Electronic Supporting Information (SI)

2-(2-Pyridyl) benzimidazole based ternary Mn(II) complex as arsenate selective turn-on fluorescence probe: ppb level determination and cell imaging studies

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1. General method of UV-Vis and fluorescence titration

Path length of the cells used for absorption and emission studies was 1 cm. For UV-Vis and fluorescence titrations, stock solution of MnPBINCO was prepared (50 μM) in methanol/water (0.5/99.5, v/v) HEPES (0.1M) buffer. Working solutions of MnPBINCO and $HAsO_4^{2-}$ were prepared from their respective stock solutions. Fluorescence measurements were performed using 5 nm x 5 nm slit width. Except time dependent spectra, all the fluorescence and absorbance spectra were taken after 5 minutes of mixing of $HAsO_4^{2-}$ to MnPBINCO.

2. Calculation of Quantum Yield

Fluorescence quantum yields (Φ) were estimated by integrating the area under the fluorescence curves using the equation,

$$\phi_{sample} = \phi_{ref} \times \frac{OD_{ref} \times A_{sample} \times \eta^2_{sample}}{OD_{sample} \times A_{ref} \times \eta^2_{ref}}$$

where A was the area under the fluorescence spectral curve, OD was optical density of the compound at the excitation wavelength[1] and η was the refractive indices of the solvent. Anthracene was used as quantum yield standard (quantum yield is 0.27 in ethanol)[2] for measuring the quantum yields of MnPBINCO and [MnPBINCO-$HAsO_4^{2-}$] systems.

Experimental

Materials and methods

High purity HEPES, 2-pyridyl benzimidazole, NaNCO, NaH_2AsO_4 and $MnCl_2.4H_2O$ were purchased from Sigma Aldrich (India). Solvents used were of spectroscopic grade. Other chemicals were of analytical reagent grade and had been used without further purification except when specified. Mili-Q Milipore® 18.2 MΩ cm^{-1} water was used throughout all the experiments. A JASCO (model V-570) UV–Vis spectrophotometer was used for recording UV-Vis spectra. FTIR spectra were recorded on a JASCO FTIR spectrophotometer (model: FTIR-H20). Mass spectra were performed on a QTOF Micro YA 263 mass spectrometer in ES positive mode. Elemental analysis was performed using Perkin Elmer CHN-Analyzer with first 2000-Analysis kit. The steady-state fluorescence emission and excitation spectra were recorded with a Perkin Elmer Precisely LS55 spectrofluorimeter. All pH measurements were performed with Systronics digital pH meter (model 335). All spectra were recorded at room temperature except for fluorescence microscope images. Time-resolved fluorescence life time measurements

were performed using a picosecond pulsed diode laser-based time-correlated single photon counting (TCSPC) spectrometer from IBH (UK) at λ_{ex} 375 nm and MCP-PMT as a detector. The emission from the sample was collected at a right angle to the direction of the excitation beam maintaining magic angle polarization (54.71).The full width at half maximum (FWHM) of the instrument response function was 250 ps and the resolution was 28 ps per channel. The data were fitted to multi exponential functions after deconvolution of the instrument response function by an iterative reconvolution technique using IBH DAS 6.2 data analysis software in which reduced w2 and weighted residuals serve as parameters for goodness of fit.

Imaging system

The imaging system was comprised of an inverted fluorescence microscope (Leica DM 1000 LED), digital compact camera (Leica DFC 420C), and an image processor (Leica Application Suite v3.3.0). The microscope was equipped with a 50 W mercury arc lamp.

Preparation and imaging of cells

Candida albicans cells (IMTECH No. 3018) from exponentially growing culture in yeast extract glucose broth medium (pH 6.0, incubation temperature, 37°C) were centrifuged at 3000 rpm for 10 minutes washed twice with 0.1 M HEPES buffer (pH 7.4). Then cells were treated with $HAsO_4^{2-}$ (100 μM) for 30 minutes in 0.1 M HEPES buffer (pH 7.4) containing 0.01 % Triton X100 as permeability enhancing agent. After incubation, the cells were washed with HEPES buffer and incubated with MnPBINCO (50 μM) for 15 minutes. Cells thus obtained were mounted on grease free glass slide and observed under

the fluorescence microscope having UV filter. Cells incubated with MnPBINCO but without $HAsO_4^{2-}$ were used as control.

Fresh pollen grains, collected from mature buds of *Allamanda puberula* (Aapocynaceae), a common ornamental plant with bell shaped bright yellow flower were crashed on a sterile petriplate and suspended in normal saline. Debris were removed by filtration through a thin layer of non-absorbent cotton. The suspended pollens were collected by centrifugation at 5000 rpm for five minutes. The pollens were then washed twice in normal saline and incubated in a solution of NaH_2AsO_4 (100 µM) for one hour at ambient temperature. After incubation, they were again washed in normal saline and photographed under fluorescence microscope using UV filter in presence and absence of MnPBINCO. Both $HAsO_4^{2-}$ treated and untreated cells were stained with MnPBINCO and observed under fluorescence microscope.

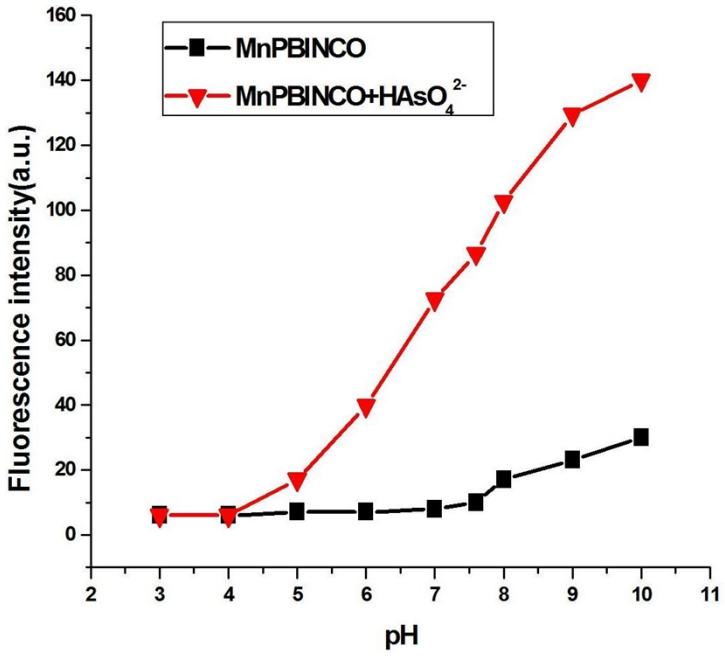

Fig.S1 Variation of emission intensities of MnPBINCO (50 µM) and MnPBINCO (50 µM) + $HAsO_4^{2-}$ (100 µM) as a function of pH.

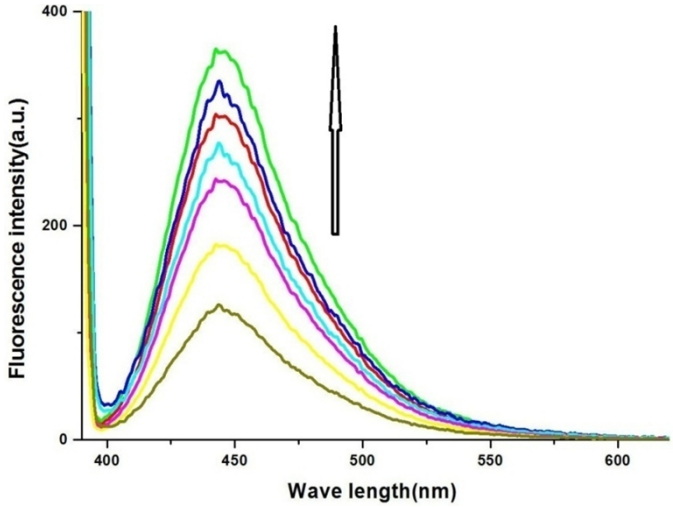

Fig.S2 Fluorescence spectral changes of MnPBINCO (50 μM) + $HAsO_4^{2-}$ (700 μM) system with solvent composition (MeOH: water, v/v), (from bottom to top) 3: 1, 2: 1, 1: 1, 1: 2, 1: 5, 1: 9, 0.5: 99.5, λ_{ex} = 370 nm, λ_{em} = 440 nm.

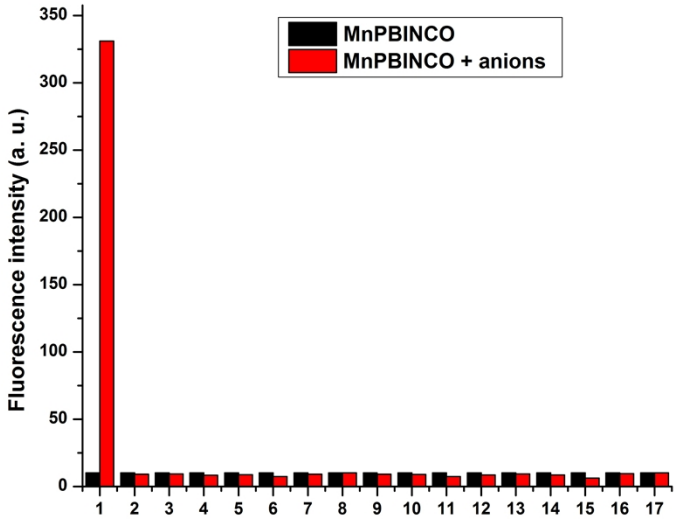

Fig.S3 Relative fluorescence intensity of the MnPBINCO (50 μM) in presence of different anions (500 μM) in HEPES buffered (0.1 M) solution (methanol/water = 0.5/99.5, v/v, pH 7.4): where anions = $HAsO_4^{2-}$ **(1)**, F^- **(2)**, Cl^- **(3)**, Br^- **(4)**, I^- **(5)**, N_3^- **(6)**, NCO^- **(7)**, NO_2^- **(8)**, NO_3^- **(9)**, SCN^- **(10)**, CN^- **(11)**, CH_3COO^- **(12)**, SO_4^{2-} **(13)**, ClO_4^- **(14)**, $H_2PO_4^{2-}$ **(15)**, S^{2-} (**16**), PPi (**17**), λ_{ex} = 370 nm, λ_{em} = 440 nm.

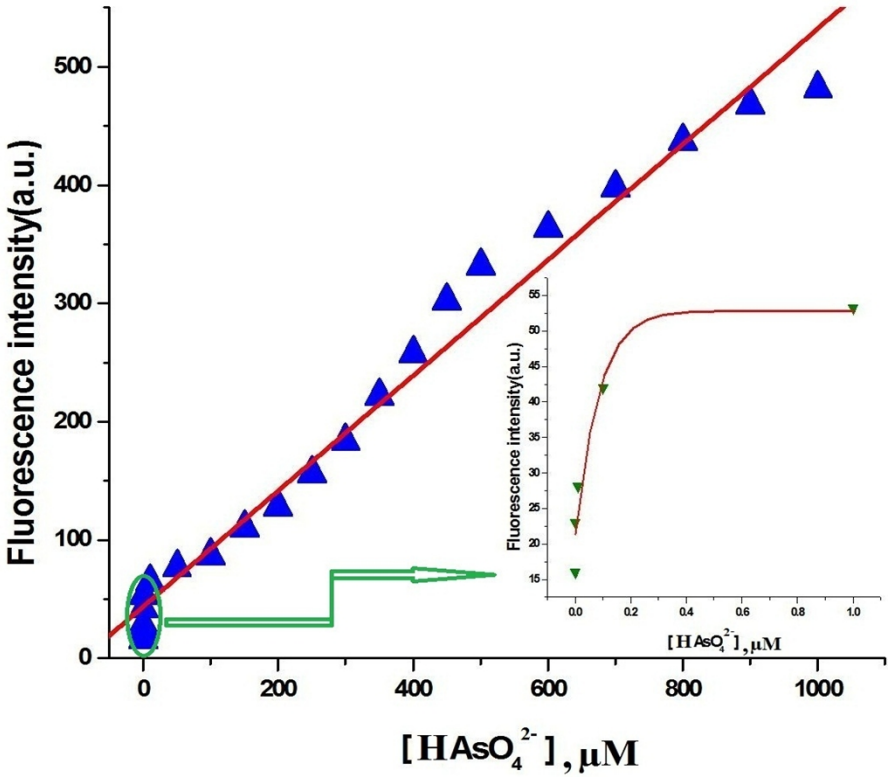

Fig.S4 Plot of emission intensities of MnPBINCO (50 μM) as a function of $HAsO_4^{2-}$ (0, 0.0001, 0.001, 0.01, 0.1, 1, 10, 50, 100, 150, 200, 250, 300, 350, 400, 450, 500, 600, 700, 800, 900, 1000 μM), $R^2 = 0.99$, inset: plot of emission intensities of MnPBINCO (50 μM) as a function of $HAsO_4^{2-}$ (0, 0.0001, 0.001, 0.01, 0.1, 1 μM), The detection limit is 1×10^{-10} M.

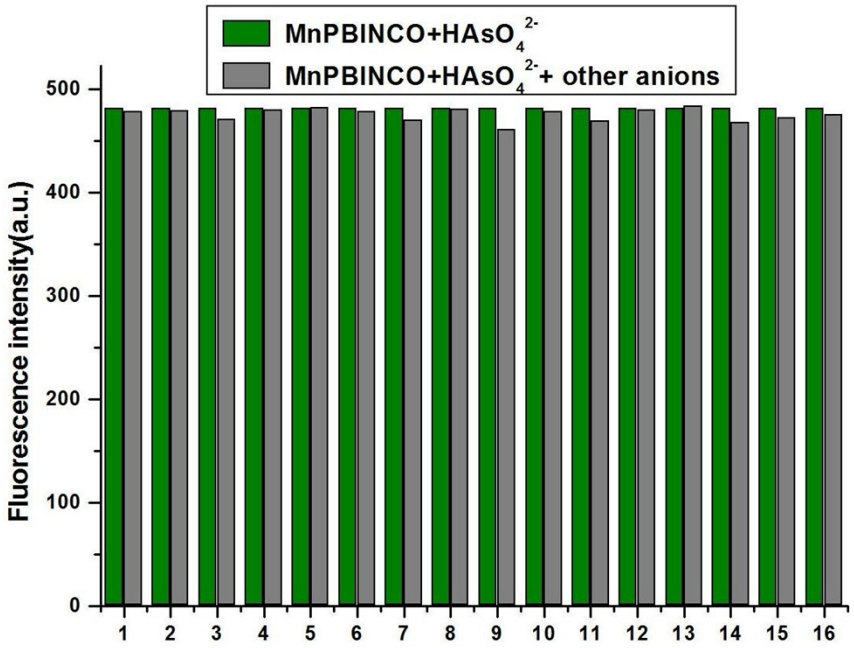

Fig.S5 Relative emission intensities of [MnPBINCO-$HAsO_4^{2-}$] system in the presence of various anions in HEPES buffered (0.1 M) solution (methanol/water = 0.5/99.5, v/v, pH 7.4). Green bar: MnPBINCO (50 μM) with 1000 equivalent of $HAsO_4^{2-}$. Gray bar: 50 μM of MnPBINCO and 1000 equivalent of $HAsO_4^{2-}$ with 1000 equiv. of anions stated, F^- **(1)**, Cl^- **(2)**, Br^- **(3)**, I^- **(4)**, N_3^- **(5)**, NCO^- **(6)**, NO_2^- **(7)**, NO_3^- **(8)**, SCN^- **(9)**, CN^- **(10)**, CH_3COO^- **(11)**, SO_4^{2-} **(12)**, ClO_4^- **(13)**, HPO_4^{2-} **(14)**, $F^- + Cl^- + Br^- + I^- + NO_2^- + SO_4^{2-}$ **(15)**, $N_3^- + NCO^- + CN^- + ClO_4^-$ **(16)**, λ_{ex} = 370 nm, λ_{em} = 440 nm.

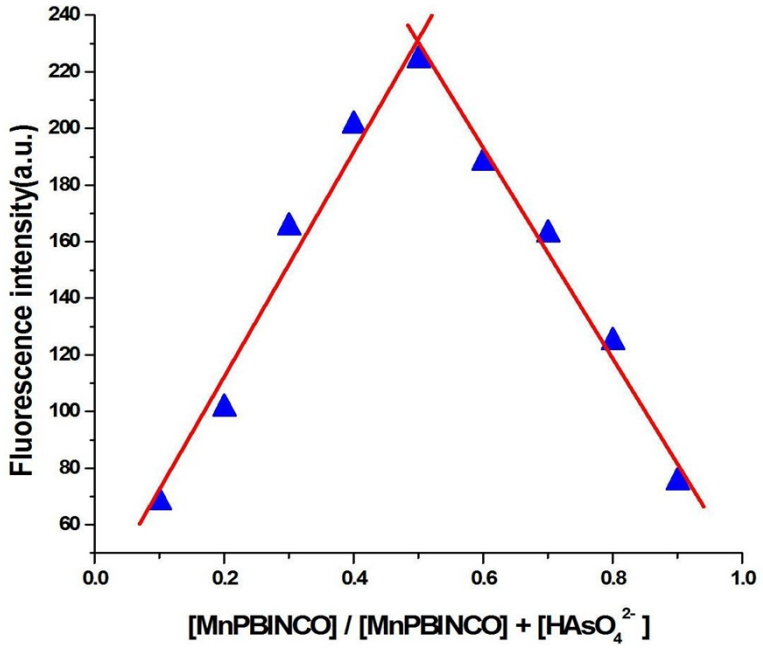

Fig.S6 Job's plot for determination of the stoichiometry of [**MnPBINCO-**$HAsO_4^{2-}$] adduct in HEPES buffer (0.1 M, methanol/ water = 0.5/ 99.5, v/v, pH 7.4).

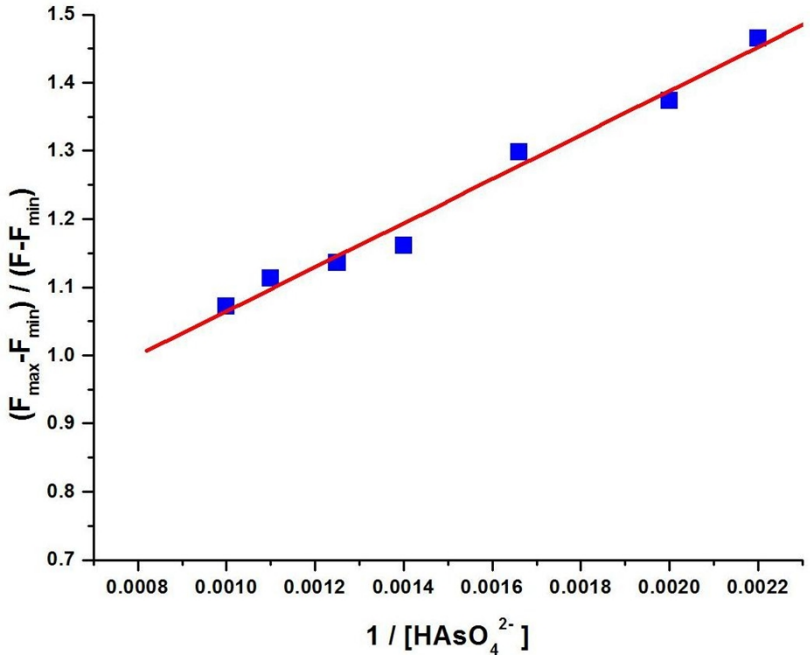

Fig.S7 Determination of binding constant between MnPBINCO and $HAsO_4^{2-}$ in HEPES buffered (0.1 M) solution (methanol/ water = 0.5/99.5, v/v, pH 7.4).

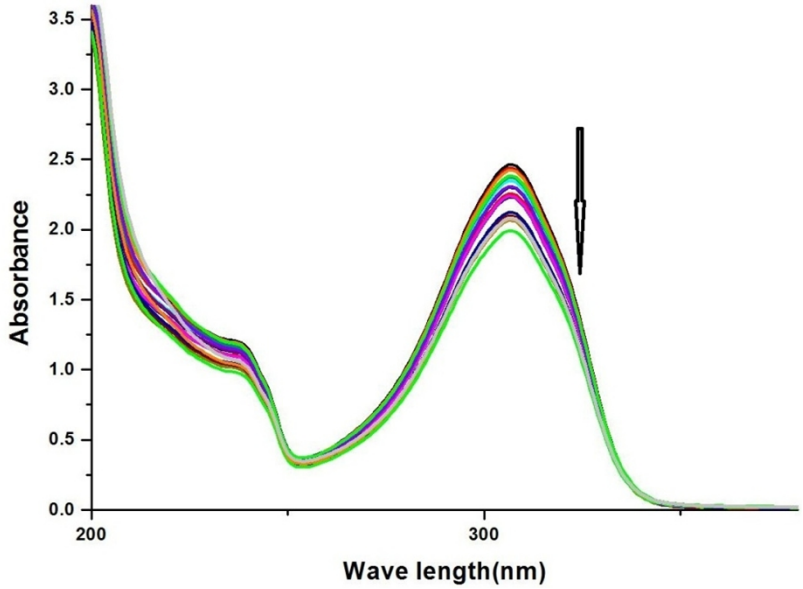

Fig.S8 Changes of absorbance of MnPBINCO (50 μM) upon addition of $HAsO_4^{2-}$ (0, 0.01, 0.1, 1, 10, 50, 100, 150, 200, 250, 300, 350, 400, 450, 500, 600, 700, 800, 900, 1000 μM) in HEPES buffered solution (0.1 M, methanol/ water = 0.5/99.5, v/v, pH 7.4).

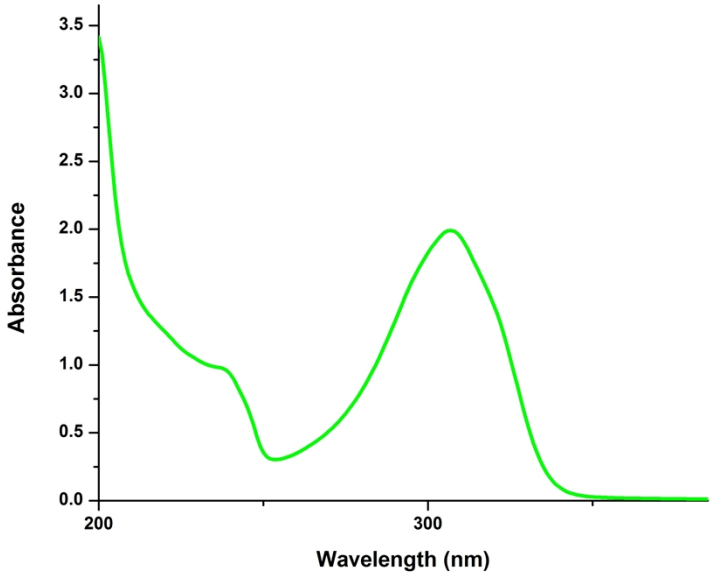

Fig.S9 Absorbance spectra of isolated MnPBINCO + $HAsO_4^{2-}$ adduct.

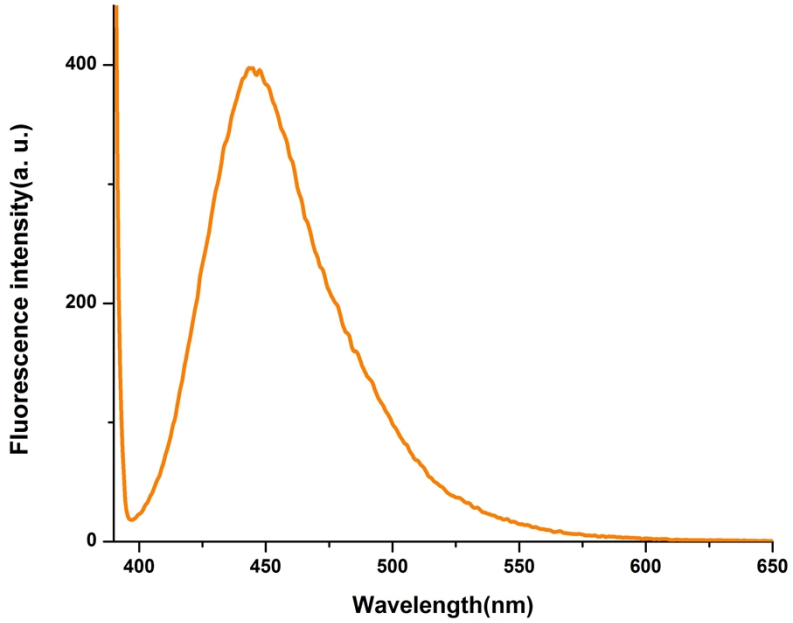

Fig.S10 Eluorescence spectra of isolated MnPBINCO + $HAsO_4^{2-}$ adduct.

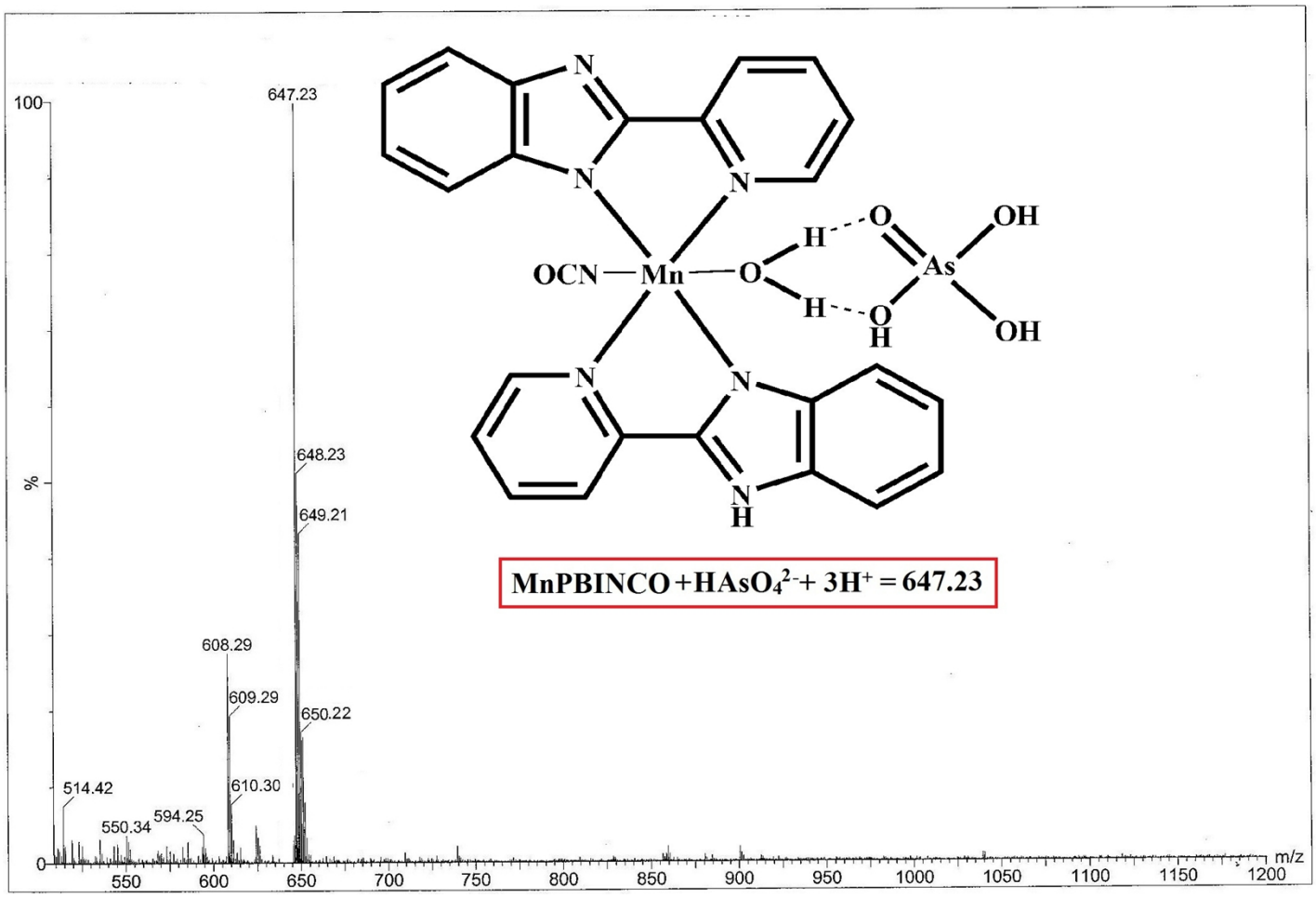

Fig.S11 QTOF mass spectrum of the [MnPBINCO + $HAsO_4^{2-}$] adduct.

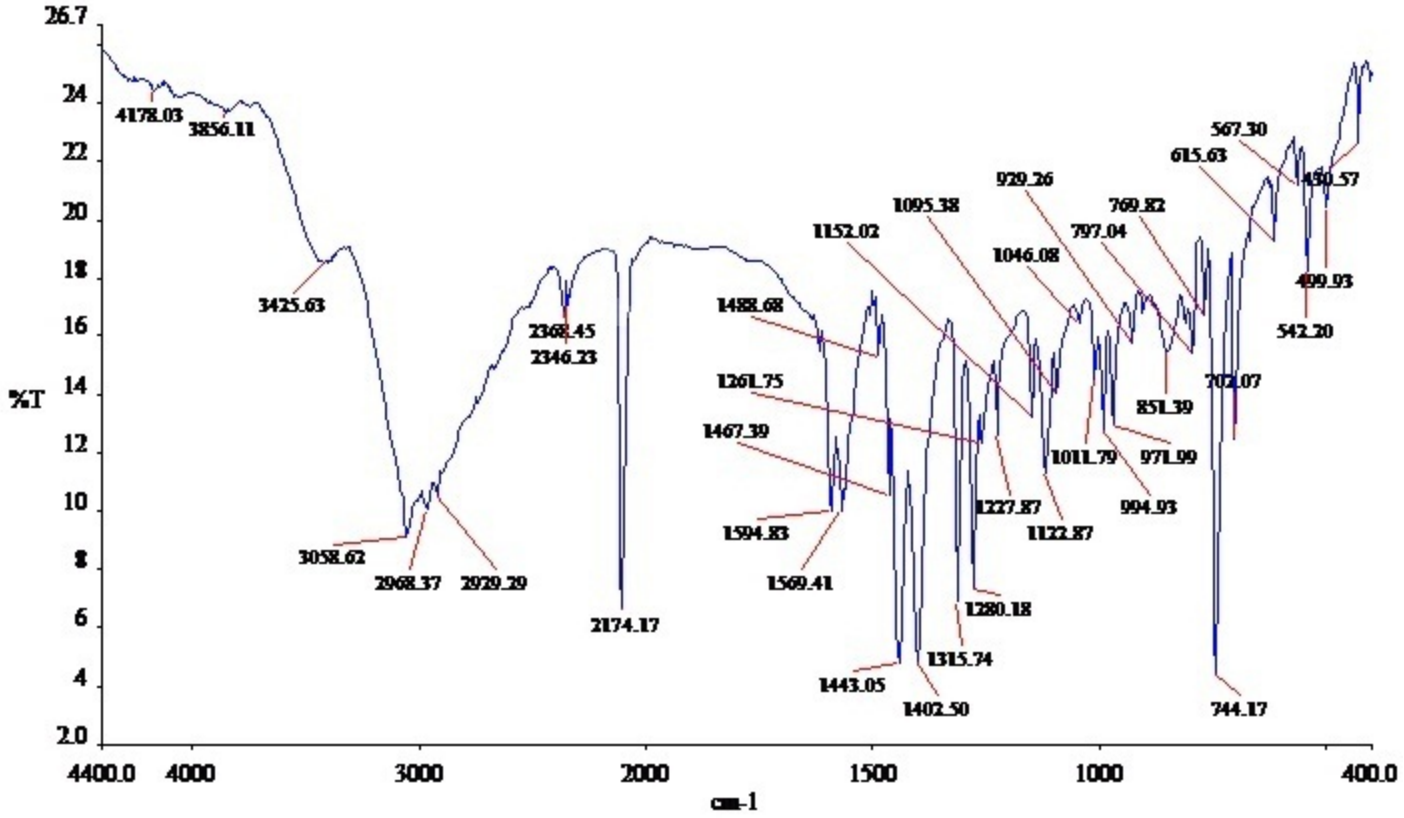

Fig.S12 FTIR spectrum of [MnPBINCO+$HAsO_4^{2-}$] adduct.

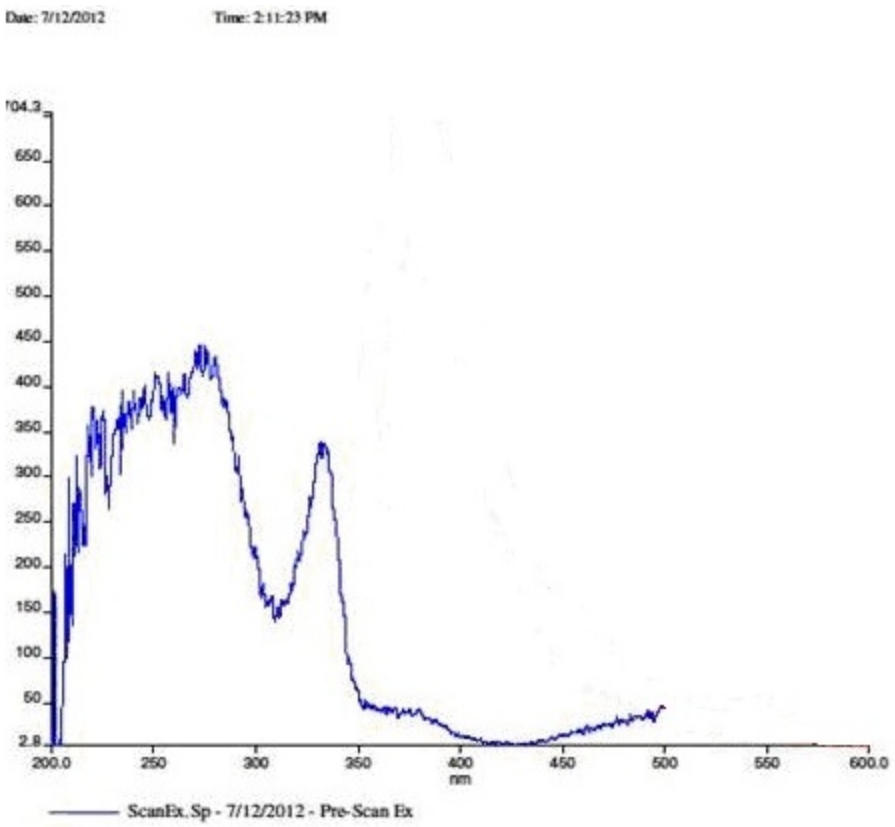

Fig.S13 Excitation and emission profile of MnPBINCO in HEPES buffered (0.1 M) solution (methanol/water = 0.5/99.5, v/v, pH 7.4).

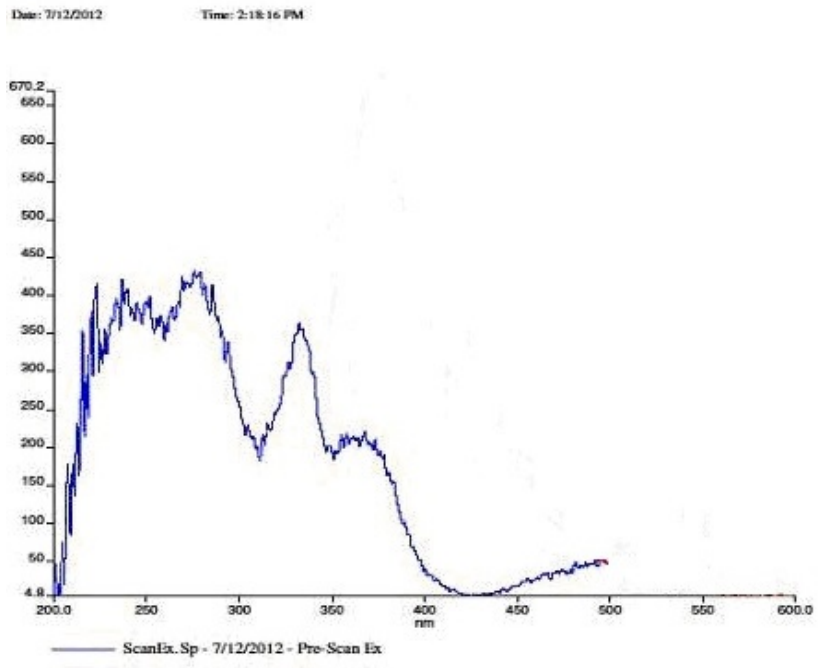

Fig.S14 Excitation and emission profile of [MnPBINCO-$HAsO_4^{2-}$] system in HEPES buffered (0.1 M) solution (methanol/water = 0.5/99.5, v/v, pH 7.4).

Characterization of MnPBINCO

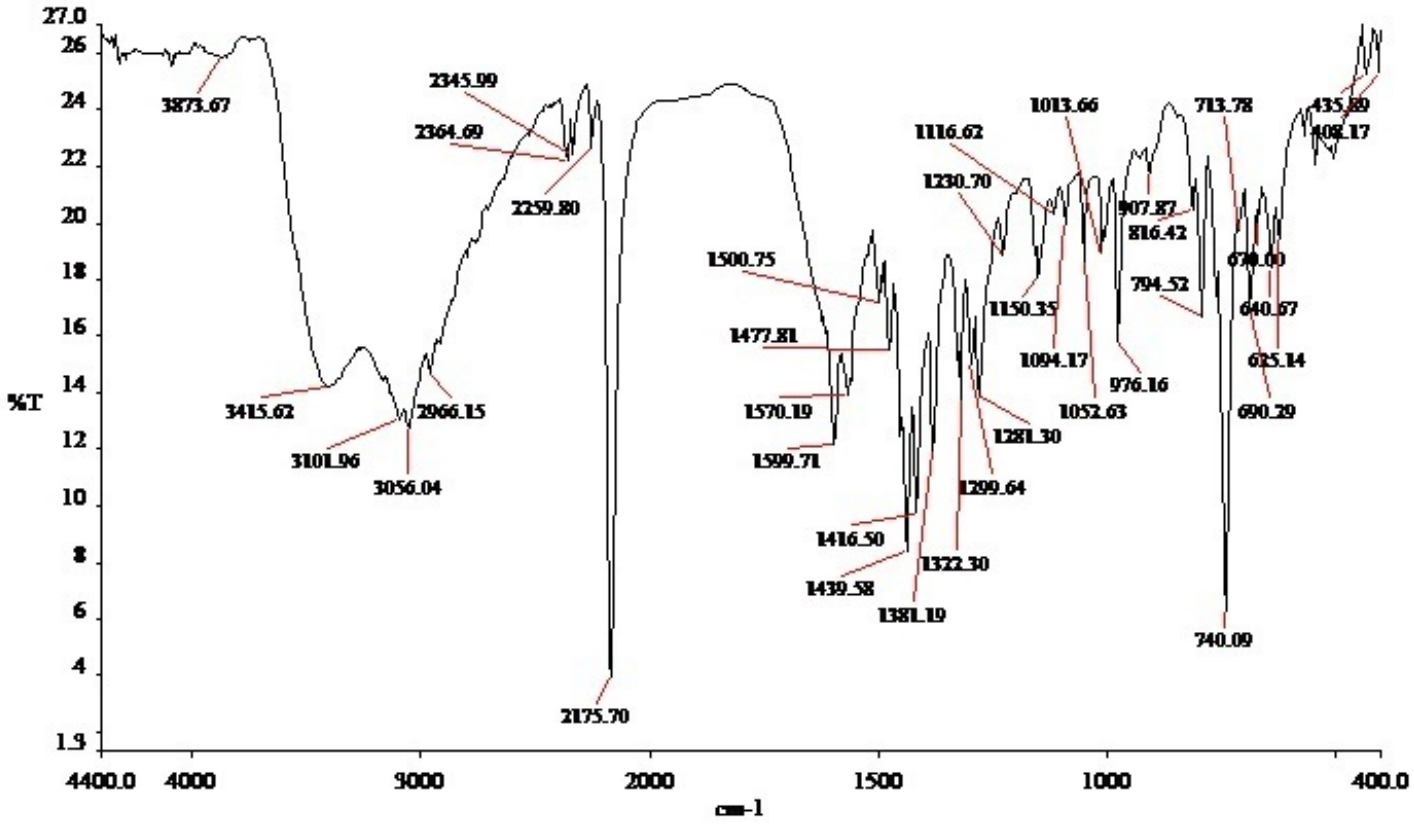

Fig.S15 FTIR spectrum of free MnPBINCO complex

Crystal structure of MnPBINCO

Data collection: APPEX2 (BRUKER AXS, 2005); cell refinement: APPEX2 (BRUKER AXS, 2005); data reduction: APPEX2 (BRUKER AXS, 2005); program(s) used to solve structure: *SIR97* (Giacovazzo *et al.*, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 1999).

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for

estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F2, conventional Rfactors R are based on F, with F set to zero for negative F2. The threshold expression of $F2 > 2\sigma(F2)$ is used only for calculating R factors (gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

To keep reasonable geometries for the minor components of both disordered ligands in MnPBINCO, bond length and angles restraints were applied using the SHELXL/SAME instruction, while bond lengths of H atoms corresponding to water molecules were restrained with DFIX instructions. Likewise, ADPs of all related disordered atoms were constrained to be identical (EADP instruction). These instructions resulted in a great number of restraints used for the refinement of the crystal structure.

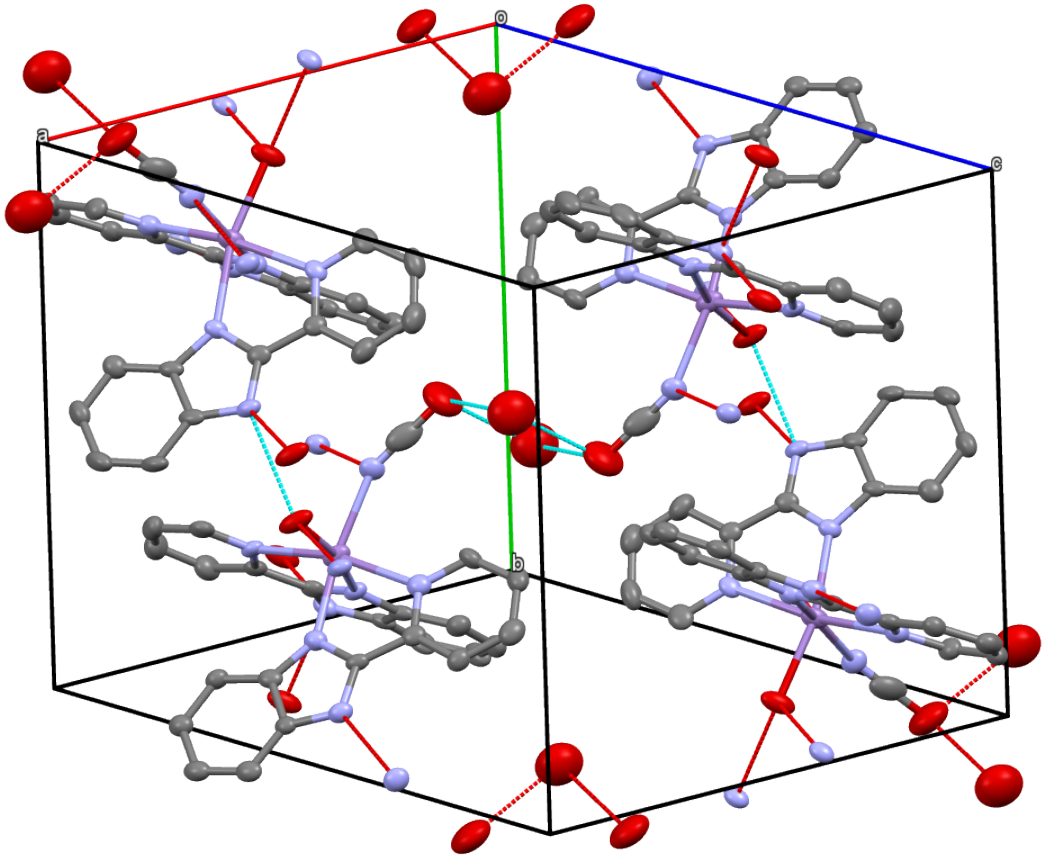

Fig.S16 H-Bonded packing diagram of MnPBINCO

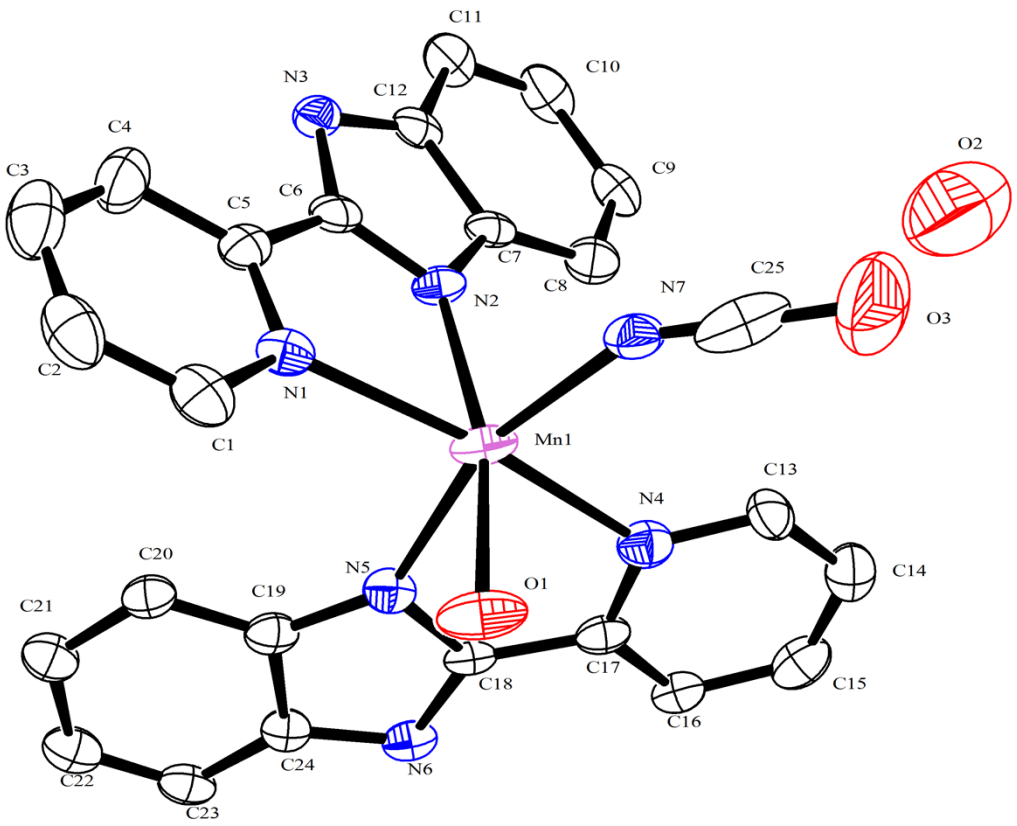

Fig. S17 ORTEP view of the molecular structure of MnPBINCO showing the atom-labeling scheme (50% thermal ellipsoid probability). Hydrogen atoms were omitted for clarity.

Table S1. Crystal data and structure refinement for MnPBINCO.

Identification code	2MnPBINCO·H_2O	
Empirical formula	C_{50} H_{40} Mn2 N_{14} O_5	
Formula weight	1026.84	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 12.144(5) Å	α= 90.000(5)°.
	b = 13.932(5) Å	β= 113.548(5)°.
	c = 14.427(5) Å	γ = 90.000(5)°.
Volume	2237.6(14) $Å^3$	
Z	4	
Density (calculated)	1.604 Mg/m^3	
Absorption coefficient	0.859 mm^{-1}	
F(000)	1100	
Crystal size	0.40 x 0.35 x 0.06 mm^3	
Theta range for data collection	1.86 to 26.02°.	
Index ranges	-14<=h<=13, 0<=k<=17, 0<=l<=17	
Reflections collected	25840	
Independent reflections	4395 [R(int) = 0.0626]	
Completeness to theta = 26.02°	100.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4395 / 85 / 428	
Goodness-of-fit on F^2	1.019	
Final R indices [I>2sigma(I)]	R1 = 0.0596, wR2 = 0.1197	
R indices (all data)	R1 = 0.0995, wR2 = 0.1377	
Largest diff. peak and hole	0.910 and -0.791 e.$Å^{-3}$	

Table S2. Bond lengths [Å] for MnPBINCO.

Mn(1)-N(2B)	2.039(17)
Mn(1)-N(5B)	2.161(10)
Mn(1)-N(2)	2.198(3)
Mn(1)-N(7)	2.199(4)
Mn(1)-N(5)	2.216(4)
Mn(1)-O(1)	2.220(3)
Mn(1)-N(1)	2.293(4)
Mn(1)-N(4)	2.337(4)
N(4)-C(17)	1.343(5)
N(4)-C(13)	1.350(6)
C(13)-C(14)	1.373(7)
C(13)-H(13)	0.9300
C(14)-C(15)	1.395(7)
C(14)-H(14)	0.9300
C(15)-C(16)	1.389(7)
C(15)-H(15)	0.9300
C(16)-C(17)	1.372(6)
C(16)-H(16)	0.9300
C(17)-C(18)	1.446(7)
C(18)-N(5)	1.345(5)
C(18)-N(6)	1.355(5)
N(5)-C(19)	1.367(6)
C(19)-C(20)	1.388(6)
C(19)-C(24)	1.435(6)
C(20)-C(21)	1.376(6)
C(20)-H(20)	0.9300
C(21)-C(22)	1.399(6)
C(21)-H(21)	0.9300
C(22)-C(23)	1.351(7)
C(22)-H(22)	0.9300
C(23)-C(24)	1.380(6)
C(23)-H(23)	0.9300
C(24)-N(6)	1.371(6)
N(6)-H(6)	0.8600

N(4B)-C(17B)	1.343(6)
N(4B)-C(13B)	1.350(6)
C(13B)-C(14B)	1.373(7)
C(13B)-H(13B)	0.9300
C(14B)-C(15B)	1.395(7)
C(14B)-H(14B)	0.9300
C(15B)-C(16B)	1.389(7)
C(15B)-H(15B)	0.9300
C(16B)-C(17B)	1.373(6)
C(16B)-H(16B)	0.9300
C(17B)-C(18B)	1.447(7)
C(18B)-N(5B)	1.345(6)
C(18B)-N(6B)	1.356(5)
N(5B)-C(19B)	1.367(6)
C(19B)-C(20B)	1.388(6)
C(19B)-C(24B)	1.435(6)
C(20B)-C(21B)	1.376(6)
C(20B)-H(20B)	0.9300
C(21B)-C(22B)	1.399(6)
C(21B)-H(21B)	0.9300
C(22B)-C(23B)	1.351(7)
C(22B)-H(22B)	0.9300
C(23B)-C(24B)	1.380(6)
C(23B)-H(23B)	0.9300
C(24B)-N(6B)	1.371(6)
N(6B)-H(6B)	0.8600
N(1)-C(1)	1.335(6)
N(1)-C(5)	1.361(6)
C(1)-C(2)	1.375(8)
C(1)-H(1)	0.9300
C(2)-C(3)	1.370(8)
C(2)-H(2)	0.9300
C(3)-C(4)	1.372(9)
C(3)-H(3)	0.9300
C(4)-C(5)	1.400(7)
C(4)-H(4)	0.9300

C(5)-C(6)	1.472(7)
C(6)-N(2)	1.337(6)
C(6)-N(3)	1.347(6)
N(2)-C(7)	1.389(6)
C(7)-C(8)	1.405(7)
C(7)-C(12)	1.407(7)
C(8)-C(9)	1.371(7)
C(8)-H(8)	0.9300
C(9)-C(10)	1.408(7)
C(9)-H(9)	0.9300
C(10)-C(11)	1.382(7)
C(10)-H(10)	0.9300
C(11)-C(12)	1.403(7)
C(11)-H(11)	0.9300
C(12)-N(3)	1.379(7)
N(1B)-C(1B)	1.34(2)
N(1B)-C(5B)	1.337(17)
C(1B)-C(2B)	1.37(2)
C(1B)-H(1B)	0.9300
C(2B)-C(3B)	1.39(2)
C(2B)-H(2B)	0.9300
C(3B)-C(4B)	1.38(2)
C(3B)-H(3B)	0.9300
C(4B)-C(5B)	1.404(19)
C(4B)-H(4B)	0.9300
C(5B)-C(6B)	1.479(19)
C(6B)-N(3B)	1.349(17)
C(6B)-N(2B)	1.354(18)
N(2B)-C(7B)	1.354(17)
C(7B)-C(8B)	1.402(19)
C(7B)-C(12B)	1.410(19)
C(8B)-C(9B)	1.361(19)
C(8B)-H(8B)	0.9300
C(9B)-C(10B)	1.402(19)
C(9B)-H(9B)	0.9300
C(10B)-C(11B)	1.372(18)

C(10B)-H(10B)	0.9300
C(11B)-C(12B)	1.402(19)
C(11B)-H(11B)	0.9300
C(12B)-N(3B)	1.381(19)
N(7)-C(25)	1.079(6)
C(25)-O(3)	1.266(7)
O(1)-H(1O)	0.822(19)
O(1)-H(2O)	0.827(19)
O(2)-H(3O)	0.84(2)
O(2)-H(4O)	0.84(2)

Table S3 Angles [°] for MnPBINCO.

N(2B)-Mn(1)-N(5B)	132.4(7)
N(2B)-Mn(1)-N(2)	49.4(5)
N(5B)-Mn(1)-N(2)	97.4(6)
N(2B)-Mn(1)-N(7)	101.9(6)
N(5B)-Mn(1)-N(7)	117.4(3)
N(2)-Mn(1)-N(7)	97.31(13)
N(2B)-Mn(1)-N(5)	95.3(6)
N(5B)-Mn(1)-N(5)	48.6(3)
N(2)-Mn(1)-N(5)	94.93(13)
N(7)-Mn(1)-N(5)	162.71(13)
N(2B)-Mn(1)-O(1)	117.2(5)
N(5B)-Mn(1)-O(1)	91.4(5)
N(2)-Mn(1)-O(1)	166.37(14)
N(7)-Mn(1)-O(1)	87.83(13)
N(5)-Mn(1)-O(1)	83.03(13)
N(2B)-Mn(1)-N(1)	24.3(5)
N(5B)-Mn(1)-N(1)	142.6(3)
N(2)-Mn(1)-N(1)	73.69(14)
N(7)-Mn(1)-N(1)	99.96(13)
N(5)-Mn(1)-N(1)	95.16(13)
O(1)-Mn(1)-N(1)	93.03(13)
N(2B)-Mn(1)-N(4)	147.4(5)
N(5B)-Mn(1)-N(4)	25.2(3)
N(2)-Mn(1)-N(4)	100.17(13)
N(7)-Mn(1)-N(4)	92.24(13)
N(5)-Mn(1)-N(4)	73.56(14)
O(1)-Mn(1)-N(4)	92.19(12)
N(1)-Mn(1)-N(4)	166.90(13)
C(17)-N(4)-C(13)	117.8(4)
C(17)-N(4)-Mn(1)	114.9(3)
C(13)-N(4)-Mn(1)	127.3(3)
N(4)-C(13)-C(14)	123.7(5)
N(4)-C(13)-H(13)	118.1
C(14)-C(13)-H(13)	118.1

C(13)-C(14)-C(15)	118.0(5)
C(13)-C(14)-H(14)	121.0
C(15)-C(14)-H(14)	121.0
C(16)-C(15)-C(14)	118.5(5)
C(16)-C(15)-H(15)	120.8
C(14)-C(15)-H(15)	120.8
C(17)-C(16)-C(15)	119.9(5)
C(17)-C(16)-H(16)	120.1
C(15)-C(16)-H(16)	120.1
N(4)-C(17)-C(16)	122.2(4)
N(4)-C(17)-C(18)	114.3(4)
C(16)-C(17)-C(18)	123.5(4)
N(5)-C(18)-N(6)	111.1(4)
N(5)-C(18)-C(17)	122.6(4)
N(6)-C(18)-C(17)	126.1(4)
C(18)-N(5)-C(19)	106.4(4)
C(18)-N(5)-Mn(1)	114.3(3)
C(19)-N(5)-Mn(1)	139.2(3)
N(5)-C(19)-C(20)	132.0(4)
N(5)-C(19)-C(24)	109.0(4)
C(20)-C(19)-C(24)	119.0(4)
C(21)-C(20)-C(19)	118.0(4)
C(21)-C(20)-H(20)	121.0
C(19)-C(20)-H(20)	121.0
C(20)-C(21)-C(22)	122.0(5)
C(20)-C(21)-H(21)	119.0
C(22)-C(21)-H(21)	119.0
C(23)-C(22)-C(21)	121.3(5)
C(23)-C(22)-H(22)	119.4
C(21)-C(22)-H(22)	119.4
C(22)-C(23)-C(24)	118.3(4)
C(22)-C(23)-H(23)	120.9
C(24)-C(23)-H(23)	120.9
N(6)-C(24)-C(23)	133.8(4)
N(6)-C(24)-C(19)	104.7(4)
C(23)-C(24)-C(19)	121.5(4)

C(18)-N(6)-C(24)	108.7(4)
C(18)-N(6)-H(6)	125.6
C(24)-N(6)-H(6)	125.6
C(17B)-N(4B)-C(13B)	117.7(4)
N(4B)-C(13B)-C(14B)	123.7(5)
N(4B)-C(13B)-H(13B)	118.2
C(14B)-C(13B)-H(13B)	118.2
C(13B)-C(14B)-C(15B)	118.0(5)
C(13B)-C(14B)-H(14B)	121.0
C(15B)-C(14B)-H(14B)	121.0
C(16B)-C(15B)-C(14B)	118.5(5)
C(16B)-C(15B)-H(15B)	120.8
C(14B)-C(15B)-H(15B)	120.8
C(17B)-C(16B)-C(15B)	119.9(5)
C(17B)-C(16B)-H(16B)	120.1
C(15B)-C(16B)-H(16B)	120.1
N(4B)-C(17B)-C(16B)	122.1(5)
N(4B)-C(17B)-C(18B)	114.3(4)
C(16B)-C(17B)-C(18B)	123.4(5)
N(5B)-C(18B)-N(6B)	111.1(4)
N(5B)-C(18B)-C(17B)	122.7(4)
N(6B)-C(18B)-C(17B)	126.0(4)
C(18B)-N(5B)-C(19B)	106.4(4)
C(18B)-N(5B)-Mn(1)	124.0(5)
C(19B)-N(5B)-Mn(1)	129.0(5)
N(5B)-C(19B)-C(20B)	132.0(5)
N(5B)-C(19B)-C(24B)	109.0(4)
C(20B)-C(19B)-C(24B)	119.0(4)
C(21B)-C(20B)-C(19B)	118.0(5)
C(21B)-C(20B)-H(20B)	121.0
C(19B)-C(20B)-H(20B)	121.0
C(20B)-C(21B)-C(22B)	121.9(5)
C(20B)-C(21B)-H(21B)	119.0
C(22B)-C(21B)-H(21B)	119.0
C(23B)-C(22B)-C(21B)	121.3(5)
C(23B)-C(22B)-H(22B)	119.4

C(21B)-C(22B)-H(22B)	119.4
C(22B)-C(23B)-C(24B)	118.3(5)
C(22B)-C(23B)-H(23B)	120.9
C(24B)-C(23B)-H(23B)	120.9
N(6B)-C(24B)-C(23B)	133.8(5)
N(6B)-C(24B)-C(19B)	104.6(4)
C(23B)-C(24B)-C(19B)	121.5(5)
C(18B)-N(6B)-C(24B)	108.7(4)
C(18B)-N(6B)-H(6B)	125.7
C(24B)-N(6B)-H(6B)	125.7
C(1)-N(1)-C(5)	118.3(4)
C(1)-N(1)-Mn(1)	126.4(3)
C(5)-N(1)-Mn(1)	115.3(3)
N(1)-C(1)-C(2)	122.5(5)
N(1)-C(1)-H(1)	118.8
C(2)-C(1)-H(1)	118.8
C(3)-C(2)-C(1)	119.5(5)
C(3)-C(2)-H(2)	120.3
C(1)-C(2)-H(2)	120.3
C(2)-C(3)-C(4)	119.7(5)
C(2)-C(3)-H(3)	120.2
C(4)-C(3)-H(3)	120.2
C(3)-C(4)-C(5)	118.6(6)
C(3)-C(4)-H(4)	120.7
C(5)-C(4)-H(4)	120.7
N(1)-C(5)-C(4)	121.4(5)
N(1)-C(5)-C(6)	114.8(4)
C(4)-C(5)-C(6)	123.8(5)
N(2)-C(6)-N(3)	117.2(5)
N(2)-C(6)-C(5)	119.1(4)
N(3)-C(6)-C(5)	123.8(4)
C(6)-N(2)-C(7)	103.4(4)
C(6)-N(2)-Mn(1)	117.0(3)
C(7)-N(2)-Mn(1)	139.4(3)
N(2)-C(7)-C(8)	130.6(4)
N(2)-C(7)-C(12)	107.5(4)

C(8)-C(7)-C(12)	122.0(4)
C(9)-C(8)-C(7)	117.5(5)
C(9)-C(8)-H(8)	121.2
C(7)-C(8)-H(8)	121.2
C(8)-C(9)-C(10)	121.1(5)
C(8)-C(9)-H(9)	119.5
C(10)-C(9)-H(9)	119.5
C(11)-C(10)-C(9)	121.8(5)
C(11)-C(10)-H(10)	119.1
C(9)-C(10)-H(10)	119.1
C(10)-C(11)-C(12)	118.1(5)
C(10)-C(11)-H(11)	120.9
C(12)-C(11)-H(11)	120.9
N(3)-C(12)-C(11)	130.7(5)
N(3)-C(12)-C(7)	109.8(4)
C(11)-C(12)-C(7)	119.5(6)
C(6)-N(3)-C(12)	102.2(4)
C(1B)-N(1B)-C(5B)	116(2)
N(1B)-C(1B)-C(2B)	127(3)
N(1B)-C(1B)-H(1B)	116.5
C(2B)-C(1B)-H(1B)	116.5
C(1B)-C(2B)-C(3B)	118(2)
C(1B)-C(2B)-H(2B)	120.9
C(3B)-C(2B)-H(2B)	120.9
C(4B)-C(3B)-C(2B)	115(2)
C(4B)-C(3B)-H(3B)	122.4
C(2B)-C(3B)-H(3B)	122.4
C(3B)-C(4B)-C(5B)	124(2)
C(3B)-C(4B)-H(4B)	118.2
C(5B)-C(4B)-H(4B)	118.2
N(1B)-C(5B)-C(4B)	120.0(19)
N(1B)-C(5B)-C(6B)	112.4(16)
C(4B)-C(5B)-C(6B)	127.6(18)
N(3B)-C(6B)-N(2B)	117.8(17)
N(3B)-C(6B)-C(5B)	121.3(16)
N(2B)-C(6B)-C(5B)	120.9(16)

C(7B)-N(2B)-C(6B)	102.3(15)
C(7B)-N(2B)-Mn(1)	132.2(14)
C(6B)-N(2B)-Mn(1)	125.5(13)
N(2B)-C(7B)-C(8B)	130.4(19)
N(2B)-C(7B)-C(12B)	108.4(15)
C(8B)-C(7B)-C(12B)	120.7(17)
C(9B)-C(8B)-C(7B)	119(2)
C(9B)-C(8B)-H(8B)	120.6
C(7B)-C(8B)-H(8B)	120.6
C(8B)-C(9B)-C(10B)	121(2)
C(8B)-C(9B)-H(9B)	119.6
C(10B)-C(9B)-H(9B)	119.6
C(11B)-C(10B)-C(9B)	120(2)
C(11B)-C(10B)-H(10B)	119.9
C(9B)-C(10B)-H(10B)	119.9
C(10B)-C(11B)-C(12B)	120(2)
C(10B)-C(11B)-H(11B)	120.2
C(12B)-C(11B)-H(11B)	120.2
N(3B)-C(12B)-C(11B)	129(2)
N(3B)-C(12B)-C(7B)	109.4(17)
C(11B)-C(12B)-C(7B)	118(2)
C(6B)-N(3B)-C(12B)	100.7(15)
C(25)-N(7)-Mn(1)	149.3(4)
N(7)-C(25)-O(3)	178.4(6)
Mn(1)-O(1)-H(1O)	114(3)
Mn(1)-O(1)-H(2O)	121(3)
H(1O)-O(1)-H(2O)	108(5)
H(3O)-O(2)-H(4O)	101(3)

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