Electronic Supplementary Material (ESI) for Environmental Science: Nano.


**Tri-metallic ZIF mediated synthesis of defect rich N-doped $Co_3O_4$/ZnO/NiO S-scheme heterostructure for detection and photocatalytic degradation of persistent organic pollutants**

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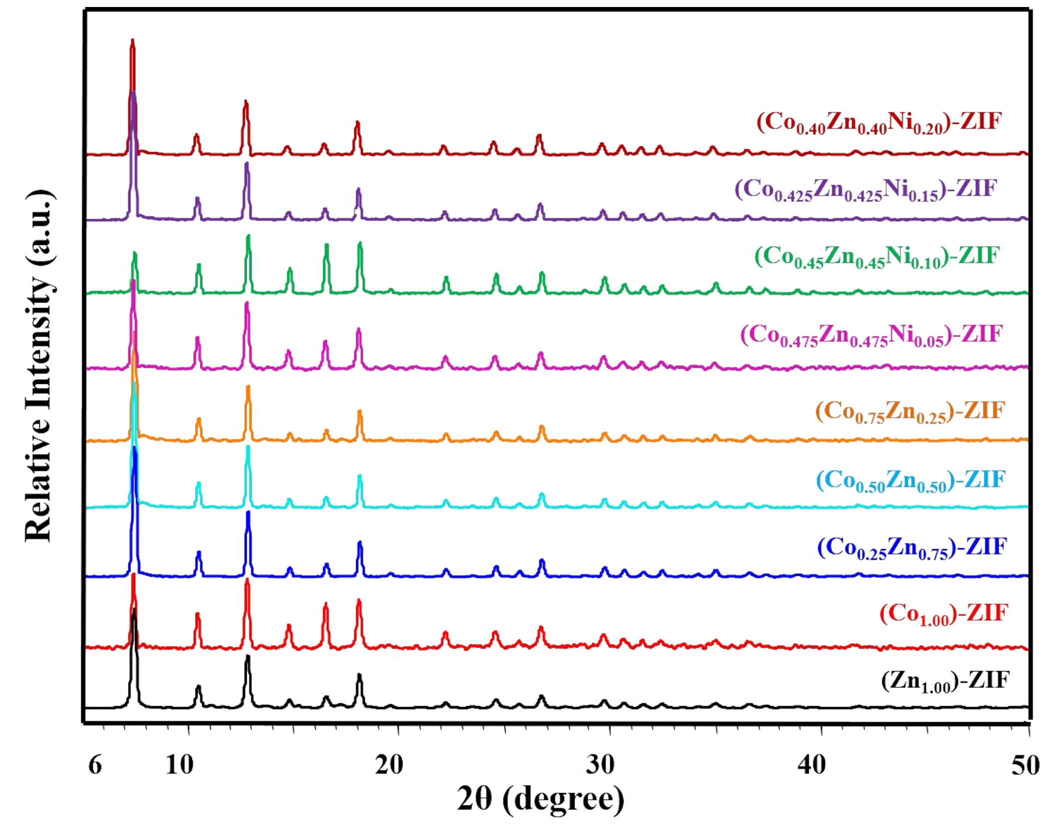


**Fig. S1 P-XRD pattern of all the synthesized mono-, bi- and tri-metallic ZIF materials**

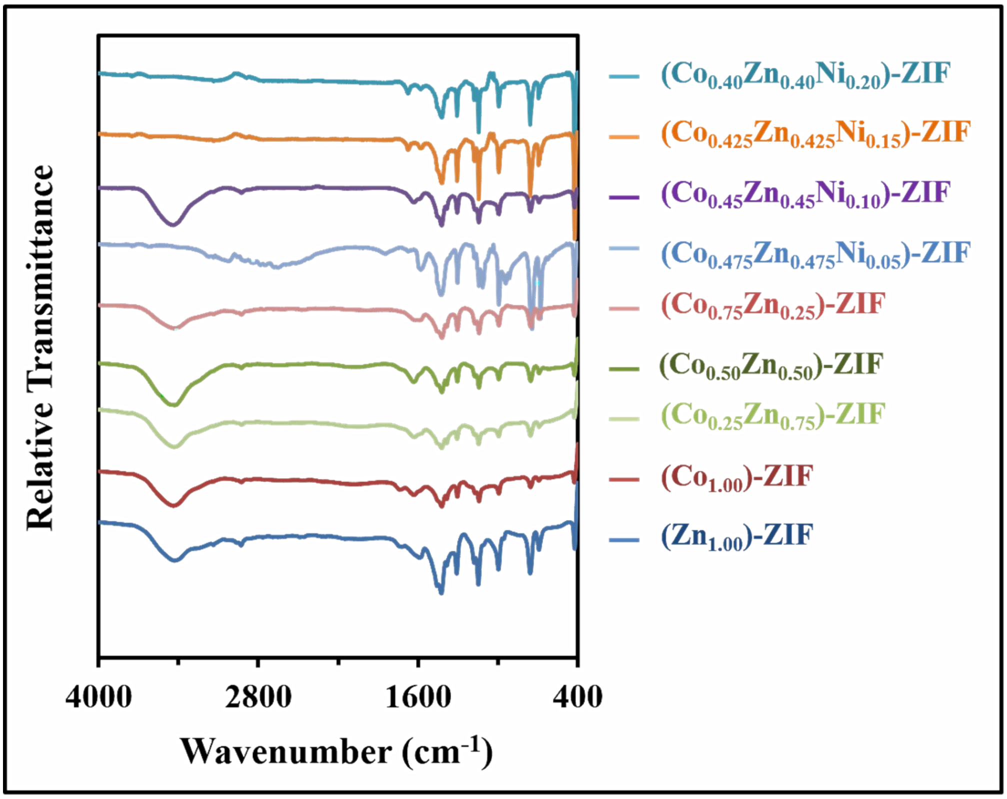


**Fig. S2 FT-IR spectra of all the synthesized ZIFs**

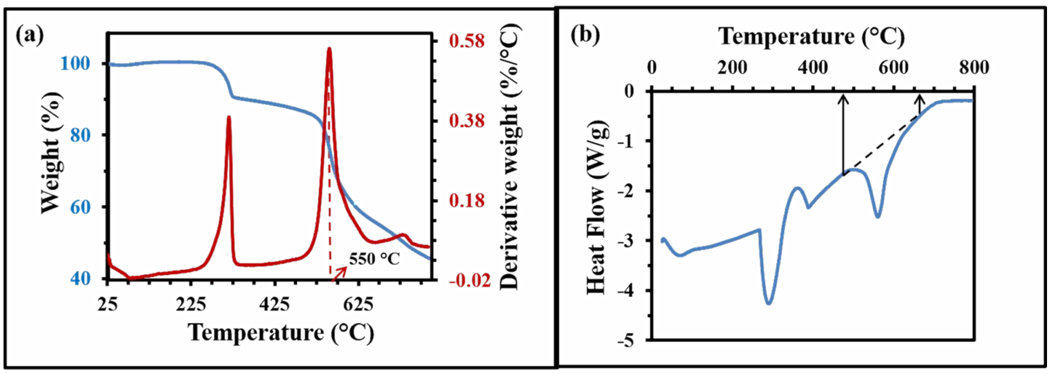


**Fig. S3 (a) Derivative weight loss curve coupled with TGA curve and (b) DSC curve of ($Co_{0.45}Zn_{0.45}Ni_{0.10}$)-ZIF**

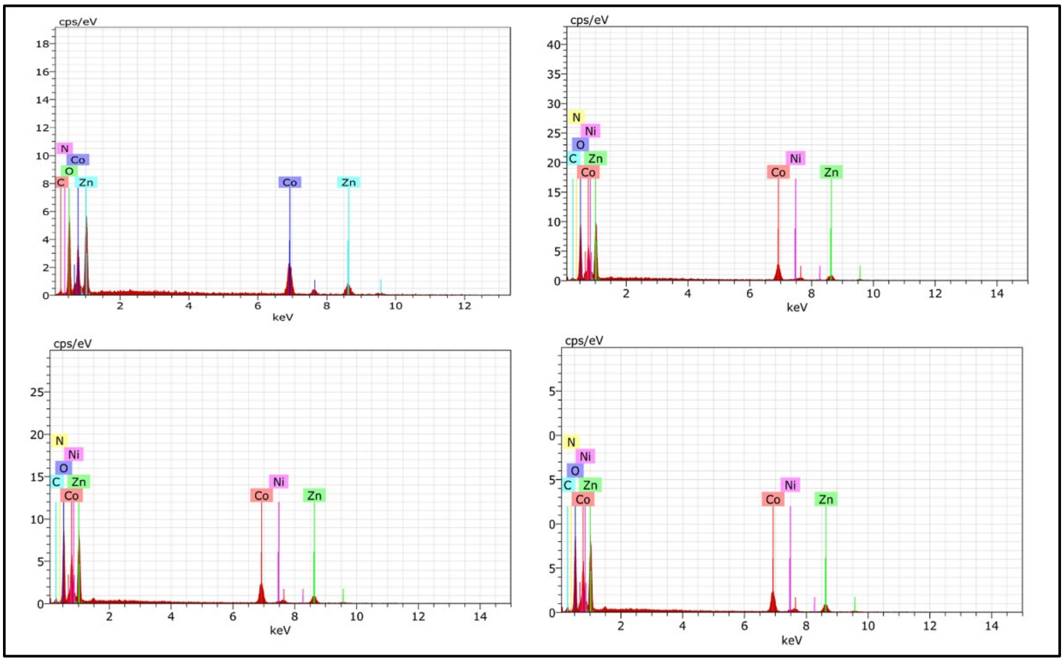


**Fig. S4 EDS spectra of : (a) ($Zn_{0.50}Co_{0.50}$)-600, (b) ($Zn_{0.475}Co_{0.475}Ni_{0.05}$)-600, (c) ($Zn_{0.425}Co_{0.425}Ni_{0.15}$)-600, and (d) ($Zn_{0.40}Co_{0.40}Ni_{0.20}$)-600**

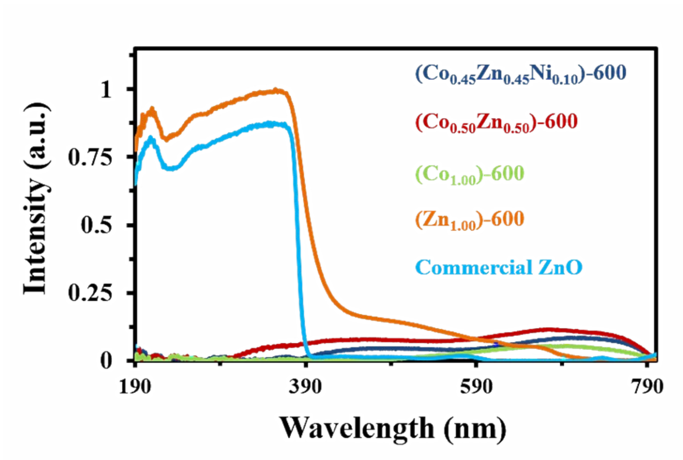


**Fig. S5 UV-Vis DRS spectra of Commercial ZnO, ($Zn_{1.00}$)-600, ($Co_{1.00}$)-600, ($Zn_{0.50}Co_{0.50}$)-600 and ($Zn_{0.45}Co_{0.45}Ni_{0.10}$)-600**

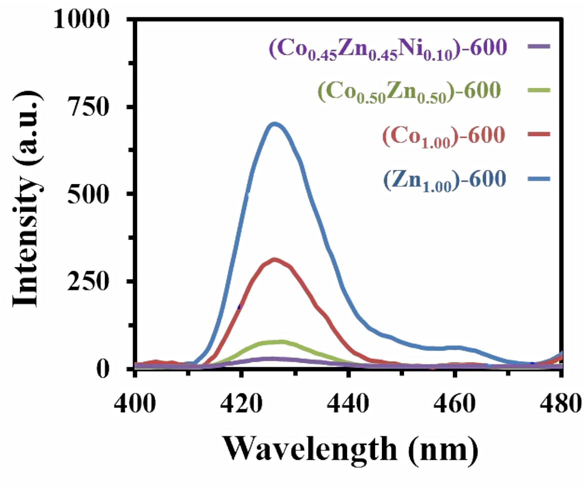


**Fig. S6 PL spectra of $(Zn_{1.00})$-600, $(Co_{1.00})$-600, $(Co_{0.50}Zn_{0.50})$-600 and $(Co_{0.45}Zn_{0.45}Ni_{0.10})$-600**

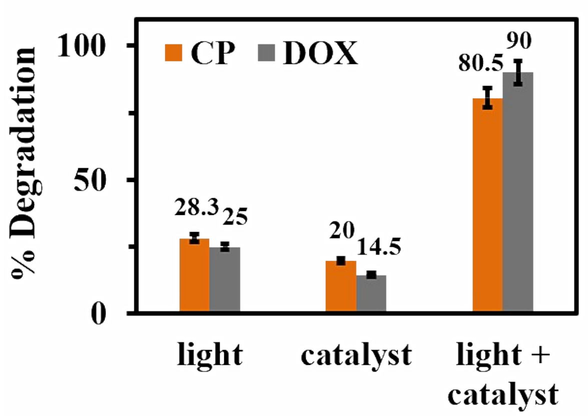


**Fig. S7 % Degradation of CP and DOX in presence of light, catalyst and both light as well as catalyst**

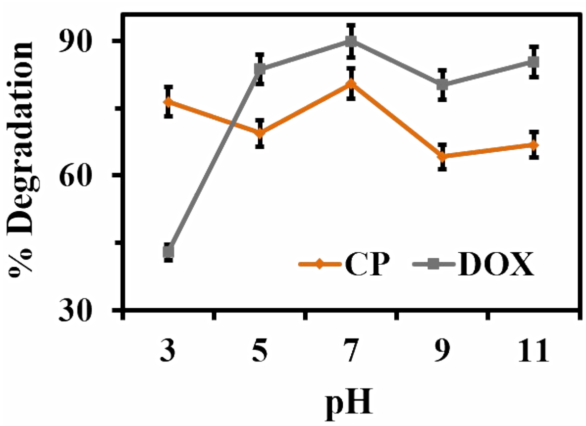


Fig. S8 Effect of pH on the photocatalytic degradation of CP and DOX by ($Co_{0.45}Zn_{0.45}Ni_{0.10}$)-600

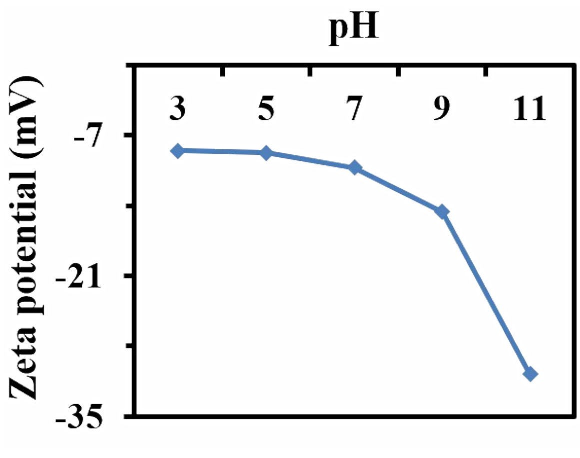


Fig. S9 Zeta potential of ($Zn_{0.45}Co_{0.45}Ni_{0.10}$)-600 at pH= 3,5,7,9 and 11

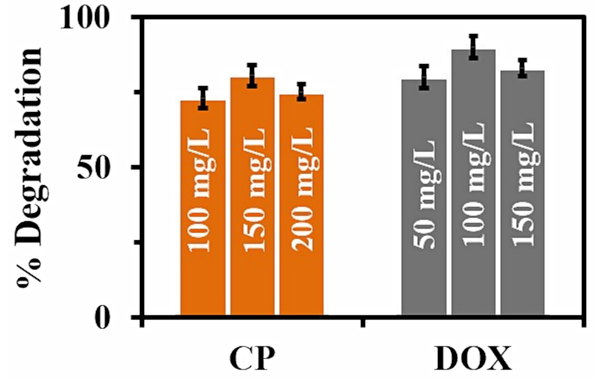


**Fig. S10 Effect of variation of ($Co_{0.45}Zn_{0.45}Ni_{0.10}$)-600 dosage on % degradation of CP and DOX**

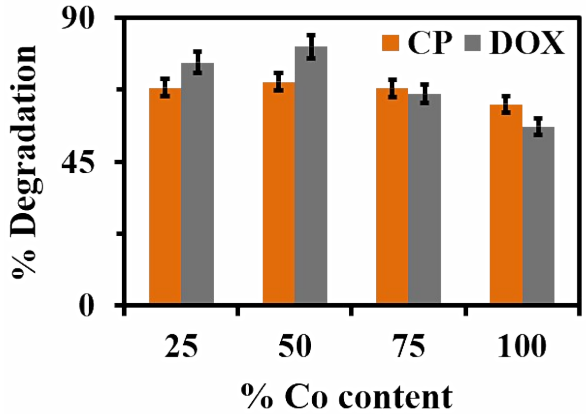


**Fig. S11 Effect of variation of Co content on % degradation of CP and DOX**

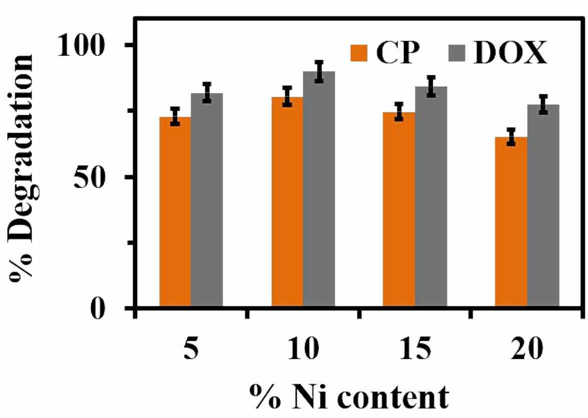


Fig. S12 Effect of variation of Ni content on % degradation of CP and DOX

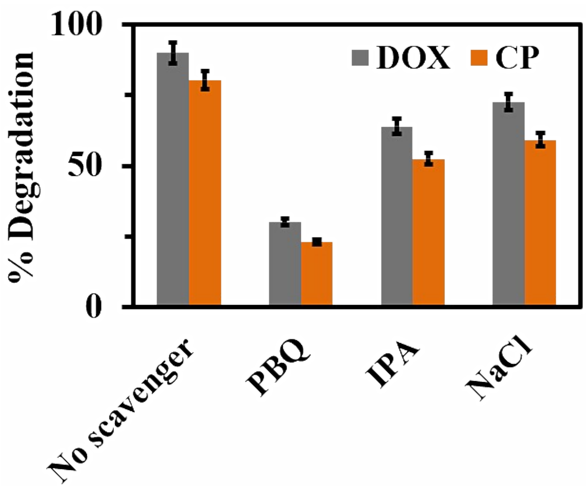


Fig.S13 Radical quenching studies for photocatalytic degradation of DOX and CP utilizing ($Co_{0.45}Zn_{0.45}Ni_{0.10}$)-600

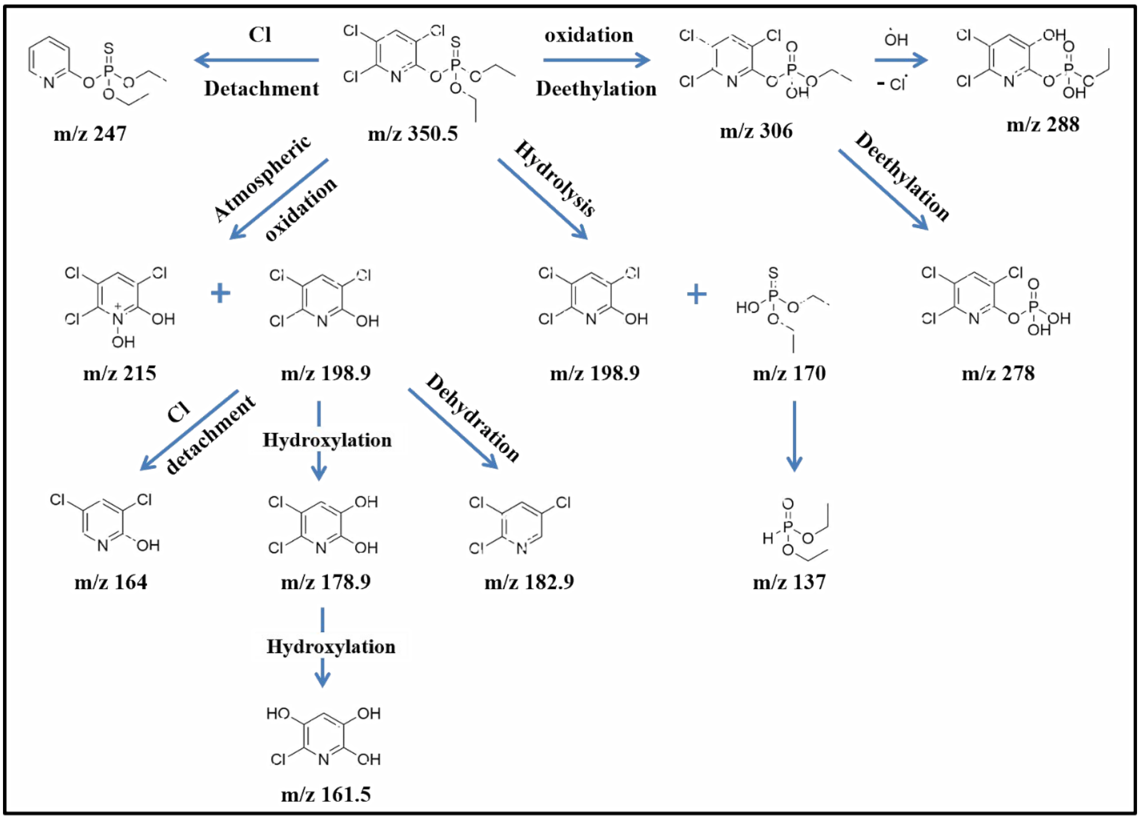


**Fig. S14 Suggested structures of intermediates and degradation pathway of CP**

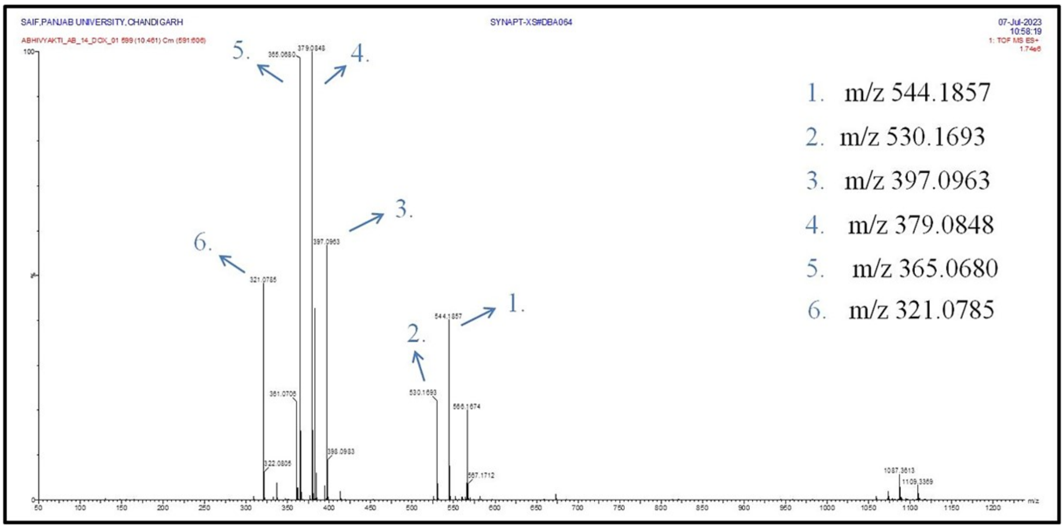


**Fig. S15 LC-MS spectra of DOX before visible light illumination**

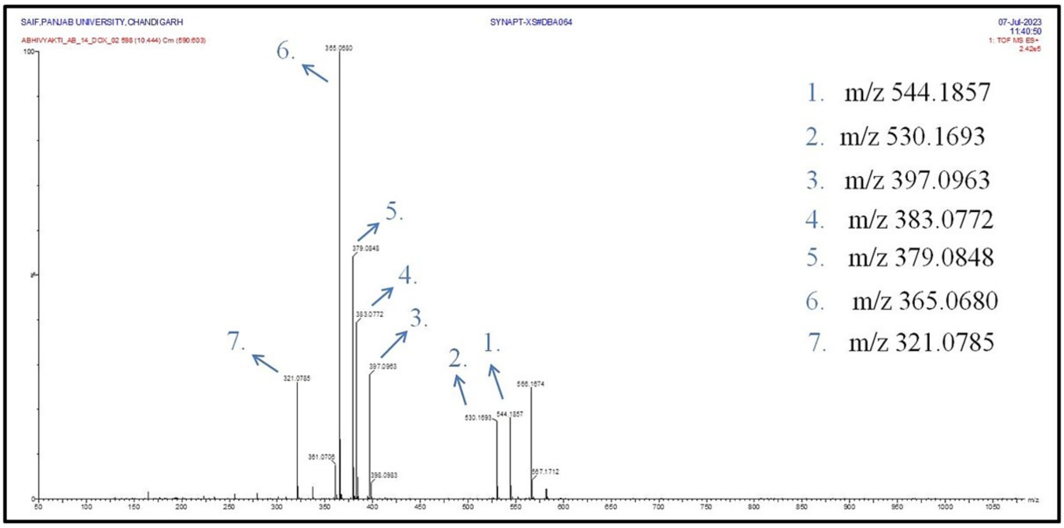


**Fig. S16 LC-MS spectra of DOX degradation after 60 min of visible light illumination**

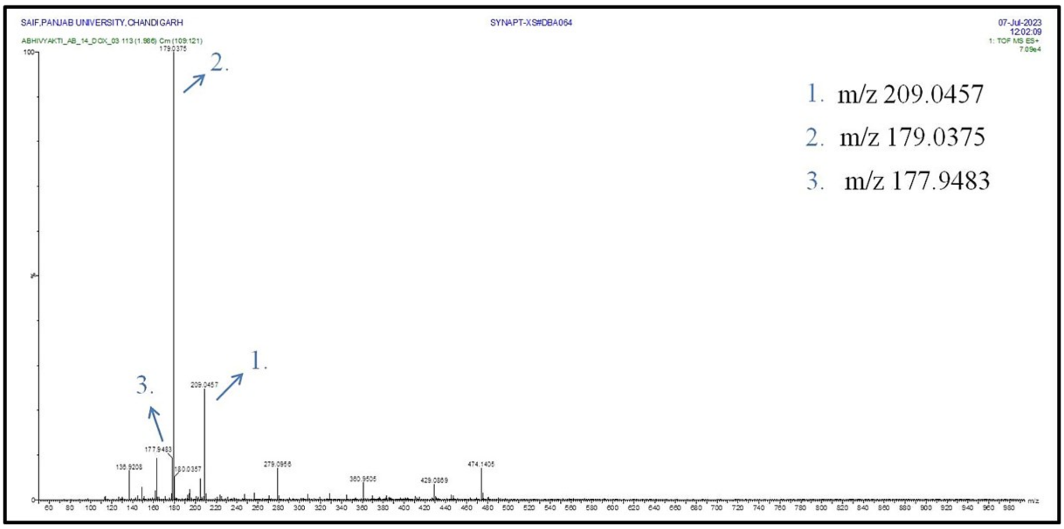


**Fig. S17 LC-MS spectra of DOX degradation after 120 min of visible light illumination**

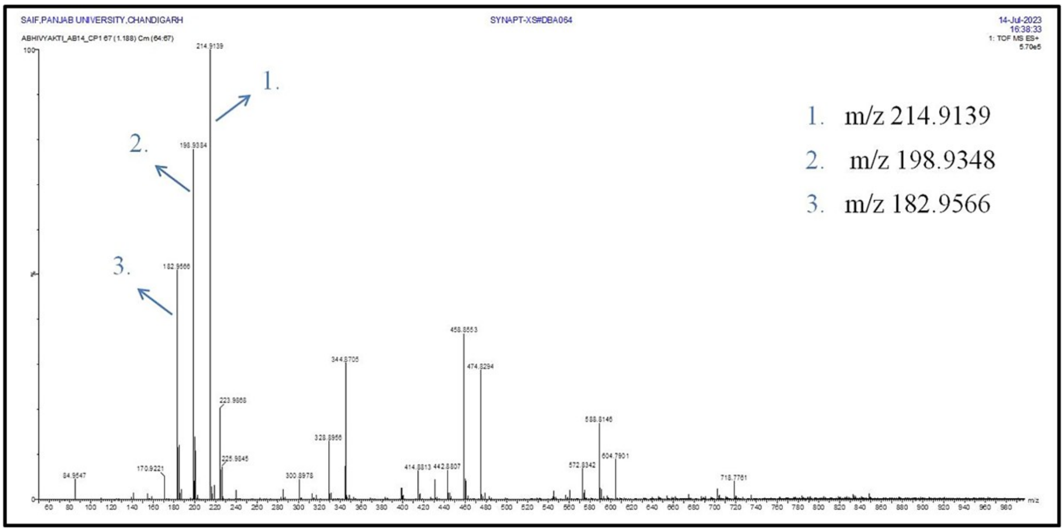


**Fig. S18 LC-MS spectra of CP before visible light illumination**

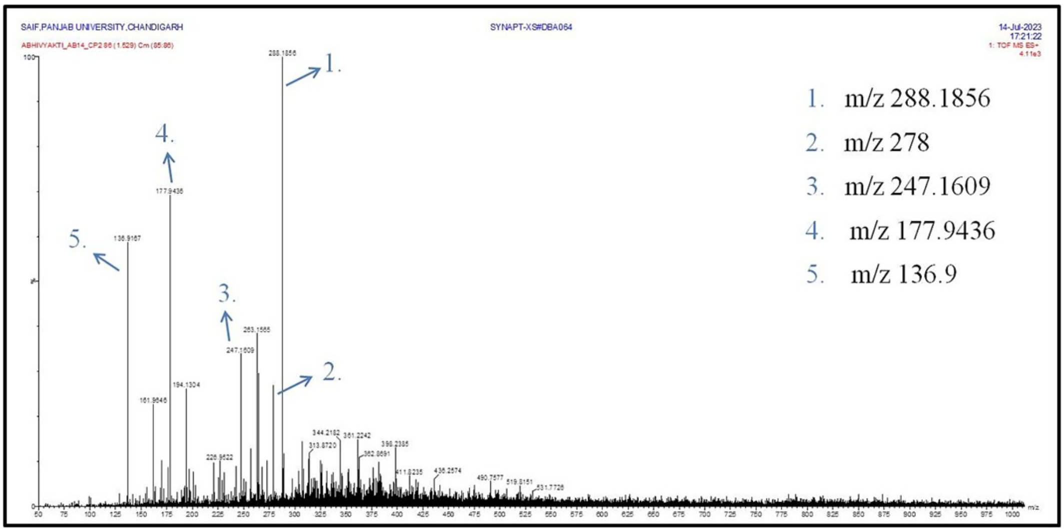


**Fig. S19 LC-MS spectra of CP degradation after 60 min of visible light illumination**

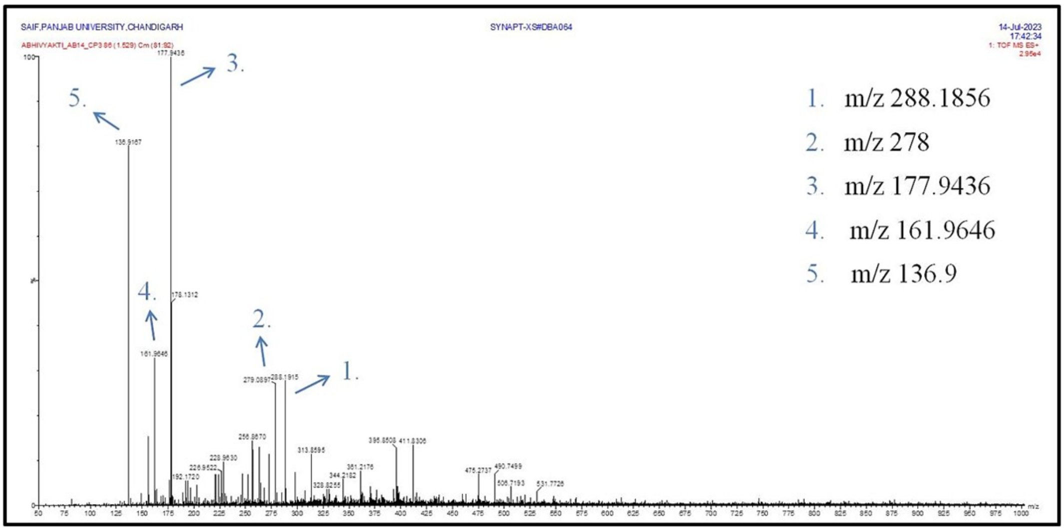


**Fig. S20 LC-MS spectra of CP degradation after 120 min of visible light illumination**

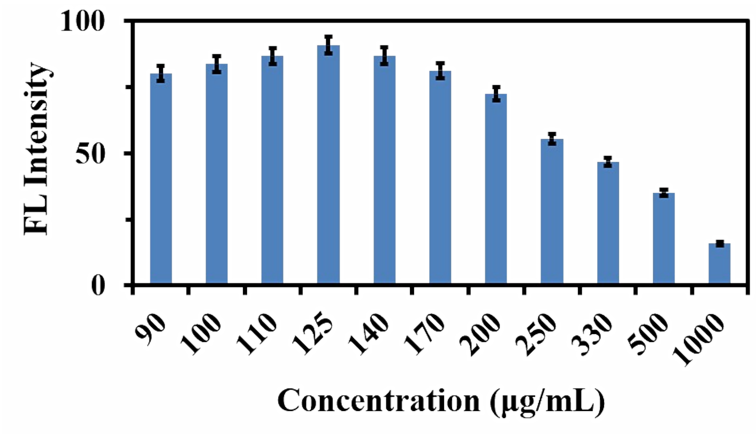


**Fig. S21 Effect of sensor concentration on fluorescence intensity**

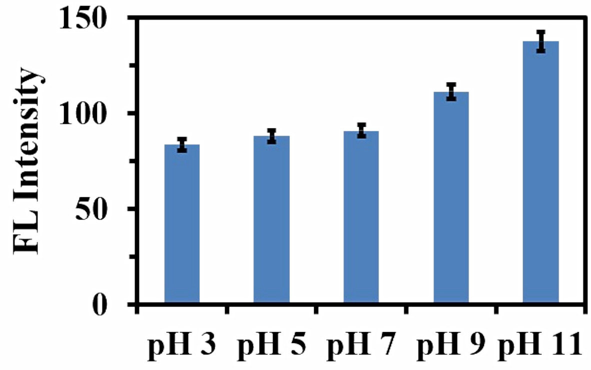


**Fig. S22 Effect of pH of the medium on fluorescence intensity of the sensor**

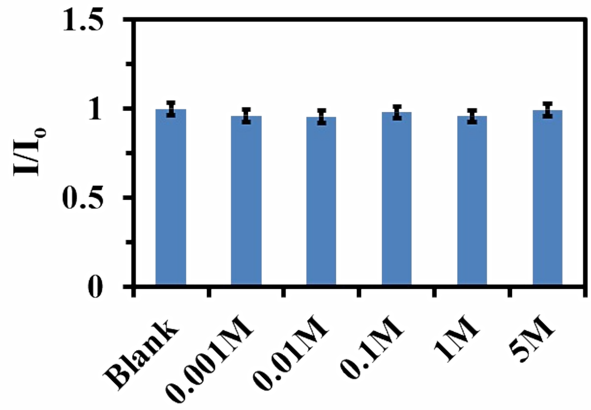


**Fig. S23 Effect of ionic strength of the medium on relative fluorescence intensity of the sensor. Blank is the relative fluorescence intensity of sensor in the absence of NaCl**

**Table S1 Band gap values estimated from tauc plot of Commercial ZnO, ($Zn_{1.00}$)-600, ($Co_{1.00}$)-600, ($Zn_{0.50}Co_{0.50}$)-600 and ($Zn_{0.45}Co_{0.45}Ni_{0.10}$)-600**

| Material | Band Gap (eV) |
|---|---|
| Commercial ZnO | 3.22 |
| ($Zn_{1.00}$)-600 | 3.10 |
| ($Co_{1.00}$)-600 | 1.35 |
| ($Zn_{0.50}Co_{0.50}$)-600 | 1.53 |
| ($Zn_{0.45}Co_{0.45}Ni_{0.10}$)-600 | 1.48 |

**Table S2 Comparison of photocatalytic efficacy of ($Co_{0.45}Zn_{0.45}Ni_{0.10}$)-600 with previously reported photocatalysts**

| Material | Pollutant | Pollutant conc. (mg/L) | Catalyst dosage (mg/L) | Degradation time (min) | % Degradation | Light source | Ref. |
|---|---|---|---|---|---|---|---|
| 2D- La doped $Bi_2O_3$ | CP | 5 | - | 120 | **67** | Vis | 1 |
| Fe- ZnO | CP | 10 | **1000** | 140 | **67** | Solar light | 2 |
| $TiO_2$ | CP | 0.37 | 20 | **1440** | 81 | **UV** | 3 |
| rGO-Ag | CP | 1 | **1000** | 105 | 75.5 | Vis | 4 |
| $BiFeO_3$ | DOX | 2 | 300 | 100 | 79 | **UV** | 5 |
| Pt-$TiO_2$ | DOX | **10** | 300 | 100 | 88 | Vis | 6 |
| N- $Co_3O_4$/ ZnO/NiO | DOX | 25 | 100 | 120 | 90 | Vis | This work |
| N- $Co_3O_4$/ ZnO/NiO | CP | 5.6 | 150 | 120 | 80.5 | Vis | This work |

**Table S3 Conduction and valence band potentials of $Co_3O_4$, ZnO and NiO**

| Materials | $\chi$ (eV) | $E_g$ (eV) | $E_{VB}$ (eV) | $E_{CB}$ (eV) |
|---|---|---|---|---|
| $Co_3O_4$ | 5.9 | 1.3 | 2.05 | 0.75 |
| ZnO | 5.79 | 3.1 | 2.84 | -0.26 |
| NiO | 3.44 | 3.5 | 0.69 | -2.81 |

## References


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[3] Budarz JF, Cooper EM, Gardner C, Hodzic E, Ferguson PL, Gunsch CK, Wiesner MR. Chlorpyrifos degradation via photoreactive TiO2 nanoparticles: assessing the impact of a multi-component degradation scenario. Journal of hazardous materials. 2019 Jun 15;372:61-8.

[4] Chinnappa K, Karuna Ananthai P, Srinivasan PP, Dharmaraj Glorybai C. Green synthesis of rGO-AgNP composite using Curcubita maxima extract for enhanced photocatalytic degradation of the organophosphate pesticide chlorpyrifos. Environmental Science and Pollution Research. 2022 Aug;29(38):58121-32.

[5] Dumitru R, Ianculescu A, Păcurariu C, Lupa L, Pop A, Vasile B, Surdu A, Manea F. BiFeO3-synthesis, characterization and its photocatalytic activity towards doxorubicin degradation from water. Ceramics international. 2019 Feb 1;45(2):2789-802.

[6] Kumar KY, Prashanth MK, Alduaij OK, Yousef TA, Abualnaja KM, Raghu MS. Mentha arvensis mediated green synthesis of platinum doped TiO2 nanocomposite for enhanced anti-cancer and photocatalytic degradation activity: Insights from molecular docking and DFT studies. Inorganic Chemistry Communications. 2021 Dec 1;134:108987.