

Supplementary Information

One-step Microwave-assisted Synthesis of MoO_{3-x} -Covalent Organic Framework (COF)-based Nanocomposite for Amplified Surface-enhanced Raman Spectroscopy in Environmental Application.

Manoj Krishnat Patil,^{a,b} Premjeet Gangadhar Wagh,^{a,b} and Shatabdi Porel Mukherjee^{,a,b}*

- a. Physical and Materials Chemistry Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune-411008, India.
- b. Academy of Scientific and Innovative Research (AcSIR), Ghaziabad-201002, India.

Email: sp.mukherjee.ncl@csir.res.in

Table of Contents

Figure S1. XPS survey scan of (a) TpTTA COF and (b) MoO_{3-x}-TpTTA COF NC.

Table S1. Values provided by CasaXPS Software Related to the Deconvolution of Figure 3d.

Figure S2. N₂ adsorption-desorption isotherm of TpTTA COF and MoO_{3-x}-TpTTA COF NC.

Figure S3. BET pore size distribution of (a) TpTTA COF and (b) MoO_{3-x}-TpTTA COF NC.

Figure S4. TGA analysis of TpTTA COF and MoO_{3-x}-TpTTA COF NC.

Figure S5. Solid state ¹³C NMR spectrum of (a) TpTTA COF and (b) MoO_{3-x}-TpTTA COF NC.

Figure S6. (a) FESEM, (b) HRTEM, (c) EDS, (d) HAADF-STEM image, and (e)-(g) elemental mapping of TpTTA COF.

Figure S7. Images of reaction mixture containing product in glass vial after microwave-assisted synthesis via (a) one-step, (b) two-step and (c) HRTEM image of the product obtained via two-step microwave-assisted synthesis.

Figure S8. (a) SERS spectra of 10⁻⁴ M MB on MoO_{3-x}-TpTTA COF NC collected from 10 random positions, and (b) intensity distribution of 1624 cm⁻¹ peak of MB (10⁻⁴ M) on MoO_{3-x}-TpTTA COF NC.

Figure S9. (a) SERS spectra of 500 ppm Mancozeb on MoO_{3-x}-TpTTA COF NC collected over a period of 4 weeks, and (b) the intensity distribution of 1140 cm⁻¹ peak of 500 ppm Mancozeb on MoO_{3-x}-TpTTA COF NC.

Table S2. Enhancement Factor (EF) calculation for MoO_{3-x}-TpTTA COF NC with respect to MB concentration (M).

Table S3. Comparison table of MoO_{3-x}-TpTTA COF NC with previously reported COF composites used for pesticide detection.

References

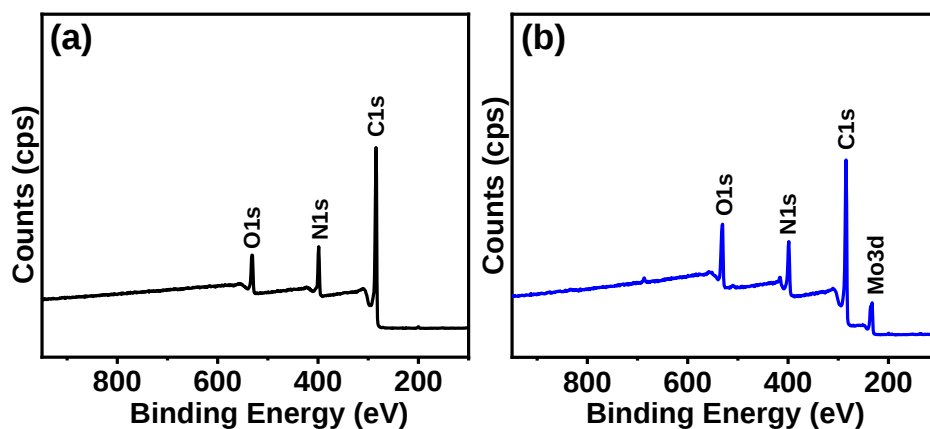


Figure S1. XPS survey scan of (a) TpTTA COF and (b) MoO_{3-x}-TpTTA COF NC.

Table S1. Values provided by CasaXPS Software Related to the Deconvolution of Figure 3d.

Mo ⁶⁺ (%)	Mo ⁵⁺ (%)
80.92	19.07

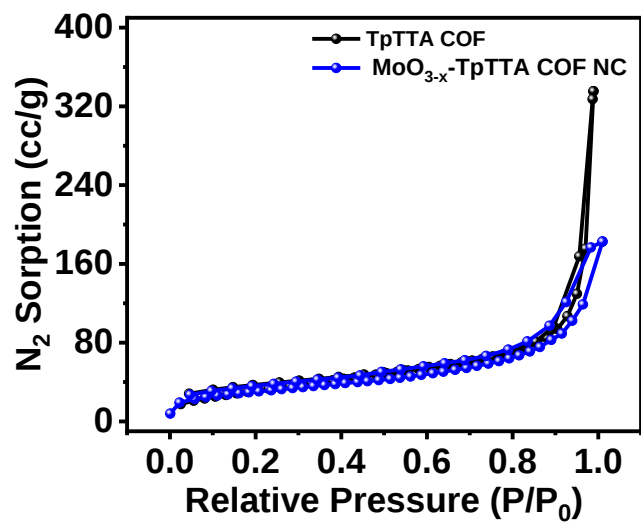


Figure S2. N₂ adsorption-desorption isotherm of TpTTA COF and MoO_{3-x}-TpTTA COF NC.

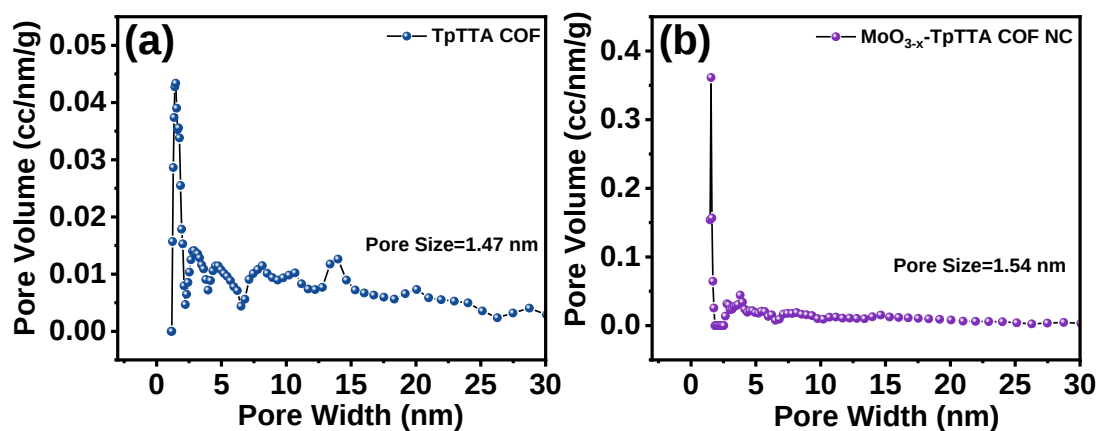


Figure S3. BET pore size distribution of (a) TpTTA COF and (b) MoO_{3-x}-TpTTA COF NC.

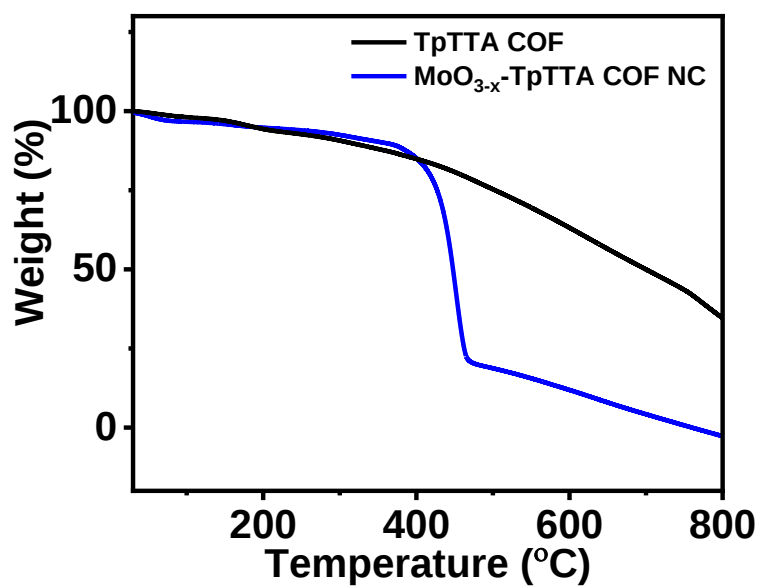


Figure S4. TGA analysis of TpTTA COF and MoO_{3-x}-TpTTA COF NC.

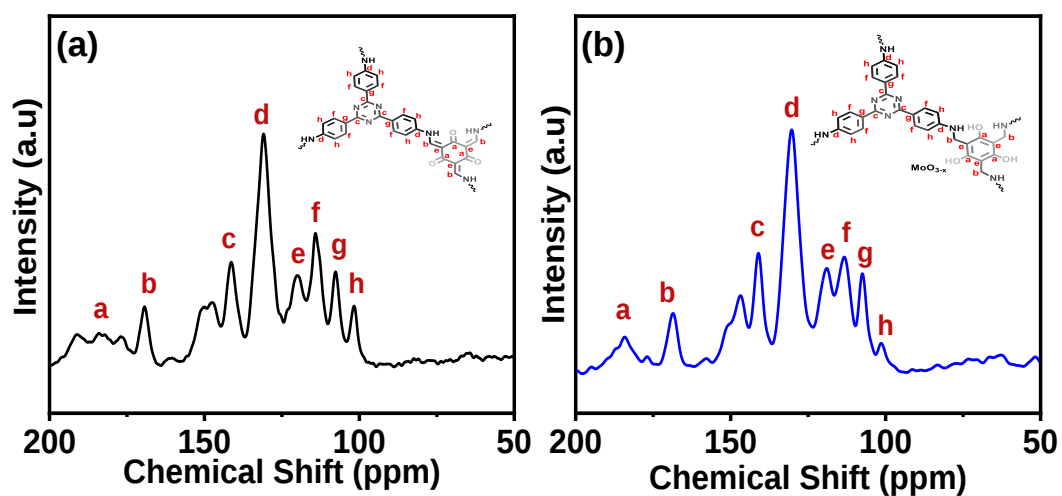


Figure S5. Solid state ^{13}C NMR Spectrum of (a) TpTTA COF and (b) $\text{MoO}_{3-x}\text{-TpTTA COF NC}$.

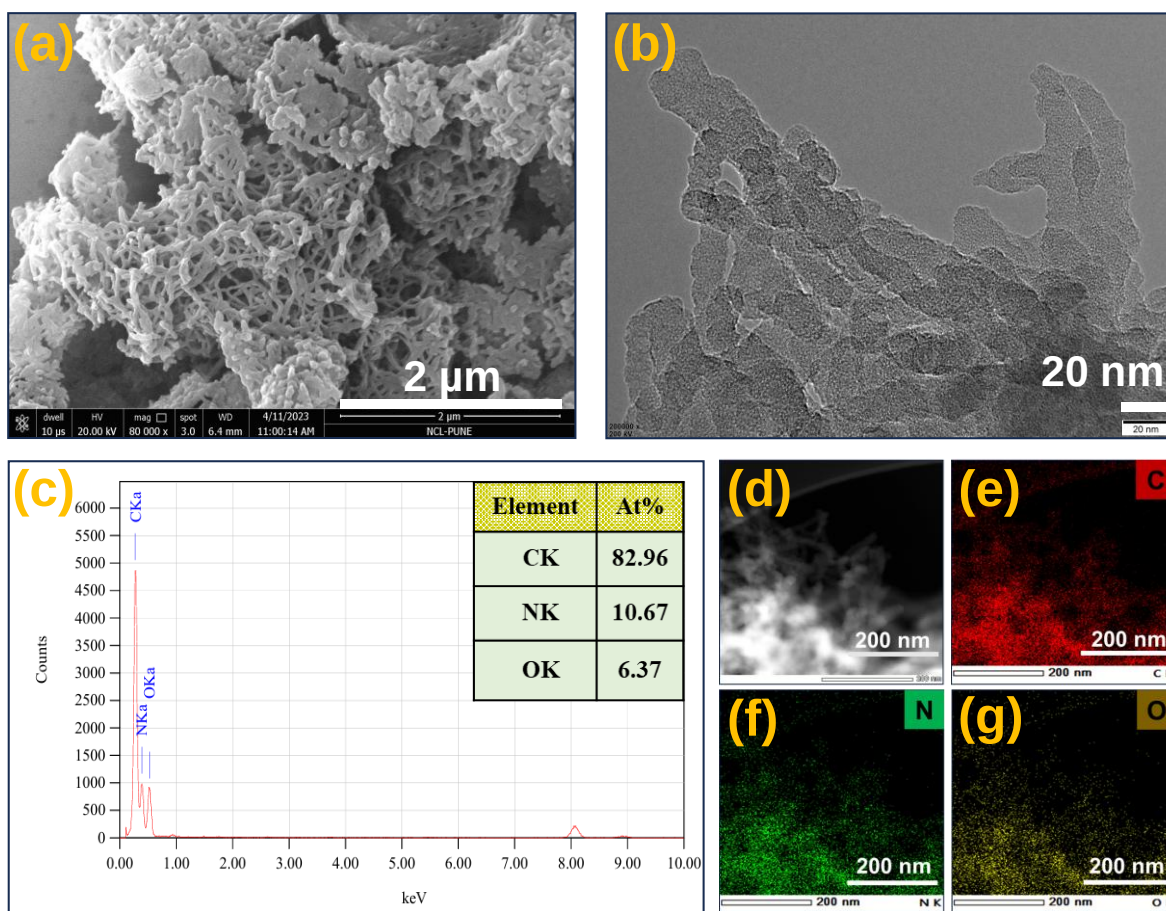


Figure S6. (a) FESEM, (b) HRTEM, (c) EDS, (d) HAADF-STEM image, and (e)-(g) Elemental mapping of TpTTA COF.

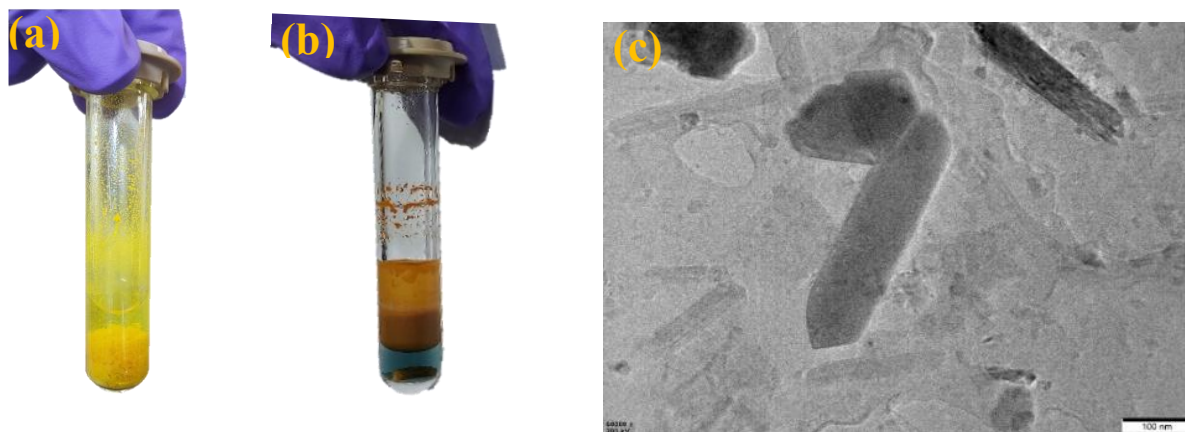


Figure S7. Images of reaction mixture containing product in glass vial after microwave-assisted synthesis via (a) one-step, (b) two-step and (c) HRTEM image of the product obtained via two-step microwave-assisted synthesis.

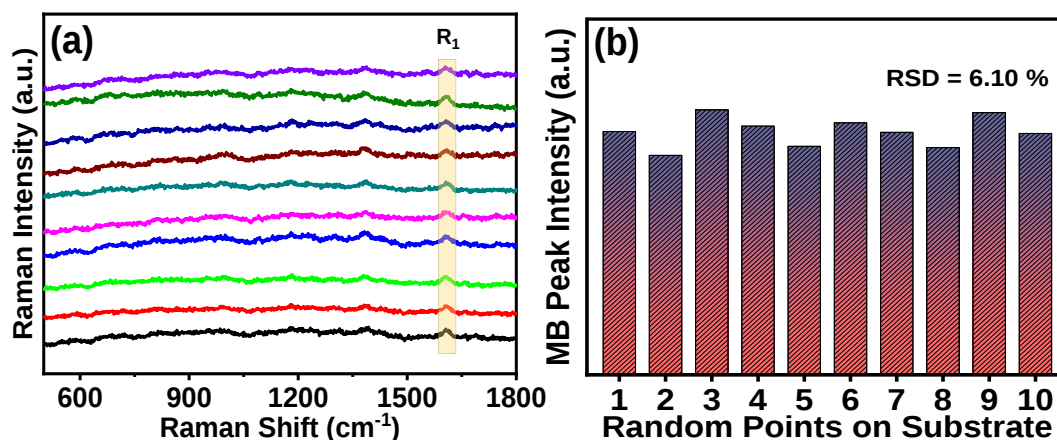


Figure S8. (a) SERS spectra of 10^{-4} M MB on MoO_{3-x} -TpTTA COF nanocomposite collected from 10 random positions, and (b) intensity distribution of 1624 cm^{-1} peak of MB (10^{-4} M) on MoO_{3-x} -TpTTA COF NC.

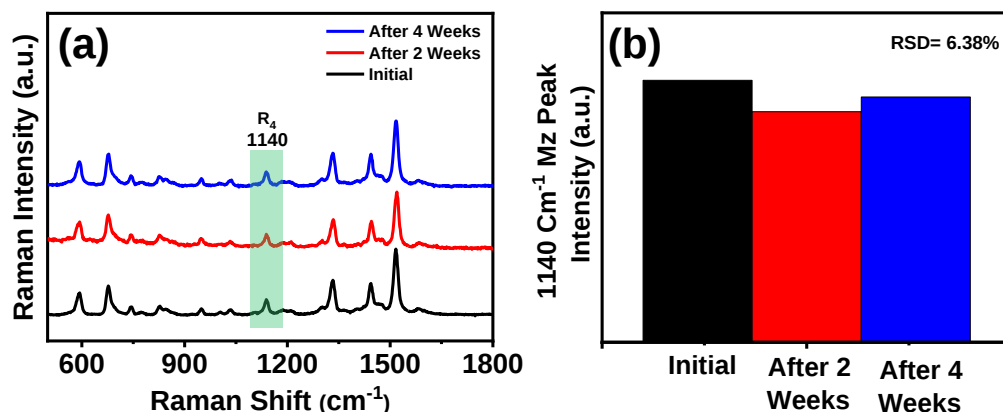


Figure S9. (a) SERS spectra of 500 ppm Mancozeb on MoO_{3-x}-TpTTA COF NC collected over a period of 4 weeks, and (b) the intensity distribution of 1140 cm⁻¹ peak of 500 ppm Mancozeb on MoO_{3-x}-TpTTA COF NC.

Table S2. Enhancement Factor (EF) calculation for MoO_{3-x}-TpTTA COF nanocomposite with respect to MB concentration (M).

Sample: MoO _{3-x} -TpTTA COF nanocomposite				
Sr. No.	Methylene Blue Concentration	N _{Bulk} /N _{SERS}	I _{SERS} /I _{Bulk}	EF=(N _{Bulk} /N _{SERS})×(I _{SERS} /I _{bulk})
1	10 ⁻¹ M	3.471	0.8799	3.05
2	10 ⁻² M	16.558	0.6315	1.05 x 10 ¹
3	10 ⁻³ M	752.139	0.214	1.61 x 10 ²
4	10 ⁻⁴ M	1506.085	0.2062	3.11 x 10 ²
5	10 ⁻⁵ M	8365.027	0.1871	1.57 x 10 ³
6	10 ⁻⁶ M	42932.026	0.1722	7.39 x 10 ³
7	10 ⁻⁷ M	531401.506	0.146	7.76 x 10 ⁴

Table S3. Comparison table of MoO_{3-x}-TpTTA COF nanocomposite with previously reported COF composites used for pesticide detection.

Sr. No.	Substrate/ Material	Synthesis Method	Analyte	Limit of Detection (LoD)	Enhancement Factor (EF)	Reference
1.	MoO _{3-x} -TpTTA COF nanocomposite	One-Step Microwave Synthesis	Methylene Blue (MB)	10 ⁻⁷ M	7.76 x 10 ⁴ (MB)	Our Work
			Commercial Mancozeb (All Care)	12.5 ppm		
2.	AgNP's-AuNP's thin film	Pulsed laser deposition (PLD)	Mancozeb	2.8 x 10 ⁻³ M (~1515 ppm)	10 ⁴	1
3.	Fe ₃ O ₄ /GO/Au	Multistep chemical synthesis	Mancozeb	0.077 ppm	-	2
4.	Ag@Au alloyed nanorods	Electroplating	Mancozeb	0.2 ppm	-	3
5.	TPDH-COF/Au NPs	Multistep electrostatic assembly	Thiabendazole	5 ppb (0.005 ppm)	2.01 x 10 ⁸ (R6G)	4
6.	Fe ₃ O ₄ @Ag@COF	Multistep chemical synthesis	4-ATP	10 ⁻¹⁰ M 0.00001252 ppm	--	5
			Methamidophos	8.3 x 10 ⁻⁵ mg/kg (0.00008 ppm)		
7.	COF-AuNPs	Multistep electrostatic assembly	Thiram	1.7 x 10 ⁻⁸ mol·L ⁻¹ (0.0041 ppm)	1.13 x 10 ⁶ (4-MBA)	6

REFERENCES

- (1) Atanasov, P. A.; Nedyalkov, N. N.; Fukata, N.; Jevasuwan, W.; Subramani, T.; Hirsch, D.; Rauschenbach, B. Au and Ag Films and Nanostructures for Detection of Fungicide Mancozeb: SERS Analyses. *AIP Conference Proceedings*, **2019**, 2075 (1), 03000 (1-8).
- (2) Wu, R., Song, X. & Tian, G. Fabrication of versatile Fe₃O₄/GO/Au composite nanomaterial as SERS-active substrate for detection of pesticide residue. *Environ Sci Pollut Res.* **2024**, 31 (32), 44759–44769.
- (3) Tsen, C. M.; Yu, C. W.; Chen, S. Y.; Lin, C. L.; Chuang, C. Y. Application of Surface-Enhanced Raman Scattering in Rapid Detection of Dithiocarbamate Pesticide Residues in Foods. *Appl. Surf. Sci.* **2021**, 558 (August 2021), 149740 (1-11).
- (4) Jiang, X.; Fu, J.; Li, D.; Xue, W.; Zhang, Y. Ultrasensitive Determination of Thiabendazole in Fruit Juice by Surface-Enhanced Raman Scattering (SERS) Using a Covalent Organic Framework (COF) Gold Nanoparticle (Au NP) Substrate. *Anal. Lett.* **2024**, 57 (15) 2455–2468.
- (5) Qin, C.; Zhang, D.; Wu, Z.; Ni, D.; Yu, Z.; Liang, P. Construction of an Efficient Molecular Enrichment and Magnetic Separation Flow with Fe₃O₄@Ag@COF for Ratiometric SERS Detection of Methamidophos. *Chem. Eng. J.* **2024**, 496 (September 2024), 154177(1-10).
- (6) Cheng, Y.; Ding, Y.; Chen, J.; Xu, W.; Wang, W.; Xu, S. Au Nanoparticles Decorated Covalent Organic Framework Composite for SERS Analyses of Malachite Green and Thiram Residues in Foods. *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* **2022**, 281 (November 2022), 121644 (1-9).