Supporting Information

Polyoxometalates immobilized carbon nanotube constructs triggered through host-guest assembly results in excellent electromagnetic interference shielding

Amit Malakar#, Samir Mondal#, Ria Sen Gupta, Sk Safikul Islam, Kunal Manna†, and Suryasarathi Bose†,**

†Department of Materials Engineering, Indian Institute of Science, Bengaluru – 560012, India

* *Corresponding Author Email address: kunalchemi17@gmail.com and sbose@iisc.ac.in)*

Supporting Information I (SI-1)
DMA Analysis:

The mechanical integrity of the Cu-POM CNT papers was evaluated using DMA. As observed, the storage modulus for the neat CNT paper is lesser as compared to the POM immobilized ones. This enhancement in mechanical properties can be attributed to the immobilization of the Cu-POMs in addition to the polymeric binder PVA.

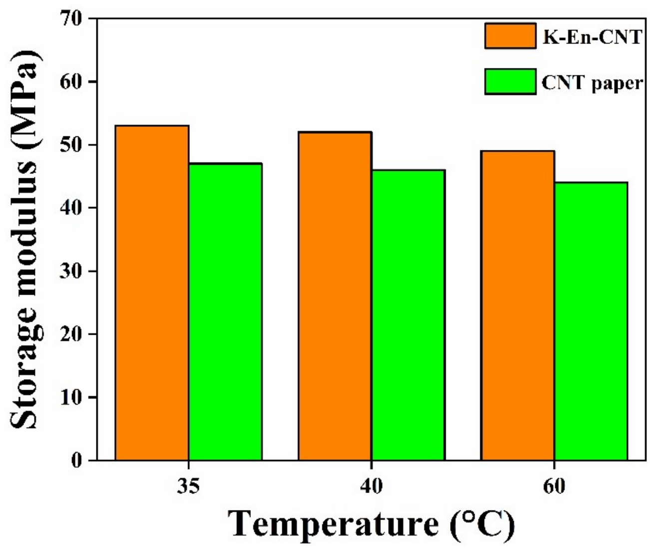

Figure S1: Plot of Storage modulus vs Temperature for CNT paper and K-En-CNT.

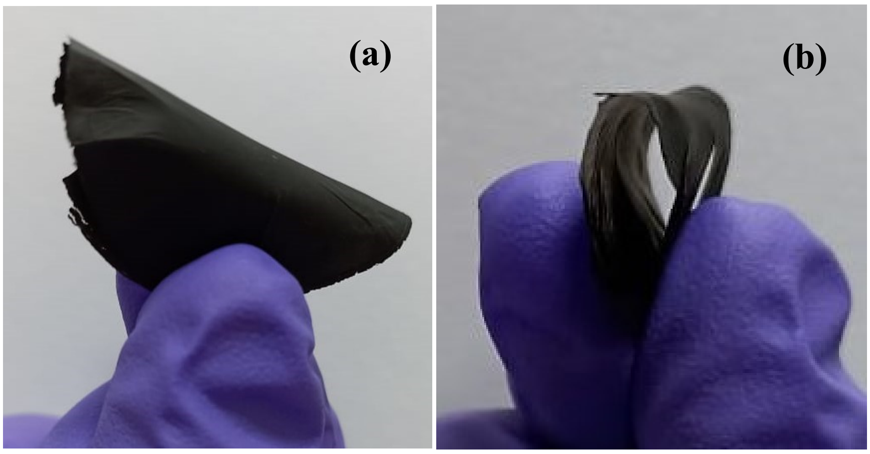

Figure S2: (a) and (b) Different folded orientations of K-En-CNT.

Supplementary Information II (SI-2)
Characterization Techniques:

The POMs immobilized CNT constructs were characterized via Fourier Transform IR spectroscopy (FTIR) from PerkinElmer Frontier in the range of mid-IR. X-ray photoelectron spectroscopy was performed on Axis Ultra with Al as the monochromatic source (1.486 keV). Morphological studies and elemental analysis were performed using Ultra55 FE-SEM Karl Zeiss scanning electron microscope equipped with an EDX detector and transmission electron microscope (TEM, FEI Technai G2). Thermogravimetric analysis was performed using TA Q500. XRD (X-ray Diffraction) analysis was performed using PANalytical X-Pert PRO instrument equipped with Cu K_α radiation (λ=1.54 A°). The Zeta-potentials of the aqueous suspension of the particles were evaluated using a Zeta-potential analyzer (Zetasizer NanoZS90, Malvern Instruments). The electrical conductivities at room temperature of the constructs and were measured on uniformly polished and compression-molded disks of a thickness of 1 mm via an Alpha-N analyzer, Novocontrol (Germany), with Vrms at 1 V in a wide frequency range of 0.1 Hz to 10^6 Hz. The EMI shielding properties of the constructs and the control samples were measured using an Agilent vector network analyzer (VNA) in X band (freq. range = 8.2 to 12.4 GHz). The VNA was coupled to a Vidyut Yantra Udyog (model KU7061; S.N. 2454) waveguide.

Supplementary Figures

Figure. S3. Digital images of the blue needle shaped Anderson type A-Cu-Al POM.

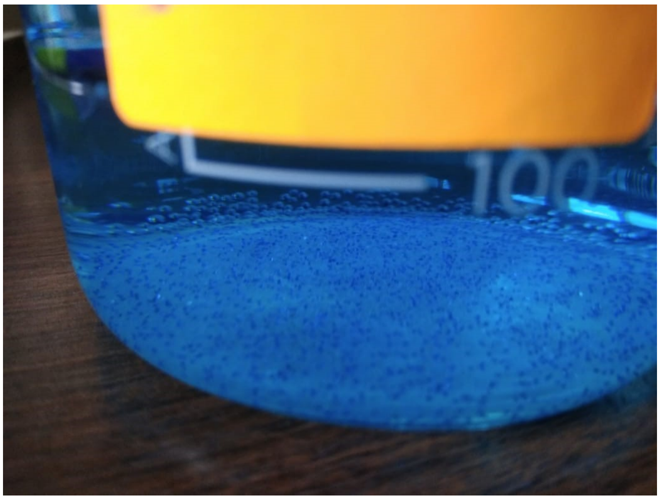

Figure. S4. Digital images of the blue block shaped Anderson type A-Cu-Cr POM.

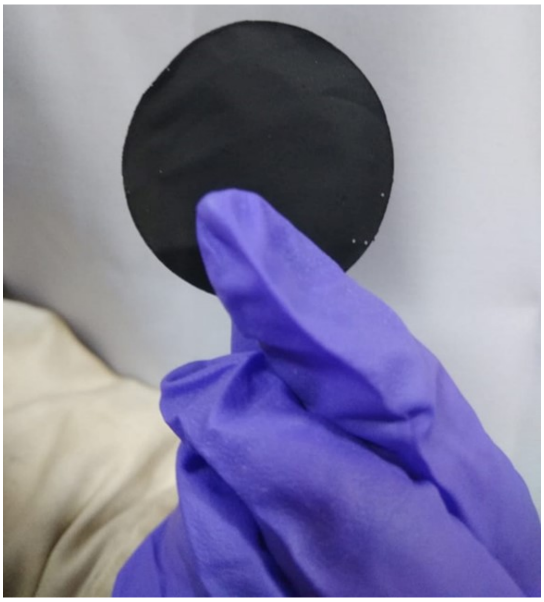

Figure S5. Digital image of Freestanding ACNT paper obtained from vacuum assisted filtration

Figure. S6. Digital images of (a) commercial PU foams (b) CNT infiltrated PU foams.

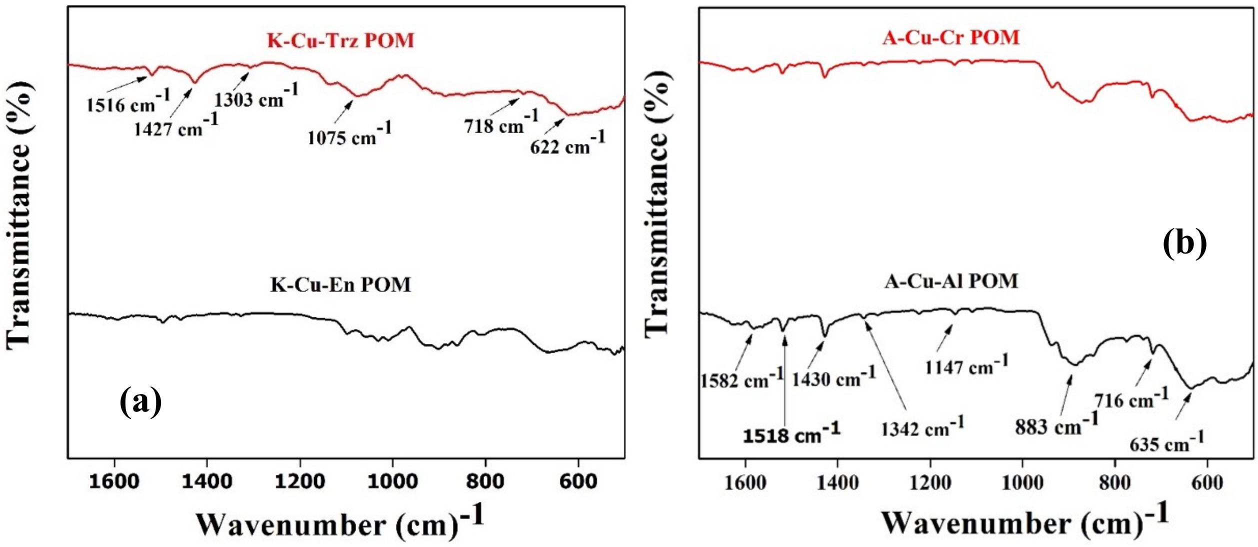

Figure S7: FTIR spectra of (a) Keggin type K-Cu-En POM and K-Cu-Trz POM, (b) Anderson type A-Cu-Cr POM and A-Cu-Al POM.

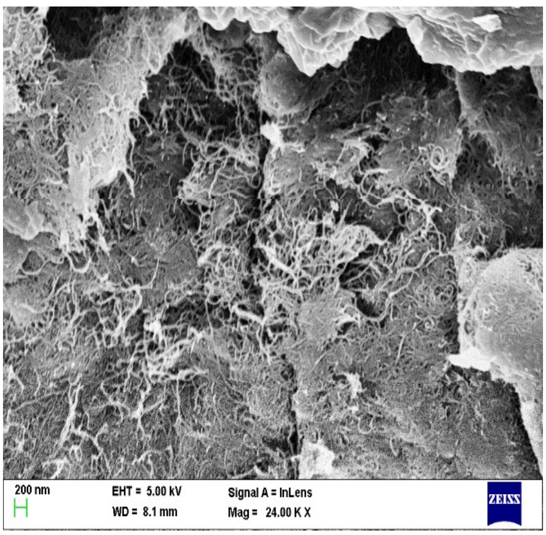

Figure. S8. FESEM image of bare ACNT paper

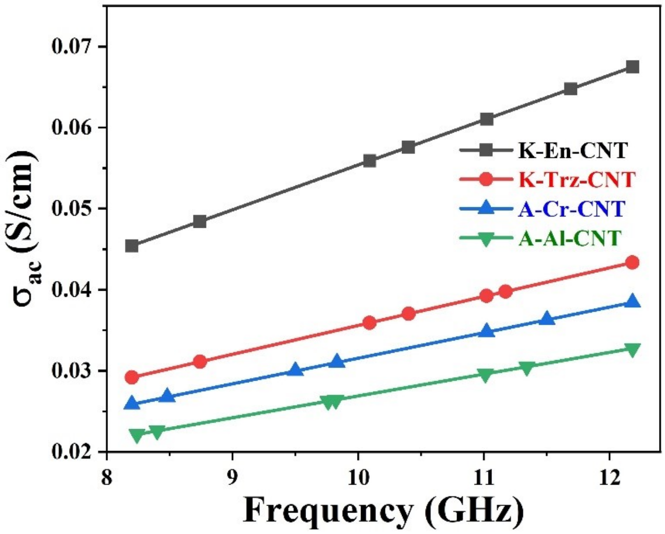

Figure S9: Room-temperature frequency dependent *ac* conductivity of Cu-POM immobilized CNT constructs at a POM loading of ACNT/PDDA : Cu-POMs =1:1.

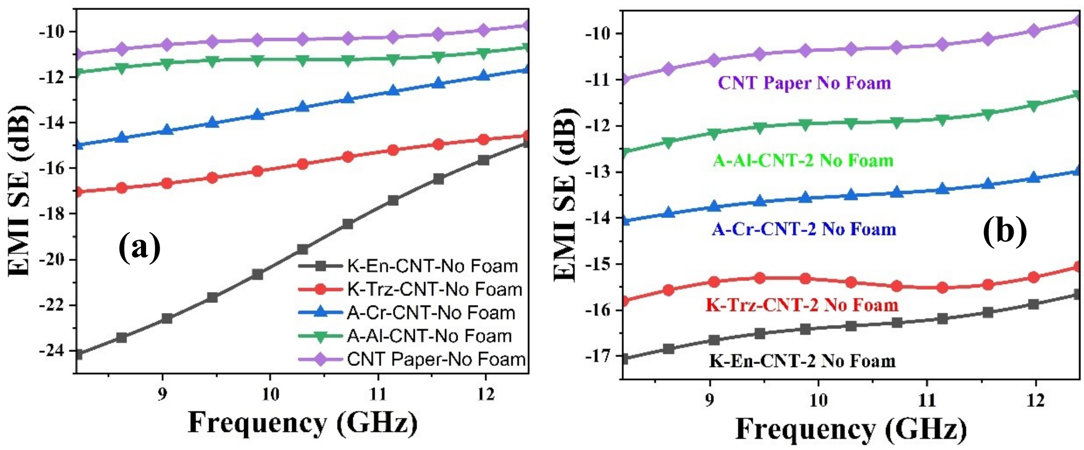

Figure S10: EMI shielding efficiency of Cu-POM immobilized CNT papers without CNT impregnated foam having various POM loading (a) ACNT/PDDA : Cu-POMs =1:1 and (b) ACNT/PDDA : Cu-POMs =1:2.

Supplementary Information III (SI-3)

Theory of Electromagnetic Interference (EMI) Shielding

EMI SE is the material's ability to attenuate the energy of the incident electromagnetic waves. When the electromagnetic radiations interact with material under test (shield), the shielding phenomenon is governed by the contributions from reflection (SE_R), absorption (SE_A), and multiple internal reflections (SE_M). The total EMI SE (SE_T) is the sum of the contributions from SE_R, SE_A and SE_M. The total SE_T can be written as;

$$SE_T = SE_R + SE_A + SE_M \tag{S1}$$

For calculations, SE_M is generally considered negligible when SE_T is higher than 15 dB. In a vector network analyzer, EMI SE is represented in terms of scattering parameters which are S_{11} (forward reflection coefficient), S_{12} (forward transmission coefficient), S_{21} (backward transmission coefficient), and S_{22} (reverse reflection coefficient). The SE_T can be evaluated from the S parameters by using the following equations

$$SE_R = 10log\left(\frac{1}{1-R}\right) = 10log\frac{1}{1-|S_{11}|^2} \quad (S2)$$

$$SE_A = 10log\left(\frac{1-R}{T}\right) = 10log\frac{1-|S_{11}|^2}{|S_{21}|^2} \quad (S3)$$

Assuming propagation of EM waves in a nonmagnetic and highly conducting medium, the Fresnel formula for reflection, absorption and multiple reflections, using equation S1, can be given as,

$$SE_T = 10log\left(\frac{1}{T}\right) = 10\log\left(\frac{1}{|S_{21}|^2}\right) = 10log\left(\frac{E_i}{E_t}\right)^2 = 20log\left|\frac{(1+N)^2}{4N}e^{-kd}[1-\left(\frac{1-N}{1+N}\right)^2e^{2ikt}]\right| \quad (S4)$$

where E_i and E_t are incident and transmitted intensities of electric field of the EM waves, respectively; N is the complex refractive index of the shield, k is the imaginary part of refractive index, and t is the shield thickness.

From equation S4, the quantitative contributions from SE_R, SE_A, and SE_M are expressed as:

$$SE_R = 20log\left(\frac{(1+N)^2}{4|N|}\right) = 50 + 10log\left(\frac{\sigma}{f}\right) \quad (S5)$$

$$SE_A = 20log\ e^{-kt} = 20log\ e^{-\alpha t} = 8.686\ \alpha t = 1.7t\sqrt{\sigma f} \quad (S6)$$

$$SE_M = \left|1-\left(\frac{1-N}{1+N}\right)^2e^{2ikt}\right| \quad (S7)$$

In equation S6, α is the attenuation constant indicating the ability of a material to absorb the associated energy of the incident EM waves.

The EMI Shielding efficiency % can be calculated by the following equation.

$$Shielding\ Efficiency\ \% = 100 - \left(10^{\frac{SE}{10}}\right)^{-1} \times 100 \quad (S8)$$

Where, *SE* stands for total shielding efficiency i.e. SE_T

Further, Skin depth (δ), which explains the intensity of penetration, can be calculated by equation S9 as below:

$$SE_A = -8.686\frac{t}{\delta} \quad (S9)$$

Where, *t* stands for shield thickness.

The EMI SE of a material is defined as the material's ability to attenuate the striking EM wave by the aids of R, A and M. Where, *R* refers to the reflection coefficient or reflectivity, A refers to the absorption coefficient or absorptivity and M multiple internal reflections.

In practice, two-port network model of Vector Network Analyzer (VNA) is used to measure the scattering parameters (S_1, S_{12}, S_{21}, and S_{22}) wherein the reflection R and transmission T coefficients are obtained from these scattering parameters using the following equations.

$$R = |S_{11}|^2 = |S_{22}|^2 \tag{S10}$$

$$T = |S_{21}|^2 = |S_{12}|^2 \tag{S11}$$

$$A = 1 - R - T \tag{S12}$$

Where, S_{11} and S_{21} represent the reflection parameter obtained using VNA port 1 and the transmission parameter from port 1 to port 2, respectively. S_{22} and S_{12} denote the reflection parameter obtained from VNA port 2 and the transmission parameter from port 2 to port 1, respectively. S_{21} refers to the forward transmission, and S_{12} refers to the reverse transmission.[37] If the shield material is uniform, $S_{11} = S_{22}$ and $S_{21} = S_{12}$. [1,2]

The absorption (SE_A) and (surface) reflections (SE_R), are also estimated from the measured S parameters. If $SE_A \gg 10$ dB, then the SE_M can be neglected and there is an effective absorption A_{eff}, as described by the following equation [1,2]

$$A_{eff}(dB) = \frac{1 - (R + T)}{1 - R} \tag{S13}$$

Then, the values of SE_R and SE_A can be calculated by the following equations:

$$SE_R(dB) = 10log\left(\frac{1}{1 - R}\right) \tag{S14}$$

$$SE_A(dB) = 10log\left(\frac{1}{1 - A_{eff}}\right) = 10log\left(\frac{1 - R}{T}\right) \tag{S15}$$

and SE_T can be expressed by

$$SE_T(dB) = SE_R + SE_A = 10log\left(\frac{1}{T}\right) \tag{S16}$$

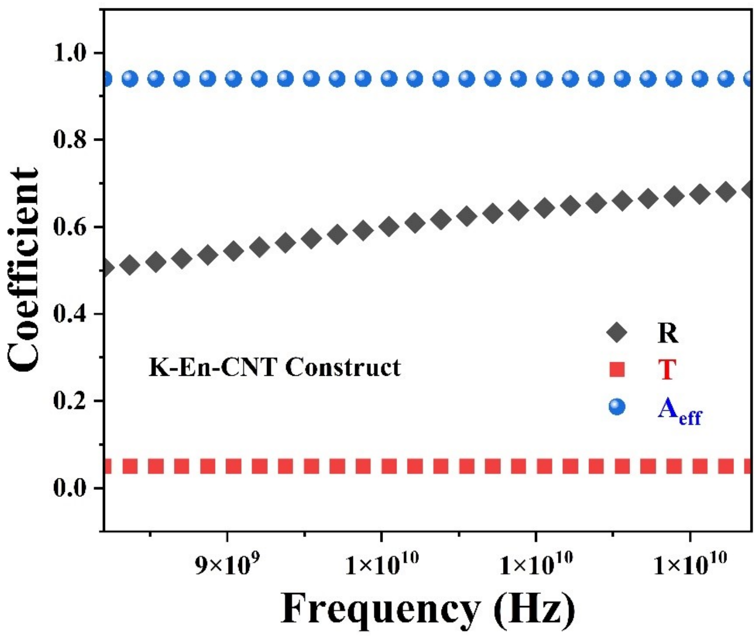

Figure S11: Plot of Reflection (R), Transmission (T) and Effective Absorption coefficient (A_{eff}) of K-En-CNT construct vs frequency.