ChemistryOPEN

Supporting Information

A New Porphyrin for the Preparation of Functionalized Water-Soluble Gold Nanoparticles with Low Intrinsic Toxicity

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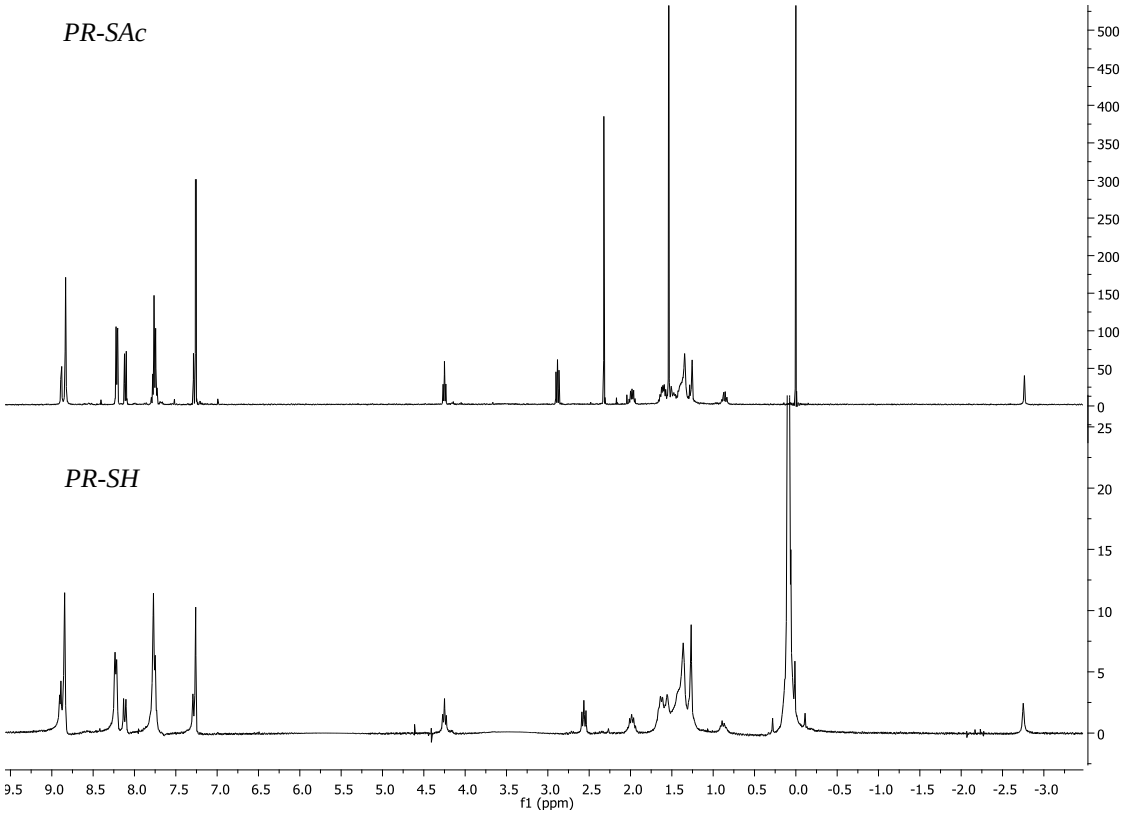


Figure S1. ^{1}H-NMR spectra of **PR-SAc** and **PR-SH** recorded in $CDCl_3$.

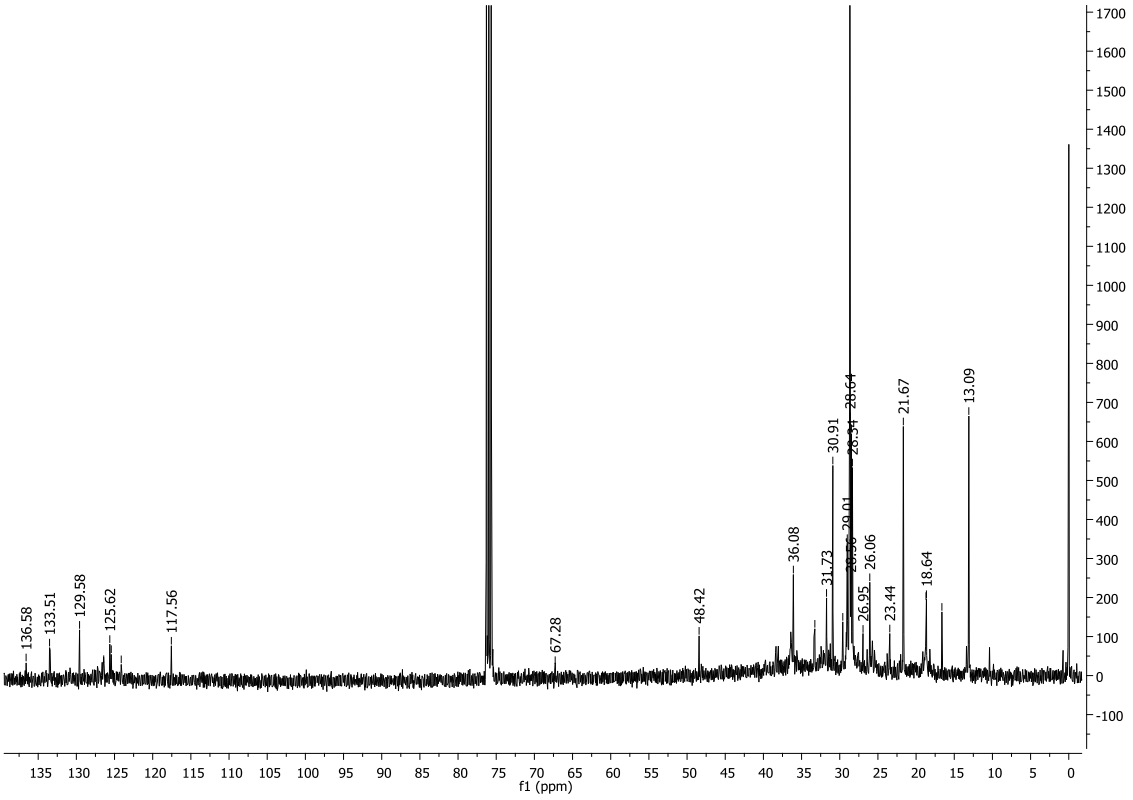


Figure S2. ^{13}C-NMR spectrum of **PR-SH** recorded in $CDCl_3$.

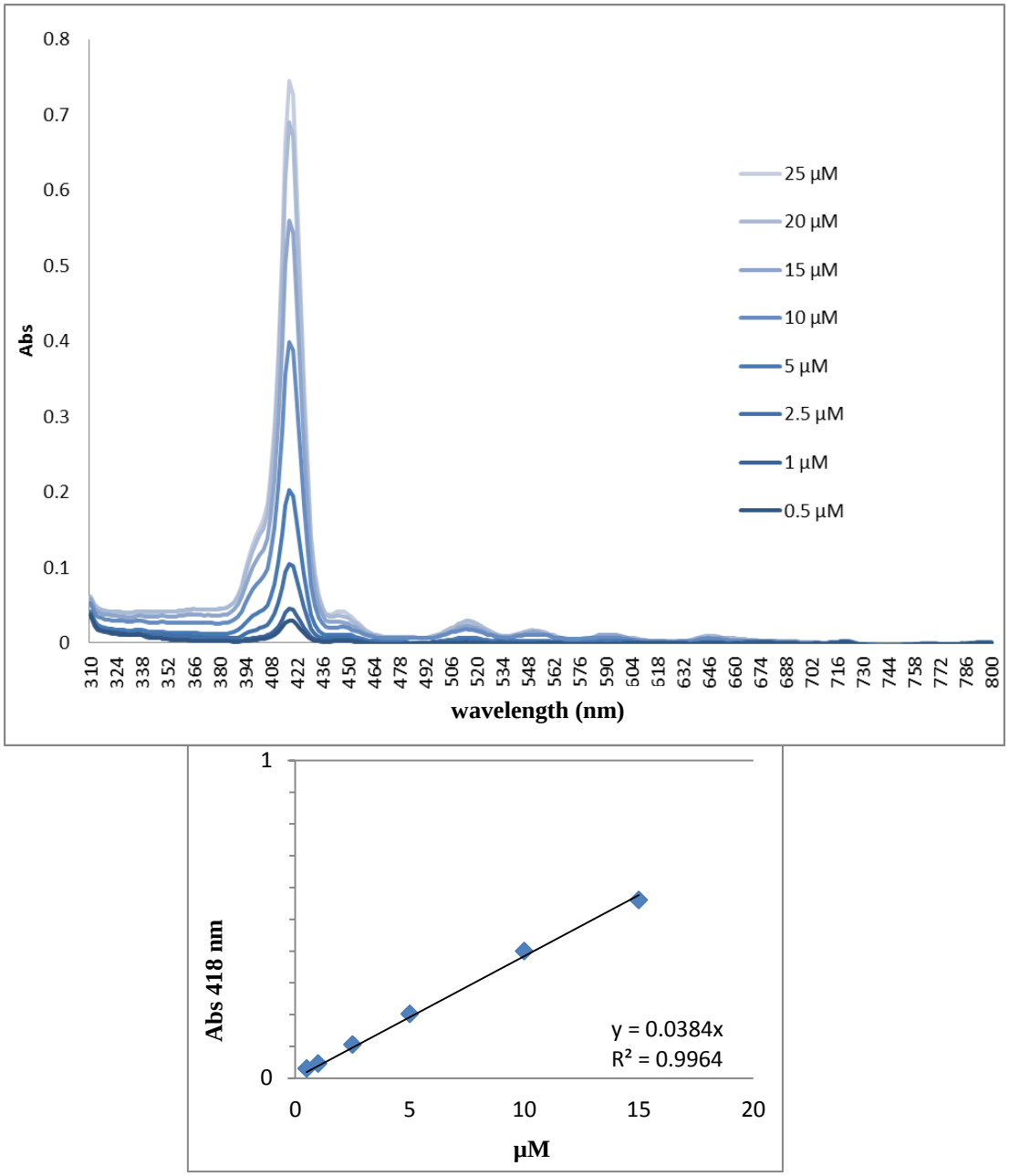
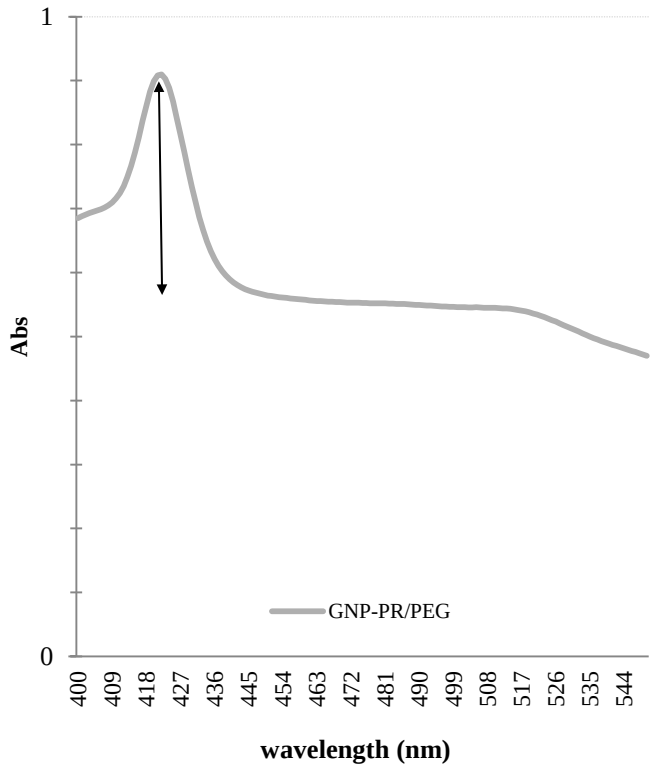


Figure S3. PR-SH UV-Vis absorption spectra at different concentrations (0.5-25 µM) in DCM and their corresponding calibration curve.



PR-SH concentration into **PR/PEG-GNP**:

Subtracting the Abs at 418 nm (0.861) – Abs at 460 nm (0.580) = 0.280 nm

If we applied the Lambert Beer law:

Abs = $\varepsilon \cdot cm \cdot C$ (ε_{418nm} = 0.03894 $mM \cdot cm^{-1}$)

We obtain C= 7.3 µM

Figure S4. UV-Vis absorption spectrum of functionalized **GNP-PR/PEG** and calculation of concentration of the functionalized porphyrin **PR-SH**.

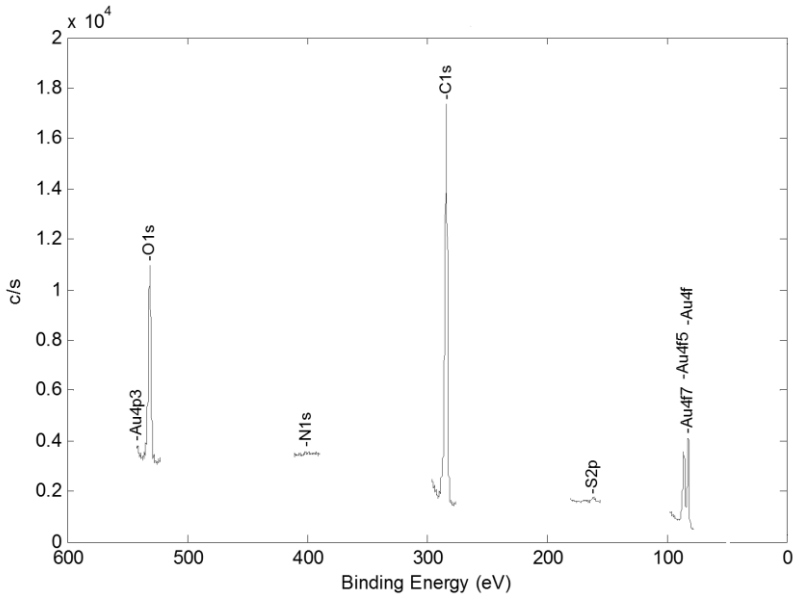


Figure S5. XPS spectrum of GNPs-**PR/PEG** after sputtering.

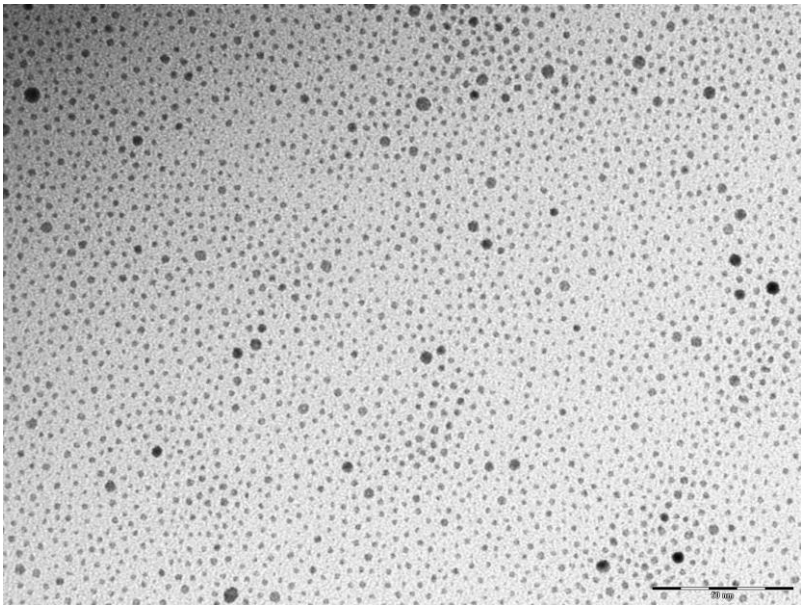


Figure S6. TEM image of **PEG-GNP**.

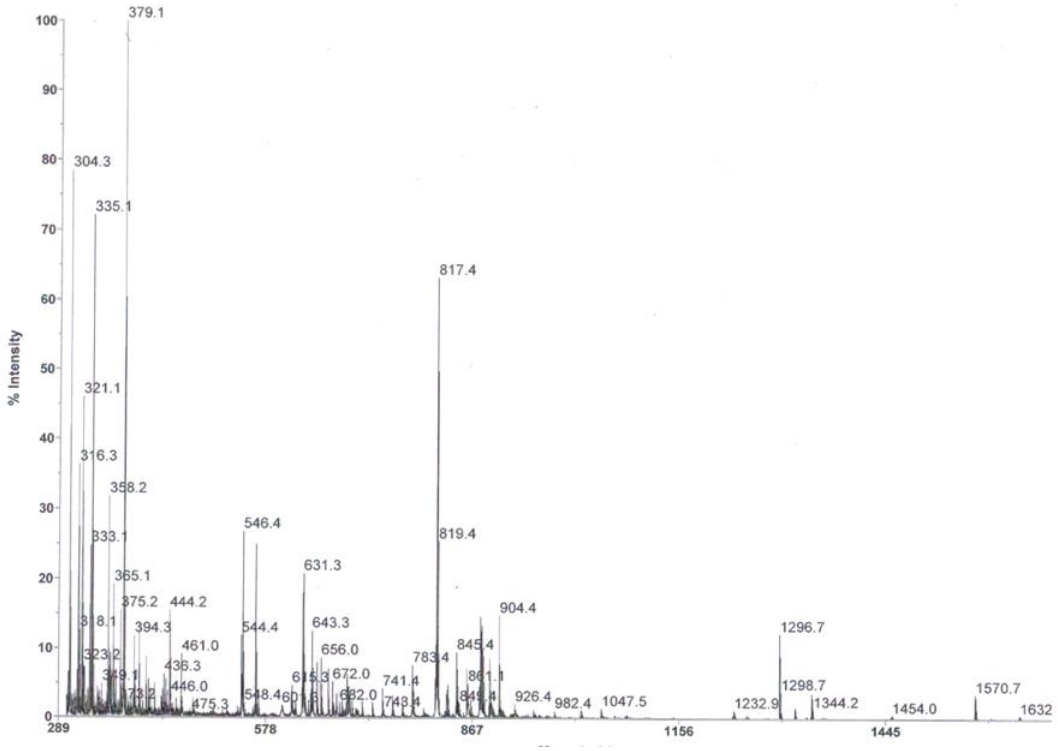


Figure S7. MALDI MS spectrum of **PR-SH**.

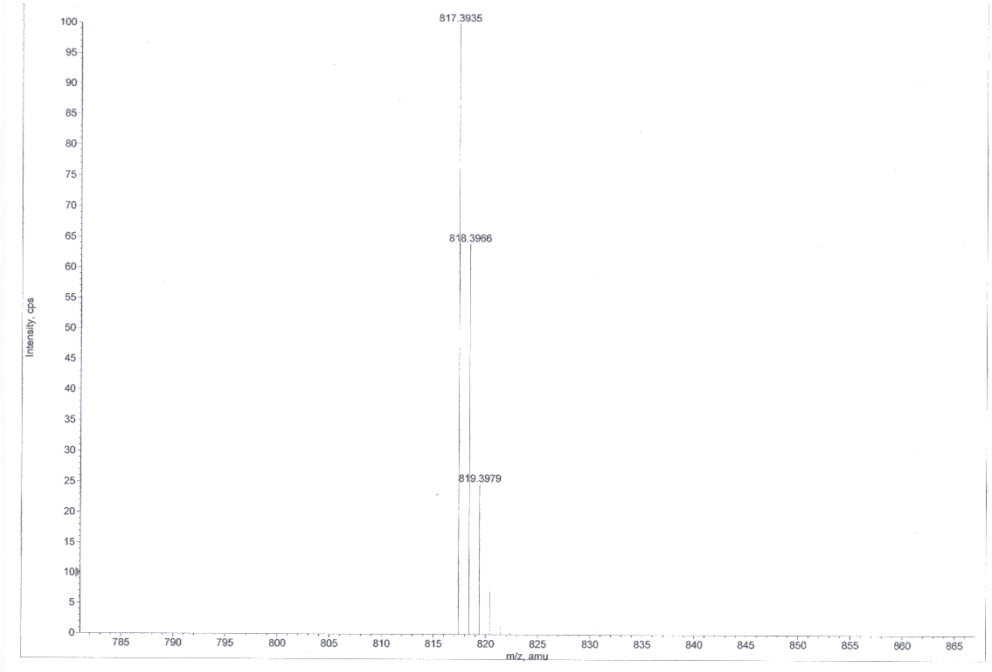


Figure S8. HR ESI-MS spectrum of **PR-SH.**

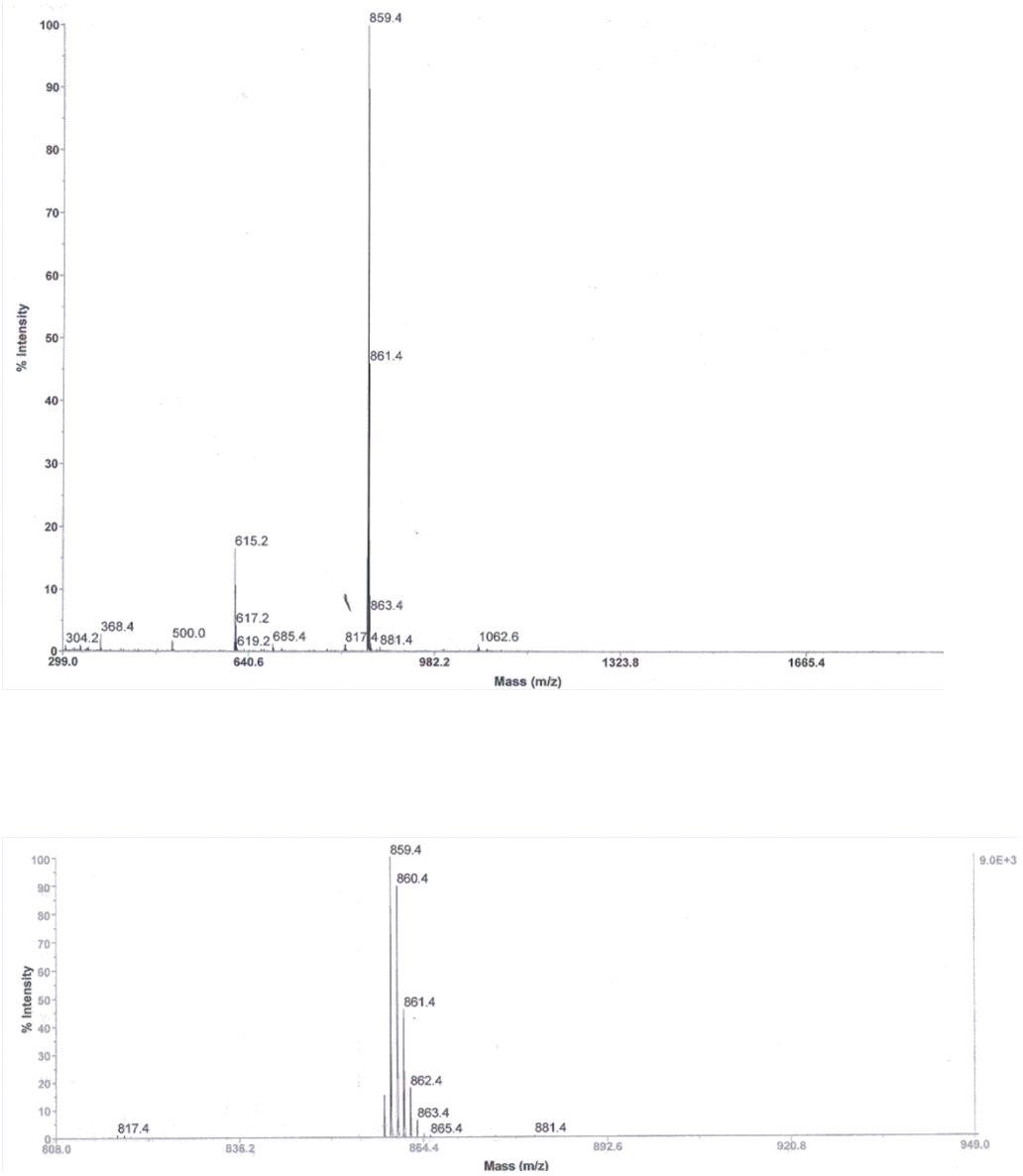


Figure S9. MALDI MS spectrum of **PR-SAc**.

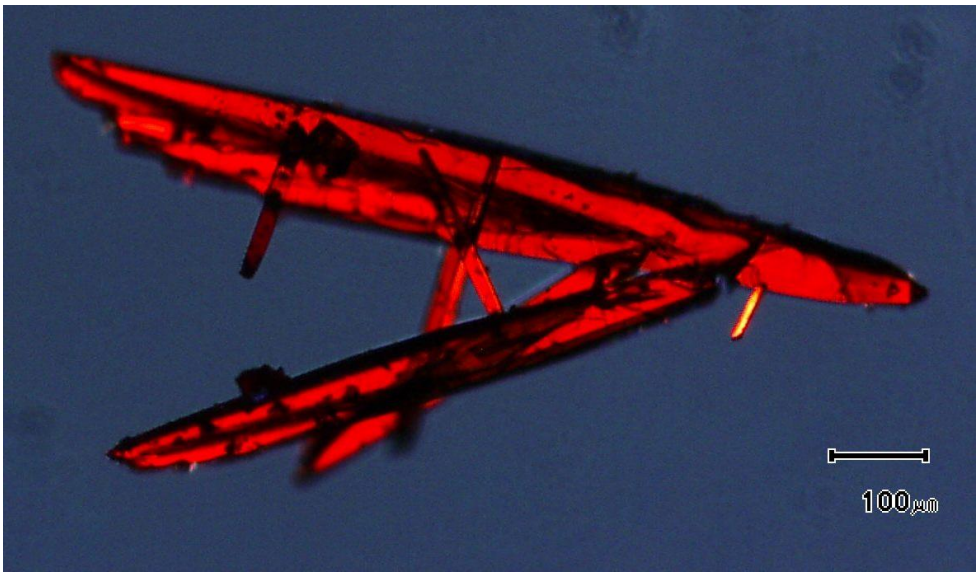


Figure S10. Polarised optical micrograph of crystals of **PR-OH**.

Crystallographic Data:

The porphyrin crystallizes in the space group P-1 with just one independent molecule in the unit cell, but where the hydroxyl group is disordered equally over the four positions where it could theoretically be located. The phenyl rings are rotated at approximately 60° (two in one helical direction and two in the other) to the tetrapyrrollic macrocycle (Figure S11).

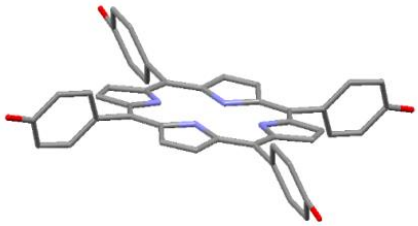


Figure S11. A view of the molecule **PR-OH** in its crystals, with the oxygen atom disordered over the four 4-positions of the phenyl rings. Hydrogen atoms are omitted for clarity.

In Figure S12 a view of the packing of the molecule is shown where local hydrogen bonds are indicated, although obviously any molecule may only possess on hydroxyl group, meaning that the intermolecular interactions of this type are present in the minority of cases. In the others, the 4-positions are either both occupied by hydrogen atoms (the majority case) or could contain a hydroxyl group next to a hydrogen atom. The hydrogen atoms at the centre of the porphyrin are also disordered in the structure. The hydroxyl oxygen atom, apart from forming a hydrogen bond with a neighbouring hydroxyl group, also forms weak hydrogen bonds with the CH groups of a pyrrole ring of an adjacent molecule (shortest C-H···O distance 2.99 Å, angle 117.6°, H···O distance 2.44 Å, not shown).

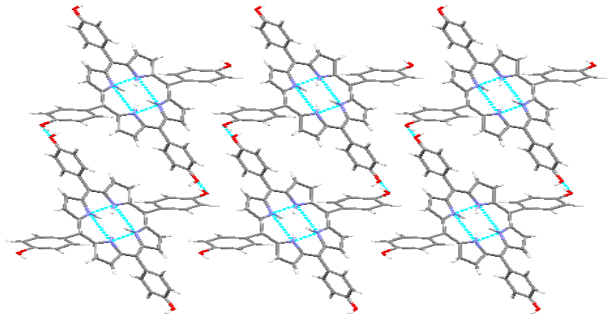


Figure S12. A view along the *a* axis of the crystal of **PR-OH** with the disordered hydrogen and oxygen atoms shown in all of their possible positions. The hydrogen bonds between neighbouring hydroxyl groups are shown in light blue, as are the close contacts between the pyrrollic nitrogen atoms at the core of the porphyrin.

The porphyrin molecules pack into sheets (Figure S13), where the hydrogen bonds between hydroxyl groups are in the plane, and weak interactions between the hydrogen atoms at the 2 and 3 positions of two of the phenyl rings with the π-bonds of the pyrrole rings in neighbouring macrocycles (approximate H···C distance 2.8 Å). There are no close contacts between the pyrrole rings, as is habitual in tetraphenyl porphyrins where the high angle formed between the aromatic segments does not allow a close approach of this type for steric reasons.

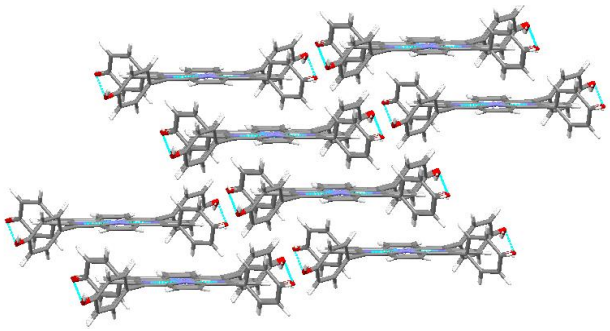


Figure S13. A view showing the sheets of porphyrin molecules in the crystal of **PR-OH** along the directions of the hydrogen bonds between molecules.

Table S1. Crystal data and structure refinement for **PR-OH** (CCDC 986636).

Empirical formula	C44 H30 N4 O	
Formula weight	630.72	
Temperature	233(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1 (no. 2)	
Unit cell dimensions	a = 6.4427(3) Å	α= 94.097(2)°.
	b = 10.3988(5) Å	β= 100.061(3)°.
	c = 12.5525(6) Å	γ = 100.294(3)°.
Volume	810.12(7) $Å^3$	
Z	1	
Density (calculated)	1.293 Mg/m^3	
Absorption coefficient	0.078 mm^{-1}	
F(000)	330	
Crystal size	0.33 x 0.11 x 0.04 mm^3	
Theta range for data collection	1.66 to 25.00°.	
Index ranges	-7<=h<=7, -12<=k<=12, -14<=l<=14	
Reflections collected	5164	
Independent reflections	2843 [R(int) = 0.0238]	
Reflections [I>2sigma(I)]	2160	
Completeness to theta = 25.00°	99.5 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2843 / 0 / 246	
Goodness-of-fit on F^2	1.032	
Final R indices [I>2sigma(I)]	R1 = 0.0446, wR2 = 0.1040	
R indices (all data)	R1 = 0.0638, wR2 = 0.1119	
Extinction coefficient	0.061(8)	
Largest diff. peak and hole	0.127 and -0.130 $e.Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **PR-OH**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	11001(9)	4883(6)	2675(5)	80(2)
O(2)	4160(10)	4247(6)	11720(4)	86(2)
C(14A)	9596(3)	4134(2)	3097(2)	59(1)
C(20A)	3947(5)	3617(2)	10790(2)	92(1)
C(14)	9596(3)	4134(2)	3097(2)	59(1)
C(20)	3947(5)	3617(2)	10790(2)	92(1)
N(1)	1297(2)	-92(1)	3577(1)	45(1)
N(2)	2622(2)	1354(1)	5746(1)	45(1)
C(1)	211(3)	-770(2)	2600(1)	47(1)
C(2)	1410(3)	-346(2)	1792(1)	54(1)
C(3)	3151(3)	568(2)	2284(2)	53(1)
C(4)	3094(2)	743(2)	3414(1)	45(1)
C(5)	4515(2)	1664(2)	4202(1)	44(1)
C(6)	4307(2)	1899(2)	5288(1)	45(1)
C(7)	5900(3)	2777(2)	6100(2)	53(1)
C(8)	5152(3)	2780(2)	7029(1)	54(1)
C(9)	3092(2)	1892(2)	6814(1)	45(1)
C(10)	1780(3)	1636(2)	7584(1)	46(1)
C(11)	6316(2)	2523(2)	3829(1)	45(1)
C(12)	7834(3)	2001(2)	3378(2)	55(1)
C(13)	9454(3)	2798(2)	3009(2)	60(1)
C(15)	8126(3)	4679(2)	3555(2)	60(1)
C(16)	6484(3)	3881(2)	3909(2)	53(1)

C(17)	2556(3)	2320(2)	8712(1)	52(1)
C(18)	4432(3)	2133(2)	9354(2)	66(1)
C(19)	5141(4)	2801(3)	10393(2)	82(1)
C(21)	2088(5)	3800(2)	10174(2)	93(1)
C(22)	1411(4)	3170(2)	9143(2)	72(1)

Table S3. Bond lengths [Å] and angles [°] for PR-OH.

O(1)-C(14A)	1.296(5)
O(1)-H(1O)	0.8300
O(2)-C(20A)	1.271(5)
O(2)-H(2O)	0.8300
C(14A)-C(13)	1.371(3)
C(14A)-C(15)	1.373(3)
C(20A)-C(21)	1.359(4)
C(20A)-C(19)	1.366(4)
N(1)-C(4)	1.373(2)
N(1)-C(1)	1.374(2)
N(1)-H(1N)	0.90(2)
N(2)-C(6)	1.369(2)
N(2)-C(9)	1.375(2)
N(2)-H(2N)	0.97(7)
C(1)-C(10)#1	1.402(2)
C(1)-C(2)	1.426(2)
C(2)-C(3)	1.355(2)
C(2)-H(2)	0.9400
C(3)-C(4)	1.426(2)
C(3)-H(3)	0.9400
C(4)-C(5)	1.403(2)
C(5)-C(6)	1.402(2)
C(5)-C(11)	1.497(2)
C(6)-C(7)	1.446(2)
C(7)-C(8)	1.338(2)
C(7)-H(7)	0.9400
C(8)-C(9)	1.445(2)

C(8)-H(8)	0.9400
C(9)-C(10)	1.401(2)
C(10)-C(1)#1	1.402(2)
C(10)-C(17)	1.497(2)
C(11)-C(12)	1.383(2)
C(11)-C(16)	1.392(2)
C(12)-C(13)	1.380(2)
C(12)-H(12)	0.9400
C(13)-H(13)	0.9400
C(15)-C(16)	1.382(2)
C(15)-H(15)	0.9400
C(16)-H(16)	0.9400
C(17)-C(18)	1.384(3)
C(17)-C(22)	1.386(3)
C(18)-C(19)	1.393(3)
C(18)-H(18)	0.9400
C(19)-H(19)	0.9400
C(21)-C(22)	1.369(3)
C(21)-H(21)	0.9400
C(22)-H(22)	0.9400

O(1)-C(14A)-C(13)	120.7(3)
O(1)-C(14A)-C(15)	119.2(3)
C(13)-C(14A)-C(15)	119.87(16)
O(2)-C(20A)-C(21)	107.6(4)
O(2)-C(20A)-C(19)	131.6(4)
C(21)-C(20A)-C(19)	120.7(2)
C(4)-N(1)-C(1)	109.45(14)
C(4)-N(1)-H(1N)	124.6(14)

C(1)-N(1)-H(1N)	125.6(14)
C(6)-N(2)-C(9)	105.96(14)
C(6)-N(2)-H(2N)	128(4)
C(9)-N(2)-H(2N)	126(4)
N(1)-C(1)-C(10)#1	126.53(15)
N(1)-C(1)-C(2)	107.01(14)
C(10)#1-C(1)-C(2)	126.29(16)
C(3)-C(2)-C(1)	108.28(15)
C(3)-C(2)-H(2)	125.9
C(1)-C(2)-H(2)	125.9
C(2)-C(3)-C(4)	108.03(15)
C(2)-C(3)-H(3)	126.0
C(4)-C(3)-H(3)	126.0
N(1)-C(4)-C(5)	126.12(15)
N(1)-C(4)-C(3)	107.22(14)
C(5)-C(4)-C(3)	126.51(15)
C(6)-C(5)-C(4)	125.32(15)
C(6)-C(5)-C(11)	117.54(14)
C(4)-C(5)-C(11)	117.02(15)
N(2)-C(6)-C(5)	126.50(15)
N(2)-C(6)-C(7)	109.84(15)
C(5)-C(6)-C(7)	123.66(15)
C(8)-C(7)-C(6)	107.28(15)
C(8)-C(7)-H(7)	126.4
C(6)-C(7)-H(7)	126.4
C(7)-C(8)-C(9)	107.04(15)
C(7)-C(8)-H(8)	126.5
C(9)-C(8)-H(8)	126.5
N(2)-C(9)-C(10)	125.65(14)

N(2)-C(9)-C(8)	109.85(15)
C(10)-C(9)-C(8)	124.49(15)
C(9)-C(10)-C(1)#1	125.67(15)
C(9)-C(10)-C(17)	118.18(14)
C(1)#1-C(10)-C(17)	116.14(15)
C(12)-C(11)-C(16)	117.84(15)
C(12)-C(11)-C(5)	121.58(14)
C(16)-C(11)-C(5)	120.57(14)
C(13)-C(12)-C(11)	121.17(15)
C(13)-C(12)-H(12)	119.4
C(11)-C(12)-H(12)	119.4
C(14A)-C(13)-C(12)	120.13(16)
C(14A)-C(13)-H(13)	119.9
C(12)-C(13)-H(13)	119.9
C(14A)-C(15)-C(16)	120.04(16)
C(14A)-C(15)-H(15)	120.0
C(16)-C(15)-H(15)	120.0
C(15)-C(16)-C(11)	120.93(16)
C(15)-C(16)-H(16)	119.5
C(11)-C(16)-H(16)	119.5
C(18)-C(17)-C(22)	117.89(17)
C(18)-C(17)-C(10)	121.44(16)
C(22)-C(17)-C(10)	120.67(16)
C(17)-C(18)-C(19)	120.3(2)
C(17)-C(18)-H(18)	119.9
C(19)-C(18)-H(18)	119.9
C(20A)-C(19)-C(18)	119.8(2)
C(20A)-C(19)-H(19)	120.1
C(18)-C(19)-H(19)	120.1

C(20A)-C(21)-C(22)	119.8(2)
C(20A)-C(21)-H(21)	120.1
C(22)-C(21)-H(21)	120.1
C(21)-C(22)-C(17)	121.6(2)
C(21)-C(22)-H(22)	119.2
C(17)-C(22)-H(22)	119.2

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z+1

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **PR-OH**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	66(4)	82(4)	80(4)	16(3)	25(3)	-29(3)
O(2)	99(5)	93(4)	47(3)	-28(3)	11(3)	-11(3)
C(14A)	48(1)	59(1)	64(1)	14(1)	11(1)	-5(1)
C(20A)	130(2)	77(2)	57(2)	-7(1)	23(2)	-13(2)
C(14)	48(1)	59(1)	64(1)	14(1)	11(1)	-5(1)
C(20)	130(2)	77(2)	57(2)	-7(1)	23(2)	-13(2)
N(1)	42(1)	43(1)	49(1)	4(1)	10(1)	4(1)
N(2)	41(1)	40(1)	51(1)	6(1)	8(1)	3(1)
C(1)	46(1)	44(1)	50(1)	2(1)	9(1)	8(1)
C(2)	54(1)	54(1)	52(1)	1(1)	15(1)	4(1)
C(3)	50(1)	51(1)	58(1)	4(1)	18(1)	3(1)
C(4)	41(1)	40(1)	56(1)	6(1)	13(1)	6(1)
C(5)	39(1)	39(1)	55(1)	9(1)	10(1)	7(1)
C(6)	38(1)	41(1)	56(1)	10(1)	8(1)	5(1)
C(7)	43(1)	52(1)	58(1)	6(1)	7(1)	-4(1)
C(8)	50(1)	53(1)	53(1)	2(1)	4(1)	-4(1)
C(9)	43(1)	40(1)	50(1)	5(1)	5(1)	5(1)
C(10)	44(1)	42(1)	50(1)	3(1)	6(1)	6(1)
C(11)	40(1)	43(1)	52(1)	7(1)	7(1)	5(1)
C(12)	46(1)	45(1)	76(1)	11(1)	15(1)	10(1)
C(13)	45(1)	63(1)	76(1)	12(1)	18(1)	11(1)
C(15)	63(1)	41(1)	71(1)	10(1)	13(1)	-1(1)
C(16)	53(1)	44(1)	63(1)	5(1)	16(1)	7(1)

C(17)	53(1)	49(1)	52(1)	5(1)	12(1)	-1(1)
C(18)	61(1)	76(1)	56(1)	6(1)	8(1)	3(1)
C(19)	77(1)	97(2)	58(1)	15(1)	0(1)	-13(1)
C(21)	134(2)	76(2)	69(2)	-11(1)	23(2)	21(2)
C(22)	85(1)	62(1)	68(1)	-1(1)	17(1)	14(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **PR-OH**.

	x	y	z	U(eq)
H(1N)	840(30)	-120(20)	4210(20)	46(6)
H(2N)	1340(110)	730(70)	5400(50)	51(19)
H(1O)	11520	4424	2264	120
H(2O)	3244	3881	12048	129
H(14)	10697	4676	2843	71
H(20)	4415	4056	11495	111
H(2)	1054	-649	1047	65
H(3)	4211	1010	1939	64
H(7)	7217	3256	5994	64
H(8)	5837	3267	7697	65
H(12)	7762	1087	3321	66
H(13)	10463	2424	2698	72
H(15)	8237	5596	3628	72
H(16)	5466	4260	4208	64
H(18)	5232	1552	9089	79
H(19)	6437	2691	10820	99
H(21)	1269	4357	10455	112
H(22)	140	3317	8717	86