Supporting Information

Gold nanocluster formation using morpholino oligomer as template and assembly agent within hybrid bio-nanomaterials†

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†*Electronic Supplementary Information (ESI) available: [MALDI-MS, EDX, P 2p and N 1s XPS, H_2O_2% from RRDE data]. See DOI: 10.1039/x0xx00000x*

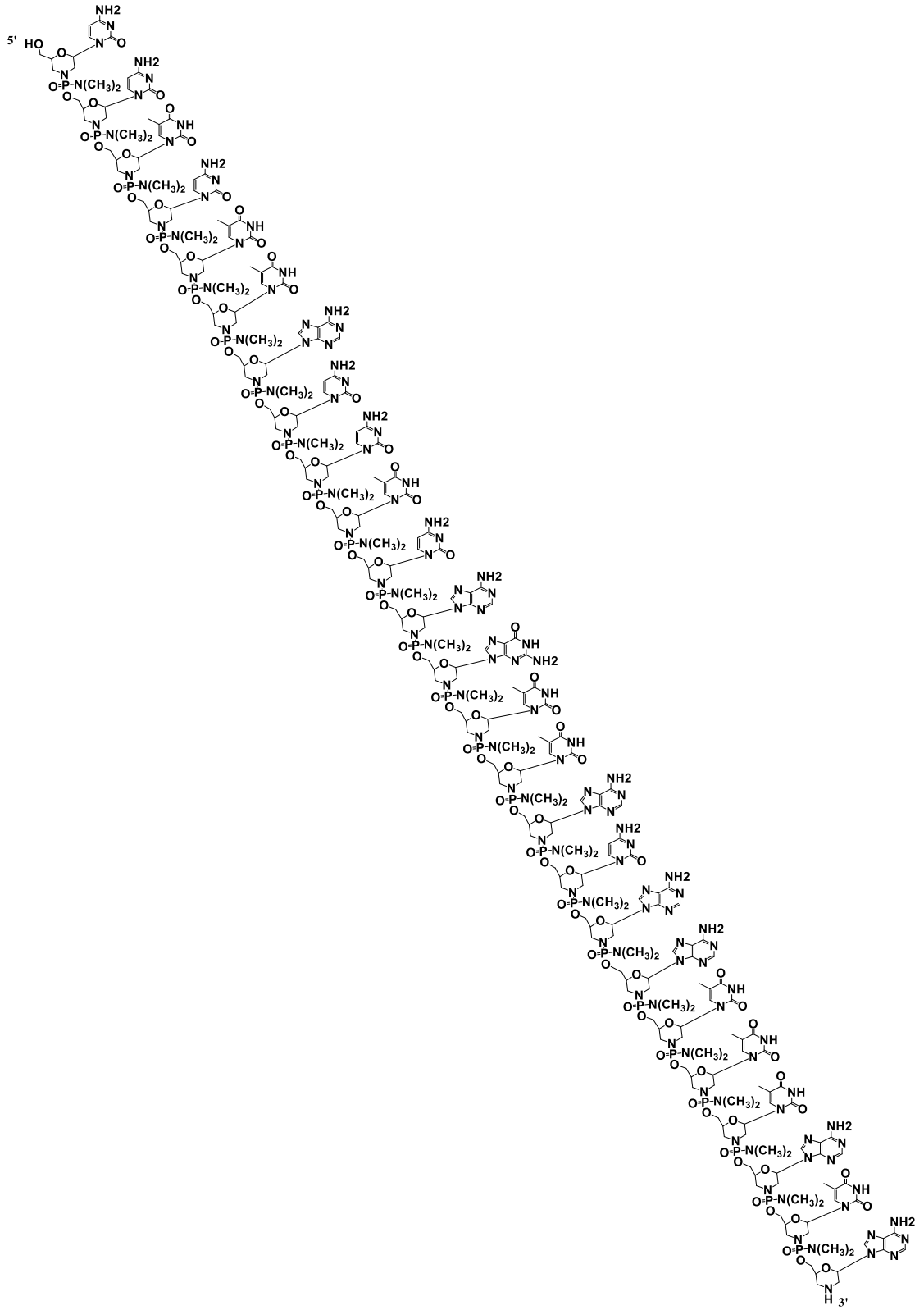

Figure S1: Chemical structure of the phosphorodiamidate morpholino oligomer (PMO).

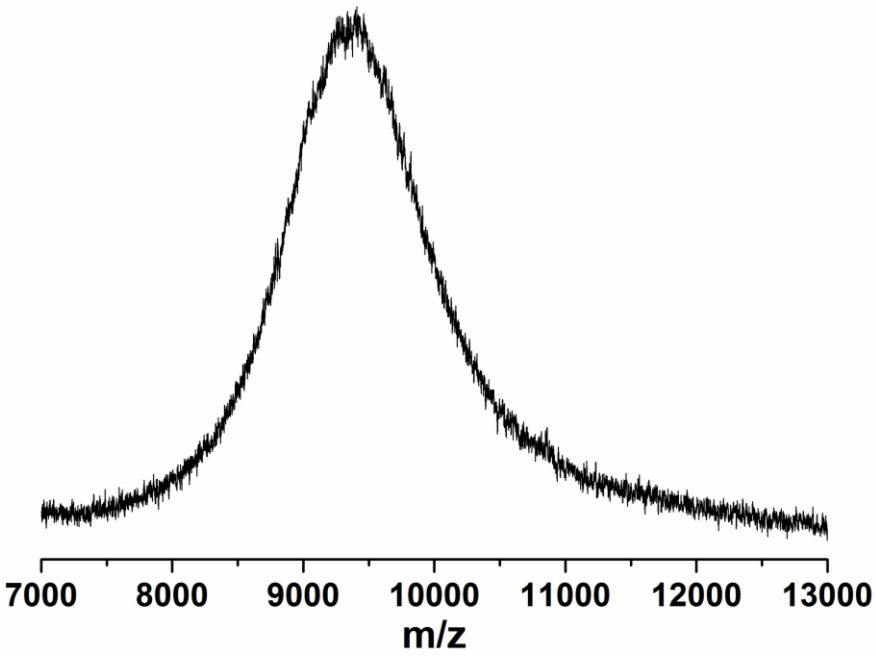

Figure S2: Negative mode MALDI-MS spectrum of PMO-AuNC (10:1 mixture of 3-indole acrylic acid:PMO-AuNC) showing a molecular weight of 9406 Da. Subtraction of the molecular weight of PMO alone (8328 Da) leads to a 6-atom Au cluster.

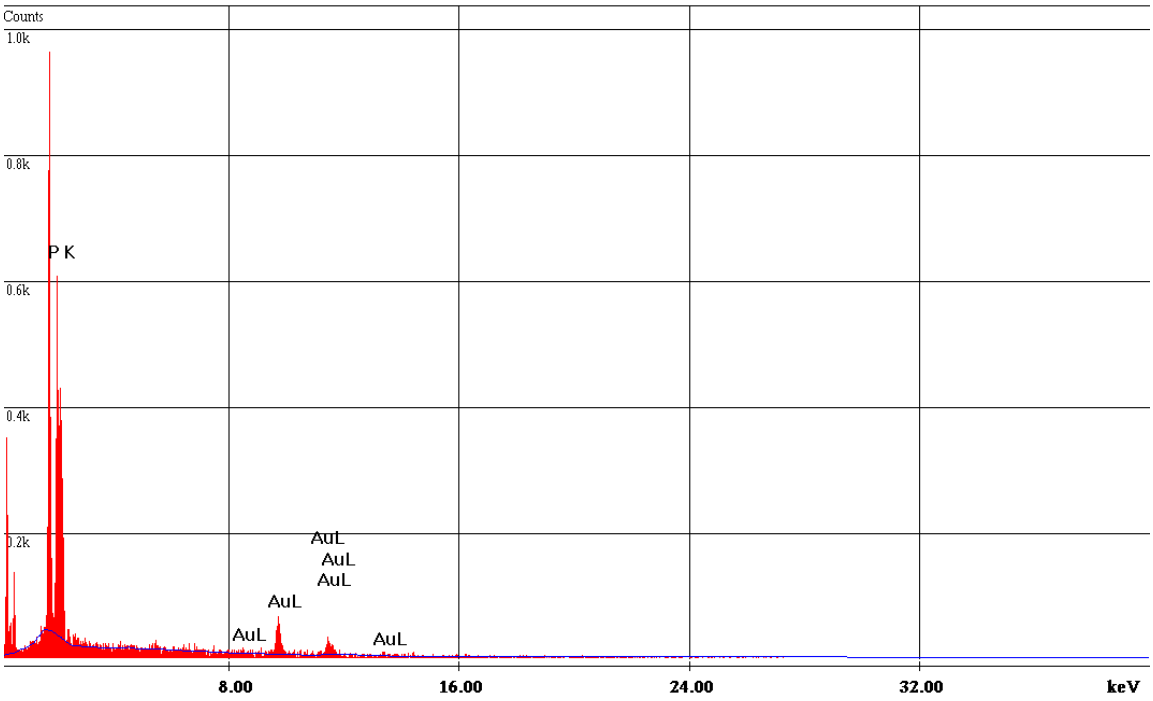

Figure S3: A representative EDX spectrum of PMO-AuNC. After subtracting the background, the % of P 2p calculated from P Kα (2.013 keV) was obtained to be 79.5%. This atomic % was then divided by the number of phosphorodiamidate groups (24) in PMO, which yielded a normalization factor of 3.3 (79.5/24) corresponding to a single piece of the oligomer. The atomic % of Au using Lα (9.712 keV) was obtained to be 20.4%, which was then used against the normalization factor to obtain the total number of Au atoms bound to a single morpholino oligomer. The number of Au atoms obtained from this analysis is 6.2±0.2.

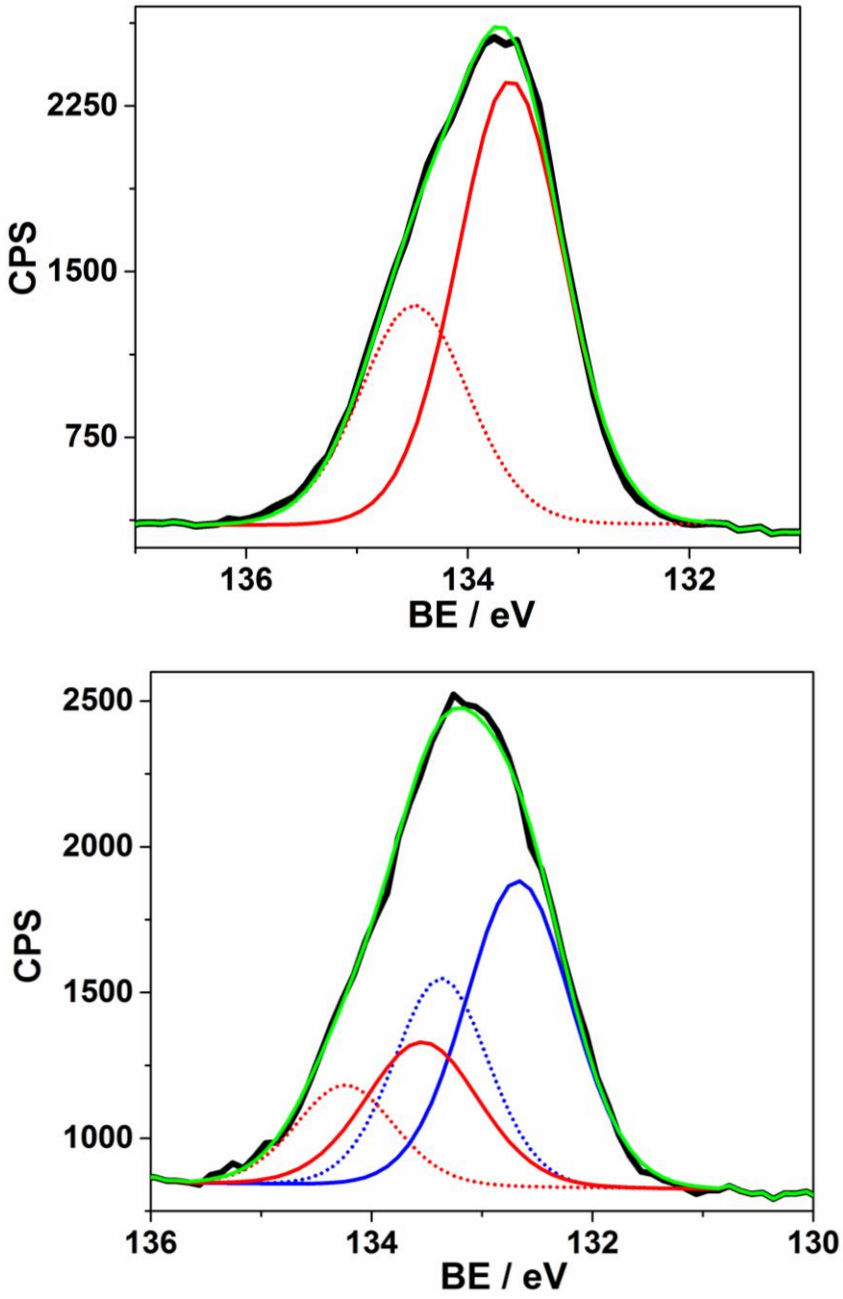

Figure S4: P 2p XPS spectra of PMO oligomer (top) and PMO-AuNC (bottom) showing the raw data (black), overall fit (green), P $2p_{3/2}$ components at 133.6 eV (solid red, top and bottom) and 132.7 eV (blue, bottom), P $2p_{1/2}$ components at 134.5 eV (dotted red, top and bottom) and 133.4 eV (dotted blue, bottom). The decrease in binding energy upon cluster formation suggests weakening of the P-N and P-O bonds of phosphorodiamidate backbone and thus increased electron density on P.

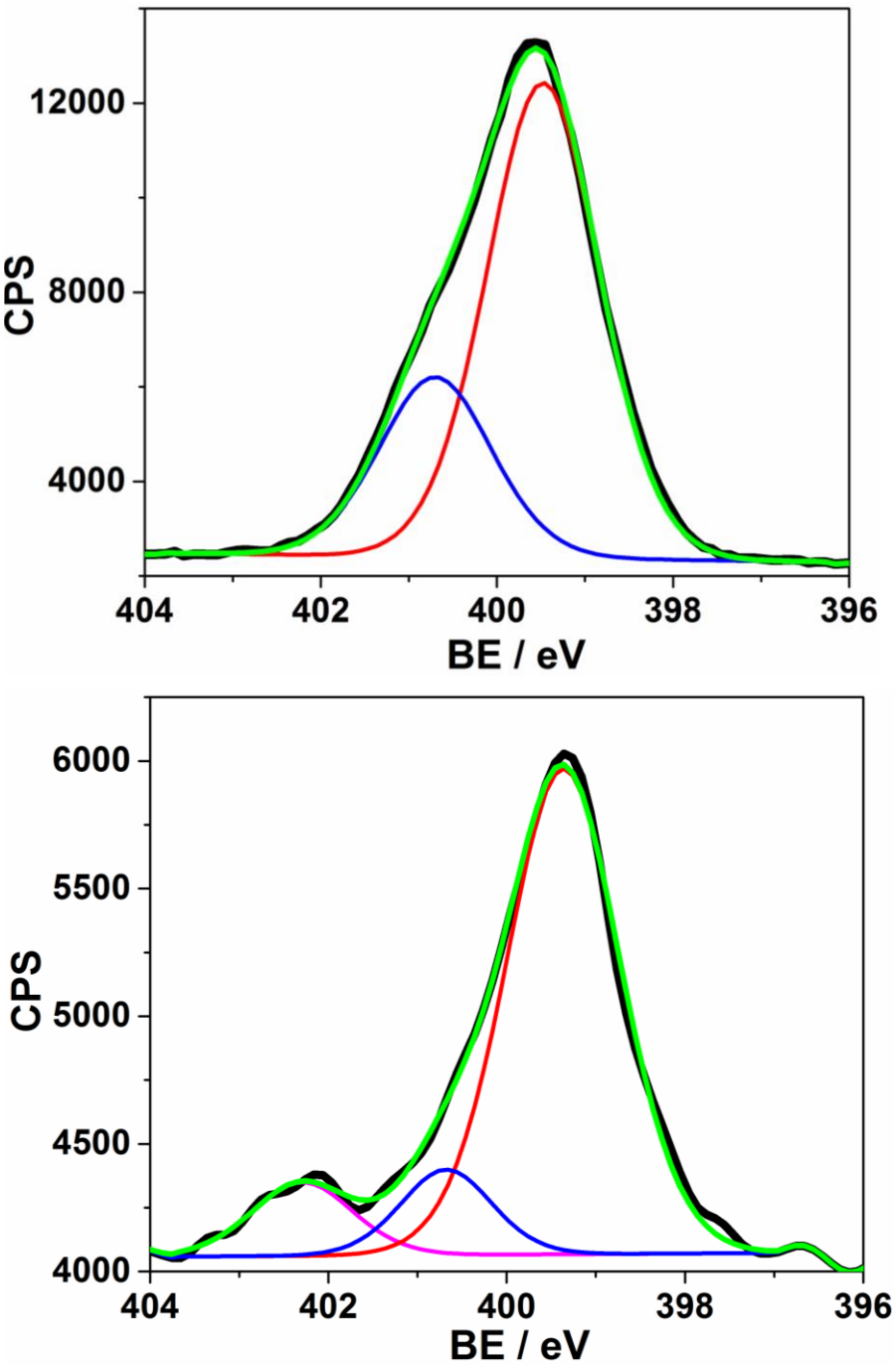

Figure S5: N 1s XPS spectra of PMO (top) and PMO-AuNC (bottom) showing the raw data (black), overall fit (green), and amine and amide groups at 393.3 eV (red) and 400.7 eV (blue) respectively. The new peak at higher binding energy upon cluster formation (402.4 eV, magenta) suggests an increased electron density on N upon cluster formation due to Au-N binding in the phosphorodiamidate (electron donation from N to Au).

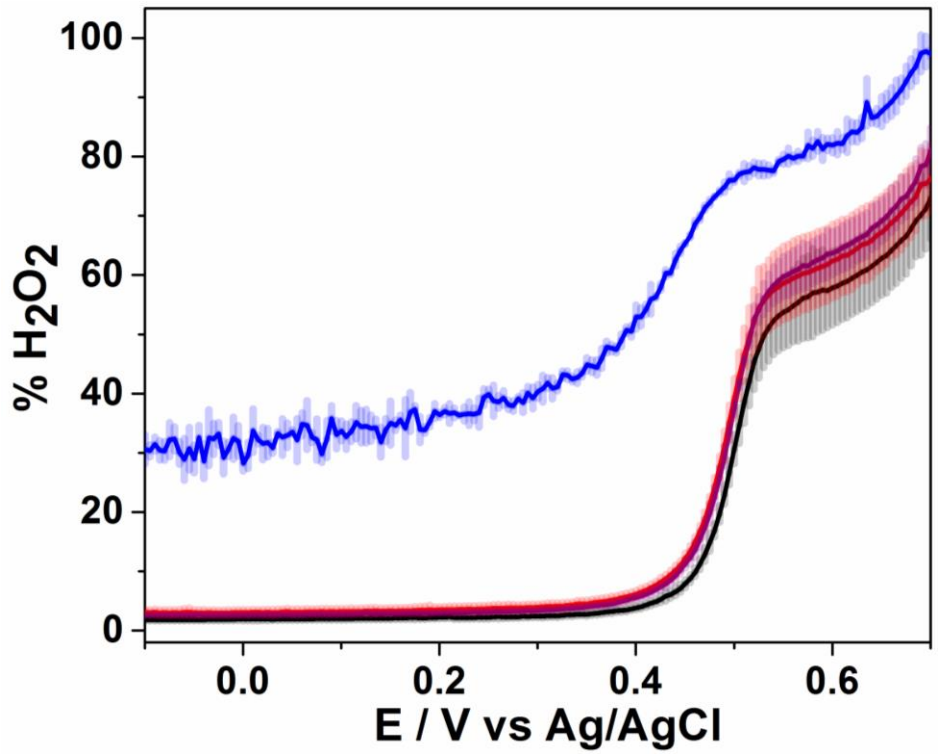

Figure S6. H_2O_2 (%) produced in RRDE experiments of various composites: 1) PMO-AuNC, SWNT and BOD (BOD-PMO-AuNC/SWNT, red curve), 2) plasmonic Au particles, SWNT and BOD (BOD-PMO-AuNP/SWNT, purple curve), 3) PMO, SWNT and BOD (PMO-BOD/SWNT, blue curve), and 4) SWNT and BOD (BOD/SWNT, black curve) in 100 mM phosphate buffer at pH 7.5, electrode rotation rate of 800 rpm, and scan rate of 10 mV/s. The ring potential was held at 0.8 V.