Supporting information

Nitrogen Enriched Mesoporous Organic Polymer Anchored Copper(II) Material: an Efficient and Reusable Catalyst for the Synthesis of Esters and Amides From aromatic systems

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^{1}H NMR data of esterification reaction:

Methyl benzoate (Table 2, entry 1): ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 3.92 (s, 3H), 7.43 (t, J = 7.6 Hz, 2H), 7.55 (t, J = 8.0 Hz, 1H), 8.05 (d, J = 7.6 Hz, 2H).

Methyl 4-Methylbenzoate (Table 2, entry 2): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 3.89 (s, 3H), 2.37 (s, 3H).

Methyl 4-methoxybenzoate (Table 2, entry 3): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.0 Hz, 2H), 6.91 (d, J = 8.0 Hz, 2H), 3.88 (s, 3H), 3.86 (s, 3H).

Methyl 2, 4-Dimethoxybenzoate (Table 2, entry 4): ^{1}H NMR (400 MHz, CDCl3) δ 7.84 (d, J = 8.0 Hz, 1H), 6.51−6.45 (m, 2H), 3.88 (s, 3H), 3.85 (s, 3H), 3.82 (s, 3H).

Methyl 3, 5-Dimethoxybenzoate (Table 2, entry 5): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, J = 4.0 Hz, 2H), 6.64 (t, J = 4.0 Hz, 1H), 3.91 (s, 3H), 3.82 (s, 6H).

Methyl 4-bromobenzoate (Table 2, entry 6): ^{1}H NMR (400 MHz, DMSO) δ ppm: 3.82 (s, 3H), 7.71 (d, J = 8.8 Hz, 2H), 7.83 (d, J = 8.4 Hz, 2H).

Methyl 4-chlorobenzoate (Table 2, entry 7): ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 3.87 (s, 3H), 7.35 (d, J = 8.4 Hz, 2H), 7.91 (d, J = 8.0 Hz, 2H).

Methyl 4-nitrobenzoate (Table 2, entry 8): ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 2.37 (s, 3H), 3.89 (s, 3H), 7.28–7.35 (m, 2H), 7.82–7.86 (m, 2H).

Methyl 4-Cyanobenzoate (Table 2, entry 9): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 8.0 Hz, 2H), 3.98 (s, 3H).

Methyl 2-chlorobenzoate (Table 2, entry 10): ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 3.90 (s, 3H), 7.29–7.31 (m, 1H), 7.37–7.44 (m, 2H), 7.79–7.82 (m, 1H).

Methyl 2-Nitrobenzoate (Table 2, entry 11): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, J = 7.8, 1.1 Hz, 1H), 7.75 (dd, J = 7.5, 1.5 Hz, 1H), 7.67 (dtd, J = 17.0, 7.4, 1.5 Hz, 2H), 3.94 (s, 3H).

Methyl Thiophene-2-carboxylate (Table 2, entry 12): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, J = 3.7, 0.8 Hz, 1H), 7.64 (dd, J = 4.9, 0.8 Hz, 1H), 7.19 (dd, J = 4.7, 4.0 Hz, 1H), 3.98 (s, 3H)

Methyl 4-Isopropylbenzoate (Table 2, entry 13): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 3.90 (s, 3H), 3.01−2.89 (m, 1H), 1.28 (s, 3H), 1.25 (s, 3H).

Methyl 2-Naphthoate (Table 2, entry 14): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.05 (dd, J = 8.6, 1.4 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 8.0 Hz, 2H), 7.58−7.49 (m, 2H), 3.98 (s, 3H).

Methyl 3-phenylpropanoate (Table 2, entry 15): ^{1}H-NMR (400MHz, $CDCl_3$) δ 2.66(t, 2H, *J*=7.9), 2.99(t, 2H, *J*=7.8), 3.70(s, 3H), 7.2-7.4(m, 5H).

Methyl 2, 6-Dimethoxybenzoate (Table 3, entry 3): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (t, J = 8.0 Hz, 1H), 6.53 (d, J = 8.0 Hz, 2H), 3.88 (s, 3H), 3.78 (s, 6H)

Methyl 2-Bromo-5-methoxybenzoate (Table 3, entry 4): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 9.0 Hz, 1H), 7.29 (d, J = 3.0 Hz, 1H), 6.86 (dd, J = 8.8, 3.1 Hz, 1H), 3.90 (s, 3H), 3.78 (s, 3H).

Methyl 3-Nitrobenzoate (Table 3, entry 7): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88−8.83 (m, 1H), 8.46−8.42 (m, 1H), 8.40−8.36 (m, 1H), 7.68 (t, J = 8.0 Hz, 1H), 4.00 (s, 3H).

Methyl 4-Acetylbenzoate (Table 3, entry 9): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.0 Hz, 2H), 8.03 (d, J = 8.0 Hz, 2H), 3.94 (s, 3H), 2.65 (s, 3H).

Methyl 1-Naphthoate (Table 3, entry 10): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (d, J = 8.0 Hz, 1H), 8.16 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.64−7.58 (m, 1H), 7.56−7.46 (m, 2H), 3.97 (s, 3H).

Methyl 4-Phenylbenzoate (Table 3, entry 12): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.0 Hz, 2H), 7.69−7.61 (m, 4H), 7.47 (t, J = 8.0 Hz, 2H), 7.41 (t, J = 8.0 Hz, 1H), 3.93 (s, 3H).

Methyl Furan-2-carboxylate (Table 3, entry 14): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.19 (d, J = 4.0 Hz, 1H), 6.55−6.50 (m, 1H), 3.92 (s, 3H).

^{1}H NMR data of amidation reaction:

N, 2-diphenylacetamide (Table 4, entry 1): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (br, 1H), δ 7.43 (d, *J* = 7.6 Hz, 2H), 7.40-7.21 (m, 7H), 7.07-7.04 (m, 1H), 3.62 (s, 2H).

2-(2-Methylphenyl)-N-phenylacetamide (Table 4, entry 2): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (br, 1H), 7.44 (t, 2H), 7.32-7.17 (m, 6H), 7.07 (t, 1H), 3.66 (s, 2H), 2.28 (s, 3H).

2-(3-Methylphenyl)-N-phenylacetamide (Table 4, entry 3): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8 Hz, 2H), 7.34-7.28 (t, 4H), 7.16-7.09 (m, 4H), 3.71 (s, 2H), 2.39 (s, 3H).

2-(4-Methylphenyl)-N-phenylacetamide (Table 4, entry 4): ^{1}H NMR (400 MHz, $CDCl_3$) δ7.43-7.44 (m, 2H), 7.04-7.31 (m, 8H), 3.70 (s, 2H), 2.38 (s, 3H).

2-(4-Metoxyphenyl)-N-phenylacetamide (Table 4, entry 5): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8 Hz, 2H), 7.31-7.26 (m, 4H), 7.12 (d, *J* = 7.6 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 3.85 (s, 3H),3.71 (s, 2H).

2-(3-(trifluoromethyl)phenyl)-N-phenylacetamide (Table 4, entry 6): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.54 (m, 4H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.14-7.11 (t, 2H), 3.81 (s, 2H).
2-(2-chlorophenyl)-N-phenylacetamide (Table 4, entry 7): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.43 (m, 4H), 7.32-7.30 (m, 5H), 7.12-7.09 (t, 1H), 3.88 (s, 2H).

2-(4-bromophenyl)-N-phenylacetamide (Table 4, entry 8): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8 Hz, 2H), 7.46 (d, *J* = 8 Hz, 2H), 7.34-7.23 (m, 5H), 7.14-7.11 (t, 1H), 3.71 (s, 2H).

N-(4-methylphenyl)-2-phenylacetamide (Table 4, entry 9): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (s, 1H),7.40-7.34 (m, 7H), 7.09 (d, *J* = 8.4 Hz, 2H), 3.68 (s, 2H), 2.32 (s, 3H).

N-(2-methylphenyl)-2-phenylacetamide (Table 4, entry 10): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8 Hz, 1H), 6.95-7.47 (m, 9H), 3.81 (s, 2H), 1.93 (s, 3H).

N-(4-bromophenyl)-2-phenylacetamide (Table 4, entry 11): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.31 (m, 9H), 7.27 (br, 1H), 3.72 (s, 2H).

N-(4-chlorophenyl)-2-phenylacetamide (Table 4, entry 12): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.34 (m, 8H), 7.24 (d, *J* = 8.8 Hz, 2H), 3.75 (s, 2H).

N-(4-fluorophenyl)-2-phenylacetamide (Table 4, entry 13): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (br, 1H), 7.37-7.25 (m, 7H), 6.96-6.92 (t, 2H), 3.67 (s, 2H).

N-phenylacetamide (Table 4, entry 14): ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.92 (br, 1H), 7.53 (d, *J* = 8 Hz, 2H), 7.33-7.27 (m, 2H), 7.13-7.09 (t, 1H), 2.15 (m, 3H).

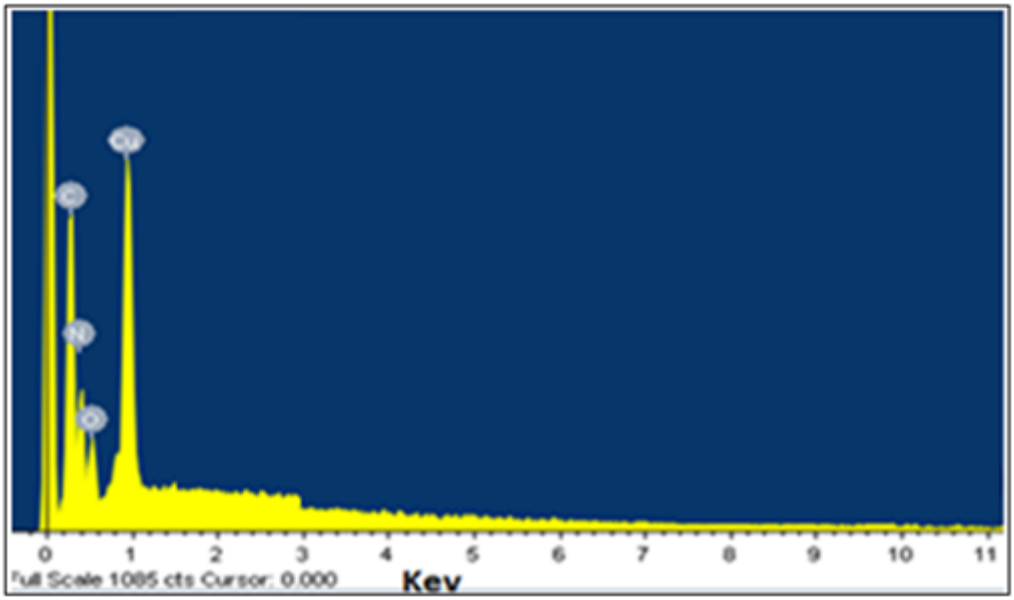

Fig.S1 Energy- dispersive X-ray spectroscopy (EDX) of the Cu-mPMF.

FT-IR analysis:

The FT-IR spectrum of mPMF (Fig. S2) shows a broad peak at 3409 cm^{-1} due to -NH- stretching which is shifted to 3405 cm^{-1} and decreased in intensity after copper acetate loading. The imine (C=N) function of the mesoporous polymer shows two stretches at 1631 and 1199 cm^{-1}. The distinct bands related to the quadrant (1554 cm^{-1}) and semicircle stretching (1476 cm^{-1}) of the triazine ring are present in the spectrum of the mPMF material, indicating the successful incorporation of melamine into the network [1].In addition, the bands at 528 cm^{-1} may be assigned to the Cu-N stretching vibration[2].

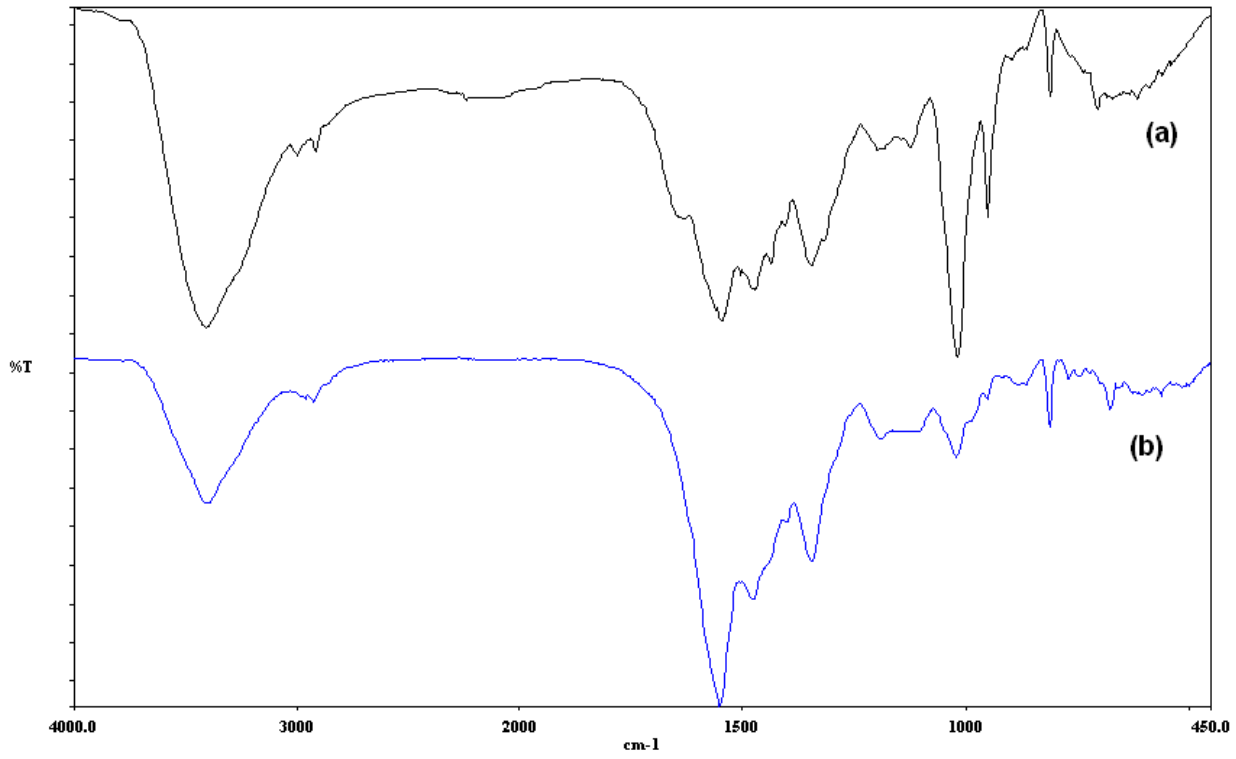

Figure S2 FT-IR Spectra of mesoporous polymer mPMF (a) and mPMF-Cu (b)

UV-vis spectroscopy study:

Optical absorption of the prepared Cu-mPMF was investigated in Fig. S3. UV-vis absorbance spectra (Fig. S3) of mPMF exhibits two strong characteristic absorbance, two peaks at 252 and 316 nm due to n→ π and π→π* transitions. But a distinguishable change in absorbance is observed in case of Cu-mPMF material. The bands at 345 nm and 370 nm arise due to LMCT. In material, the bands around 410-435 nm are due to d-d transition[3].

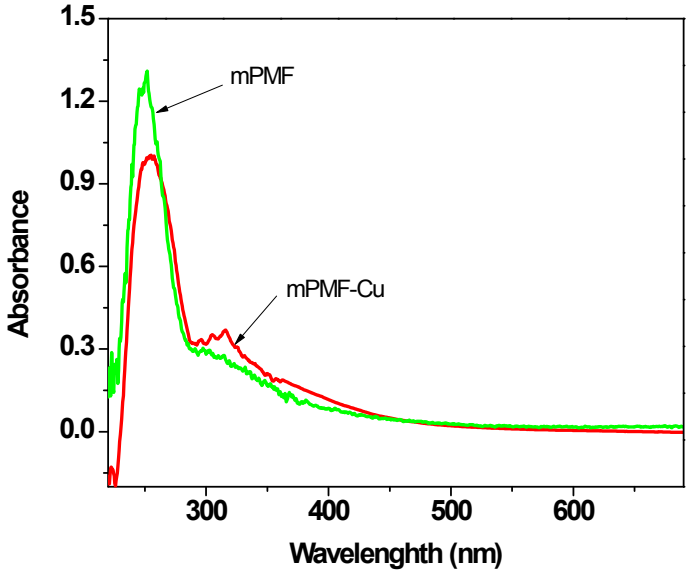

Figure S3 DRS-UV-visible absorption spectra of the mPMF and Cu-mPMF materials.

Thermal analysis:

The quantitative determination of the organic content and the framework stability of the Cu-mPMF sample are obtained from the thermogravimetric (TG) and differential thermal analysis (DTA) under N_2 flow. TGA-DTA curve of Cu-mPMF material is shown in Figure S4. The TGA of this material showed the first weight around 100 ^{0}C due to desorption of physisorbed water. This was followed by a gradual decrease in the weight after 340 ^{0}C. Thus this thermal analysis data suggested that Cu-mPMF sample is stable up to 340 ^{0}C.

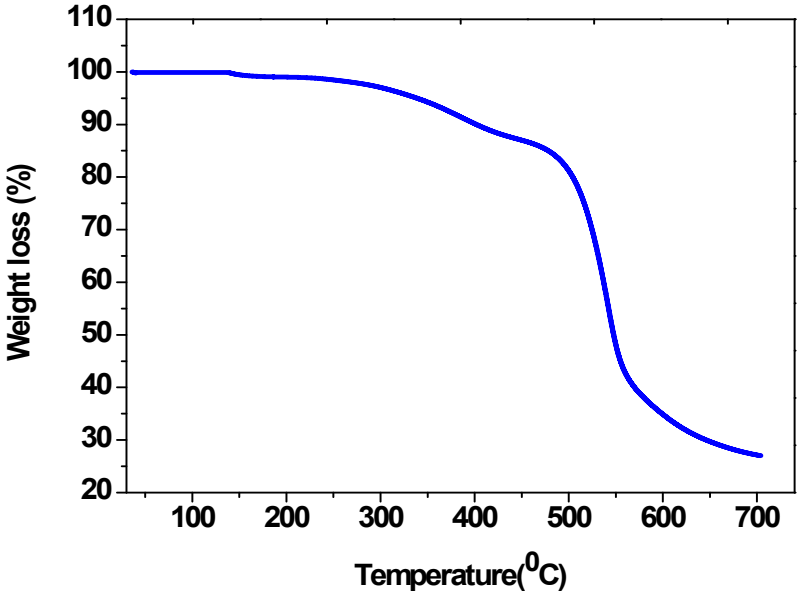

Figure S4 Thermogravimetric weight loss plots for Cu-mPMF.

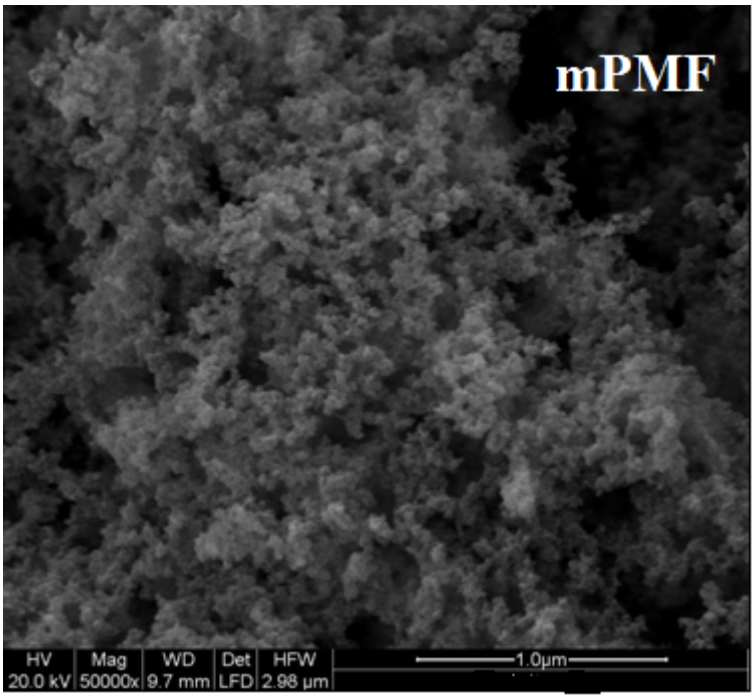

Figure S5. FE-SEM image of mPMF material

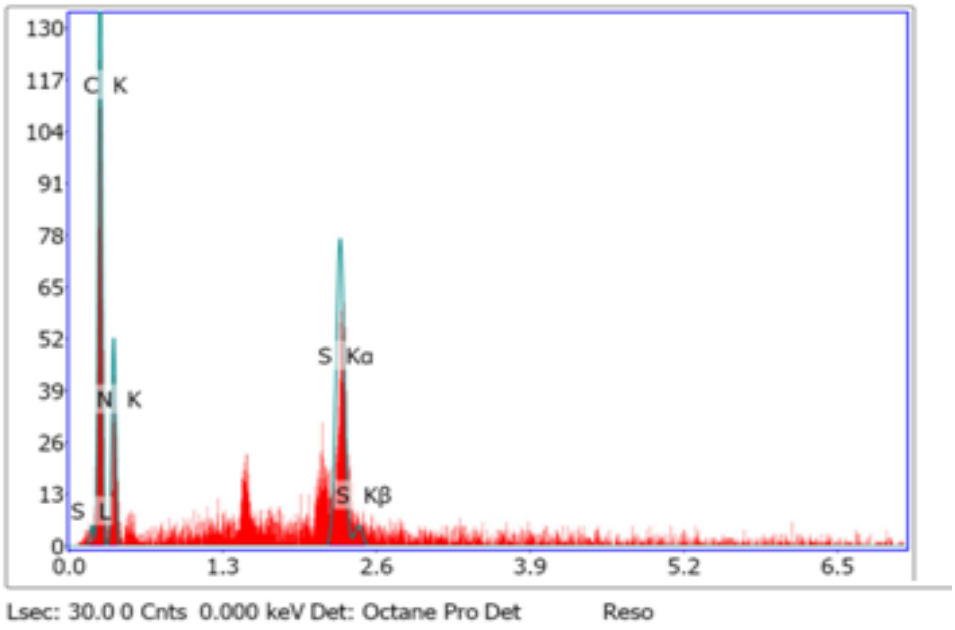

Figure S6. EDX image of mPMF material

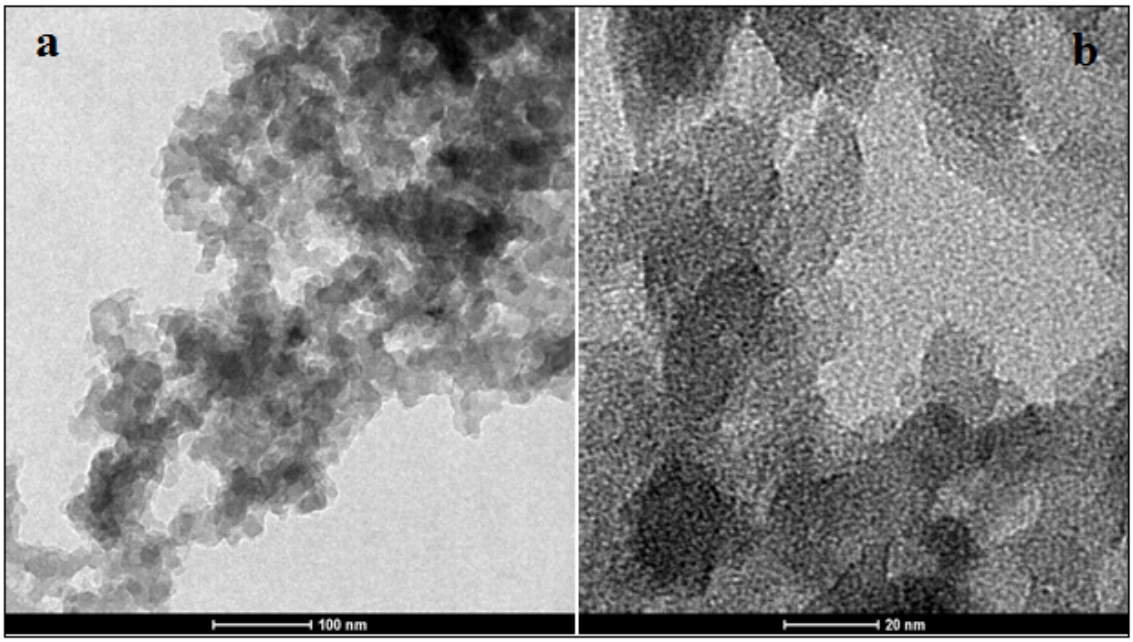

Figure S7. HR-TEM images of mPMF material

^{13}C cross-polarization magic-angle spinning (CP-MAS) NMR: The ^{13}C cross-polarization magic-angle spinning (CP-MAS) NMR spectral study was performed to confirm the chemical structure of the Cu-mPMF (Fig. S8). In the ^{13}C CP-MAS NMR spectrum of Cu-mPMF, a remarkable peak at 21.3 ppm originates from the methyl (CH_3-) carbon atoms of copper acetate particles bounded by mPMF. The other resonance signals detected at 176.4, 166.2, 48.2-54.3 and 29.3 ppm belong to four types of carbon species of Cu-mPMF i.e acetate carbonyl carbon, triazine carbon, bridging CH_2 groups and DMSO respectively. Two peaks at 176.4 and 21.3 ppm confirmed the presence of copper acetate particles in Cu-mPMF.

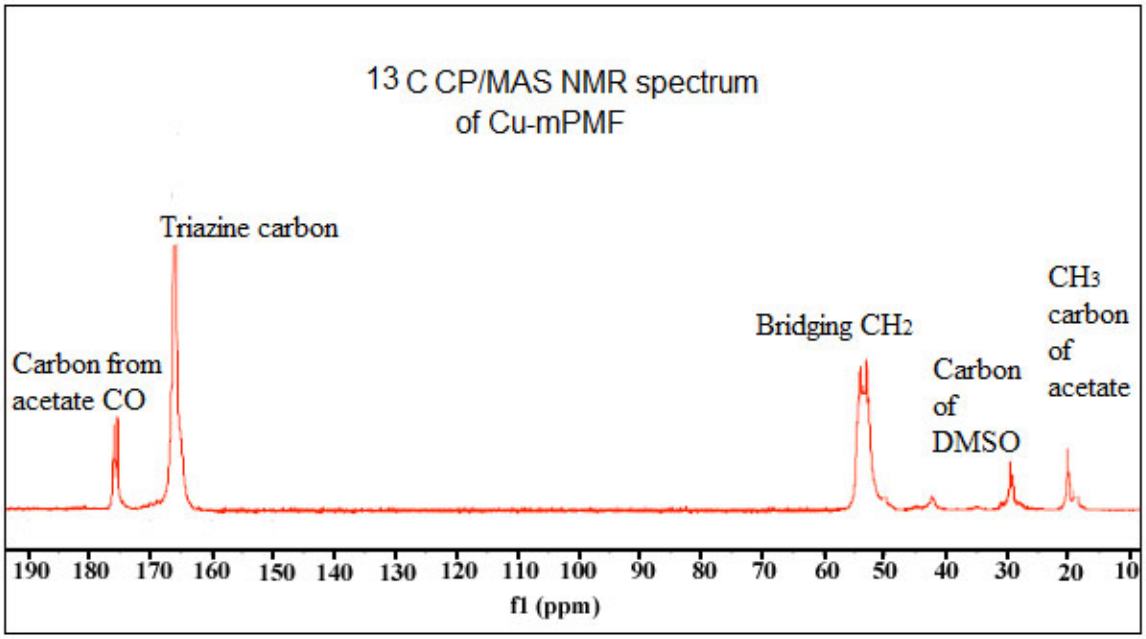

Figure S8. ^{13}C cross-polarization magic-angle spinning (CP-MAS) NMR of Cu-mPMF

References

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