Electronic Supplementary Information (ESI)

Prompt Synthesis of Iridium Organosol on DNA for Catalysis and SERS Applications

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Reagents and instruments.

Double stranded deoxyribonucleic acid (low molecular weight ~10K base pairs) from salmon sperm, metal precursor iridium trichloride ($IrCl_3$. xH_2O), tetra butyl ammoniumborohydride ($TBABH_4$) and Sodium borohydride ($NaBH_4$) were bought from Sigma Aldrich and used as received. Ethanol (EtOH)was purchased from SRL India used for the entire synthesis and application purposes. Rose Bengal (RB) dye was purchased from Qualigens, India. Different nitroarenes, namely, 4-nitrophenol (4-NP), 4-nitrobenzaldehyde (4-NBA), 4-nitroaniline (4-NA), 2-nitroaniline (2-NA) and 2-nitrophenol (2-NP) were procured from Sigma-Aldrich and used as received. The produced Ir organosol was characterized using various spectroscopic and microscopic techniques such as Microwave oven, UV-Visible, XRD, HR-TEM, XPS, Laser Raman and FT-IR analyses. The Microwave oven irradiation used for generating Ir NPs is of a domestic purpose-based from Samsung Company, DE68-03714B. The output power of MW oven was 100–900 W and the operating frequency was 2450 MHz. The UV-Visible (UV-Vis) absorption spectra were documented in a Unico (model 4802) UV-Vis-NIR spectrophotometer armed with a 1 cm quartz cuvette holder for liquid samples. The X-ray diffraction (XRD) analysis was done using a PAN analytical Advanced Bragg-Brentano X-ray powder diffractometer (XRD) with Cu K_α radiation (λ = 0.154 nm) with a scanning rate of 0.020 s^{-1} in the 2θ range 10-90°. The high-resolution transmission electron microscopy (HR-TEM) analysis was done with a Tecnai model TEM instrument (Tecnai^{TM} G2 F20, FEI) with an accelerating voltage of 200 KV. The LASER Raman measurements were carried out with the green emitting semiconductor laser source of 540 nm. The excitation light intensity in front of the objective was ~10 mW with a spectral collection time of 1 sec for Raman experiment.The integration time for our measurement was set to 10 sec.The FT-IR analysis was done with the modelNexus 670 (FTIR), Centaurms 10X (Microscope) having spectral Range 4,000 to 400 cm^{-1} with aMCT-B detector.

Preparation of samples for various other characterizations.

The synthesized Ir NPs @DNA and IrO_x NPs @DNA were characterized using UV-Vis, TEM, XRD, XPS, Laser Raman and FT-IR studies. The as-synthesized Ir NPs @DNA and IrO_2 NPs @DNA were diluted (as required), drop casted over carbon coated copper grids, dried in air and finally analyzed with TEM instrument. For UV-Vis spectroscopic analysis the as-synthesized Ir NPs @DNA and IrO_2 NPs @DNA was used directly. For FT-IR analysis, 10 µL of Ir NPs @DNA was mixed with KBr, the reaction mixture was

palletized and analyzed immediately with FT-IR instrument, same thing followed for IrO_2 NPs @DNA also. For XRD and XPS analysis, a thin film was prepared by repeatedly pouring 200 μL of Ir NPs @DNA and IrO_2 NPs @DNA separately over glass slide and by drying at room temperature. The process is repeated for more than 15 times. The dried thin film was used for analysis.

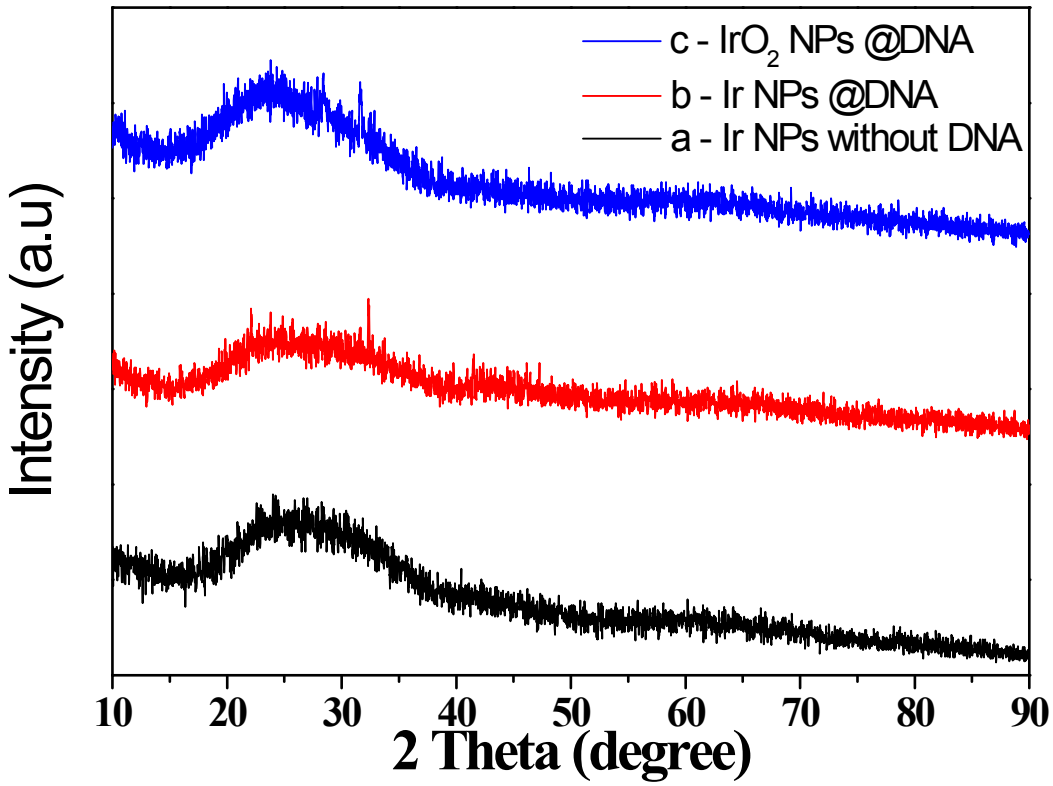


Figure S1: The X-ray diffraction pattern for the Ir NPs without DNA (curve a), Ir NPs on DNA scaffold (curve b) and IrO_2 NPs on DNA scaffold (curve c) were depicted.

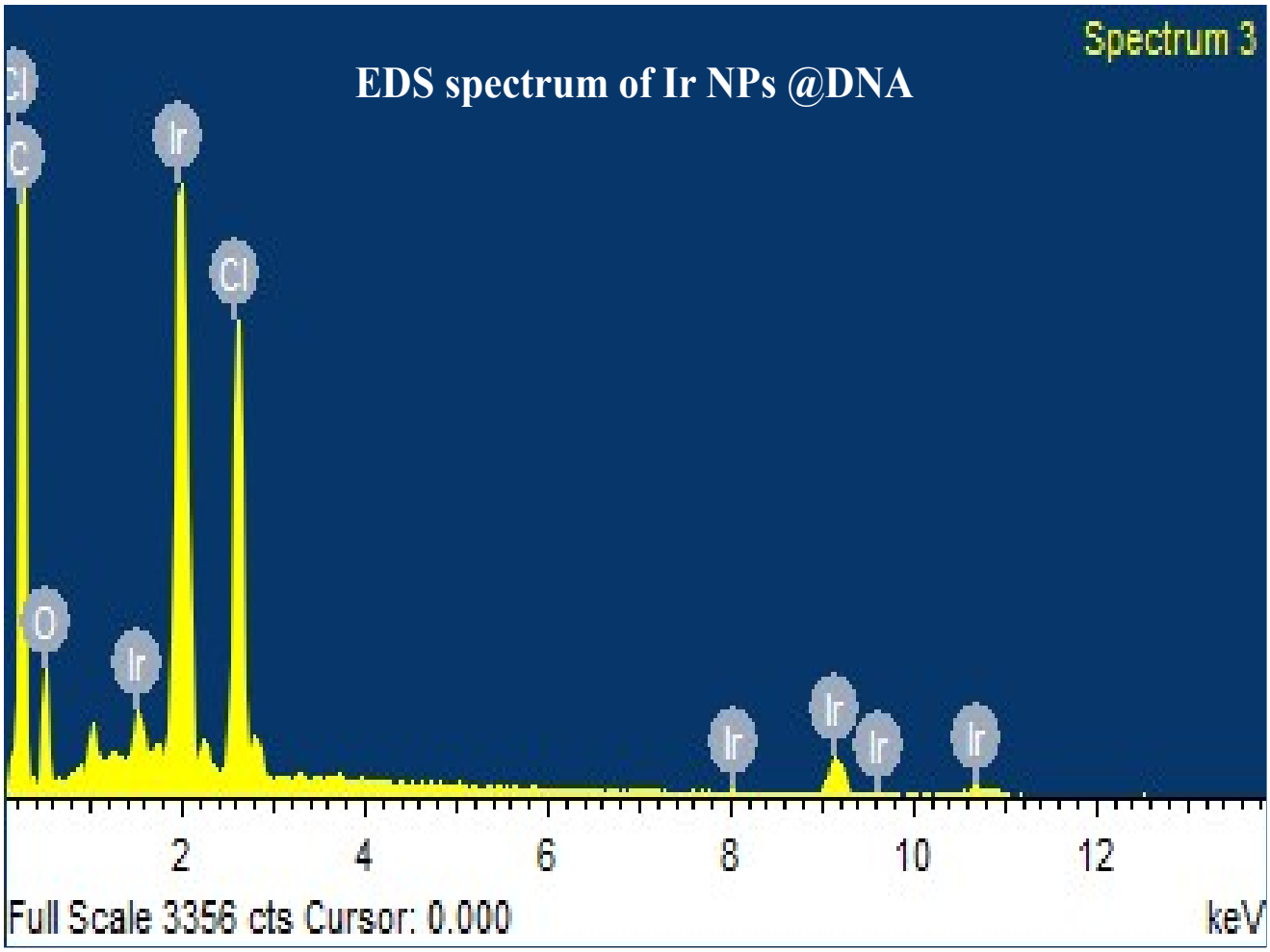


Figure S2a: The energy dispersive X-ray spectroscopic (EDS) studies of the Ir NPs on DNA scaffold, the elements like, Cl, C, O and Ir are originated in this spectrum.

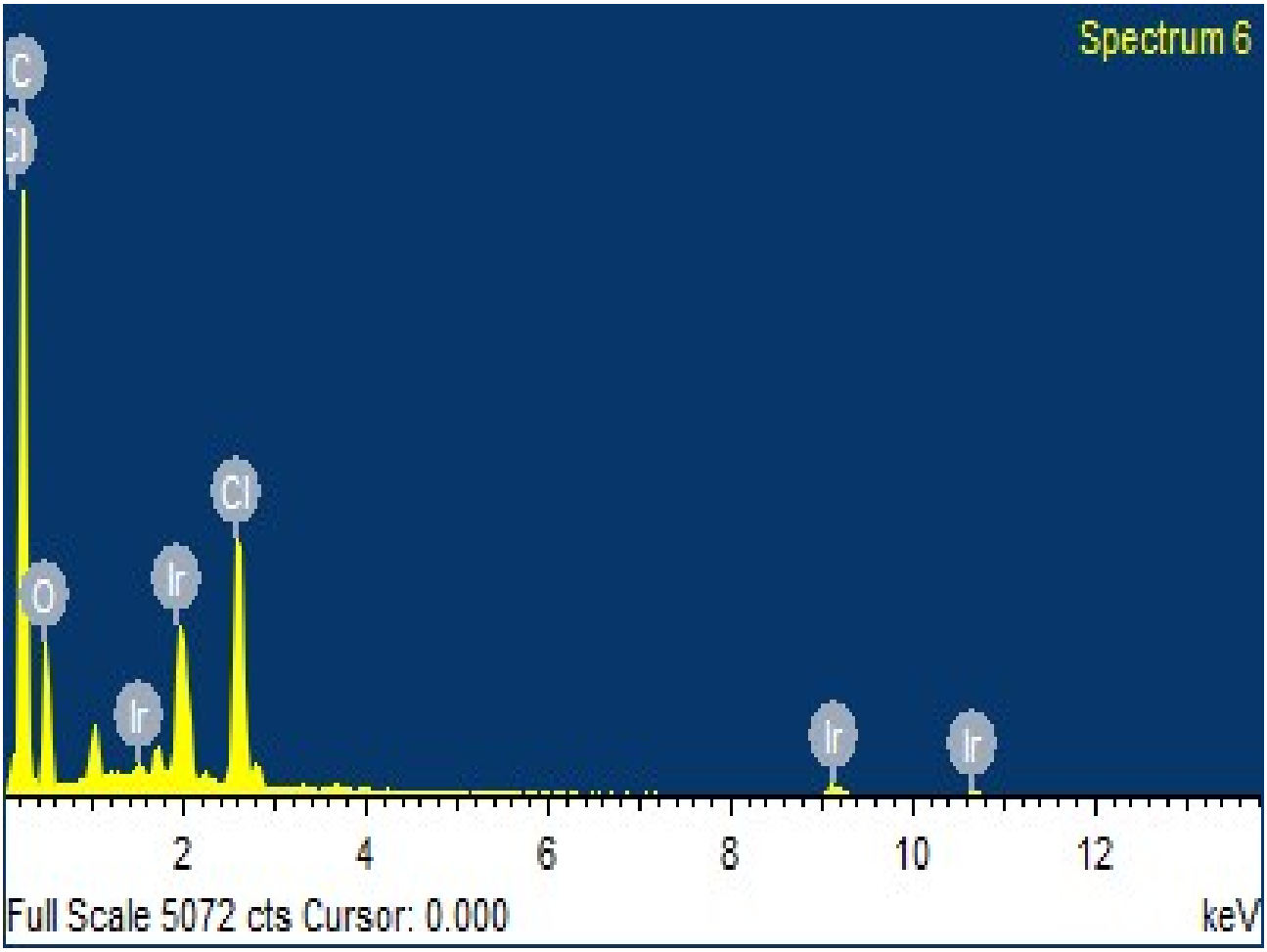


Figure S2b: The energy dispersive X-ray spectroscopic (EDS) studies of the IrO_2 NPs on DNA scaffold, the elements like Cl, C, O and Ir are originated in this spectrum.

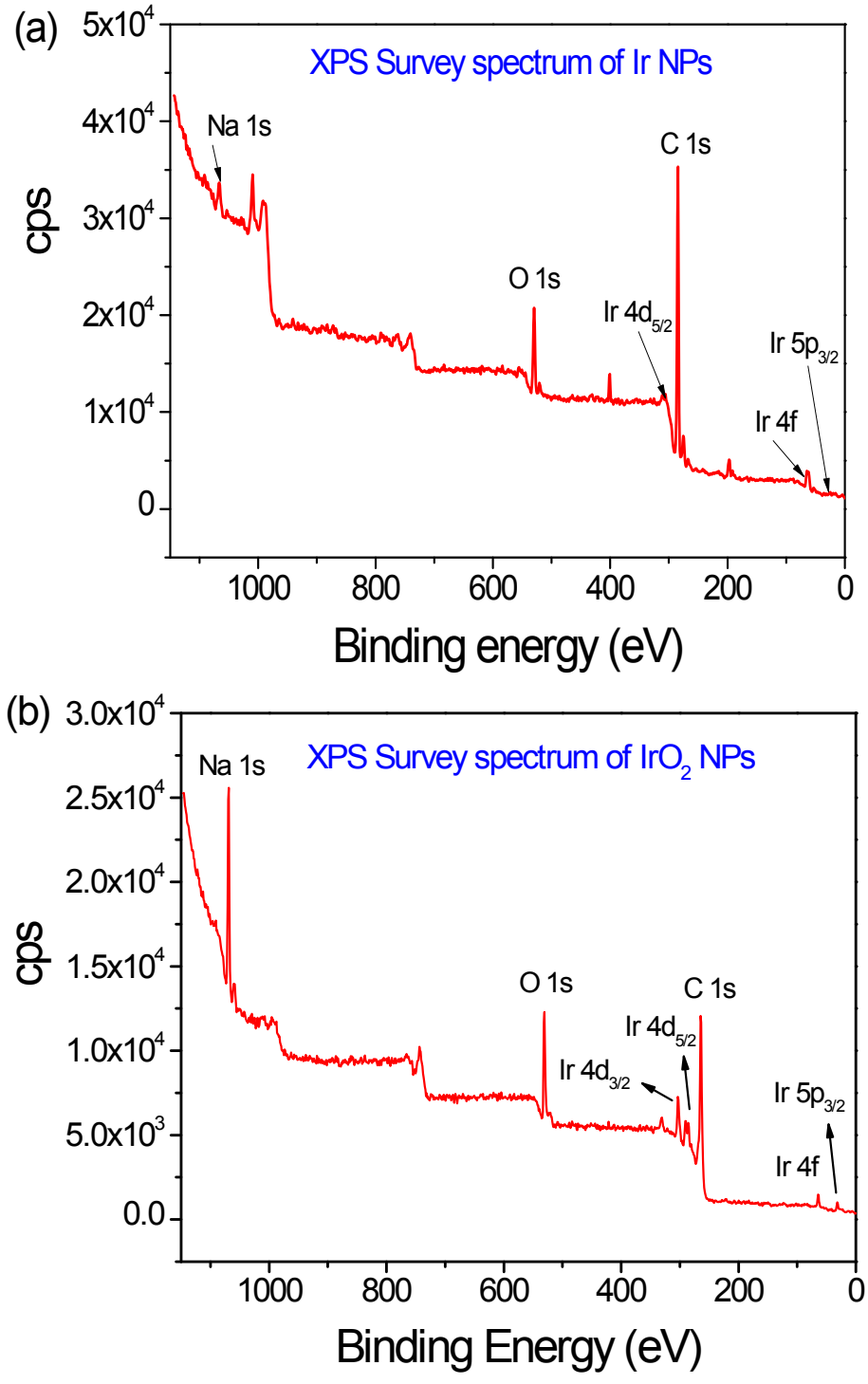
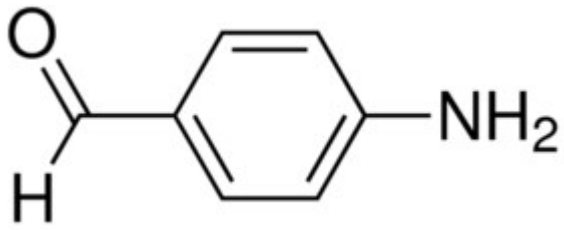
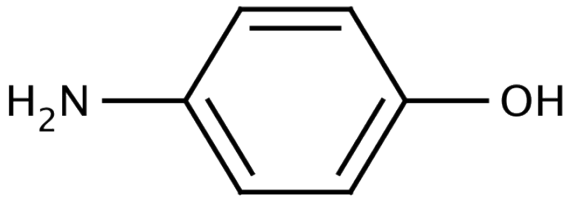


Figure S3: The XPS survey spectra of Ir NPs on DNA scaffold (figure S-3A) and IrO_2 NPs on DNA scaffold (figure S-3B) are depicted.

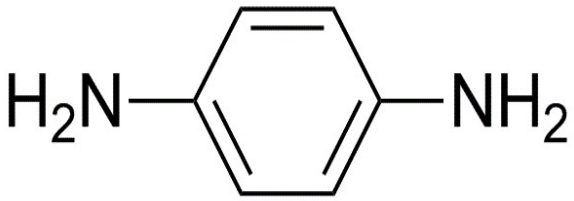
^{1}H NMR Spectral data of the amine products obtained from the catalytic reduction of aromatic nitro compounds:



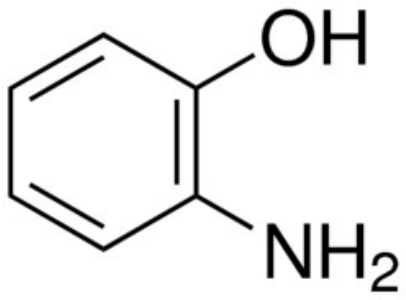
4-Amino benzaldehyde: ^{1}H NMR (400 MHz, D_2O): δ(ppm) = 8.29 (s, 1H), 7.07 (d, J = 8 Hz, 2H), 6.69(d, J = 8Hz, 2H), 3.21 (s, 2H).



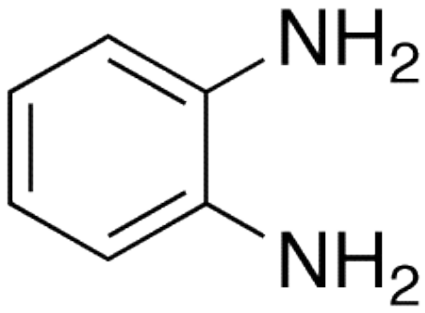
4-Amino phenol: ^{1}H NMR (400 MHz, D_2O): δ(ppm) = 6.59 (d, J = 8 Hz, 2H), 6.47 (d, J = 8 Hz, 2H), 4.84 (s, 1H), 3.23 (s, 2H).



1, 4 Di Amino benzene: ^{1}H NMR (400 MHz, D_2O): δ(ppm) = 6.62 (s, 4H), 3.23 (s, 4H).



2-Amino phenol: ^{1}H NMR (400 MHz, D_2O): δ(ppm) = 7.20 (d, J = 8Hz, 1H), 7.00 (t, J = 8 Hz, 1H), 6.65 (d, J = 8Hz, 1H), 6.53 (t, J = 8Hz, 1H), 4.51 (s, 1H), 3.25 (s, 2H).



1, 2 Di Amino benzene: ^{1}H NMR (400 MHz, D_2O): δ(ppm) = 6.73 (d, J = 8Hz, 2H), 6.68 (d, J = 8Hz, 2H), 3.23 (s, 4H).

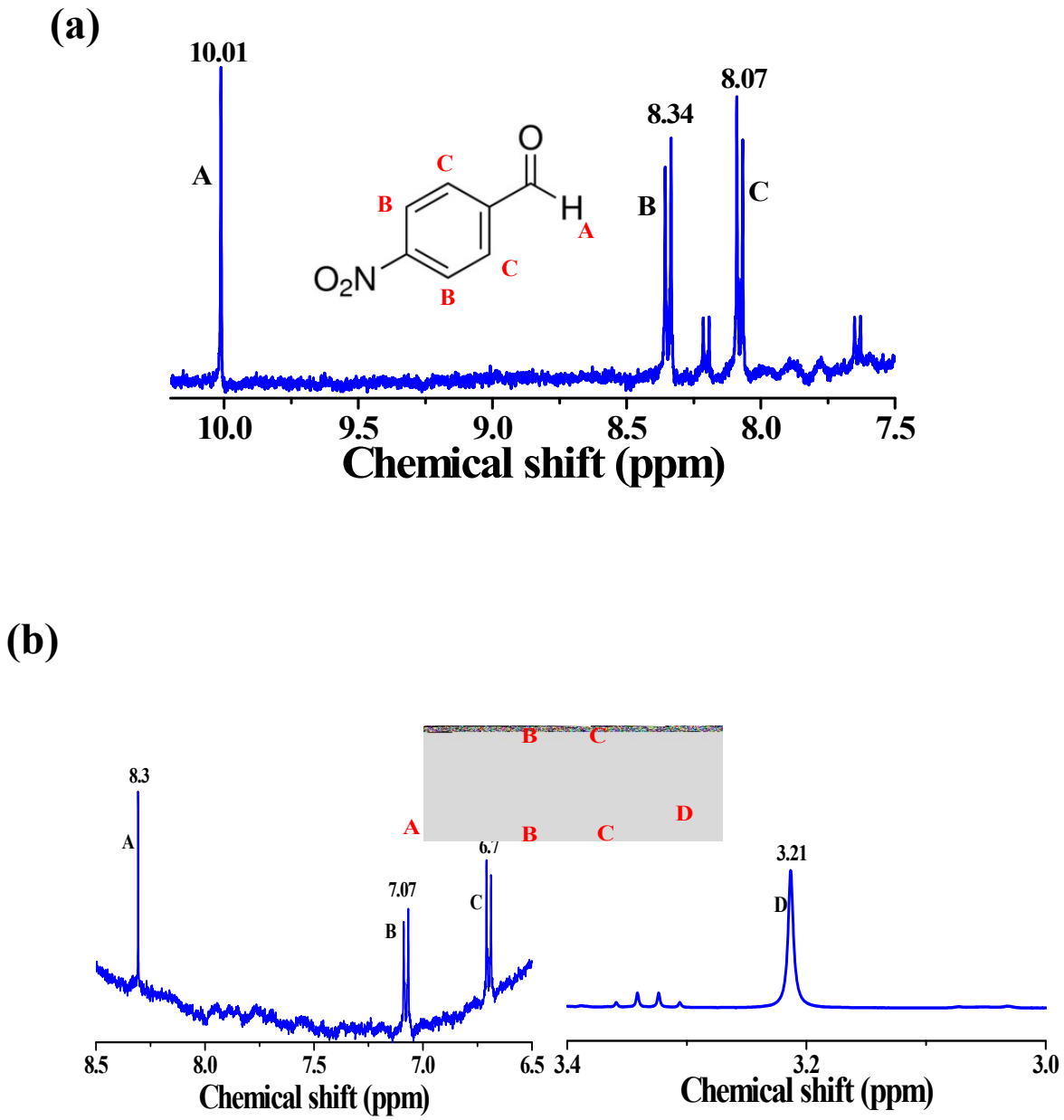


Figure S4: ^{1}H NMR spectra of the 4-Nitro benzaldehyde (a) and its corresponding amine product (b) after reduced by Ir@DNA catalyst.

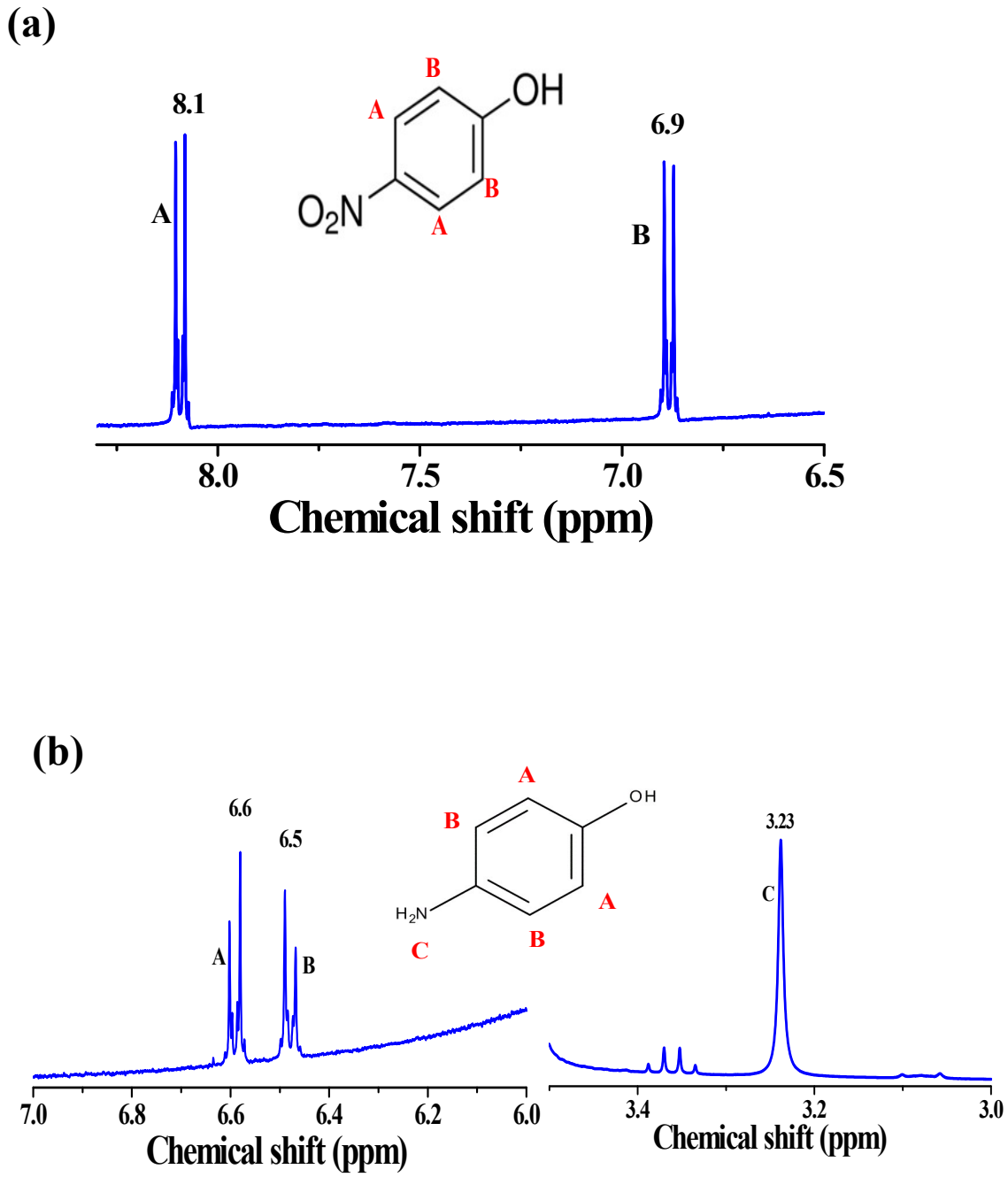


Figure S5: ^{1}H NMR spectra of the 4-Nitro phenol (a) and its corresponding amine product (b) after reduced by Ir@DNA catalyst.

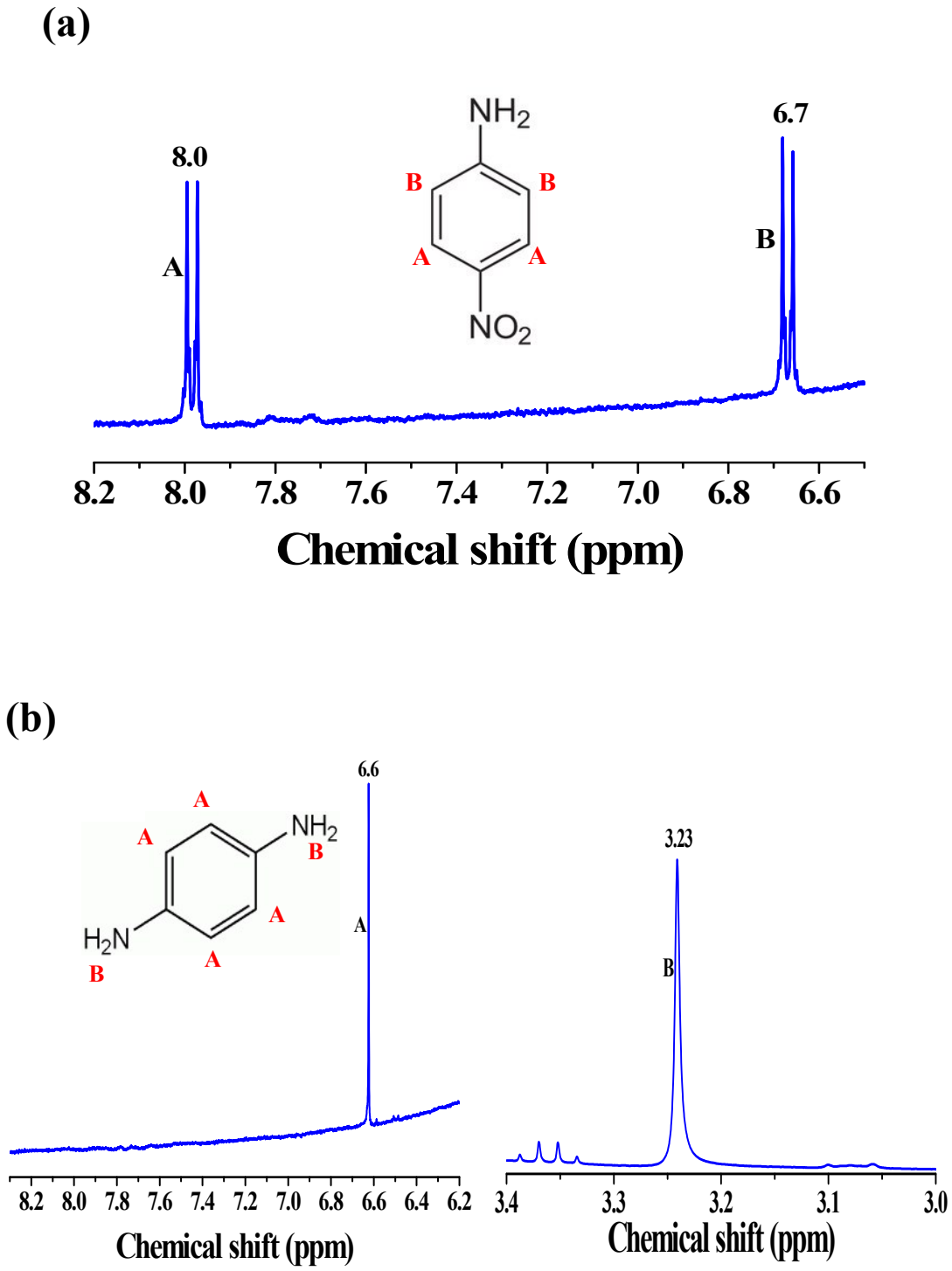


Figure S6: ^{1}H NMR spectra of the 4-Nitro aniline (a) and its corresponding amine product (b).

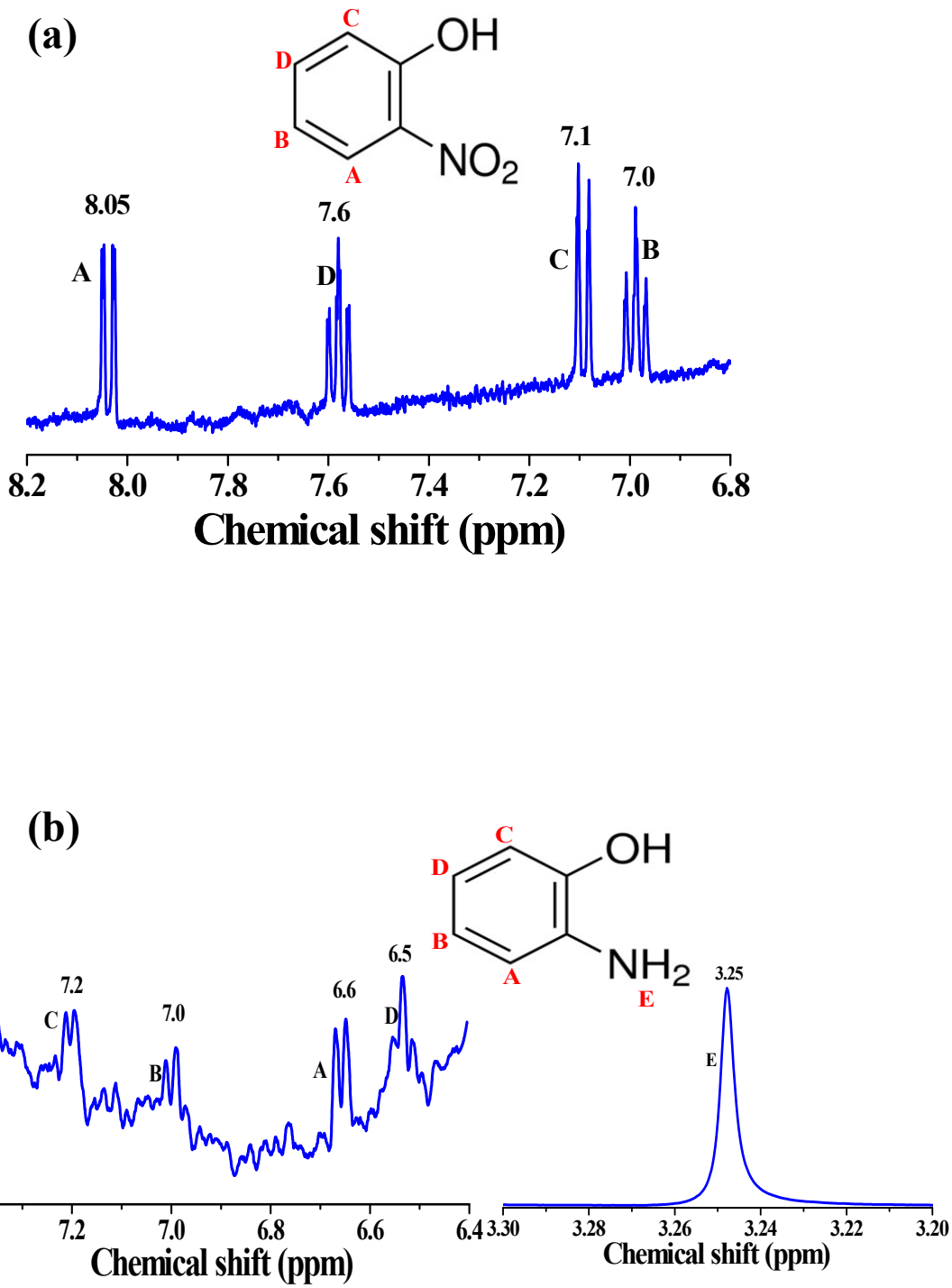


Figure S7: ^{1}H NMR spectra of the 2-Nitro phenol (a) and its corresponding amine product (b) after reduced by Ir@DNA catalyst.

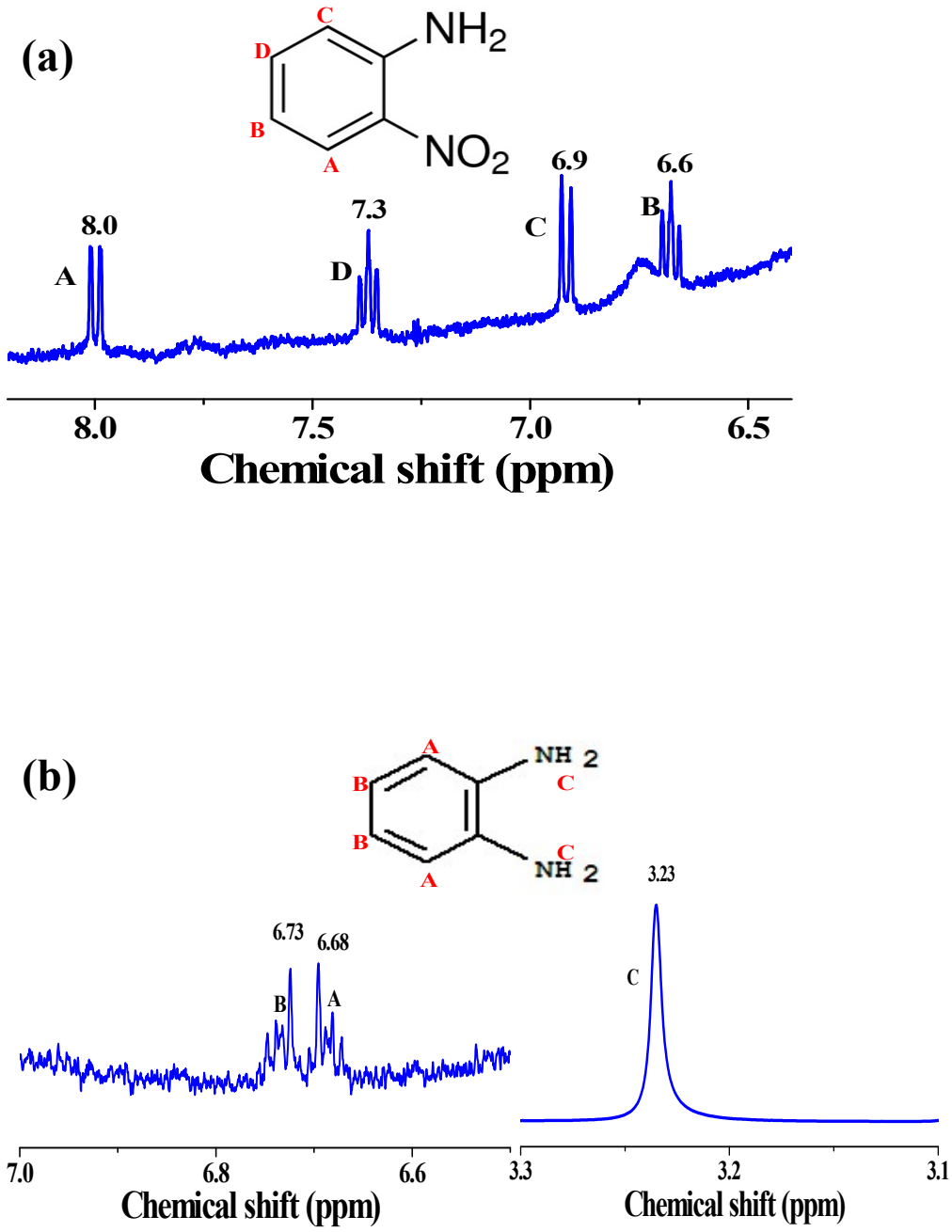


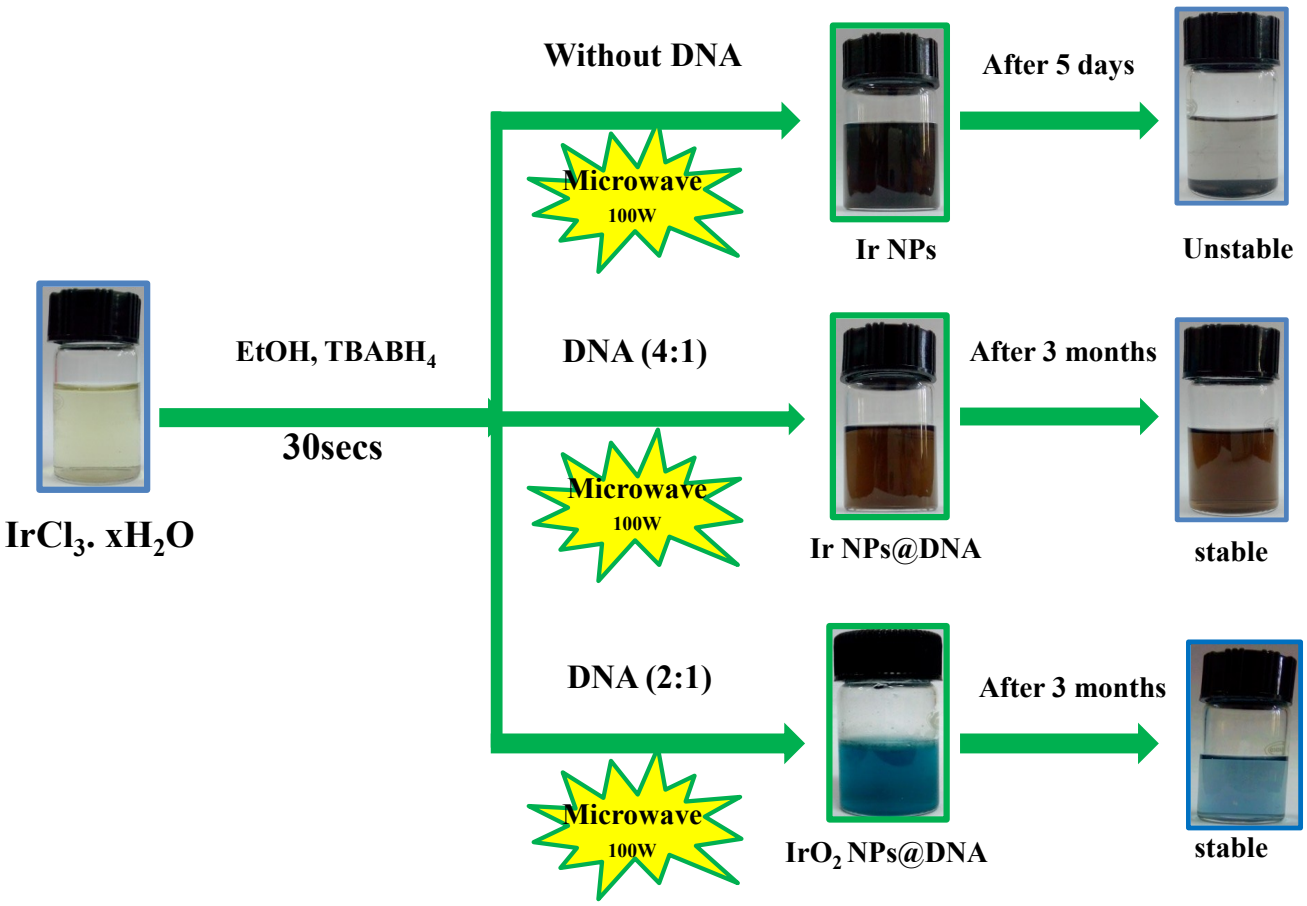
Figure S8: [1]H NMR spectra of the 2-Nitro aniline (a) and its corresponding amine product (b) after reduced by Ir@DNA catalyst.

Table S1: The concentrations of the entire reagents used to synthesize the Ir and IrO_2NPs@DNA and their morphology are summarized.

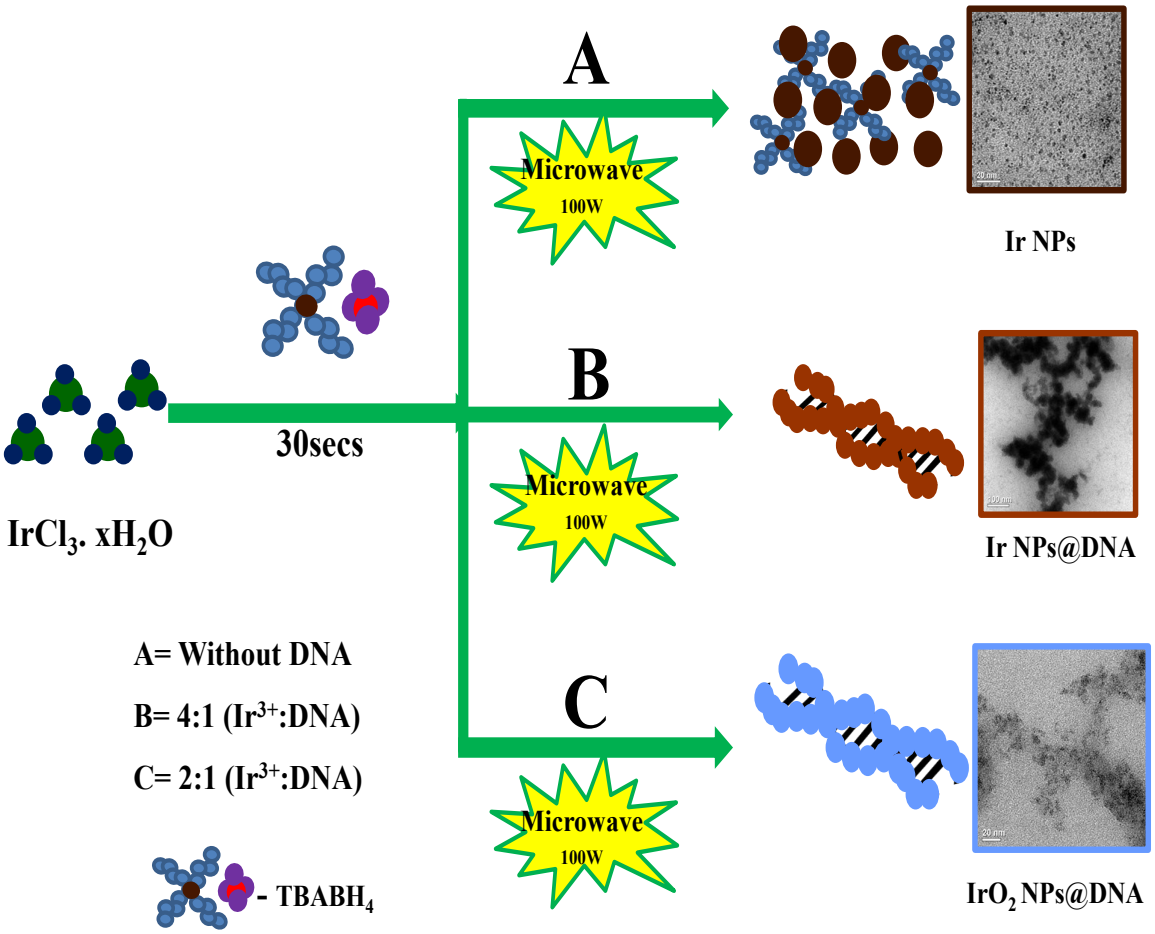
S.No.	Initial Conc. Of $IrCl_3.xH_2O$ (mM)	Ratio of Ir^{3+}:DNA	Volume of EtOH (mL)	Amount of $TBABH_4$ (mg)	Final conc. Of $IrCl_3.xH_2O$ ($\times 10^{-4}$ M)	Microwave time (100W)	Results
1.	2.68	**4 : 0**	8	15	5.36	30 sec	5 days Stable **Ir NPs**
2.	2.68	**4 : 1**	7.5	15	5.36	30 sec	More than 3 months stable **Ir@DNA NPs**
3.	2.68	3 : 1	7.3	15	5.36	30 sec	More than 2 months stable **Ir@DNA NPs**
4.	2.68	**2 : 1**	7	15	5.36	30 sec	More than 3 months stable **IrO_2@DNA NPs**
5.	2.68	4 : 3	6.5	15	5.36	30 sec	More than a month stable **IrO_2@DNA NPs**
6.	2.68	1 : 1	6	25	5.36	5min	No reaction
7.	2.68	2 : 3	5	35	5.36	10min	No reaction

Table S2: The comparisons of EF values from the SERS study for our Ir NPs@DNA with other similar organic mediated NPs are depicted.

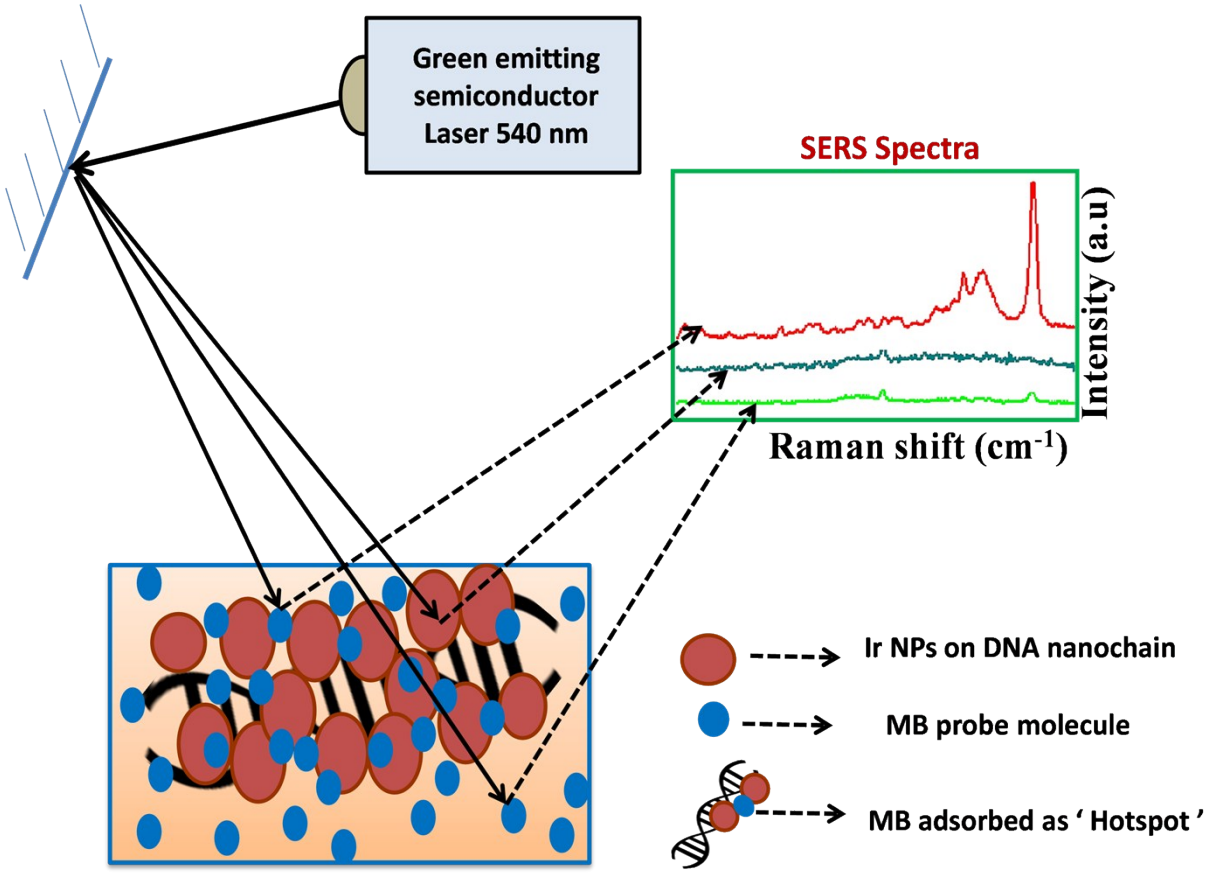
S. No.	Metal NPs	Medium	SERS Probe	EF	Ref No.
1.	Au	Amide-based molten solvent	R6G	10^7	46
2.	Au	EtOH	3,5-PDCA	1.4×10^5	47
3.	Ag	Mercaptoacetic acid	R6G	--	48
4.	Os	Acetone	MB	1.6×10^5	49
5.	Cu	Benzyl alcohol	PMBA	--	50
6.	Re	Acetonitrile	MB	3.3×10^6	29
7.	Ir	Aqueous	4-MPy	--	20
8.	Ir @DNA	EtOH	MB	8×10^5	This work



Scheme S1: Schematic representation of formation of Ir and IrO_2 nanoparticles.



DNA scaffold are depicted.for SERS spectra of MB dye adsorbed on Ir NPs@The schematic representations **:Scheme S3Scheme S2:** Schematic representation of assembling of Ir and IrO_2



nanoparticles over DNA.

Calculation of Analytical Enhancement Factor (AEF) value in SERS

The concentration of the stock probe molecule used for SERS study was 10^{-6} (M). We used 500 µl of it and final volume was 1000 µl. So the final concentration of the probe was 5 × 10^{-7} (M).

So, 1 litre of 5 × 10^{-7} mole contains 6.023 × 10^{23} number of molecules.

Then, 1000 ml of 5 × 10^{-7} mole contains 6.023 × 10^{23} number of molecules.

Then, 1 ml of 1 mole contains 3 × 10^{14} number of molecules.

So the 1 µl of the same solution contains 3 × 10^{11} number of molecules.

For deposition on substrate, we take 10 µl solutions, so it contains 3 × 10^{12} number of molecules.

When we deposit 10 µl solutions, it approximately covers 3 mm circular area on the substrate. So the diameter is 3 mm = 3 × 10^{3} µm.

So the number of molecule per µm area = 3 × 10^{12} / π $(3/2 \times 10^{3})^2$

= 4.24 × 10^{5}, so calculated $\mathbf{C_{SERS} = 4.24 \times 10^5}$

The approximate diameter of the LASER spot = 1 µm and the number of molecule inside the LASER spot ($\mathbf{C_{SERS}}$) = $\mathbf{4.24 \times 10^5}$

For calculation of $C_{RS,}$ we used 10^{-2} (M) probe solution and in similar way when we calculate the number of molecule per µm area ~ 10^{9}.

So the calculated $\mathbf{C_{RS}}$ **is =** $\mathbf{10^9}$

Now if we calculated the AEF for the peak position at 1363 cm^{-1} using the following equation,

$$\mathbf{AEF} = \frac{\mathbf{I_{SERS}/C_{SERS}}}{\mathbf{I_{RS}/C_{RS}}}$$

This work@DNA8MPyAqueousIr7.2963.3×10MBAcetonitrileRe6.50

$$\frac{\mathbf{4429/4.24 \times 10^5}}{\mathbf{13/10^9}}$$

It will be, = $\mathbf{8 \times 10^5}$

So the AEF value at peak position 1623 cm^{-1} is $\mathbf{8 \times 10^5}$**.** In similar way, the AEF values for other peak position were also calculated.