Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supporting Information

Silk fibroin nanoparticles as biocompatible nanocarriers of a novel light-responsive CO-prodrug

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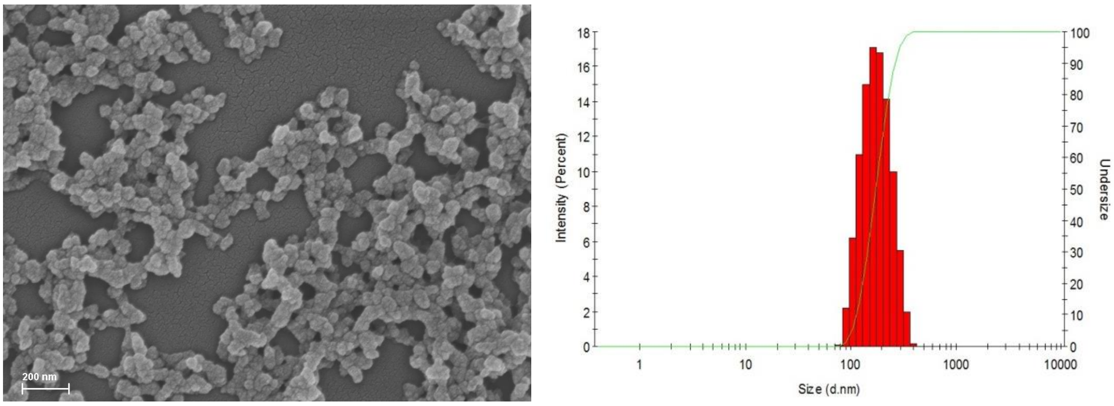

Figure S1. SEM image (left) and DLS size distribution profile (right) of silk fibroin nanoparticles (SFNs).

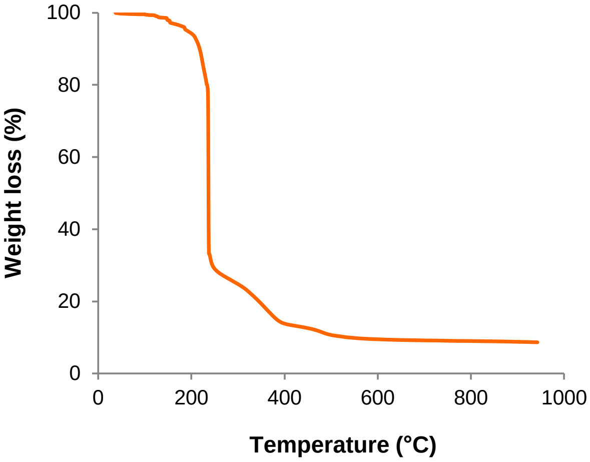

Figure S2. Thermogravimetric analysis of [Mn(CO)$_3$(bpy)(PPh$_3$)](ClO$_4$) (**1**).

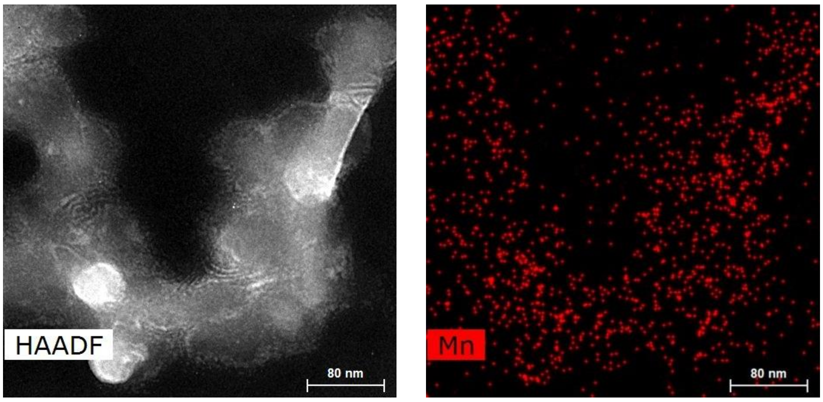

Figure S3. Elemental mapping obtained by EDX-TEM of **1@SFNs**. The presence of manganese into the nanoparticles is confirmed.

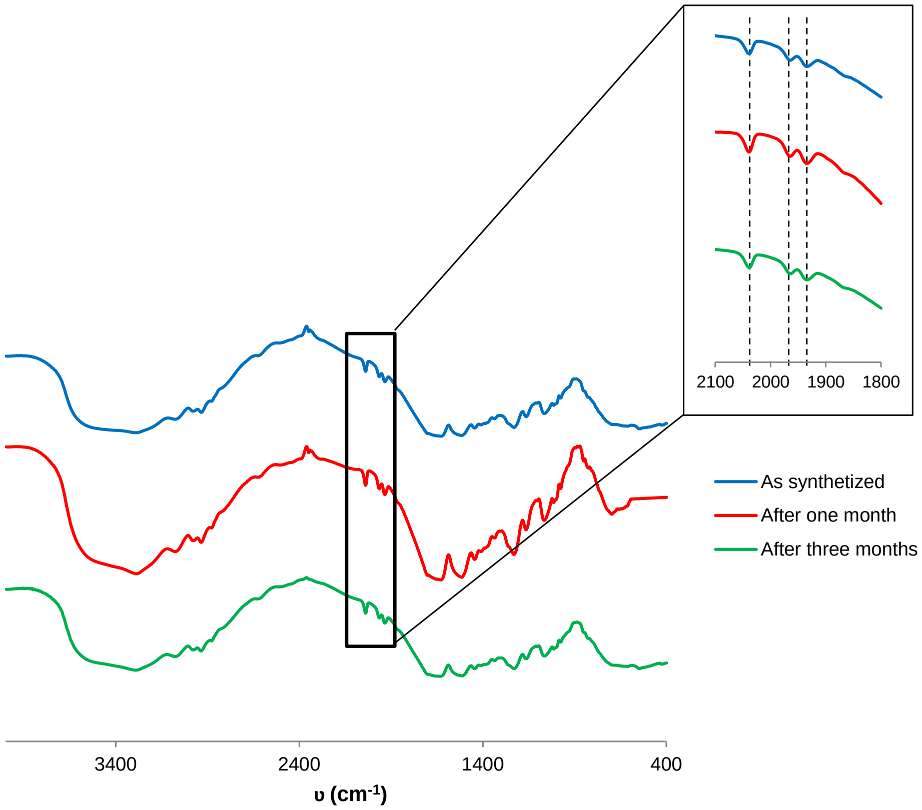

Figure S4. Storage stability studies of **1@SFNs** by means of quantitative IR spectroscopy.

Table S1. Quantification of $[Mn(CO)_3(bpy)(PPh_3)](ClO_4)$ (**1**) loading in the hybrid materials.

CORM/SFNs ratio	Incubation time	CORM cargo (mg per 100 mg)
1/10	30 min	1.18 ± 0.17
1/50	30 min	0.60 ± 0.05
	1 h	0.63 ± 0.03
	3 h	0.57 ± 0.02
1/100	30 min	0.48 ± 0.05

Table S2. Quantification of $[Mn(CO)_3(bpy)Br]$ loading in the hybrid materials as control.

CORM/SFNs ratio	Incubation time	CORM cargo (mg per 100 mg)
1/10	30 min	0.90 ± 0.08
1/50	30 min	0.41 ± 0.01
1/100	30 min	0.33 ± 0.01

EXPERIMENTAL SECTION

1. General methods

Elemental (C, H, N) analyses were obtained in a THERMO SCIENTIFIC Flash 2000 instrument (CIC, University of Granada). Thermogravimetric analyses were performed using a Mettler Toledo TGA/DSC STAR system under oxygen flow (10 mL min^{-1}) running from RT to 950 ºC with a heating rate of 20 ºC min^{-1} (CIC, University of Granada). The infrared spectra data were collected with a Fourier transform infrared spectrophotometer Bruker Tensor 27. Single X-ray diffraction data were recorded in a Bruker D8 Venture with an area detector Photon 100 (CMOS) (CIC, University of Granada). Solid state fluorescence spectra were registered in a Varian Cary Eclipse and reflectance diffuse in a Varian Cary-5E (CIC, University of Granada). Inductively Coupled Plasma Mass spectrometry (ICP-MS) was carried out in an AGILENT 7500a (CICT, University of Jaén). UV−vis spectra were collected on a Shimadzu UV spectrophotometer. Scanning Electron Microscopy images were recorded using a MERLINTM VP COMPACT Carl Zeiss Microscopy (Catholic University of Murcia). A 10 µL aliquot of an aqueous suspension of nanoparticles was dropped onto a clean glass wafer, fixed onto an aluminium stub by a double tapered carbon film before drying overnight and then were sputter-coated with 5 nm platinum high-vacuum coater Leica EM ACE 600. TEM-EDX elemental mapping were performed using a JEOL JEM-1400 (Central Services Research Support, University of Malaga). Samples were prepared by dispersing by sonication a small amount of the material (2 mg) in water (1 mL). A drop of the suspension was deposited on a copper grid. DLS and Z-potential measurements were carried out in a Zetasizer NanoZS (Malvern) instrument of the Department of Applied Physics of the University of Granada.

2. Synthesis and characterization of materials

All chemical and solvents were commercially available and used without further purification.

2.1. Silk fibroin extraction

Silk fibroin was obtained from white silk cocoons from *Bombyx mori* silkworms reared at the facilities of the IMIDA (Murcia, Spain) fed on *M. alba L.* fresh leaves under GMP compliances in a clean room. Five days after spinning the cocoon, the pupae were extracted alive from the cocoons by cutting open the cocoons, in order to avoid the SF contamination in further steps.

2.2. Preparation of liquid silk fibroin

Prior to silk fibroin (SF) dissolution, the silk cocoons were boiled in a 0.05 M Na_2CO_3 aqueous solution for 45 minutes to remove the sericins. The resultant cotton-like SF fibers were rinsed thoroughly with ultrapure water and left to dry at room temperature overnight. Then, SF was dissolved at 10% (w/v) in Ajisawa's reagent,[1] composed of a mixture of $CaCl_2$/ethanol/H_2O (1:2:8), and left for 4 h at 65 ºC. To remove salts, small peptides and other impurities, the hydro-alcoholic silk solution was dialyzed for 48

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[1] A. Ajisawa, *J. Seric. Sci. Jpn.*, **1998**, *67*, 91–94.

h against ultra-pure water using a cellulose semi-permeable membrane (cut-off 3.5 KD). This gave a final SF concentration of 2 wt.% in ultrapure water.

2.3. Preparation of silk fibroin nanoparticles (SFNs)

SFNs were prepared following an adaptation of the previously described method by Zhang *et al.*[2,3] Briefly, the freshly prepared SF aqueous solution was slowly dropped into a vigorously stirred methanolic solution. The nanoparticles suspension was centrifuged at 8 °C (15 min, 12000 *g*) and the pellet was repeatedly washed (3 x 20 mL) by resuspending it by vigorous stirring (using a vortex and ultrasonication for 5 min) in ultrapure water. Finally, the SFNs were maintained in ultrapure water (20 mg/mL) at 4 ºC until use.

2.4. Synthesis of $[Mn(CO)_3(bpy)(PPh_3)]ClO_4$ (1)

All manipulations were performed under inert atmosphere, using standard Schlenk-line techniques, and in darkness in order to avoid the photoactivation of the carbonyl metal complexes. Prior to use, all solvents were degassed by bubbling a N_2 flow.

The manganese-tricarbonyl complex $[Mn(CO)_3(bpy)(PPh_3)]ClO_4$ (1) (bpy = 2'2'-bipyridyl, PPh_3= triphenylphosphane) was synthesized in 3 different steps. Firstly, $[Mn(CO)_3(bpy)Br]$ was prepared according to a previously reported procedure,[4] by reacting $[Mn(CO)_5Br]$ (100.0 mg, 0.36 mmol) with a 20 % excess of 2,2'-bipyridine (67.5 mg, 0.43 mmol) in 30 mL of refluxing hexane during 30 min. The yellow precipitate was collected by filtration and washed with hexane. Afterwards, $[Mn(CO)_3(bpy)Br]$ (30.0 mg, 0.11 mmol) and $AgClO_4$ (34.0, 0.14 mmol) were stirred in 5 mL of acetone at room temperature during 20 minutes. After removing AgBr, the mother solution was concentrated under reduced pressure to a thick syrup. Addition of diethlylether led to $[Mn(CO)_3(bpy)(solv)]ClO_4$ which was collected by filtration. Finally, a mixture of $[Mn(CO)_3(bpy)(solv)]ClO_4$ (15 mg, 0.04 mmol) and an excess of triphenylphosphane (14.9 mg, 0.06 mmol) was stirred in 3 mL of acetone during 3 h at room temperature. The solvent was evaporated and the as-synthesized solid was recrystallized in dichloromethane-ethanol (1:1) giving rise to orange crystals suitable for X-ray structure analysis.

Anal. Calc. for $[Mn(CO)_3Br]$ (neutral precursor): N 7.47, C 41.63, H 2.15; found: N 7.38, C: 40.42, H; 2.19. M.W: 375.1 g/mol. Calculated residue (MnO) after thermal treatment: 19.9 %; found: 23.4 %.

Anal. Calc. for $[Mn(CO)_3(bpy)(PPh_3)]ClO_4$ (**1**): N 4.26, C 56.68, H 3.53; found: N 4.41, C: 56.97, H; 3.79. M.W: 656.9 g/mol. Calculated residue (MnO) after thermal treatment: 10.8 %; found: 8.7 %.

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[2] Y. Zhang, W. Shen, R. Xiang, L. Zhuge, W. Gao W. Wang, *J. Nanopart. Res*. **2007**, *9*, 885-900.

[3] A. A. Lozano-Pérez, H. Correa Rivero, M. C. Pérez Hernández, A. Pagán, M. G. Montalbán, G. Víllora and J. L. Cénis, *Int. J. Pharm*., **2017**, *518*, 11-19.

[4] R. Usón, V. Riera, J. Gimeno and M. Laguna, *Transit. Met. Chem.*, **1977**, *2*, 123-130.

2.5. Preparation of the hybrid material

Screening studies

Initially, an aqueous suspension of silk fibroin nanoparticles (20 mg mL^{-1}) and a methanolic solution of **1** (0.2 mg mL^{-1}) were prepared. Then, 500 µL of 1 was mixed with different volumes of silk fibroin stock suspension (see below) to a final volume of 1 mL. In all cases, the MeOH:H_2O ratio was kept constant to 1:1. The suspensions were incubated at room temperature, under orbital stirring and in darkness, during 30 min. Additionally, in the case of 1/50 CORM/SFNs w/w ratio, two extra incubation periods were also assayed (1 and 3 h). After each incubation time, the corresponding solids were collected by centrifugation (10 min, 16000 *g*), washed with MeOH:H_2O (3 x 1 mL) and dried under N_2 flow.

Sample	Volume of **1** (µL)	Volume of **SFNs** (µL)	Volume H_2O (µL)
1/10	500	50	450
1/50	500	250	250
1/100	500	500	0

Mn quantification was determined by ICP-MS (see Table S1). Prior to measurement, 2 mg of **1@SFNs** was degraded in 1 mL of concentrated HNO_3 (69 %). Then, 579 µL of this solution was diluted with water to a final concentration of 4 % in HNO_3.

*Scale-up synthesis of **1@SNFs***

In a typical procedure, 0.5 mL of an aqueous suspension of silk fibroin nanoparticles (20 mg mL^{-1}) was diluted with 4.5 mL of ultrapure water and then, mixed with 5 mL of a methanolic solution of **1** (0.2 mg mL^{-1}). The suspension was incubated at room temperature, under orbital stirring and in darkness, during 30 min. The solid was collected by centrifugation (10 min, 16000 *g*), washed with MeOH:H_2O (3 x 10 mL) and dried under N_2 flow.

4. Determination of CO-release by Myoglobin Assay.

The CO release from **1** and **1@SFNs** was studied, as previously described,[5,6] by monitoring the conversion of deoxy-myoglobin (deoxy-Mb) to carbonmonoxy-myoglobin (CO-Mb). The amount of CO-Mb was quantified by measuring the absorbance at 423 nm at different times. Firstly, myoglobin stock solution from equine heart (100 µM), sodium dithionite (24 mg mL^{-1}), and stock suspension of **1@SFNs** (0.2 mM, based on **1**) were freshly prepared in degassed PBS (10 mM, pH = 7.4). In the case of **1**, and due to solubility reasons, a 0.2 mM stock solution was obtained by mixing 100 µL of methanol and 900 µL of degassed PBS. In a typical experiment, 100 µL of myoglobin stock solution, 100 µL of sodium dithionite stock solution, 790 µL of degassed PBS and 10 µL of **1** or **1@SFNs** were

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[5] D. E. Bikiel, E. G. Solveyra, F. Di Salvo, H. M. S. Milagre, M. N. Eberlin, R. S. Corrêa, J. Ellena, D. A. Estrin and F. Doctorovich, *Inorg. Chem.*, **2011**, *50*, 2334–2345.

[6] R. Motterlini, J. E. Clark, R. Foresti, P. Sarathchandra, B. E. Mann and C. J. Green, *Circ. Res.*, **2002**, *90*, e17–e24.

added in a sealed quartz cuvette, under inert atmosphere, and kept at 37 ºC under visible light (luminous flux, 600 lm; color temperature, 4000 K, distance between lamp and cuvette, 5 cm). The concentration of CO-Mb was recorded at different times (0, 15, 30, 45, 60, 75, 90, 105, 120 min) with the aim to determine the total amount of released CO. Additional experiments, up to 180 min, were performed in darkness in order to demonstrate the photoactivable properties of both **1** and **1@SFNs**. Once each experiment was finalized, the solutions were bubbled with CO and the concentration of CO-Mb was calculated. All the experiments were performed in quintuplicate.

SINGLE X-RAY DIFFRACTION DATA

Table S3. Crystal data and structure refinement for $[Mn(CO)_3(bpy)(PPh_3)](ClO_4)$ (**1**) (bpy = 2,2'-bipyridine; PPh_3 = triphenylphosphane).

Empirical formula	$C_{31}H_{23}ClMnN_2O_7P$	
Formula weight	656.87	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 10.5698(4) Å	α = 90°
	b = 21.1564(9) Å	β= 100.017(1)°
	c = 12.7711(5) Å	γ = 90°
Volume	2812.33(19) $Å^3$	
Z	4	
Density (calculated)	1.551 mg/m^3	
Absorption coefficient	0.675 mm^{-1}	
F(000)	1344	
Crystal size	0.140 x 0.120 x 0.120 mm^3	
Theta range for data collection	2.313 to 28.747°	
Index ranges	$-13 \le h \le 11$, $-23 \le k \le 28$, $-17 \le l \le 15$	
Reflections collected	20536	
Independent reflections	7076 [R(int) = 0.0733]	
Completeness to theta = 25.242°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7458 and 0.6424	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7076 / 0 / 388	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2sigma(I)]	R1 = 0.0505, wR2 = 0.0824	
R indices (all data)	R1 = 0.0994, wR2 = 0.0954	
Largest diff. peak and hole	0.461 and -0.531 e.$Å^{-3}$	

Table S4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for $[Mn(CO)_3(bpy)(PPh_3)](ClO_4)$ (**1**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Mn	1825(1)	4063(1)	1272(1)	11(1)
C(1)	301(3)	4136(1)	1716(2)	16(1)
O(1)	-688(2)	4165(1)	1969(2)	26(1)
C(2)	1745(2)	4858(1)	756(2)	15(1)
O(2)	1700(2)	5363(1)	409(2)	26(1)
C(3)	953(3)	3785(1)	-27(2)	18(1)
O(3)	370(2)	3663(1)	-838(2)	32(1)
P	2916(1)	4488(1)	2924(1)	10(1)
C(11A)	4411(2)	4901(1)	2817(2)	12(1)
C(12A)	5458(2)	4576(1)	2531(2)	13(1)
C(13A)	6561(2)	4896(1)	2398(2)	16(1)
C(14A)	6642(3)	5548(1)	2524(2)	18(1)
C(15A)	5610(3)	5876(1)	2795(2)	17(1)
C(16A)	4507(2)	5559(1)	2942(2)	14(1)
C(21A)	3275(2)	3886(1)	3964(2)	12(1)
C(22A)	2247(3)	3692(1)	4445(2)	18(1)
C(23A)	2401(3)	3210(1)	5187(2)	23(1)
C(24A)	3563(3)	2901(1)	5443(2)	22(1)
C(25A)	4583(3)	3084(1)	4967(2)	21(1)
C(26A)	4450(3)	3578(1)	4235(2)	17(1)
C(31A)	2052(2)	5082(1)	3575(2)	12(1)
C(32A)	988(2)	5404(1)	3032(2)	13(1)
C(33A)	404(2)	5879(1)	3531(2)	17(1)
C(34A)	902(3)	6046(1)	4573(2)	18(1)
C(35A)	1953(3)	5725(1)	5122(2)	20(1)
C(36A)	2522(3)	5245(1)	4631(2)	17(1)
N(1B)	3526(2)	3843(1)	816(2)	11(1)
C(2B)	4138(3)	4194(1)	181(2)	16(1)
C(3B)	5308(3)	4024(1)	-75(2)	19(1)
C(4B)	5886(3)	3474(1)	350(2)	20(1)
C(5B)	5255(3)	3097(1)	976(2)	17(1)
C(5AB)	4066(2)	3283(1)	1181(2)	12(1)
C(6B)	3663(3)	2330(1)	2259(2)	18(1)
C(6AB)	3284(2)	2908(1)	1794(2)	12(1)
C(7B)	2829(3)	1994(1)	2765(2)	19(1)
C(8B)	1632(3)	2245(1)	2805(2)	19(1)
C(9B)	1322(3)	2831(1)	2353(2)	15(1)
N(10B)	2121(2)	3166(1)	1861(2)	12(1)
Cl	2637(1)	2453(1)	8410(1)	18(1)
O(1P)	2032(2)	2933(1)	7683(2)	27(1)
O(2P)	2372(2)	2571(1)	9459(2)	33(1)
O(3P)	2130(2)	1844(1)	8052(2)	42(1)
O(4P)	3992(2)	2464(1)	8448(2)	52(1)

Table S5. Bond lengths [Å] for [Mn(CO)$_3$(bpy)(PPh$_3$)](ClO$_4$) (**1**).

Mn-C(2)	1.804(3)
Mn-C(1)	1.805(3)
Mn-C(3)	1.848(3)
Mn-N(1B)	2.038(2)
Mn-N(10B)	2.045(2)
Mn-P	2.3968(7)
C(1)-O(1)	1.148(3)
C(2)-O(2)	1.154(3)
C(3)-O(3)	1.139(3)
P-C(21A)	1.832(3)
P-C(11A)	1.832(3)
P-C(31A)	1.836(3)
C(11A)-C(16A)	1.402(4)
C(11A)-C(12A)	1.403(3)
C(12A)-C(13A)	1.384(4)
C(13A)-C(14A)	1.390(4)
C(14A)-C(15A)	1.386(4)
C(15A)-C(16A)	1.386(4)
C(21A)-C(26A)	1.393(3)
C(21A)-C(22A)	1.400(4)
C(22A)-C(23A)	1.383(4)
C(23A)-C(24A)	1.380(4)
C(24A)-C(25A)	1.382(4)
C(25A)-C(26A)	1.392(4)
C(31A)-C(32A)	1.392(3)
C(31A)-C(36A)	1.397(4)
C(32A)-C(33A)	1.391(4)
C(33A)-C(34A)	1.389(4)
C(34A)-C(35A)	1.383(4)
C(35A)-C(36A)	1.386(4)
N(1B)-C(2B)	1.345(3)
N(1B)-C(5AB)	1.360(3)
C(2B)-C(3B)	1.382(4)
C(3B)-C(4B)	1.380(4)
C(4B)-C(5B)	1.381(4)
C(5B)-C(5AB)	1.385(4)
C(5AB)-C(6AB)	1.468(4)
C(6B)-C(7B)	1.378(4)
C(6B)-C(6AB)	1.386(4)
C(6AB)-N(10B)	1.361(3)
C(7B)-C(8B)	1.382(4)
C(8B)-C(9B)	1.381(4)
C(9B)-N(10B)	1.340(3)
Cl-O(4P)	1.425(2)
Cl-O(2P)	1.438(2)
Cl-O(3P)	1.438(2)
Cl-O(1P)	1.447(2)

Table S6. Bond angles [°] for [Mn(CO)$_3$(bpy)(PPh$_3$)](ClO$_4$) (**1**).

C(2)-Mn-C(1)	92.72(12)
C(2)-Mn-C(3)	89.10(12)
C(1)-Mn-C(3)	88.68(12)
C(2)-Mn-N(1B)	95.52(10)
C(1)-Mn-N(1B)	171.60(11)
C(3)-Mn-N(1B)	89.86(10)
C(2)-Mn-N(10B)	173.91(10)
C(1)-Mn-N(10B)	92.96(11)
C(3)-Mn-N(10B)	93.23(10)
N(1B)-Mn-N(10B)	78.87(8)
C(2)-Mn-P	87.47(9)
C(1)-Mn-P	90.58(8)
C(3)-Mn-P	176.45(9)
N(1B)-Mn-P	91.37(6)
N(10B)-Mn-P	90.28(6)
O(1)-C(1)-Mn	177.3(2)
O(2)-C(2)-Mn	178.7(2)
O(3)-C(3)-Mn	174.3(2)
C(21A)-P-C(11A)	108.25(11)
C(21A)-P-C(31A)	101.77(12)
C(11A)-P-C(31A)	102.15(12)
C(21A)-P-Mn	112.62(8)
C(11A)-P-Mn	113.77(8)
C(31A)-P-Mn	117.04(9)
C(16A)-C(11A)-C(12A)	118.1(2)
C(16A)-C(11A)-P	120.72(19)
C(12A)-C(11A)-P	121.0(2)
C(13A)-C(12A)-C(11A)	120.8(2)
C(12A)-C(13A)-C(14A)	120.5(3)
C(15A)-C(14A)-C(13A)	119.3(3)
C(16A)-C(15A)-C(14A)	120.6(3)
C(15A)-C(16A)-C(11A)	120.7(2)
C(26A)-C(21A)-C(22A)	118.7(2)
C(26A)-C(21A)-P	124.7(2)
C(22A)-C(21A)-P	116.34(19)
C(23A)-C(22A)-C(21A)	120.6(3)
C(24A)-C(23A)-C(22A)	120.4(3)
C(23A)-C(24A)-C(25A)	119.6(3)
C(24A)-C(25A)-C(26A)	120.7(3)
C(25A)-C(26A)-C(21A)	120.0(3)
C(32A)-C(31A)-C(36A)	118.8(2)
C(32A)-C(31A)-P	122.1(2)
C(36A)-C(31A)-P	118.98(19)
C(33A)-C(32A)-C(31A)	120.7(2)
C(34A)-C(33A)-C(32A)	119.9(2)
C(35A)-C(34A)-C(33A)	119.8(3)
C(34A)-C(35A)-C(36A)	120.3(3)
C(35A)-C(36A)-C(31A)	120.5(2)
C(2B)-N(1B)-C(5AB)	118.0(2)
C(2B)-N(1B)-Mn	125.90(18)
C(5AB)-N(1B)-Mn	116.05(17)
N(1B)-C(2B)-C(3B)	122.8(3)
C(4B)-C(3B)-C(2B)	118.7(3)
C(3B)-C(4B)-C(5B)	119.3(3)
C(4B)-C(5B)-C(5AB)	119.4(3)
N(1B)-C(5AB)-C(5B)	121.6(2)
N(1B)-C(5AB)-C(6AB)	114.4(2)

C(5B)-C(5AB)-C(6AB)	124.0(2)
C(7B)-C(6B)-C(6AB)	119.7(3)
N(10B)-C(6AB)-C(6B)	121.6(2)
N(10B)-C(6AB)-C(5AB)	114.5(2)
C(6B)-C(6AB)-C(5AB)	123.9(2)
C(6B)-C(7B)-C(8B)	118.9(3)
C(9B)-C(8B)-C(7B)	118.7(3)
N(10B)-C(9B)-C(8B)	123.2(3)
C(9B)-N(10B)-C(6AB)	117.8(2)
C(9B)-N(10B)-Mn	126.52(18)
C(6AB)-N(10B)-Mn	115.58(17)
O(4P)-Cl-O(2P)	108.83(14)
O(4P)-Cl-O(3P)	110.02(16)
O(2P)-Cl-O(3P)	109.22(15)
O(4P)-Cl-O(1P)	109.83(15)
O(2P)-Cl-O(1P)	109.88(13)
O(3P)-Cl-O(1P)	109.05(12)

Table S7. Anisotropic displacement parameters ($Å^2$x 10^3) for [$Mn(CO)_3$(bpy)(PPh_3)](ClO_4) (**1**). The anisotropic displacement factor exponent takes the form: $-2p^2$[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}
Mn	9(1)	11(1)	13(1)	0(1)	1(1)	2(1)
C(1)	14(2)	13(2)	20(1)	1(1)	-2(1)	0(1)
O(1)	15(1)	23(1)	42(1)	0(1)	12(1)	3(1)
C(2)	12(1)	21(2)	14(1)	1(1)	3(1)	5(1)
O(2)	27(1)	19(1)	32(1)	11(1)	9(1)	9(1)
C(3)	12(1)	16(2)	24(2)	1(1)	3(1)	8(1)
O(3)	27(1)	39(1)	24(1)	-12(1)	-12(1)	12(1)
P	8(1)	9(1)	12(1)	1(1)	2(1)	2(1)
C(11A)	11(1)	12(1)	11(1)	3(1)	0(1)	1(1)
C(12A)	10(1)	15(1)	13(1)	-1(1)	0(1)	3(1)
C(13A)	10(1)	24(2)	15(1)	-1(1)	2(1)	2(1)
C(14A)	12(1)	26(2)	15(1)	2(1)	1(1)	-7(1)
C(15A)	18(2)	12(1)	19(1)	1(1)	0(1)	-5(1)
C(16A)	15(1)	13(1)	13(1)	1(1)	3(1)	2(1)
C(21A)	15(1)	9(1)	12(1)	-1(1)	0(1)	0(1)
C(22A)	15(2)	20(2)	18(2)	4(1)	1(1)	-1(1)
C(23A)	25(2)	22(2)	20(2)	7(1)	2(1)	-6(1)
C(24A)	39(2)	11(2)	15(2)	5(1)	2(1)	1(1)
C(25A)	27(2)	19(2)	17(2)	2(1)	2(1)	13(1)
C(26A)	19(2)	18(2)	16(1)	2(1)	6(1)	6(1)
C(31A)	12(1)	9(1)	16(1)	1(1)	5(1)	2(1)
C(32A)	16(1)	10(1)	14(1)	0(1)	2(1)	0(1)
C(33A)	12(1)	12(1)	26(2)	-1(1)	2(1)	3(1)
C(34A)	18(2)	13(2)	25(2)	-1(1)	11(1)	4(1)
C(35A)	25(2)	21(2)	14(1)	-4(1)	6(1)	3(1)
C(36A)	17(2)	18(2)	15(1)	3(1)	2(1)	4(1)
N(1B)	10(1)	13(1)	9(1)	0(1)	0(1)	1(1)
C(2B)	19(2)	17(2)	14(1)	1(1)	3(1)	1(1)
C(3B)	18(2)	28(2)	14(1)	-4(1)	7(1)	-2(1)
C(4B)	11(1)	30(2)	20(2)	-7(1)	4(1)	2(1)
C(5B)	16(2)	18(2)	16(1)	-5(1)	0(1)	5(1)
C(5AB)	13(1)	12(1)	11(1)	-3(1)	-1(1)	2(1)
C(6B)	17(2)	13(1)	24(2)	-2(1)	-1(1)	4(1)

C(6AB)	12(1)	12(1)	12(1)	-5(1)	0(1)	2(1)
C(7B)	26(2)	10(1)	20(2)	2(1)	-1(1)	1(1)
C(8B)	22(2)	15(2)	19(2)	1(1)	5(1)	-4(1)
C(9B)	14(1)	14(1)	17(1)	-2(1)	3(1)	-4(1)
N(10B)	12(1)	9(1)	12(1)	-4(1)	-1(1)	1(1)
Cl	17(1)	18(1)	19(1)	-2(1)	4(1)	-2(1)
O(1P)	38(1)	18(1)	25(1)	6(1)	2(1)	-4(1)
O(2P)	34(1)	49(2)	17(1)	-1(1)	8(1)	2(1)
O(3P)	66(2)	17(1)	35(1)	-2(1)	-16(1)	-6(1)
O(4P)	16(1)	83(2)	58(2)	-2(2)	12(1)	2(1)

Table S8. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for [Mn(CO)$_3$(bpy)(PPh$_3$)](ClO$_4$) (**1**).

	x	y	z	U(eq)
H(12A)	5409	4132	2428	16
H(13A)	7268	4669	2219	20
H(14A)	7397	5767	2425	22
H(15A)	5659	6322	2882	20
H(16A)	3808	5789	3130	16
H(22A)	1436	3894	4260	21
H(23A)	1702	3091	5523	27
H(24A)	3661	2564	5942	26
H(25A)	5383	2871	5141	25
H(26A)	5161	3704	3920	20
H(32A)	658	5298	2314	16
H(33A)	-334	6089	3160	20
H(34A)	521	6379	4909	22
H(35A)	2286	5835	5838	24
H(36A)	3238	5024	5016	20
H(2B)	3748	4576	-103	20
H(3B)	5708	4280	-534	23
H(4B)	6709	3356	213	24
H(5B)	5633	2713	1264	20
H(6B)	4493	2167	2228	22
H(7B)	3073	1596	3080	23
H(8B)	1033	2020	3138	23
H(9B)	503	3004	2393	18