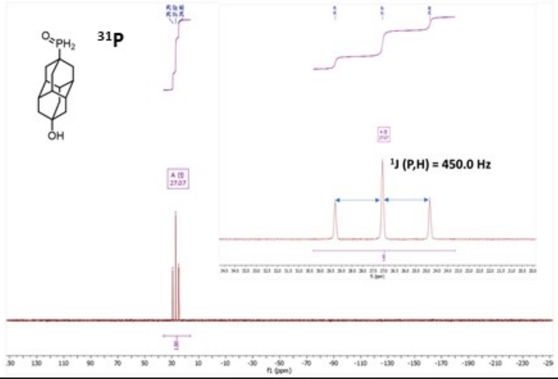
320.2 mg (1 mmol, 1 eq.) of (9-hydroxydiamant-4-yl) phosphoryl dichloride (**1a** achieved from literature report ***J. Org. Chem. 2016, 81, 8759−8769***) were dissolved with 1.5 mL (0.02 mol, 20 eq.) of freshly distilled thioacetic acid and 50 µL (0.6 mmol, 0.6 eq.) of TfOH (triflic acid). The solution was stirred during 18h at room temperature; after addition of 2 mL of water and extraction three times with 5 mL of DCM, the organic phases were washed three times with water (3x5 mL) and dried over sodium sulfate. The phase was filtered and the solvent was evaporated. The colorless solid was obtained by purification on silica column with diethyl ether:n-pentane (1:4) giving 310.2 mg (82 %) of (9-thioacetyldiamant-4-yl) phosphoryl dichloride (**1b**).

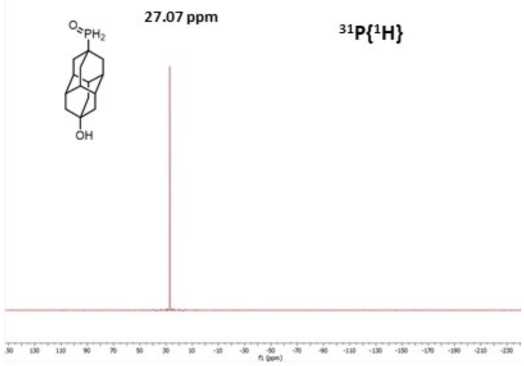
100 mg (0.26 mmol, 1 eq.) of (9-thioacetyldiamant-4-yl) phosphoryl dichloride (**1b**) were weighed and poured into a Schlenk tube having a magnetic bar, previously dried under vacuum

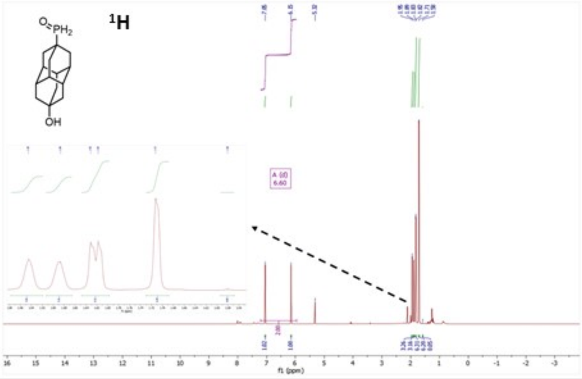
and placed under a flow of nitrogen. The Schlenk was isolated and a nitrogen-vacuum sweep cycle is carried out three times, while initiating magnetic stirring. The Schlenk was then cooled to –60 °C using an acetone-liquid nitrogen bath. 2 mL of THF was poured, followed by a dropwise addition of 0.44 mL of LiAlH4 (2.4 M in THF, 1.06 mmol, 4 eq.). Stirred for 5 hours at –20 ° C. At the end of the 5 hours of stirring, 1 mL of HCl (5 %, or saturated NH_4Cl) was added to the mixture. Extraction then takes place with frozen dichloromethane (3x6 mL), followed by drying with $MgSO_4$ and filtered through a funnel and cotton wool into a 100 mL flask. The solvent was evaporated by rotary evaporator. The compound phosphinodiamantane-4-thiol (**3**, 57.74 mg, 89 % yield) as a white powder was dried under vacuum and kept under argon in a fridge at –28 ° C.

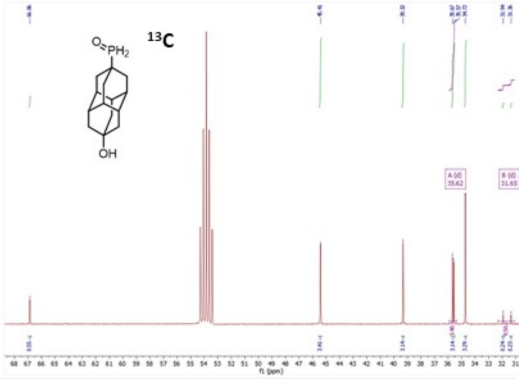
NMR characterization of (9-hydroxydiamant-4-yl)phosphine oxide, 4

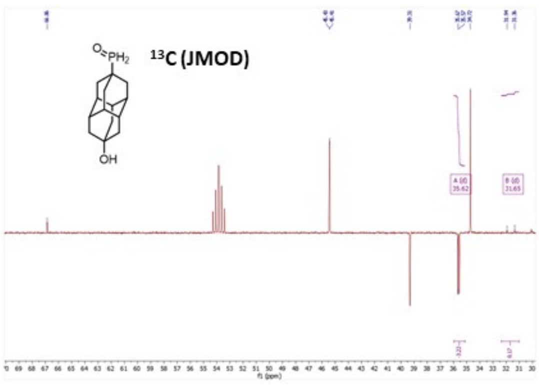
Figure S1c. ^{31}P, ^{1}H and ^{13}C NMR of **4**











^{1}H NMR (500 MHz, 298 K, CD_2Cl_2) δ = 6.60 (d, ^{1}J(P,H) = 450.0 Hz, 2H, O=PH), 1.98 – 1.92 (m, 3H, CH, H-2,6,12), 1.92 – 1.87 (m, 3H, CH, H-1,7,11), 1.85 – 1.79 (m, 6H, CH_2, H-3,5,13), 1.73 – 1.68 (m, 6H, CH_2, H-8,10,14), 1.58 (s, 1H, O-H) ppm.

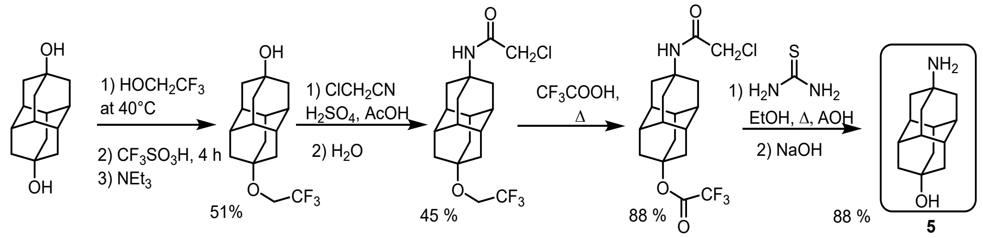
^{13}C NMR (125.7 MHz, 298K, CD_2Cl_2) δ = 66.86 (s, 1C, C_q, C-9), 45.52 – 45.33 (m, 3C, CH_2, C-8,10,14), 39.42 – 39.22 (m, 3C, CH, C-1,7,11), 35.62 (d, ^{3}J(C,P) = 13.0 Hz, 3C, CH, C-2,6,12), 34.8 – 34.62 (m, 3C, CH_2, C-3,5,13), 31.65 (d, ^{1}J(C,P) = 73.2 Hz, 1C, C-4).

^{31}P NMR (202 MHz, 298 K, CD_2Cl_2) δ = 27.07 (t, ^{1}J(P-H) = 450.0 Hz, O=PH) ppm.

Synthesis of difunctionalized diamondoid 5

Figure S2.

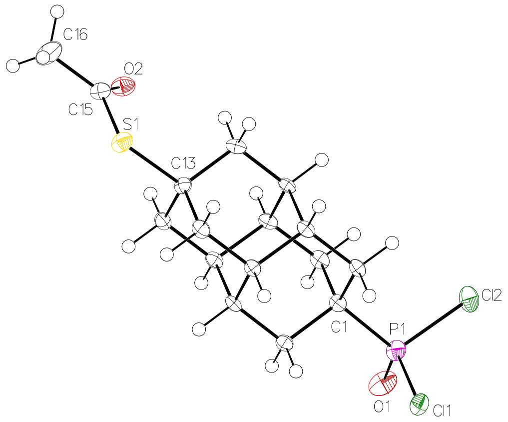
H. Schwertfeger, C. Würtele, M. Serafin, H. Hausmann, R. M. K. Carlson, J. E. P. Dahl, and P. R. Schreiner, J. Org. Chem. 2008, 73, 7789–7792.



XRD of (9-thioacetyldiamant-4-yl)phosphoryl dichloride

Compound	POCl2-Diam-SAc
Formula	$C_{16}H_{21}Cl_2O_2PS$
$D_{calc.}$/ g cm^{-3}	1.468
μ/mm^{-1}	0.597
Formula Weight	379.26
Color	clear light colorless
Shape	needle-shaped
Size/mm^3	0.66x0.08x0.08
T/K	110.0(1)
Crystal System	monoclinic
Space Group	$P2_1/n$
a/Å	6.6911(2)
b/Å	21.7491(8)
c/Å	12.1069(5)
α/°	90
β/°	103.068(2)
γ/°	90
V/Å^3	1716.23(11)
Z	4
Z'	1
Wavelength/Å	0.71073
Radiation type	Mo $K_{\alpha 1}$
Θ_{min}/°	3.211
Θ_{max}/°	27.533
Measured Refl's.	44968
Indep't Refl's	3950
Refl's I≥2 σ(I)	3103
R_{int}	0.0618
Parameters	200
Restraints	0
Largest Peak	0.457
Deepest Hole	-0.263
GooF	1.079
wR_2 (all data)	0.0834
wR_2	0.0754
R_1 (all data)	0.0556
R_1	0.0363

Figure S3. Crystal Data and Experimental (R_1 = 3.63%)



Experimental. Single clear, colorless needle-shaped crystals of 9-thioacetyldiamant-4-yl)phosphoryl dichloride recrystallized from a mixture of diethyl ether and pentane by slow evaporation. A suitable crystal with dimensions 0.66 x 0.08 x 0.08 mm^3 was selected and mounted on a MITIGEN holder oil on a Nonius Kappa Apex II diffractometer. The crystal was kept at a steady T = 110.0(1) K during data collection. The structure was solved with the **ShelXT** 2018/2 (Sheldrick, 2018) solution program using dual methods and by using **Olex2** 1.5 (Dolomanov et al., 2009) as the graphical interface. The model was refined with **ShelXL** 2018/3 (Sheldrick, 2015) using full matrix least squares minimization on F^2.

Crystal Data. $C_{16}H_{21}Cl_2O_2PS$, M_r = 379.26, monoclinic, $P2_1/n$ (No. 14), a = 6.6911(2) Å, b = 21.7491(8) Å, c = 12.1069(5) Å, β = 103.068(2)°, $\alpha = \gamma$ = 90°, V = 1716.23(11) Å^3, T = 110.0(1) K, Z = 4, Z' = 1, μ(Mo $K_{\alpha 1}$) = 0.597, 44968 reflections measured, 3950 unique (R_{int} = 0.0618) which were used in all calculations. The final wR_2 was 0.0834 (all data) and R_1 was 0.0363 (I≥2 σ(I)).

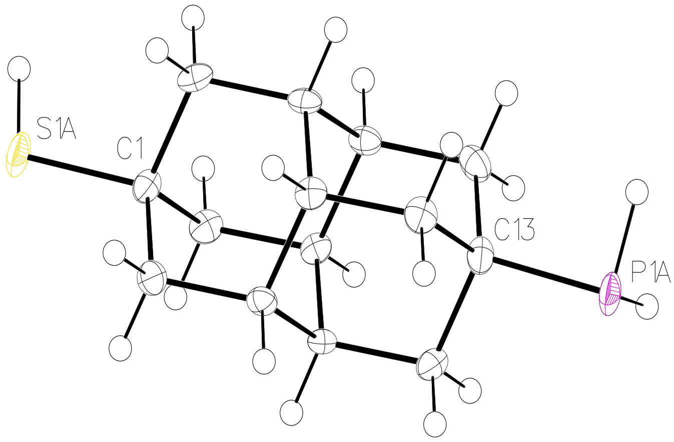
Structure Quality Indicators

Reflections:	d min (Mo) $2\Theta=55.1°$ 0.77	I/σ(I) 31.1	Rint 6.18%	Full 50.5° 99.9
Refinement:	Shift 0.000	Max Peak 0.5	Min Peak -0.3	GooF 1.079

A clear, colorless needle-shaped-shaped crystal with dimensions 0.66 x 0.08 x 0.08 mm^3 was mounted on a MITIGEN holder oil. Data were collected using a Nonius Kappa Apex II diffractometer operating at T = 110.0(1) K. Data were measured using ϕ and ω scans with Mo $K_{\alpha 1}$ radiation. The diffraction pattern was indexed and the total number of runs, and images was based on the strategy calculation from the program APEX4 (Bruker, 2021). The maximum resolution that was achieved was Θ = 27.533° (0.77 Å). The unit cell was refined using SAINT V8.40B (Bruker, 2016) on 8103 reflections, 18% of the observed reflections. Data reduction, scaling and absorption corrections were performed using SAINT V8.40B (Bruker, 2016). The final completeness is 99.90 % out to 27.533° in Θ. SADABS-2016/2 (Bruker, 2016) was used for absorption correction. wR_2(int) was 0.0674 before and 0.0558 after correction. The ratio of minimum to maximum transmission was 0.9108. The $\lambda/2$ correction factor is not present. The absorption coefficient μ of this material is 0.597 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.833 and 0.914. The structure was solved, and the space group $P2_1/n$ (# 14) determined by the ShelXT 2018/2 (Sheldrick, 2018) structure solution program using using dual methods and refined by full matrix least squares minimization on $\boldsymbol{F}^2$ using version 2018/3 of **ShelXL** 2018/3 (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Hydrogen atom positions were calculated geometrically and refined using the riding model. There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 4 and Z' is 1.

XRD of 9-phosphinothioldiamantan-4-ol, 2

Figure S4. Crystal Data and Experimental (R_1=3.75%)



Compound	**PH_2–Diam–SH**
Formula	$C_{14}H_{21}PS$
$D_{calc.}$/ g cm^{-3}	1.300
μ/mm^{-1}	0.346
Formula Weight	252.34
Color	clear light colorless
Shape	needle-shaped
Size/mm^3	0.34x0.14x0.07
T/K	110.0(1)
Crystal System	monoclinic
Space Group	$P2_1/c$
a/Å	7.7405(4)
b/Å	13.6302(7)
c/Å	12.6387(6)
$\alpha/^\circ$	90
$\beta/^\circ$	104.820(3)
$\gamma/^\circ$	90
V/Å^3	1289.08(11)
Z	4
Z'	1
Wavelength/Å	0.71073
Radiation type	Mo $K_{\alpha 1}$
$\Theta_{min}/^\circ$	2.239
$\Theta_{max}/^\circ$	27.498
Measured Refl's.	25147
Indep't Refl's	2954
Refl's I≥2 σ(I)	2209
R_{int}	0.0474
Parameters	155
Restraints	0
Largest Peak	0.382
Deepest Hole	-0.519
GooF	1.021
wR_2 (all data)	0.1051
wR_2	0.0913
R_1 (all data)	0.0613
R_1	0.0375

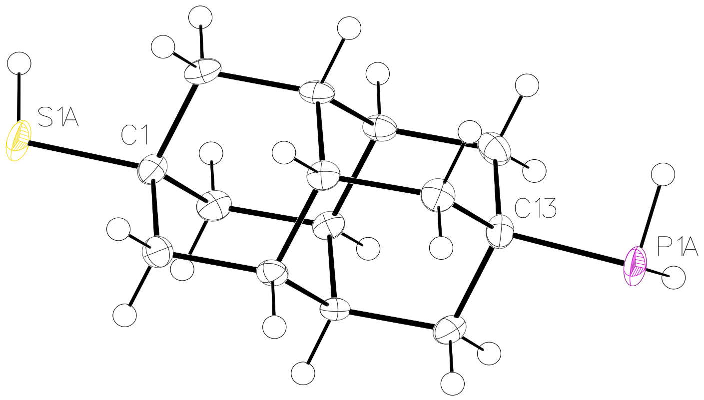
Experimental. Colorless needle-shaped crystals of 9-thioacetyldiamant-4-yl)phosphoryl dichloride recrystallized from DCM by slow evaporation. A suitable crystal with dimensions 0.34 x 0.14 x 0.07 mm^3 was selected and mounted on a MITIGEN holder oil on a Nonius Kappa Apex II diffractometer. The crystal was kept at a steady T = 110.0(1) K during data collection. The structure was solved with the **ShelXT** 2018/2 (Sheldrick, 2018) solution program using dual methods and by using **Olex2** 1.5 (Dolomanov et al., 2009) as the graphical interface. The model was refined with **ShelXL** 2018/3 (Sheldrick, 2015) using full matrix least squares minimization on $\boldsymbol{F^2}$.

Crystal Data. $C_{14}H_{21}PS$, M_r = 252.34, monoclinic, $P2_1/c$ (No. 14), a = 7.7405(4) Å, b = 13.6302(7) Å, c = 12.6387(6) Å, β = 104.820(3)°, $\alpha = \gamma$ = 90°, V = 1289.08(11) Å^3, T = 110.0(1) K, Z = 4, Z' = 1, μ(Mo $K_{\alpha 1}$) = 0.346, 25147 reflections measured, 2954 unique (R_{int} = 0.0474) which were used in all calculations. The final wR_2 was 0.1051 (all data) and R_1 was 0.0375 (I≥2 σ(I)).

Structure Quality Indicators

Reflections:	d min (Mo) 2Θ=55.0° 0.77	I/σ(I) 31.9	Rint 4.74%	Full 50.5° 100
Refinement:		Max Peak 0.4	Min Peak -0.5	GooF 1.021

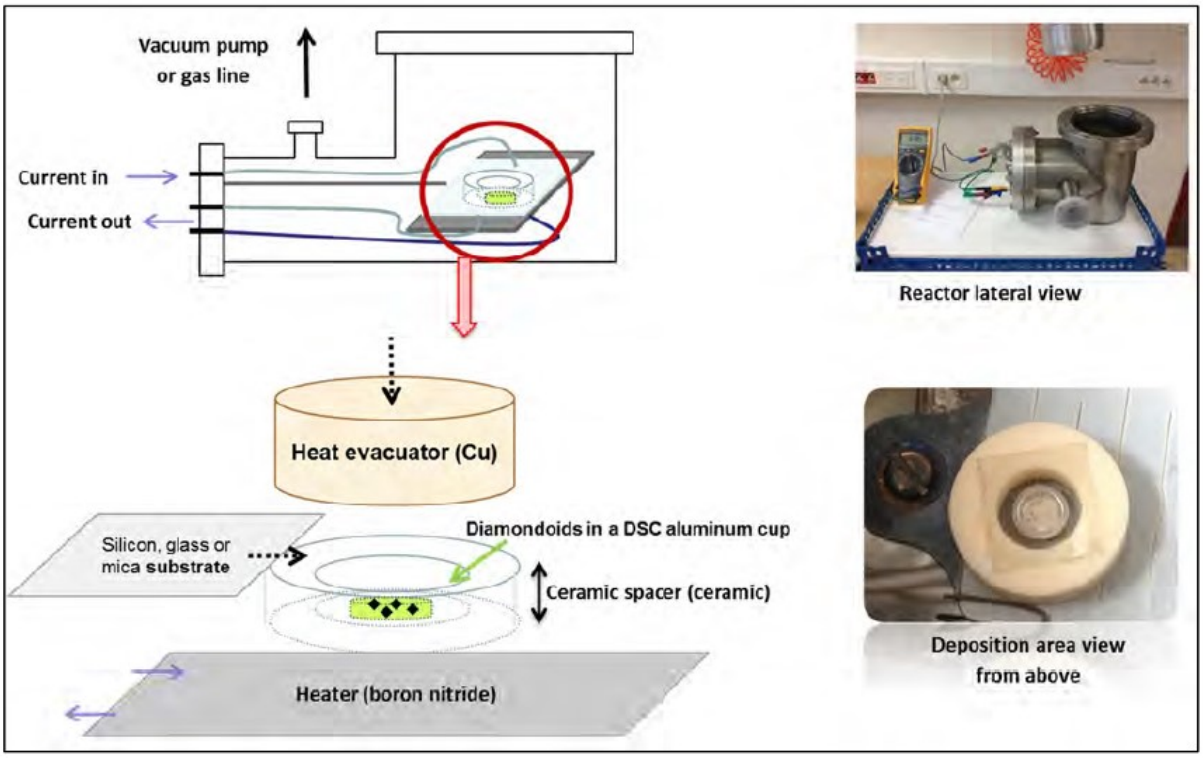
A colorless needle-shaped-shaped crystal with dimensions 0.34 x 0.14 x 0.07 mm^3 was mounted on a MITIGEN holder oil. Data were collected using a Nonius Kappa Apex II diffractometer operating at T = 110.0(1) K. Data were measured using ϕ and ω scans with Mo K$_{\alpha 1}$ radiation. The diffraction pattern was indexed and the total number of runs, and images was based on the strategy calculation from the program **APEX4** (Bruker, 2021). The maximum resolution that was achieved was Θ= 27.498° (0.77 Å). The unit cell was refined using **SAINT V8.40B** (Bruker, 2016) on 5410 reflections, 22% of the observed reflections. Data reduction, scaling and absorption corrections were performed using **SAINT V8.40B** (Bruker, 2016). The final completeness is 100.00 % out to 27.498° in Θ. **SADABS-2016/2** (Bruker, 2016) was used for absorption correction. wR_2(int) was 0.0543 before and 0.0500 after correction. The ratio of minimum to maximum transmission was 0.8998. The absorption coefficient μ of this material is 0.346 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions were 0.862 and 0.958. The structure was solved, and the space group $P2_1/c$ (# 14) determined by the **ShelXT 2018/2** (Sheldrick, 2018) structure solution program using dual methods and refined by full matrix least squares minimization on F^2 using version 2018/3 of **ShelXL** 2018/3 (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically, excepted minor disordered part (54(1)% / 46(1)%). Hydrogen atom positions were calculated geometrically and refined using the riding model, excepted H atoms on phosphorus atom, there were located in the Fourier difference maps. Their positional parameters were either fixed with U$_{iso}$(H) = 1.2U$_{eq}$(P). There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 4 and Z' is 1.



ORTEP view of major disordered part of title compound. Thermal ellipsoids are drawn at 50 % probability plot.

Physical vapor deposition of diamantane derivatives and conditions

Figure S5. Vapor Deposition under Controlled atmosphere (VD-CA)

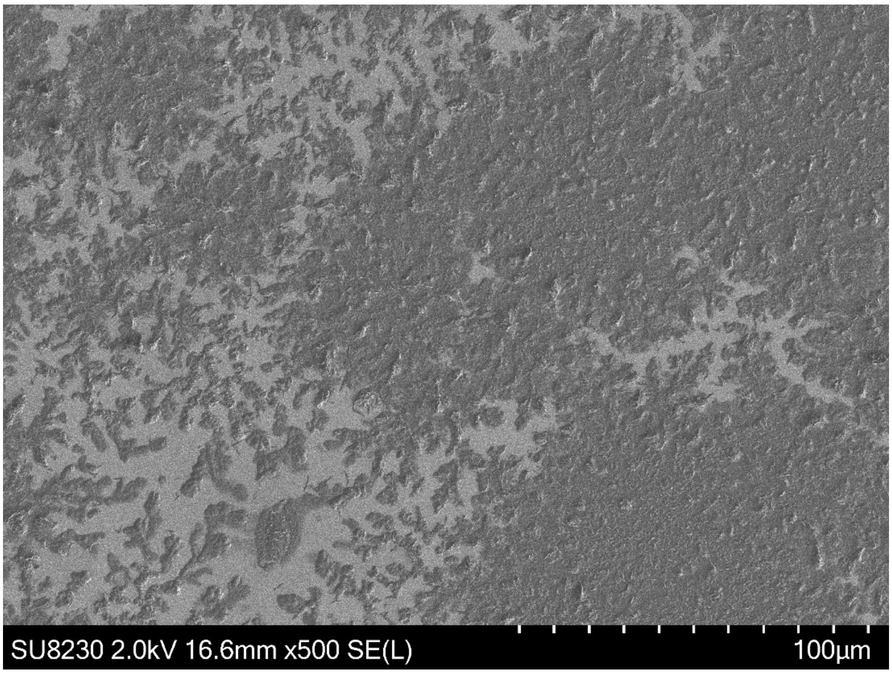


Functionalized diamondoids are deposited on silicon substrates by PVD. <100> silicon wafers bought from TED PELLA, INC. are pre-cut into 10 x 10 mm. Si-chips were polished on one side and pre-cleaned but without removal of native SiO_2 overlayer. The wafer thickness is between 460 and 530 µm. The device for the deposition of diamondoids allows the sublimation of diamondoids under controlled atmosphere and their condensation on a substrate which is cooled by heat dissipation. This home-made chamber is called VD-CA (for "Vapor Deposition under Controlled Atmosphere") and is detailed in **Figure S5**. Full details on this home-made apparatus are described in *Nanoscale, 2015, 7, 1956–1962* and its electronic supporting information ESI.

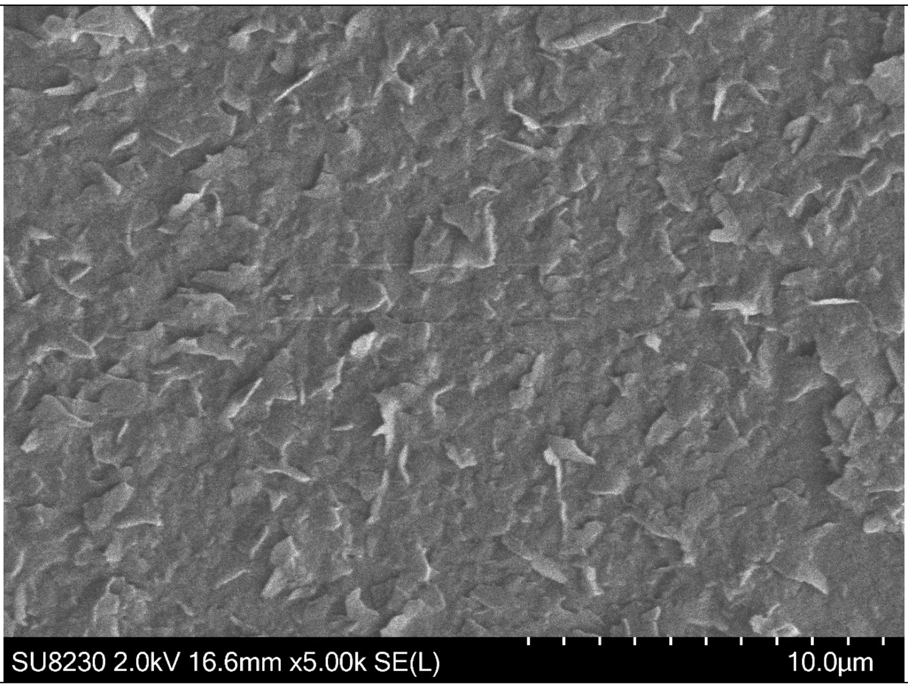
SEM micrography &EPMA analysis of the deposit from PVD of diamantane 2

Figure S6a. Lower temperature conditions

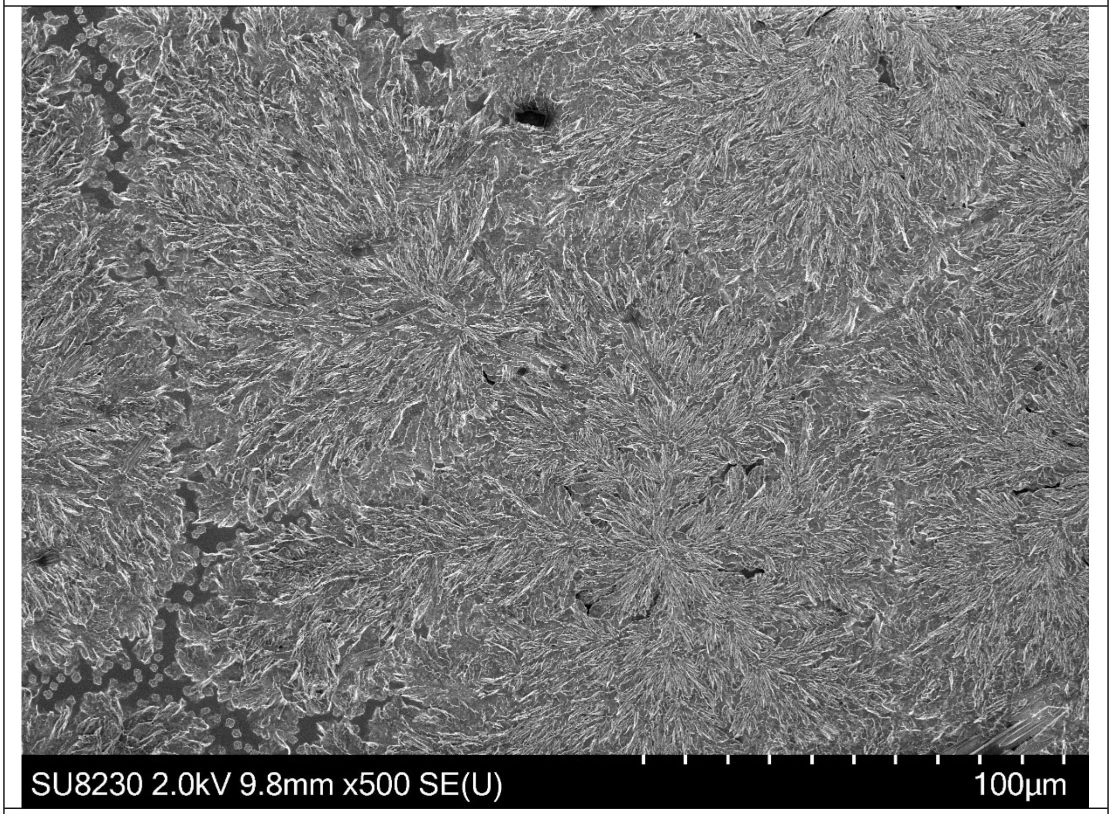
Compound 2 (x500) - deposition conditions: 8 min / 1A (Tmax = 76.5 °C)



Compound 2 (x5.0 k) - deposition conditions: 8 min / 1A (Tmax = 76.5 °C)



Compound 2 (x500) - deposition conditions: 2 min / 2A (Tmax = 86.3°C)



Compound 2 (x5.0k) - deposition conditions: 2 min / 2A (Tmax = 86.3°C)

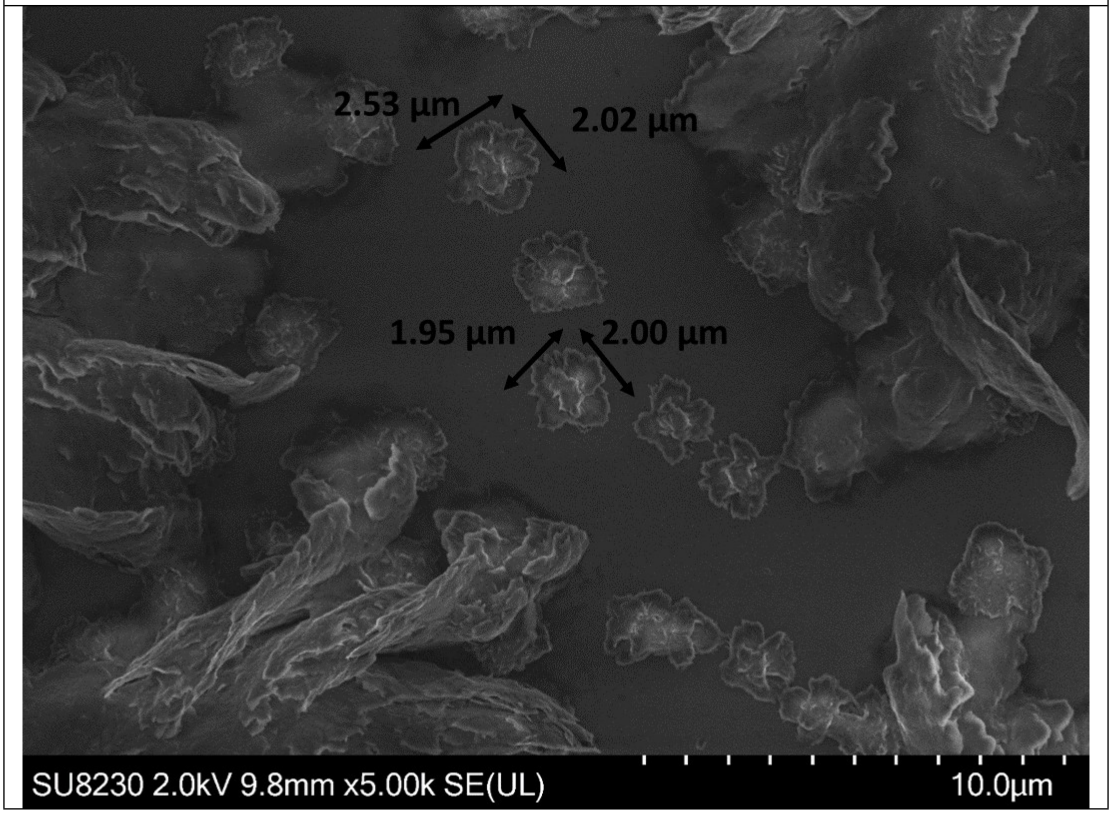
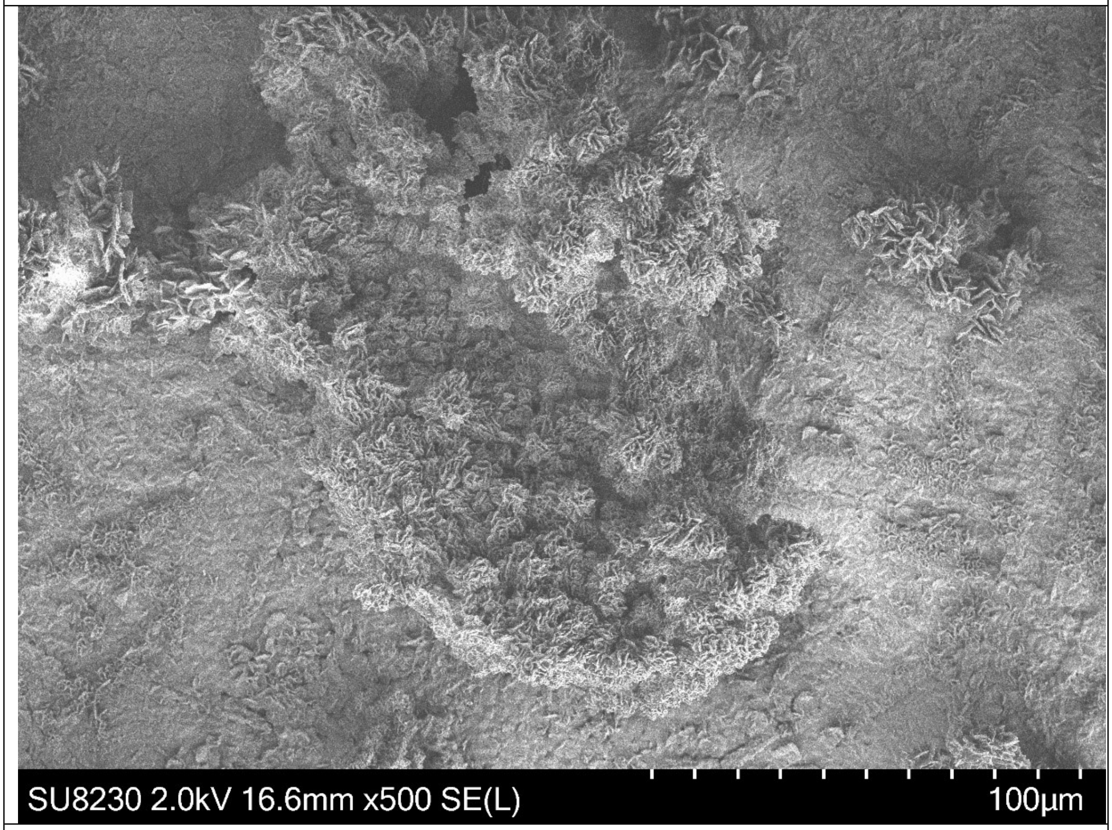
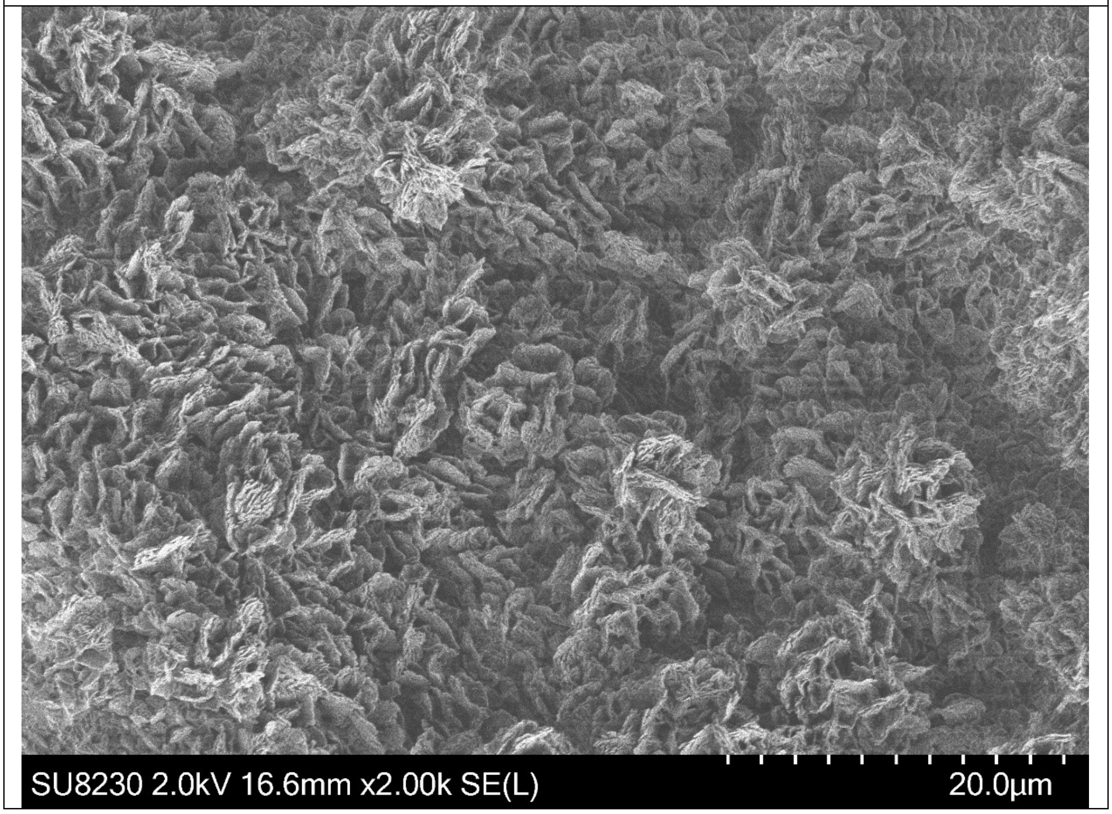


Figure S6b. Higher temperature conditions

Compound 2 (x500) - deposition conditions: 2 min / 3A (Tmax = 130.2 °C)



Compound 2 (x2.0k) - deposition conditions: 2 min / 3A (Tmax = 130.2°C)



Compound 2 (x5.0k) - deposition conditions: 2 min / 3A (Tmax = 130.2°C)

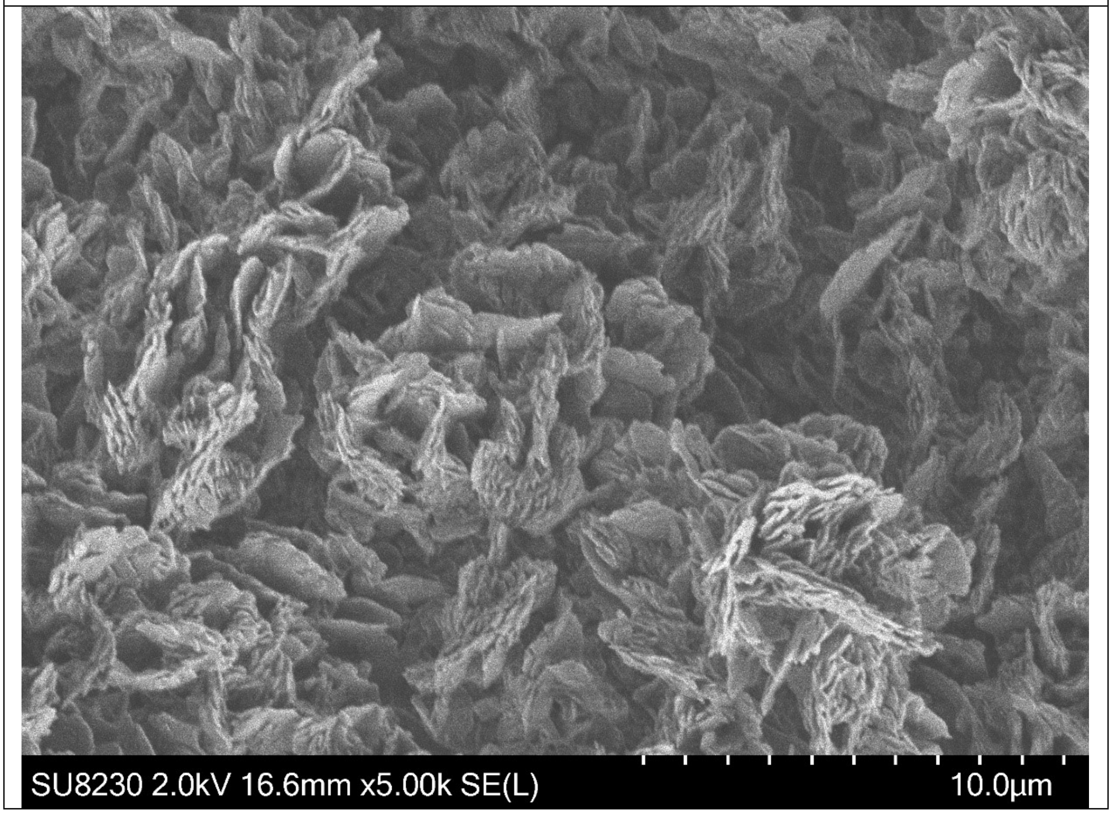
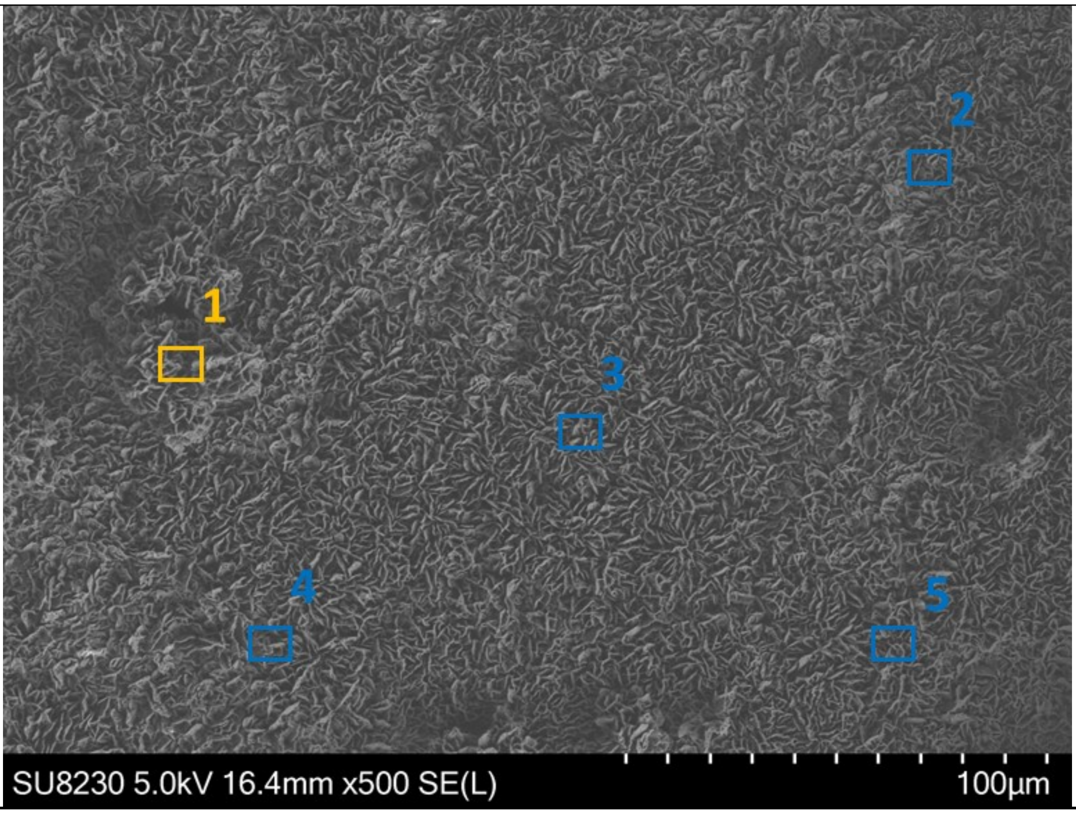


Figure S6c. EPMA analysis of 2 deposited at 120 °C

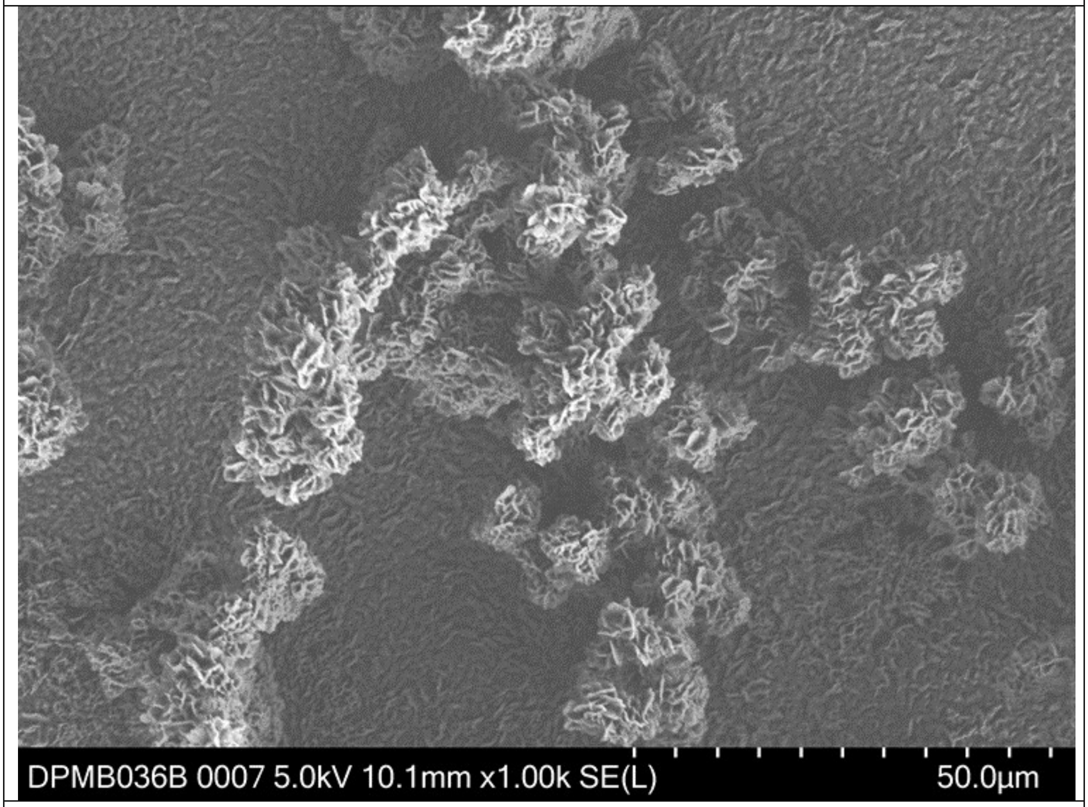
c) Compound 2 (x500) Deposition conditions: 4min / 2A (T_{max} = 122.1°C)



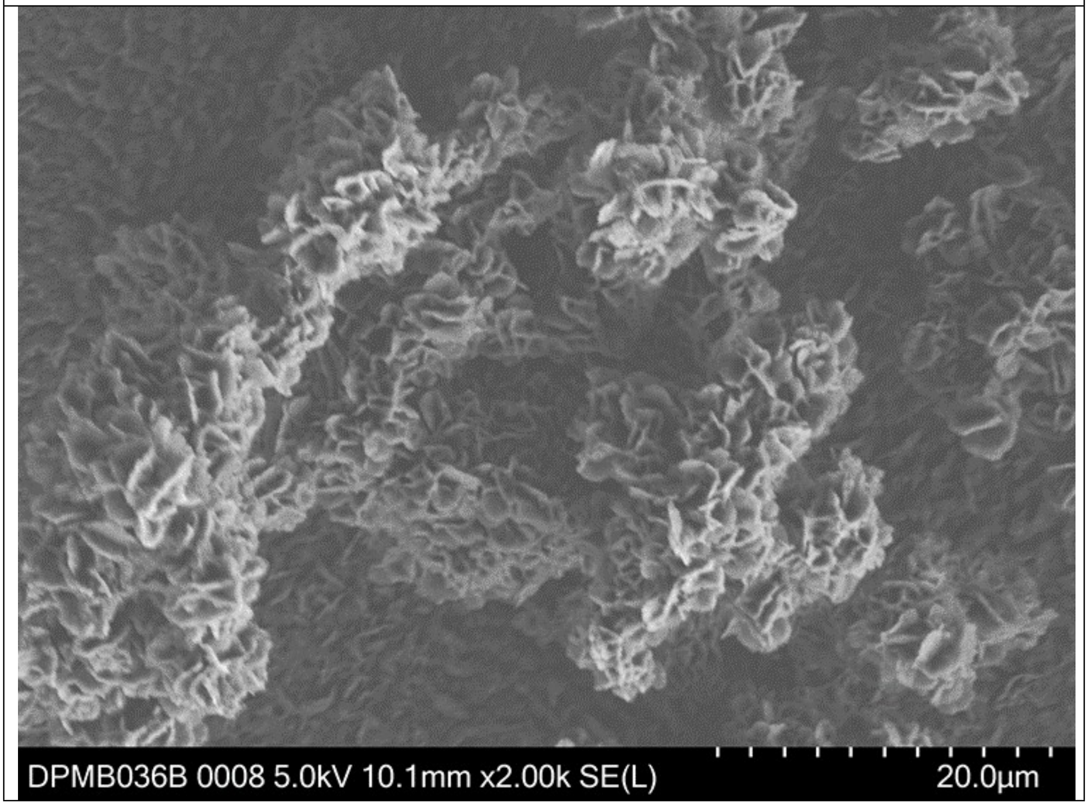
at.%	C	O	P	S	Si
Expected	82.3	5.9	5.9	5.9	0
Area 1	64.5	9.9	12.5	12.1	0.6
Area 2	69.5	10.7	11.0	8.2	0.6
Area 3	69.8	10.0	9.2	8.6	2.4
Area 4	67.1	10.7	11.5	10.0	0.6
Area 5	66.8	10.4	11.8	10.2	0.7

Figure S6d. SEM micrograph of Au MOCVD on 2

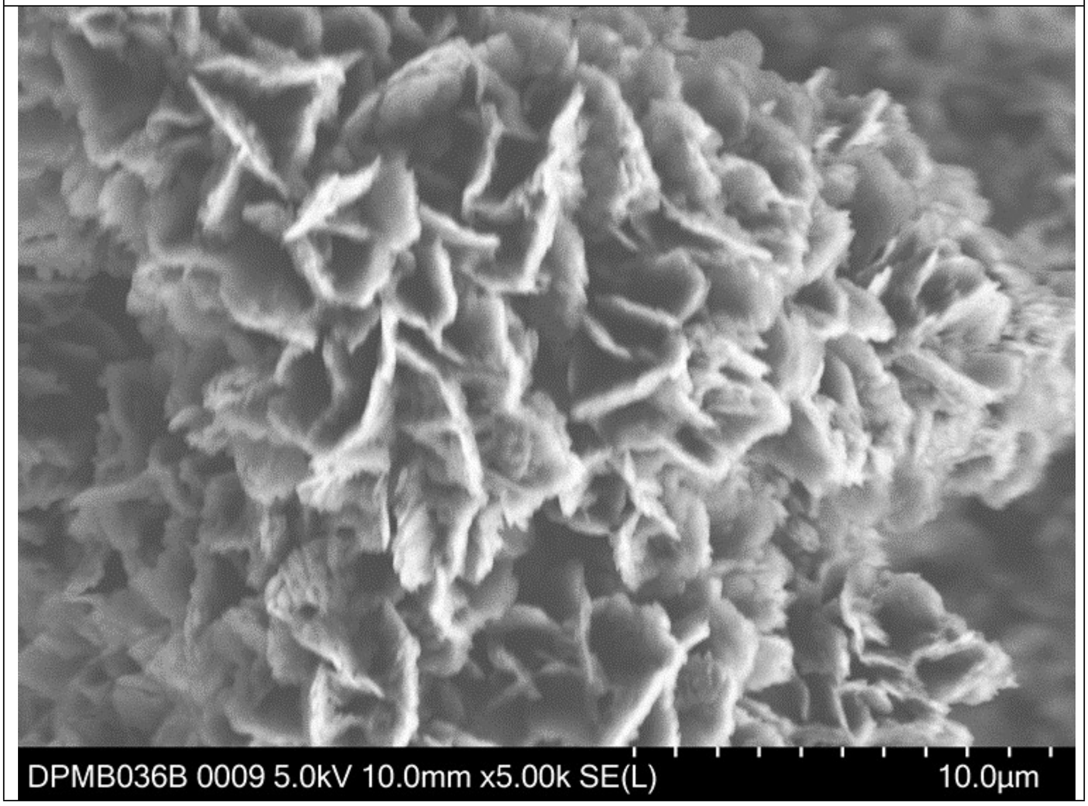
Gold deposition on 2 (x1.0k) – PVD conditions: 4 min / 2A (Tmax = 116 °C) – MOCVD Au condition: 60 °C – 1h



(x2.0k) – PVD conditions: 4 min / 2A (Tmax = 116 °C) – MOCVD Au condition: 60°C – 1h



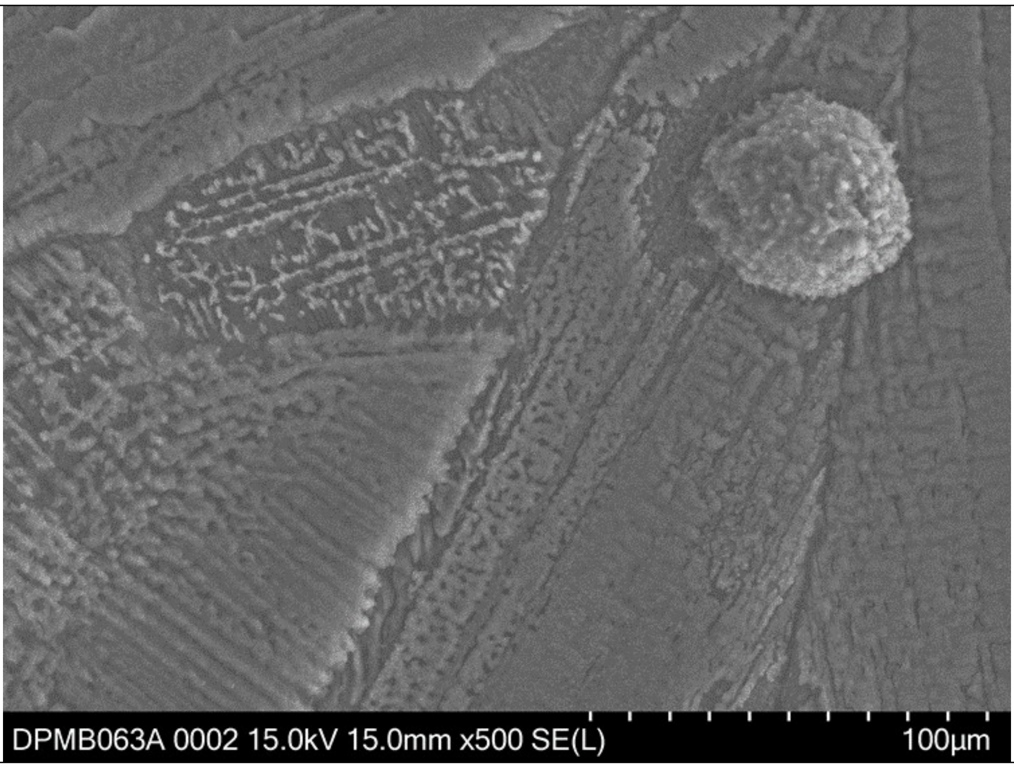
(x5.0k) – PVD conditions: 4 min / 2A (Tmax = 116 °C) – MOCVD Au condition: 60°C – 1h



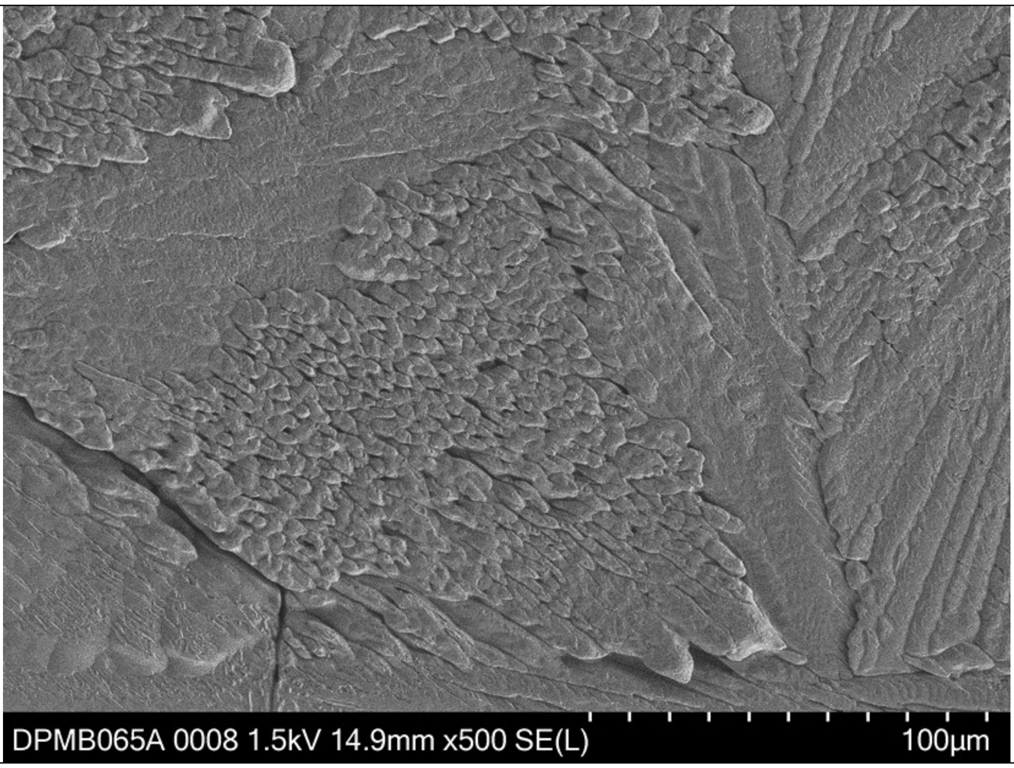
SEM micrography of the deposit from physical vapor deposition of diamantane 3

Figure S7a. Deposition of 3 at *ca* 75 °C, 100°C and 120 °C

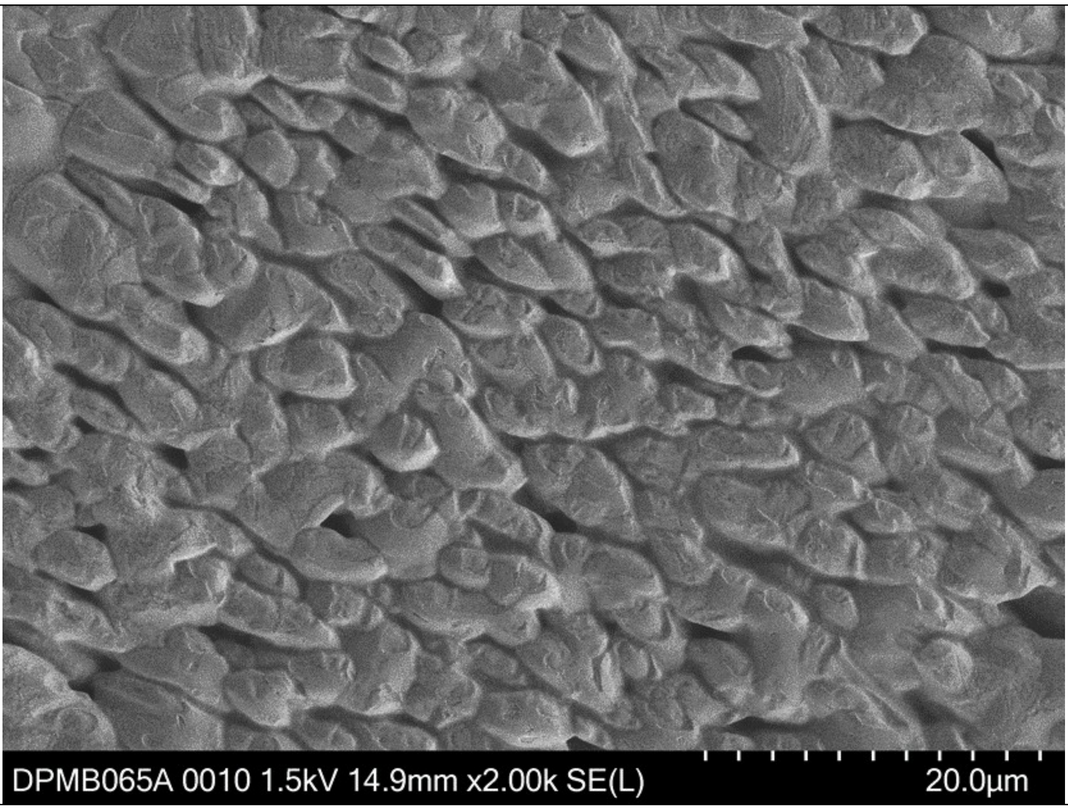
Compound 3 (x500) - deposition condition: 2 min / 2 A (Tmax = 75.9 °C)



Compound 3 (x500) - deposition condition: 3 min / 2 A (Tmax = 98.5 °C)



Compound 3 (x2.0k) - deposition condition: 3 min / 2 A (Tmax = 98.5 °C)



Compound 3 (x250) -deposition condition: 4 min / 2 A (T_{max} = 117 °C)

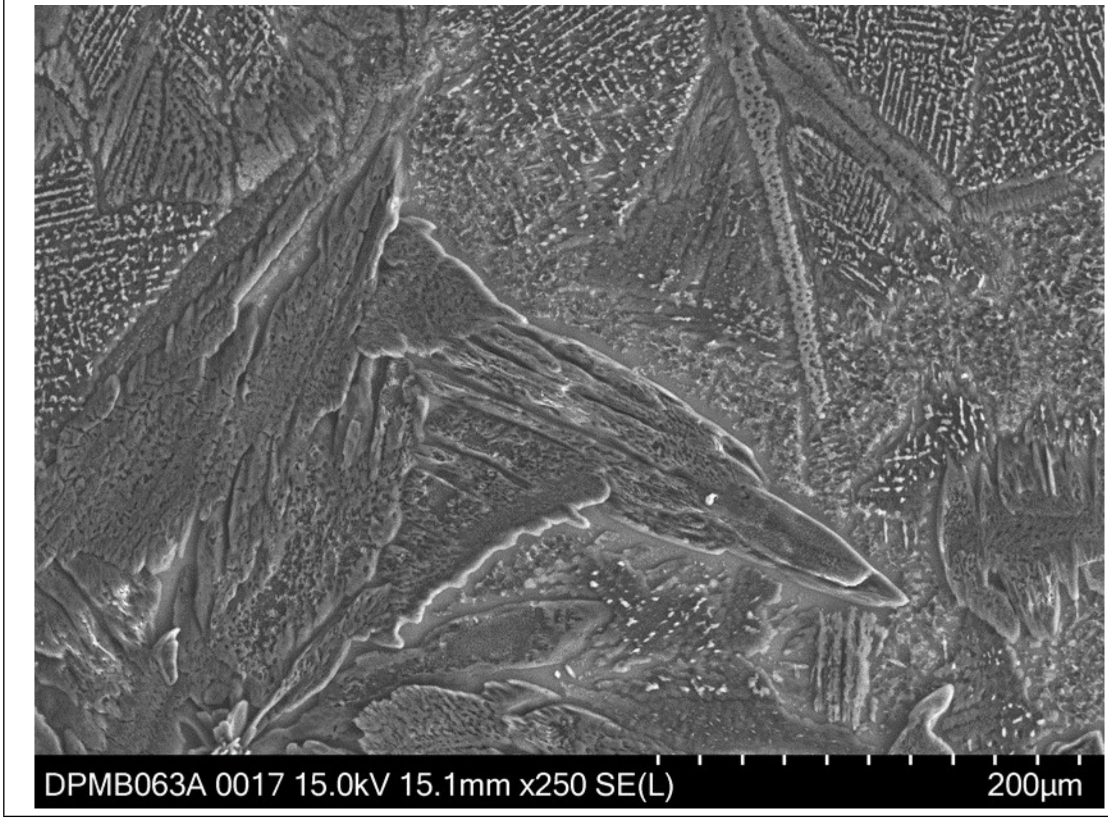
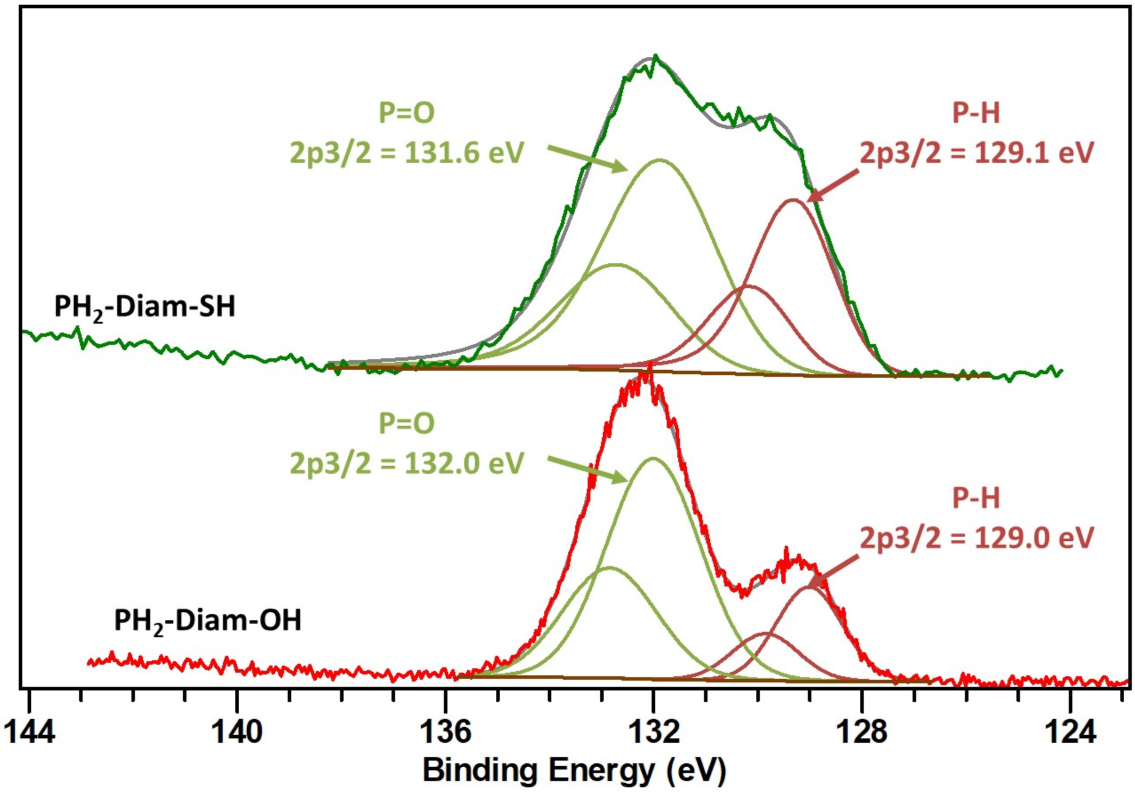


Figure S7b. High-resolution XPS spectra at P2p core level of 3

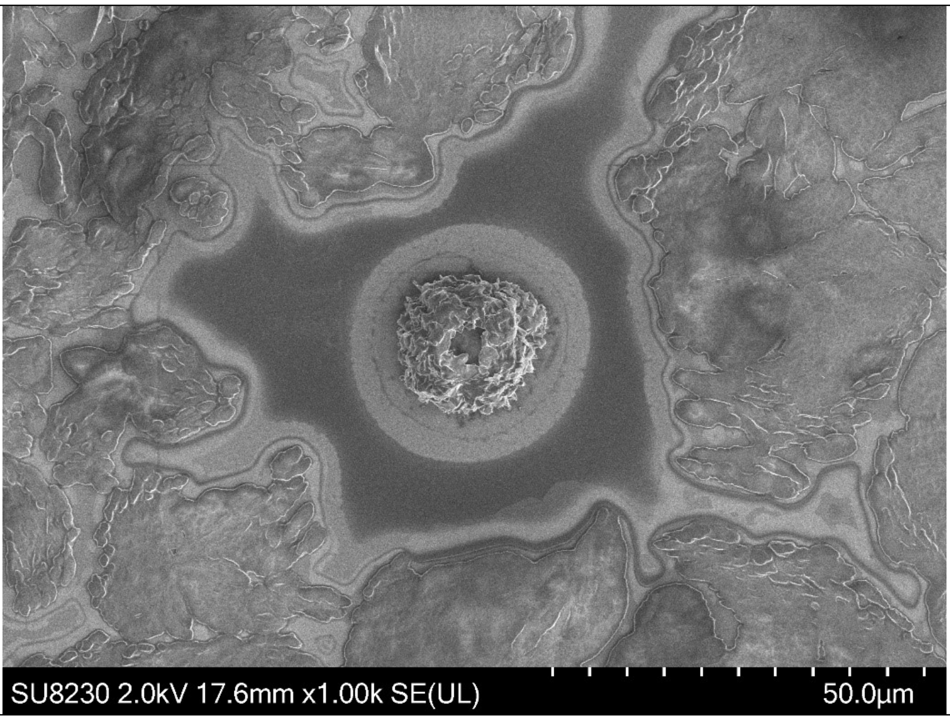


Note: *The proportion of reduced phosphine compared to its oxidized form measured on a PVD deposit of compound **3** (top, green) is equal to 40%; whereas this proportion was only 20% for a PVD deposit of compound **1** (bottom, red) (exposure to atmospheric air is the cause of these oxidation rates).*

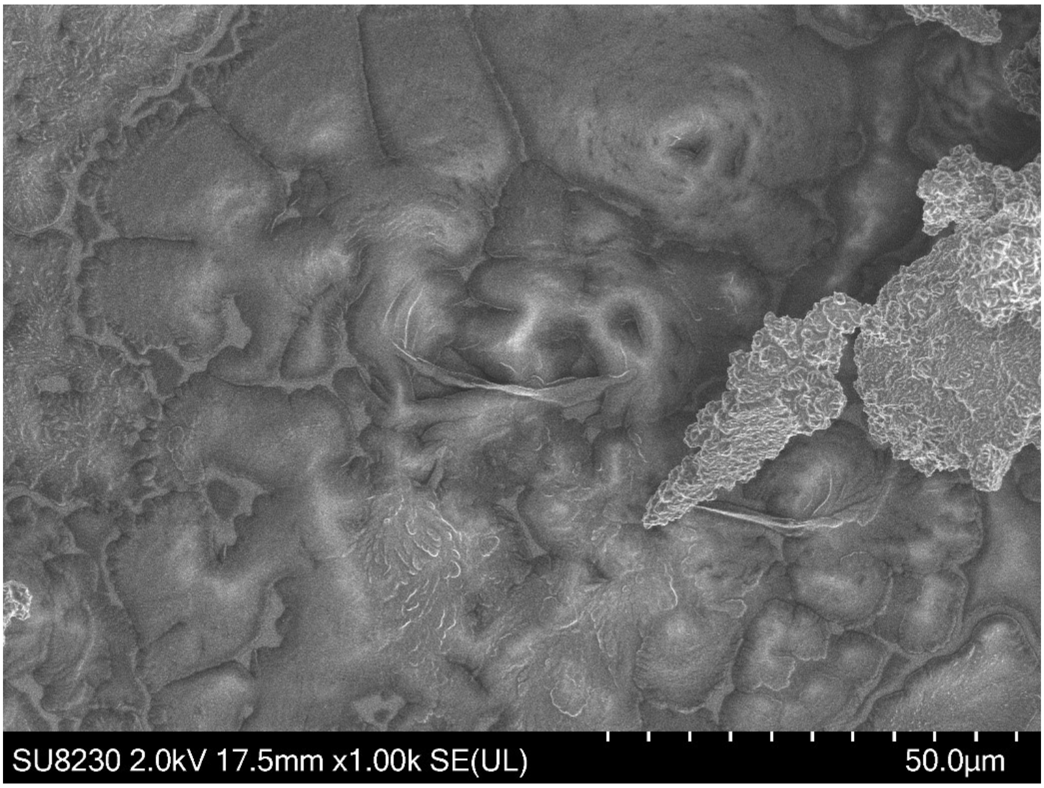
SEM micrography of the deposit from physical vapor deposition of diamantane 4

Figure S8a. Deposition of 4 at 85 °C, 125°C and 145 °C

Compound 4 (x500) - deposition conditions: 2 min / 2 A (Tmax = 82.9 °C)



Compound 4 (x1.0k) - deposition condition: 4 min / 2 A (Tmax = 124.9 °C)



Compound 4 (x1.0k) -deposition condition: 6 min / 2 A (T_{max} = 146.4°C)

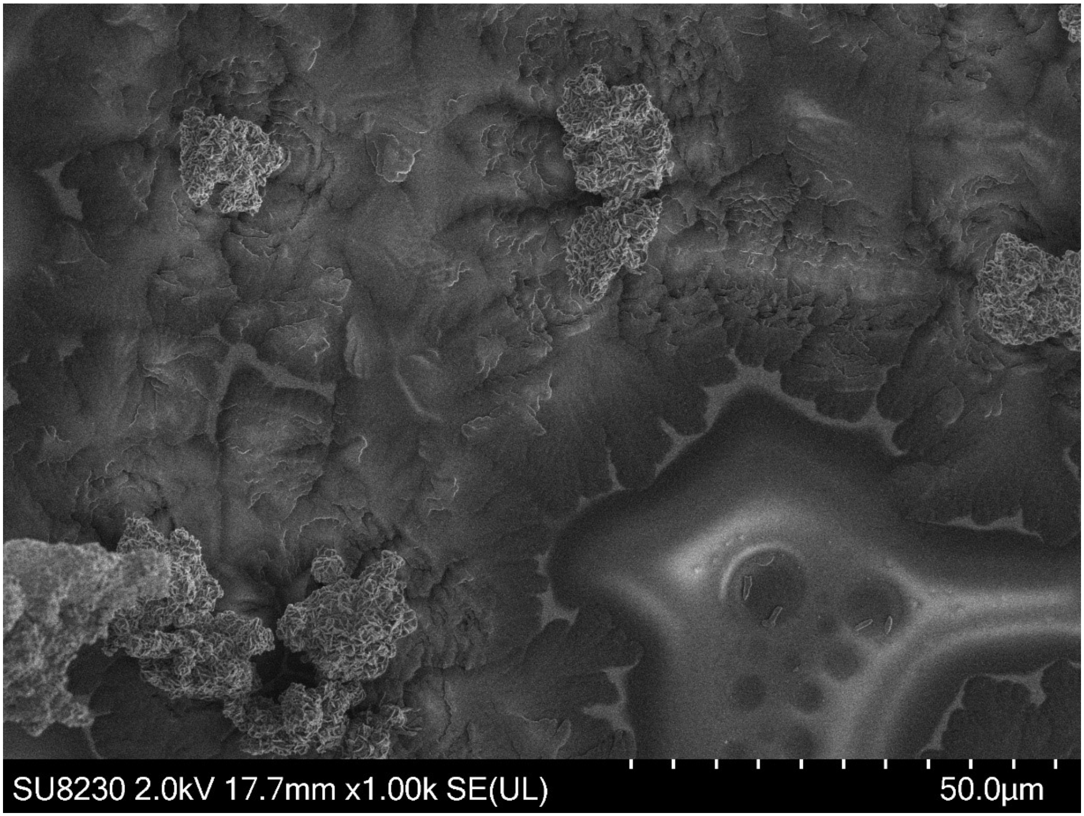
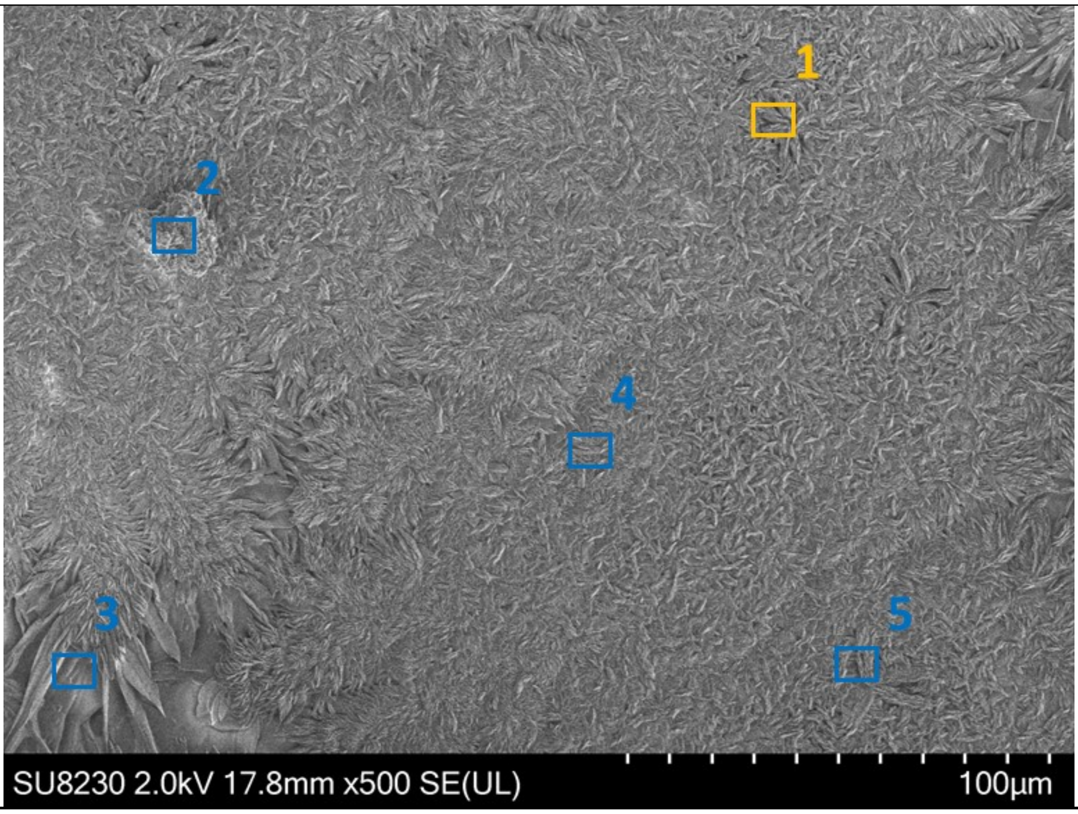


Figure S8b. EPMA analysis of 4 deposited at 170 °C

Compound 4 (x500) Deposition condition: 8 min / 2 A (T_{max} = 172.4 °C)

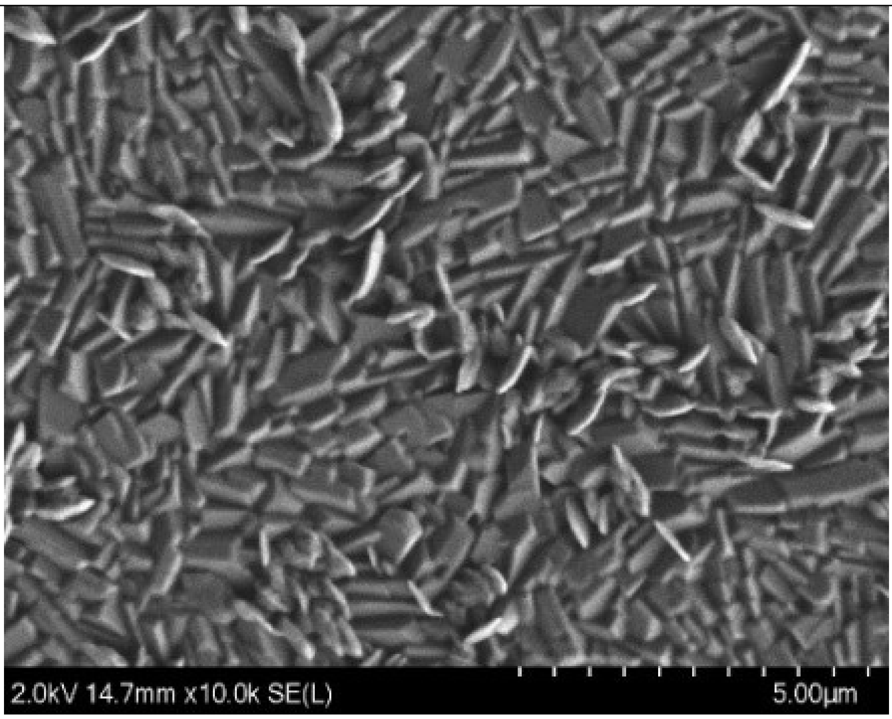


at.%	C	O	P	Si
Expected	82.3	11.8	5.9	0
Area 1	69.1	20.3	9.1	1.5
Area 2	62.7	19.9	11.3	3.3
Area 3	69.4	19.2	8.8	2.6
Area 4	69.9	20.0	9.4	0.7
Area 5	70.2	20.0	9.1	0.7

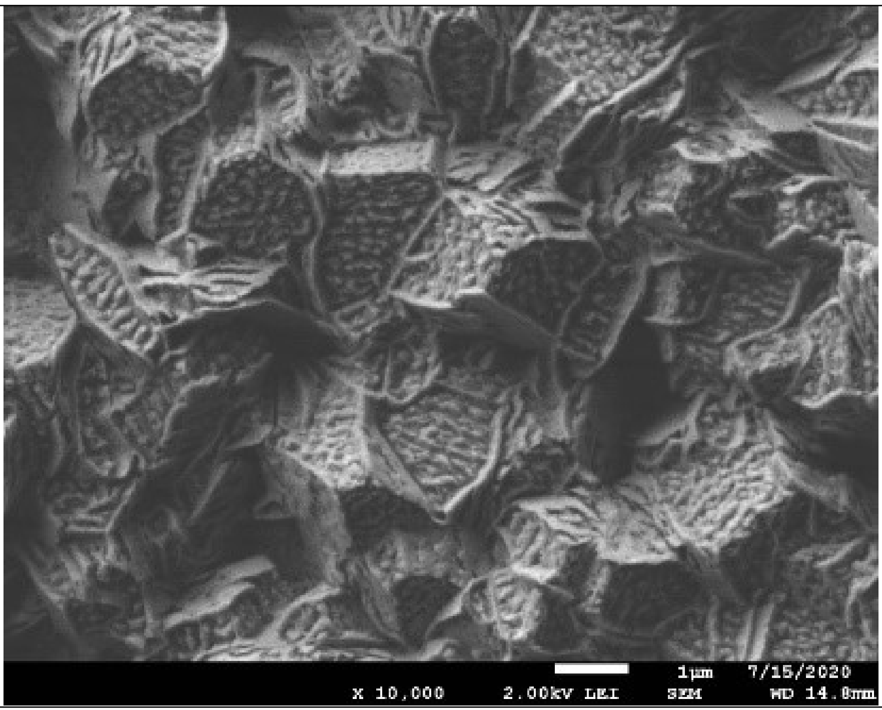
SEM micrography of the deposit from physical vapor deposition of diamantane 5

Figure S9a. Deposition of 5 at 116 °C, 125 °C and 145 °C

Compound 5 (x10.0k) – Deposition conditions: 4 min / 2A (Tmax = 116 °C)



Compound 5 (x10.0k) – Deposition condition: 2 min / 3A (Tmax = 127.1 °C)



Compound 5 (x10.0k) – Deposition conditions: 6min / 2A (Tmax = 147.8 °C)

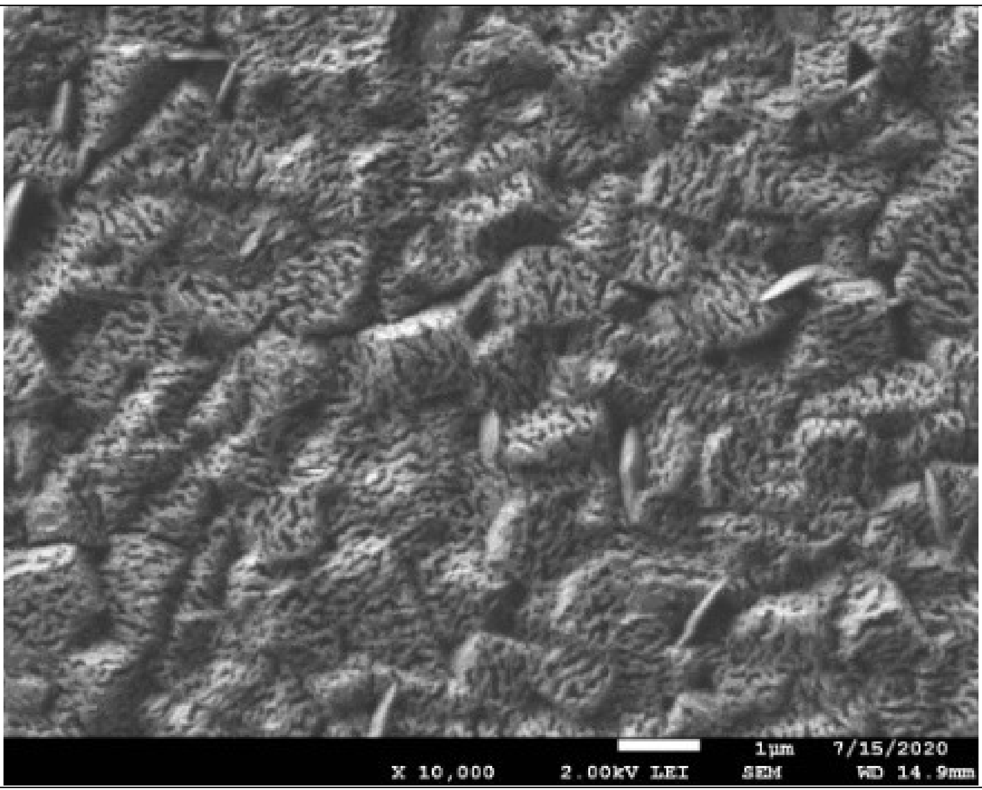
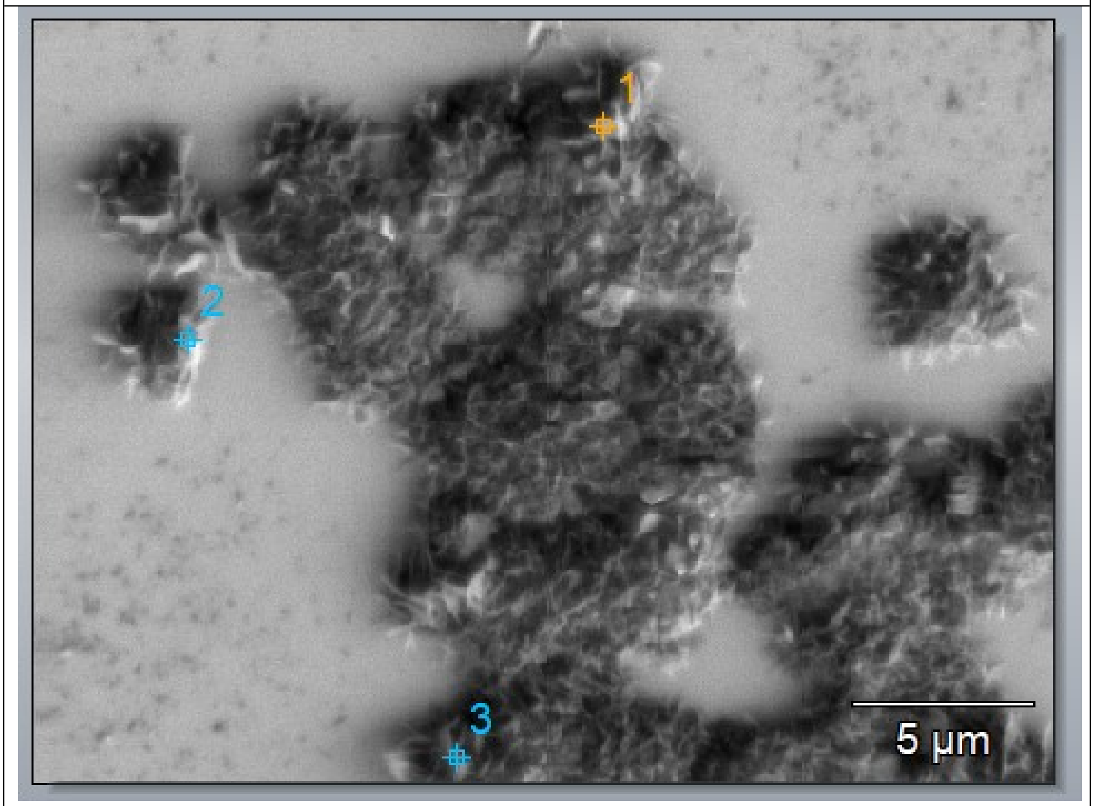


Figure S9b. EPMA of 5 deposited at 75°C

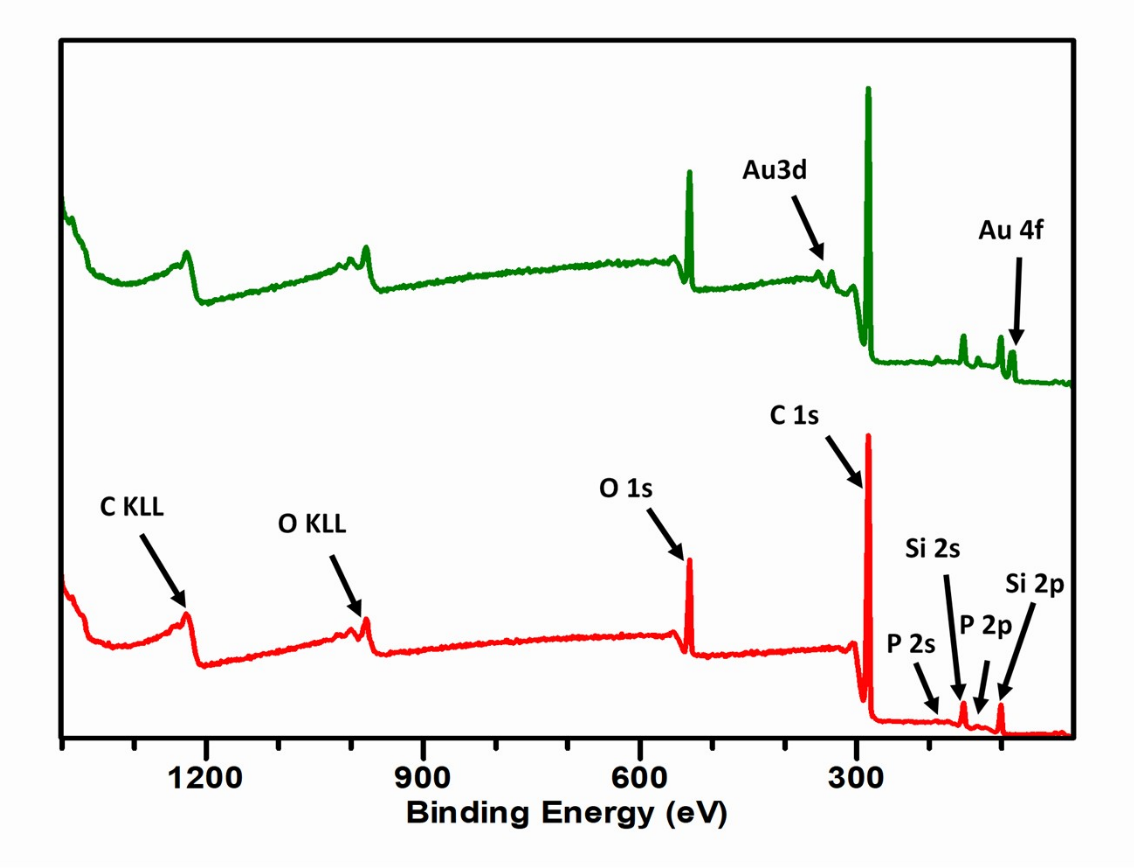
Compound 5 – Deposition conditions: 2min / 2A (T_{max} = 75.8 °C)



wt.%	C	O	N
Expected	76.6	7.3	6.4
Area 1	72.8	10.3	7.2
Area 2	73.5	10.4	6.4
Area 3	74.3	9.3	6.9

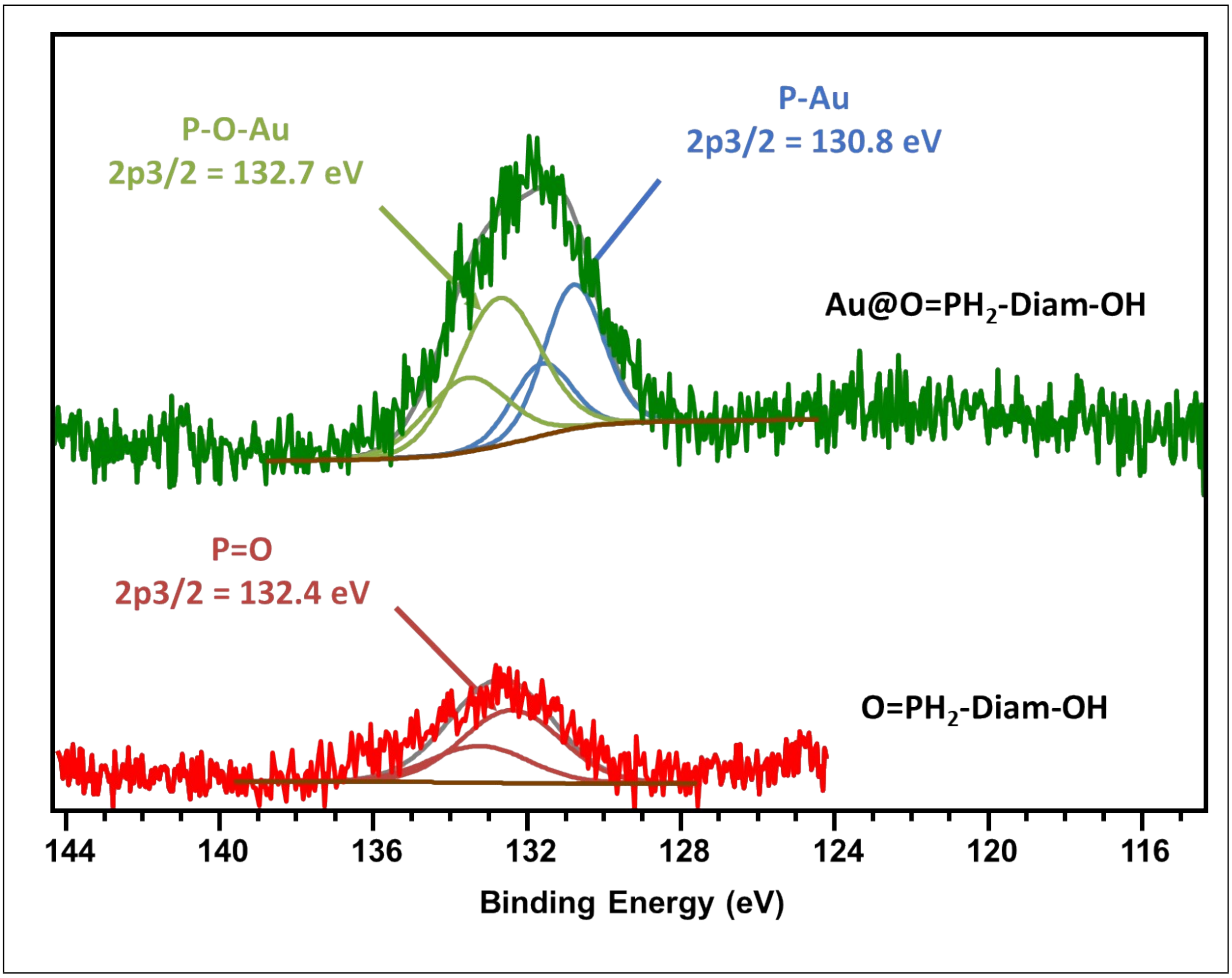
XPS data of the deposit from PVD of diamantane 4 and its composite after gold MOCVD

Figure S10a. XPS survey spectra of 4 before (red) and after (green) deposition of gold; and comparison of atomic percentages of elements detected by XPS



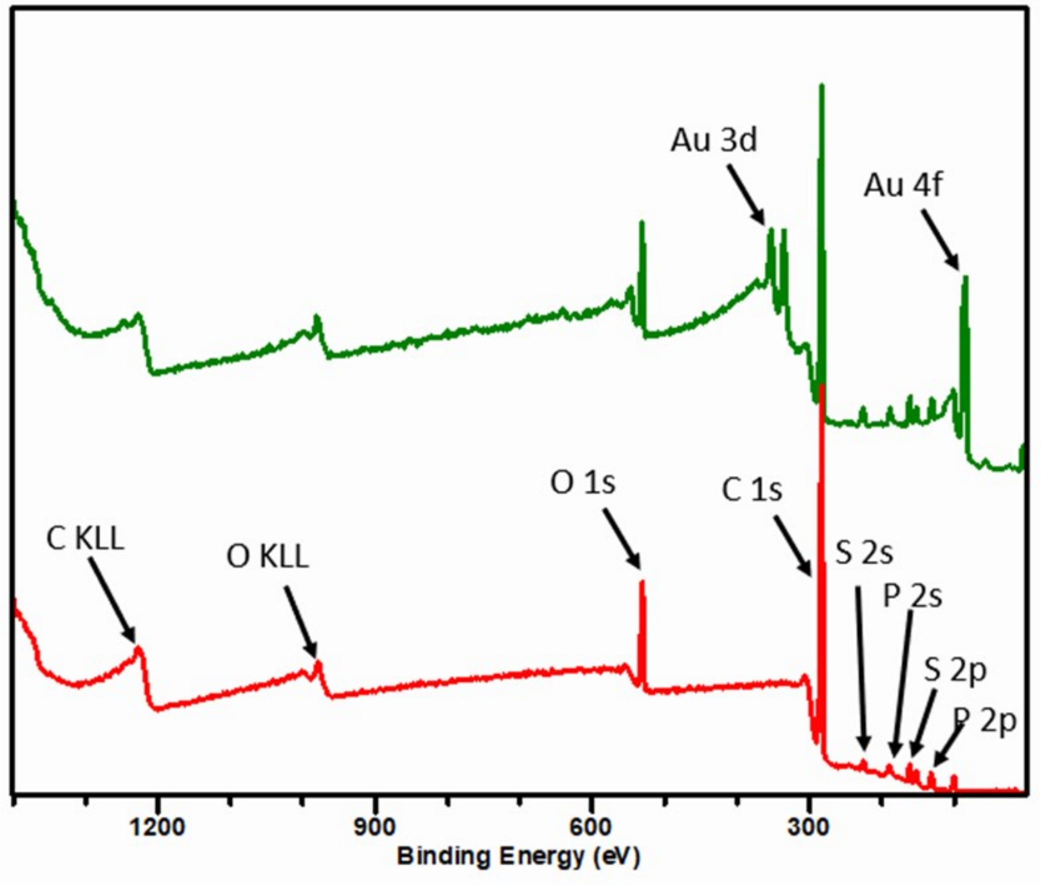
	C1s	O1s	P2p	Si2p	Au4f	[M] / P ([M] : P)
Au@OPH$_2$-Diam-OH (at.%)	76.9	13.9	1.5	7.1	0.6	0.4 (2 : 5)
OPH$_2$-Diam-OH (at.%)	81.7	11.5	0.6	6.2	0	0
Theoretical atomic percentage (native)	82.3	11.8	5.9			

Figure S10b. High-resolution XPS spectra at P2p core level of gold-based organohybrid diamantane phosphine oxide 4 (Au@OPH2-Diam-OH, green) and before gold deposition (OPH2-Diam-OH, red).



XPS data of the deposit from physical vapor deposition of diamantane 2 and its organohybrid after gold MOCVD

Figure S11a. XPS survey spectra of 2 before (red) and after (green) deposition of gold; and comparison of atomic percentages of elements detected by XPS



	C1s	O1s	P2p	S2p	S / P	Metal [M]	[M] / S ([M] : S)
Au@SPH$_2$-Diam-OH (at.%)	78.1	11.5	3.8	3.3	0.87	3.3	1 (1 : 1)
Native (at.%)	83.8	9.8	3.6	2.8	0.78	0	0
Theoretical atomic percentage (native)	82.3	5.9	5.9	5.9	1		

Figure S11b. High-resolution XPS spectra at P2p (top) and S2p (bottom) core levels of gold-based organohybrid diamantane phosphine oxide 4 (Au@SPH$_2$-Diam-OH, green) and before gold deposition (SPH$_2$-Diam-OH, red).

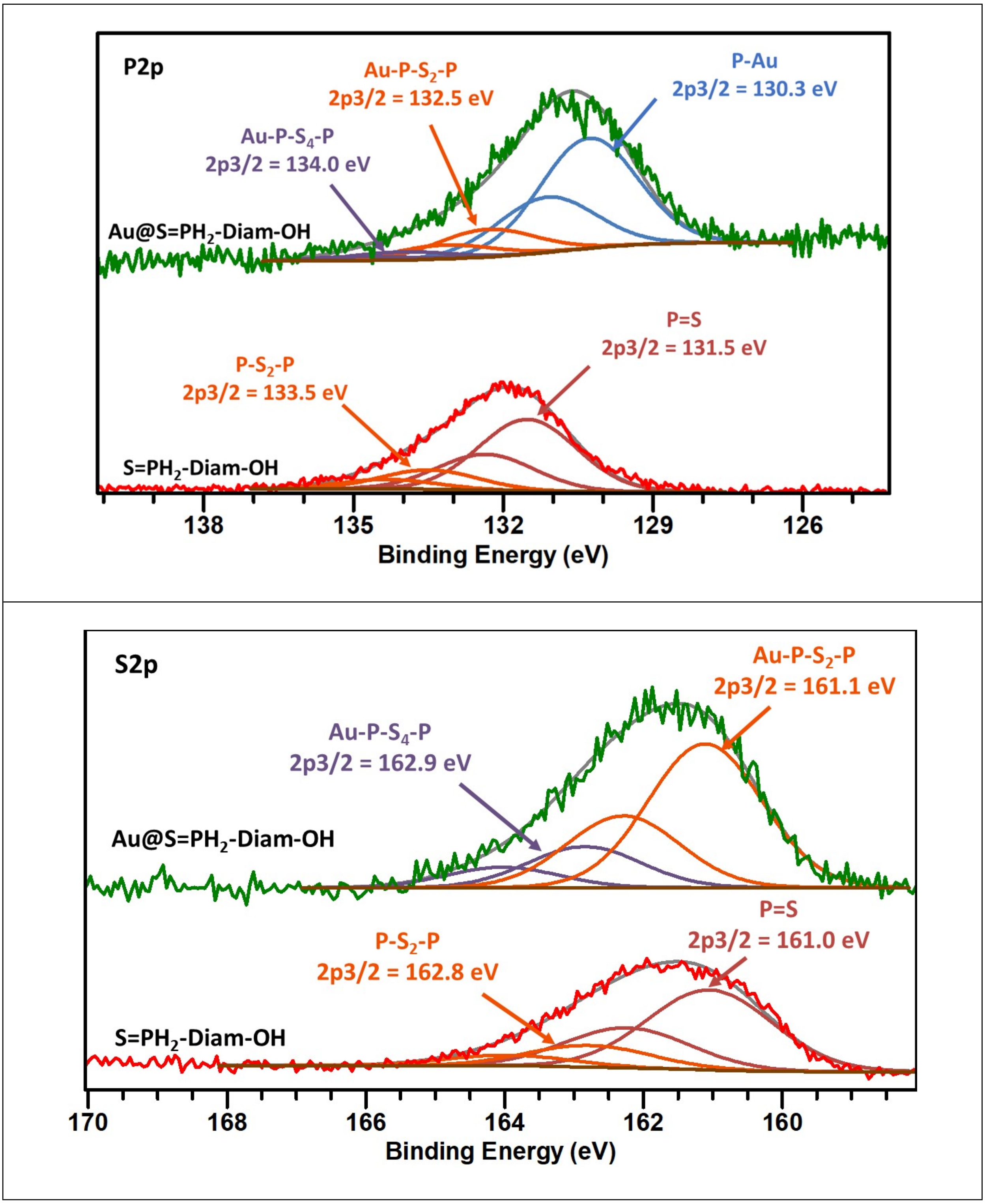
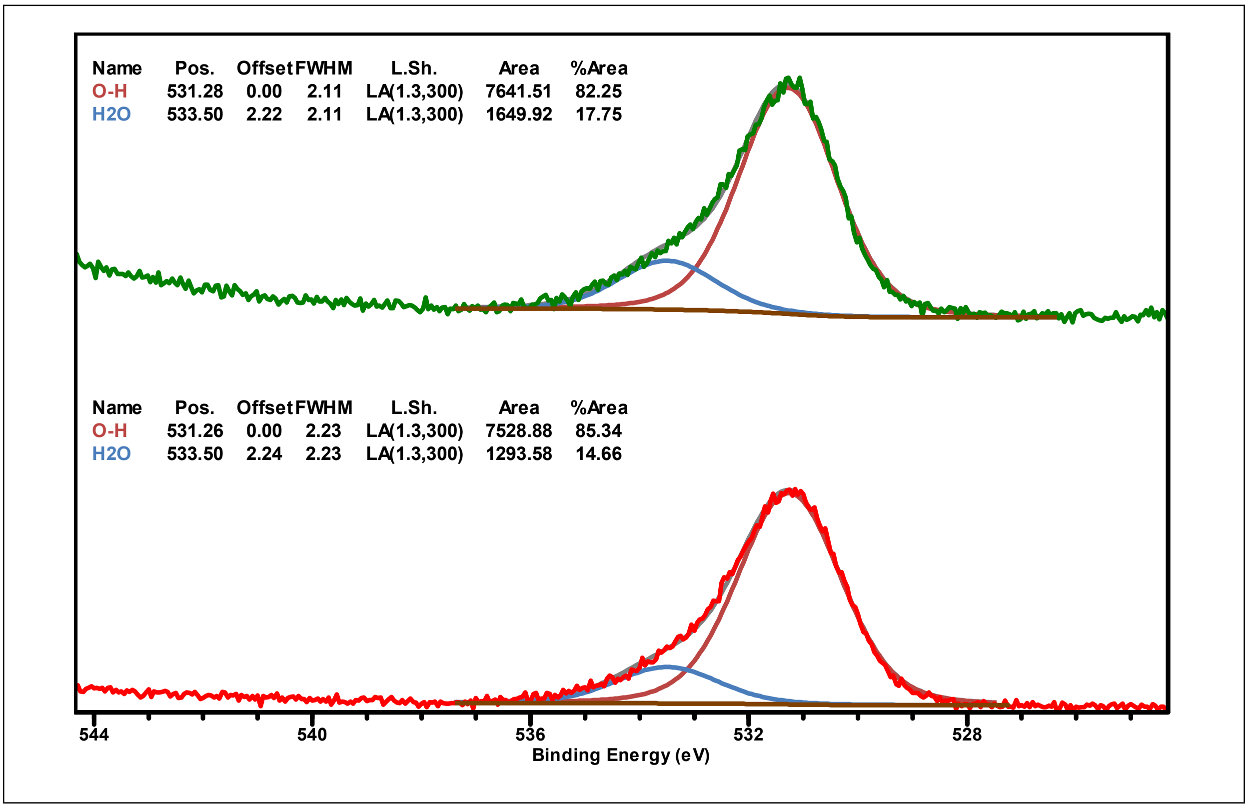


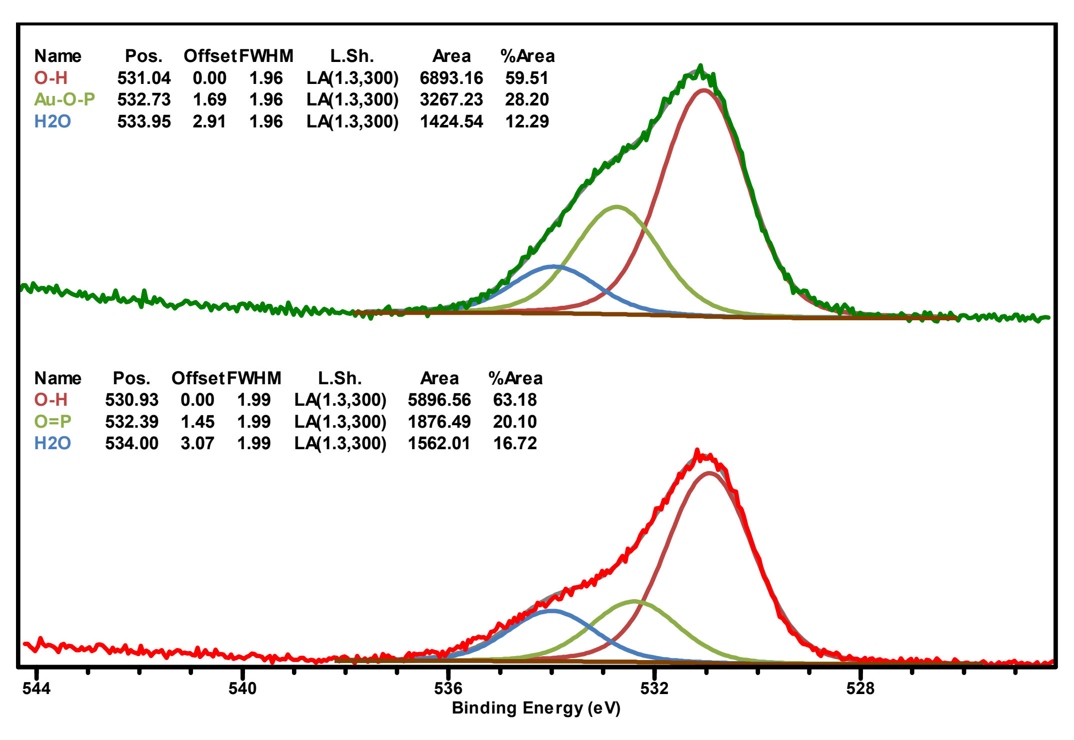
Figure S11c. High-resolution XPS spectra at O1s core levels of gold-based organohybrid diamantane phosphine 2 (Au@S=PH$_2$-Diam-OH, green) and before gold deposition (S=PH$_2$-Diam-OH, red).



Name	Pos.	Offset	FWHM	L.Sh.	Area	%Area
O-H	531.28	0.00	2.11	LA(1.3,300)	7641.51	82.25
H2O	533.50	2.22	2.11	LA(1.3,300)	1649.92	17.75

Name	Pos.	Offset	FWHM	L.Sh.	Area	%Area
O-H	531.26	0.00	2.23	LA(1.3,300)	7528.88	85.34
H2O	533.50	2.24	2.23	LA(1.3,300)	1293.58	14.66

Figure S11d. High-resolution XPS spectra at O1s core levels of gold-based organohybrid diamantane phosphine oxide 4 (Au@O=PH$_2$-Diam-OH, green) and before gold deposition (O=PH$_2$-Diam-OH, red).



Name	Pos.	Offset	FWHM	L.Sh.	Area	%Area
O-H	531.04	0.00	1.96	LA(1.3,300)	6893.16	59.51
Au-O-P	532.73	1.69	1.96	LA(1.3,300)	3267.23	28.20
H2O	533.95	2.91	1.96	LA(1.3,300)	1424.54	12.29

Name	Pos.	Offset	FWHM	L.Sh.	Area	%Area
O-H	530.93	0.00	1.99	LA(1.3,300)	5896.56	63.18
O=P	532.39	1.45	1.99	LA(1.3,300)	1876.49	20.10
H2O	534.00	3.07	1.99	LA(1.3,300)	1562.01	16.72

Thermogravimetric analyses (TGA/DSC)

Thermogravimetric analyses have been performed by Simultaneous Differential Thermal Analysis (SDT), which combine both Thermogravimetric Analysis (TGA) both Differential Scanning Calorimetry (DSC) in one run. 2 mg of the compound to be analysed have been added to a platinum DSC cup and transferred to the furnace of the SDT Q600 instrument (TA instrument). An isotherm at 30 °C is applied for 5 minutes to stabilise the mass measurement. An increase of 5 °C per min have been then applied up to 400 or 800 °C. An isotherm at 100 °C for 30 min was implemented in order to eliminate sorption of water on our compounds. The curve of mass as a function of temperature is plotted as a black solid line and its derivative in blue short dash. The optimum temperature applied during PVD deposition is indicated on the curve of the mass derivative as a function of temperature.

Figure S12a. SDT data of difunctionalized diamantane 1

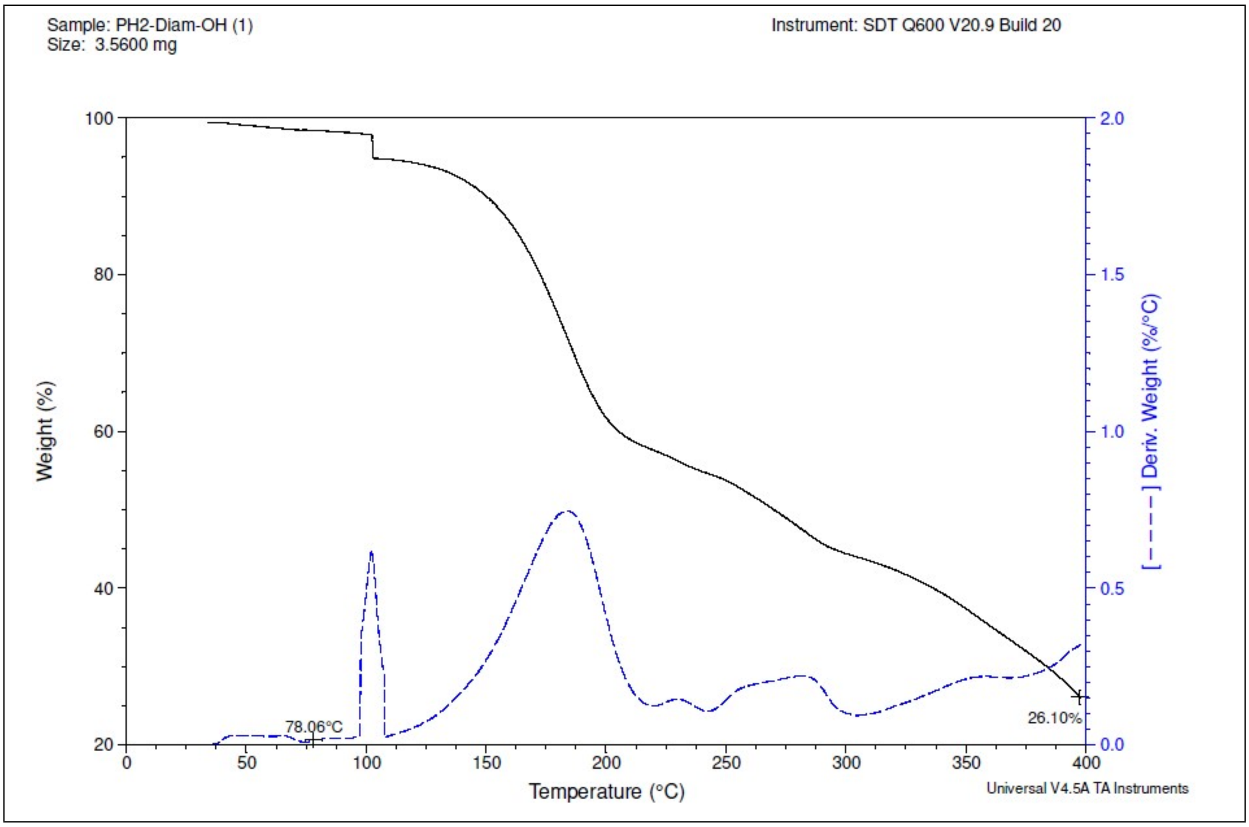


Figure S12b. SDT data of difunctionalized diamantane 2

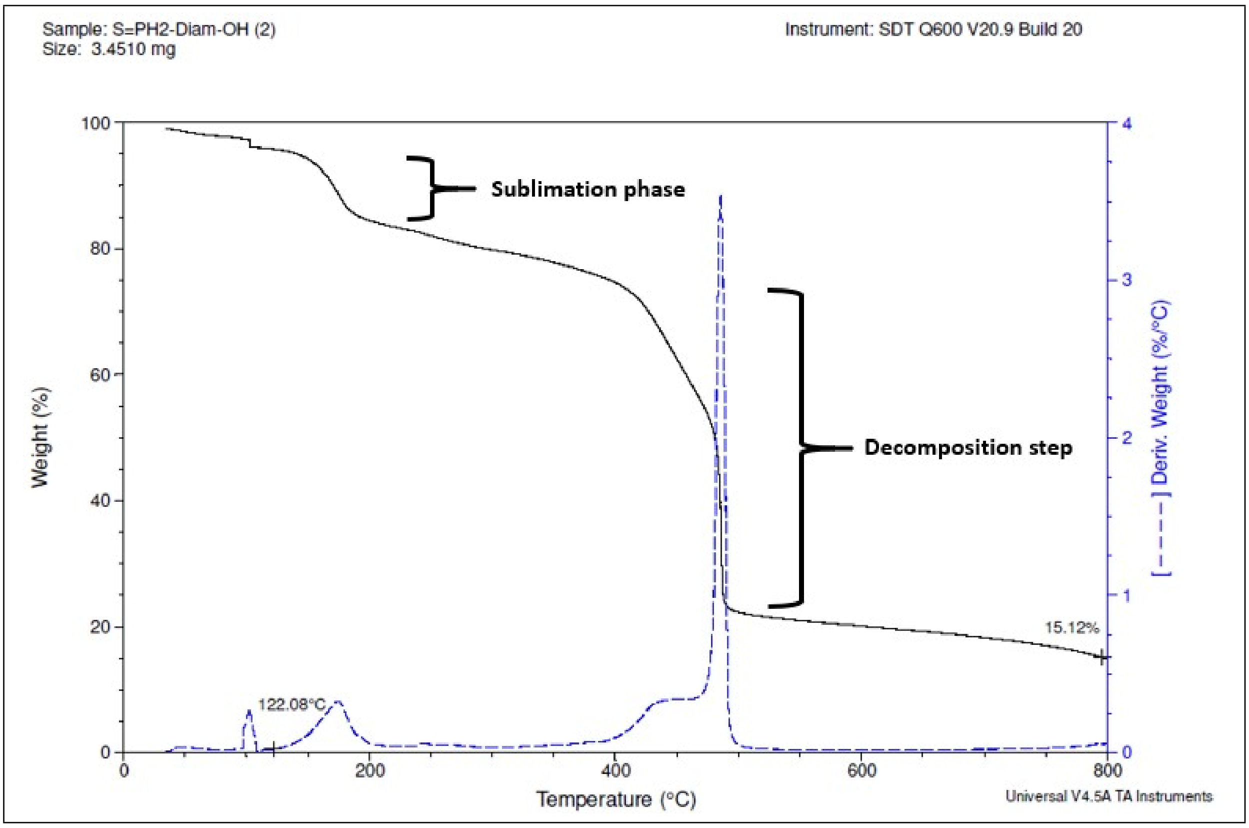


Figure S12c. SDT data of difunctionalized diamantane 3

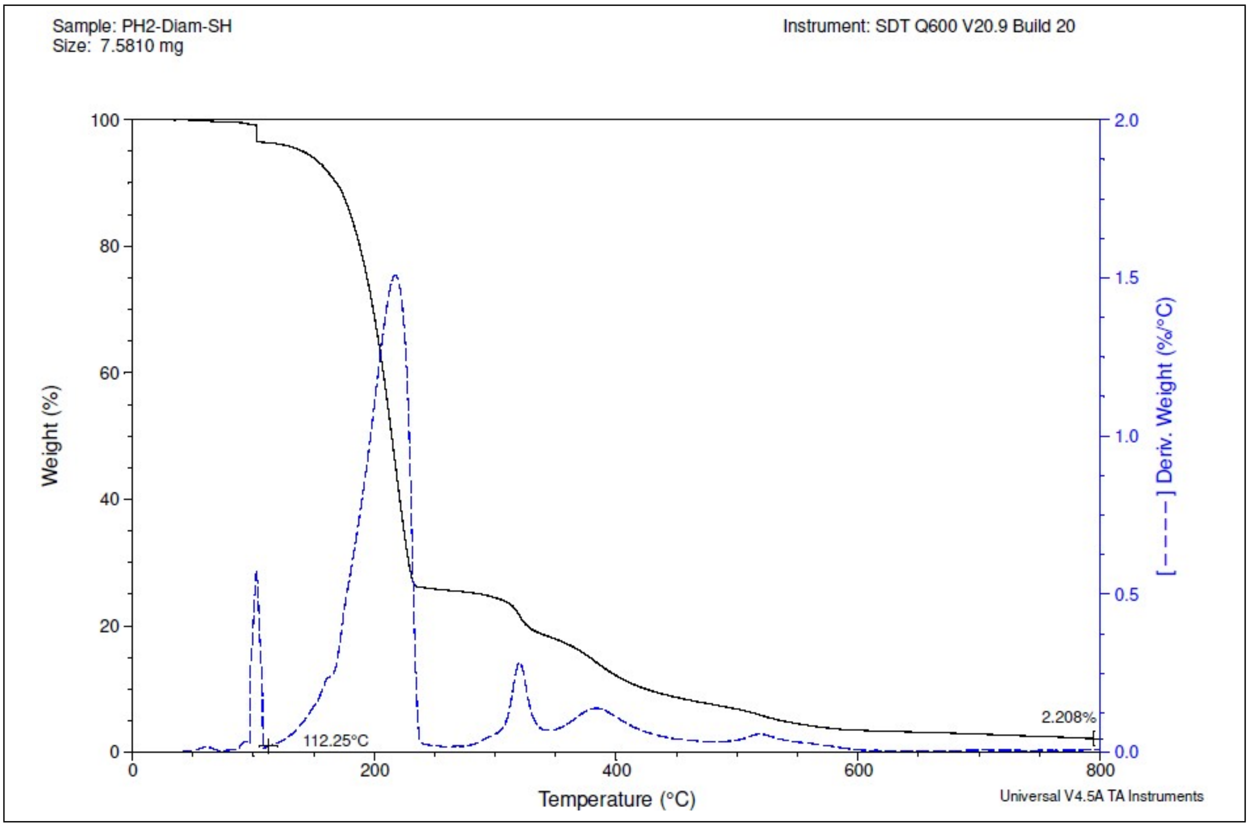


Figure S12d. SDT data of difunctionalized diamantane 4

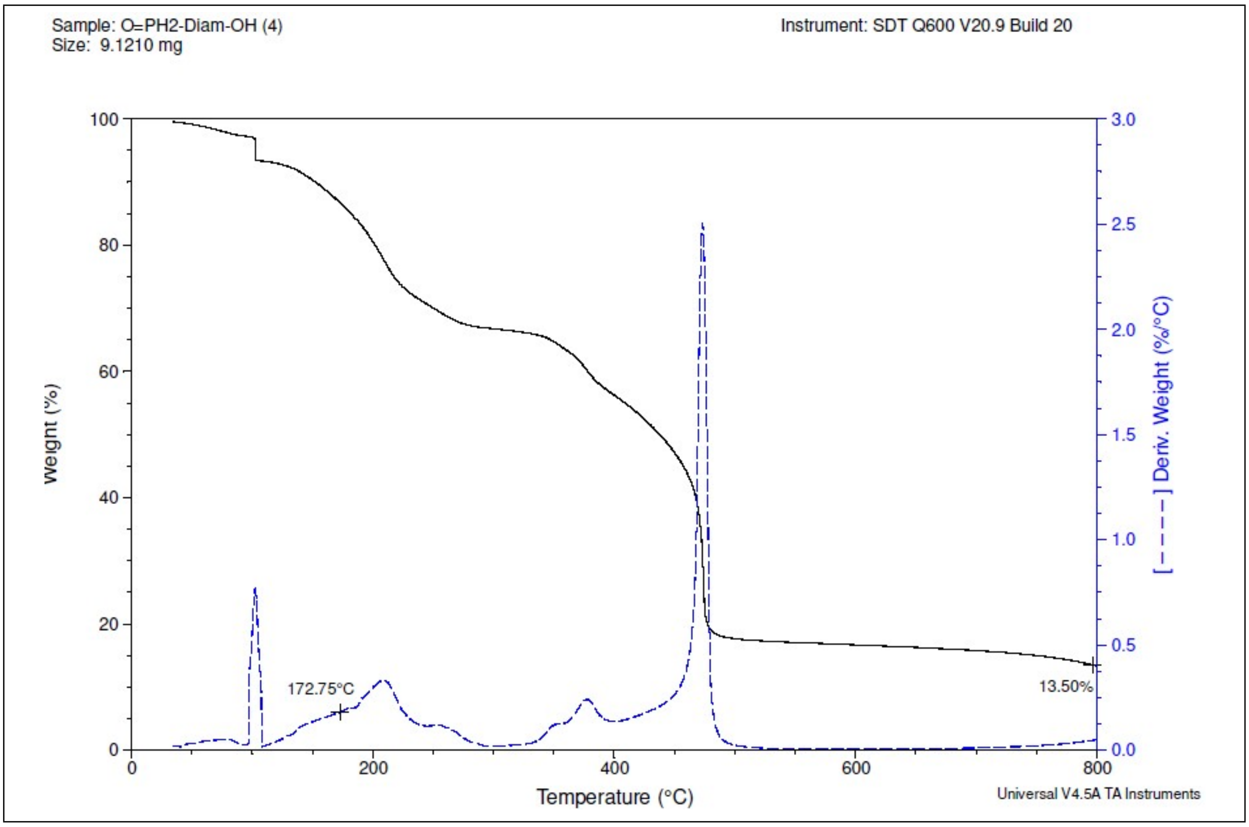


Figure S12e. SDT data of difunctionalized diamantane 5

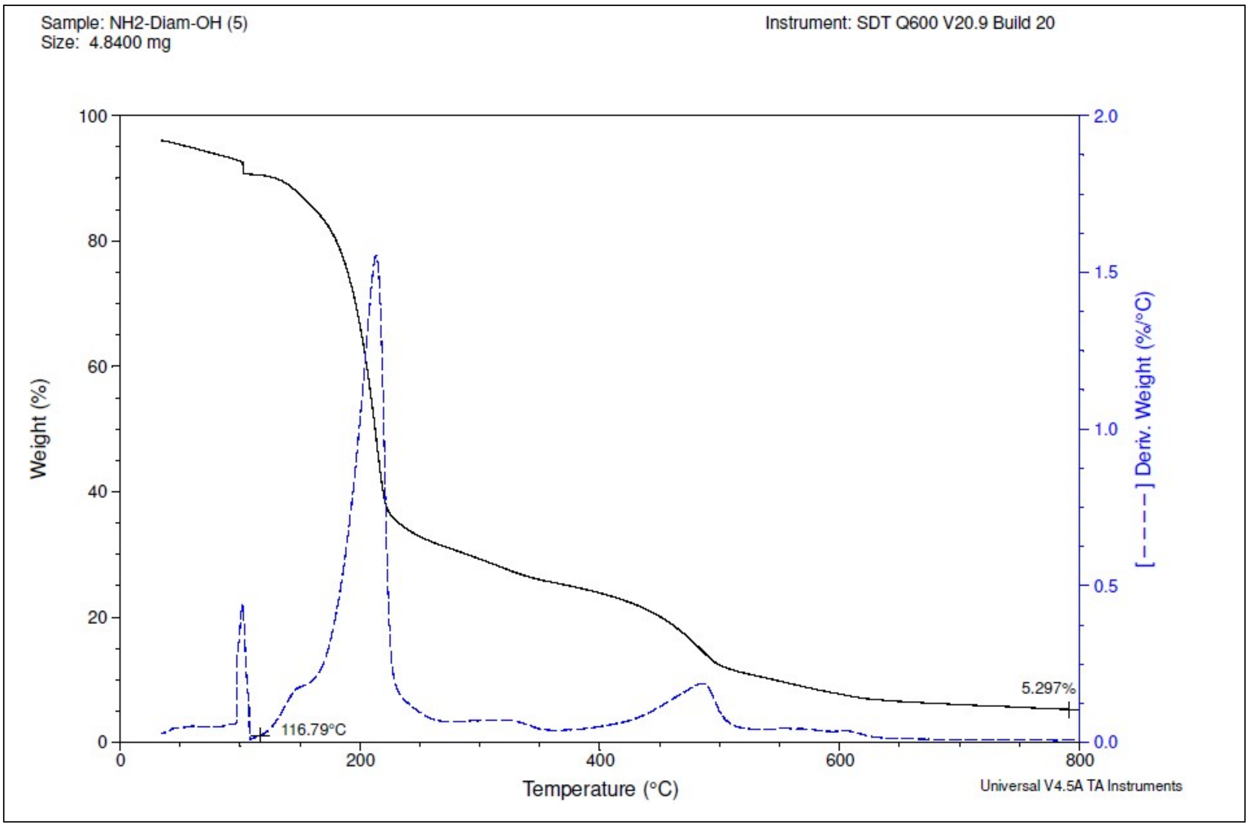
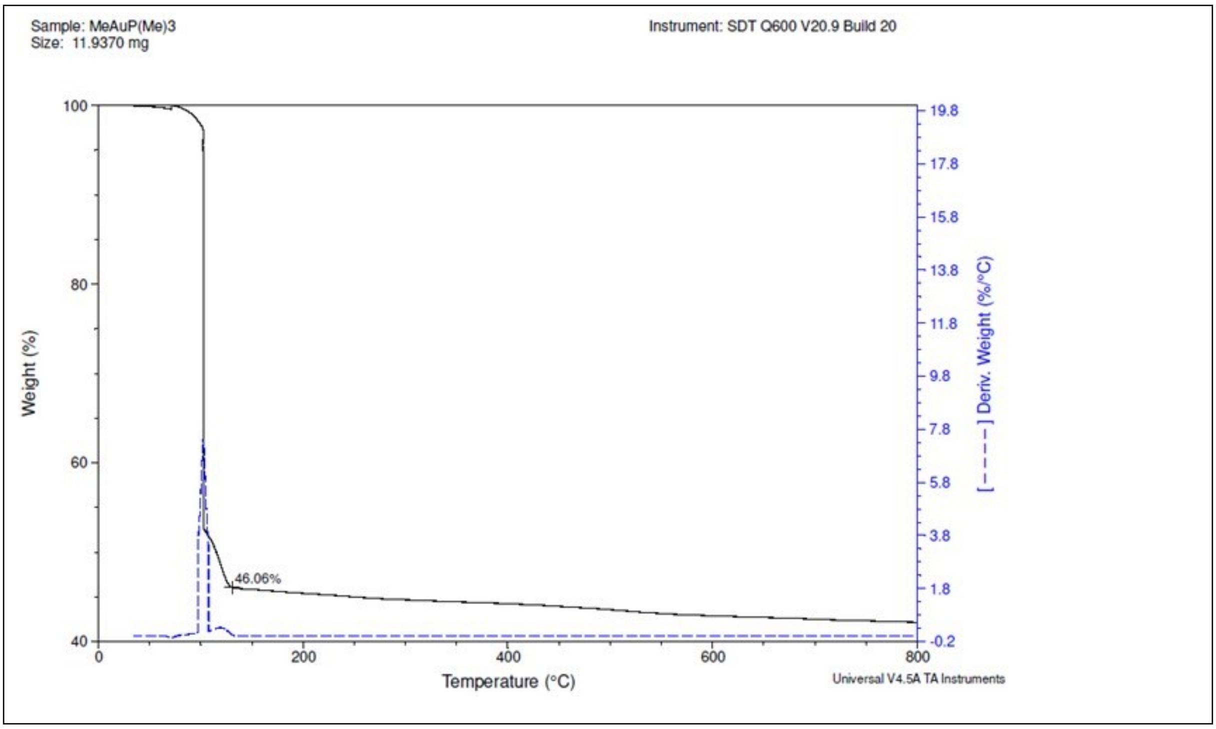
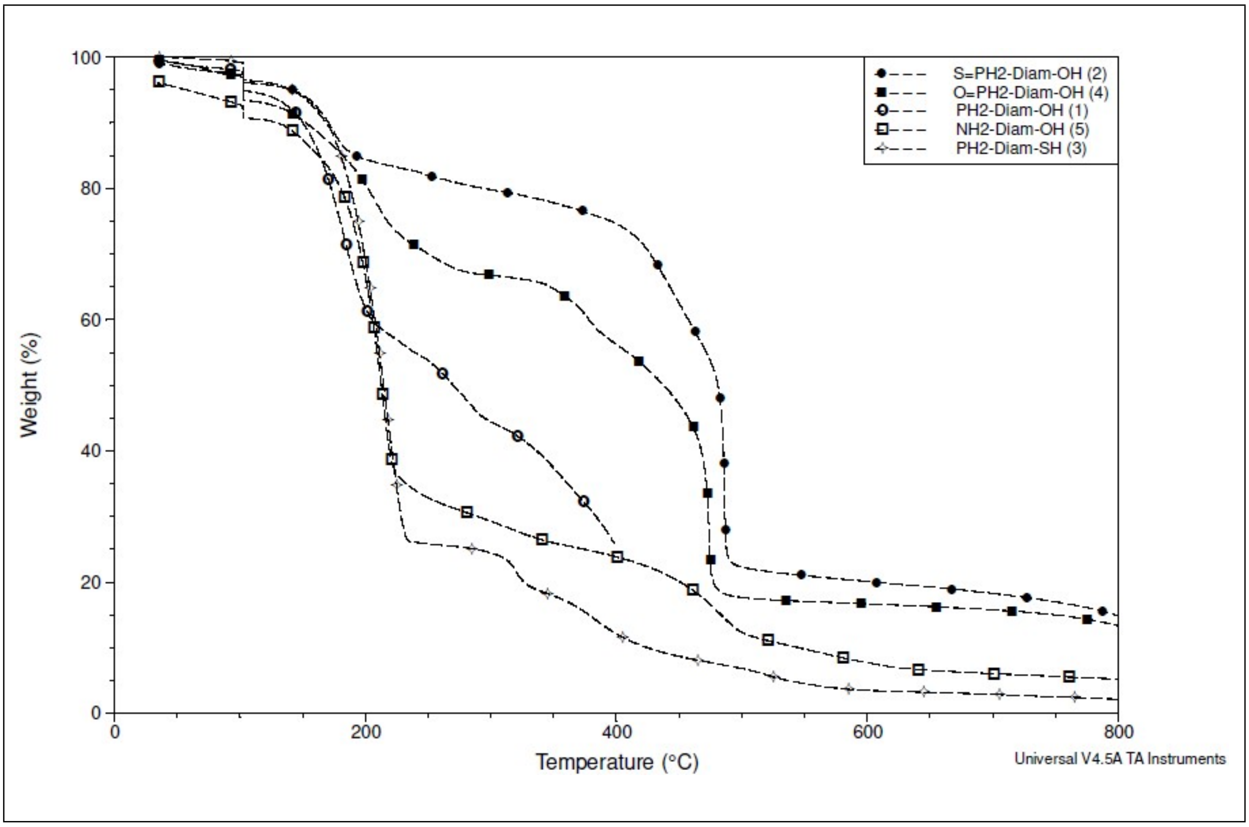


Figure S12f. SDT data of organometallic complex MeAuP(Me)$_3$



The SDT analyses of organometallic complex MeAuP(Me)$_3$ show a significant loss of mass from 95°C to 130°C, attributed to sublimation of the complex, with a remaining percentage of 46.06%. From pure decomposition the expected percentage of gold in the complex should be 68.39% (molecular weight of gold, equal to 196.97 g.mol-1, divided by the total molecular mass of the organometallic complex, equal to 288.03 g.mol-1). This percentage of only 46.06 % of gold is due to a decomposition step which starts at around 115 °C while the complex evaporation step takes place starting at 95°C.

Figure S12g. Overlay of SDT data of difunctionalized diamantane 1 to 5



The overlay of SDT data of difunctionalized diamantane **1** to **5** highlights the differences in the thermal stability (and volatility) of difunctionalized diamantane as a function of chemical modifications carried out either on the phosphine group or on the hydroxyl group. Interestingly, the difunctionalized diamantane **2** shows the greatest thermal up to 400 °C.