Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.
This journal is © the Partner Organisations 2017

Supporting Information

Robust Microporous Hyper-cross-linked Polymer (HCP): An Efficient Cationic Dye Scavenger from Aqueous Medium

ParthaSamanta, Priyanshu Chandra, Aamod V. Deasi and SujitK. Ghosh*

*Indian Institute of Science Education and Research (IISER), Pashan, Pune, Maharashtra 411008, India

E-mail: *sghosh@iiserpune.ac.in* ***Fax:*** *+91-20-25898022* ***Tel:*** *+91-20- 25908076*

Table of Contents

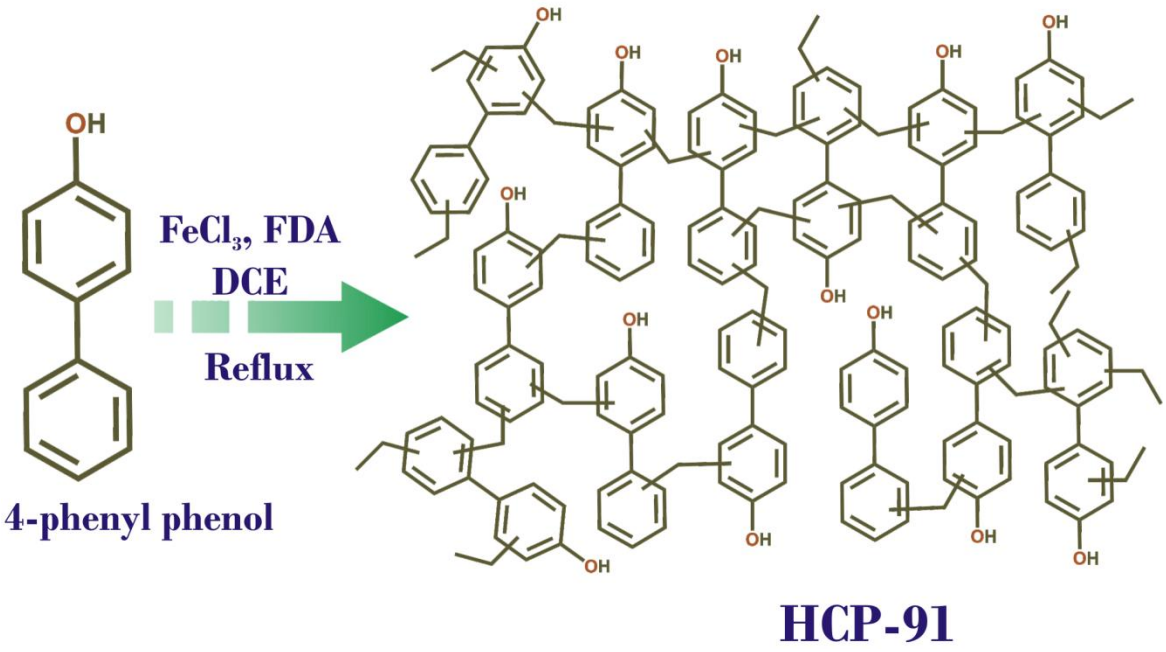
Experimental Section:

Materials: 4-phenylphenol, $FeCl_3$, formaldehyde dimethyl acetal (FDA), methylene blue, crystal violet and rhodamine B were purchased from Sigma-Aldrich. Methyl orange andremaining solvents were obtained locally. These chemicals were used without further purification.

Physical Measurements: All Infra-red Spectra were acquired by using NICOLET 6700 FT-IR spectrophotometer using KBr pellet in 400-4000 cm^{-1} range. Gas adsorption measurements were studied using BelSorp-max instrument from Bel Japan.. FESEM was done by using FEI Quanta 3D dual beam ESEM at 30KV.UV spectra were recorded on Shimadzu UV 2600 Spectrophotometer. Solid state UV-Vis studies have been carried out on Shimadzu UV 3600 plus UV-VIS-NIR Spectrophotometer

Synthesis of HCP-91:

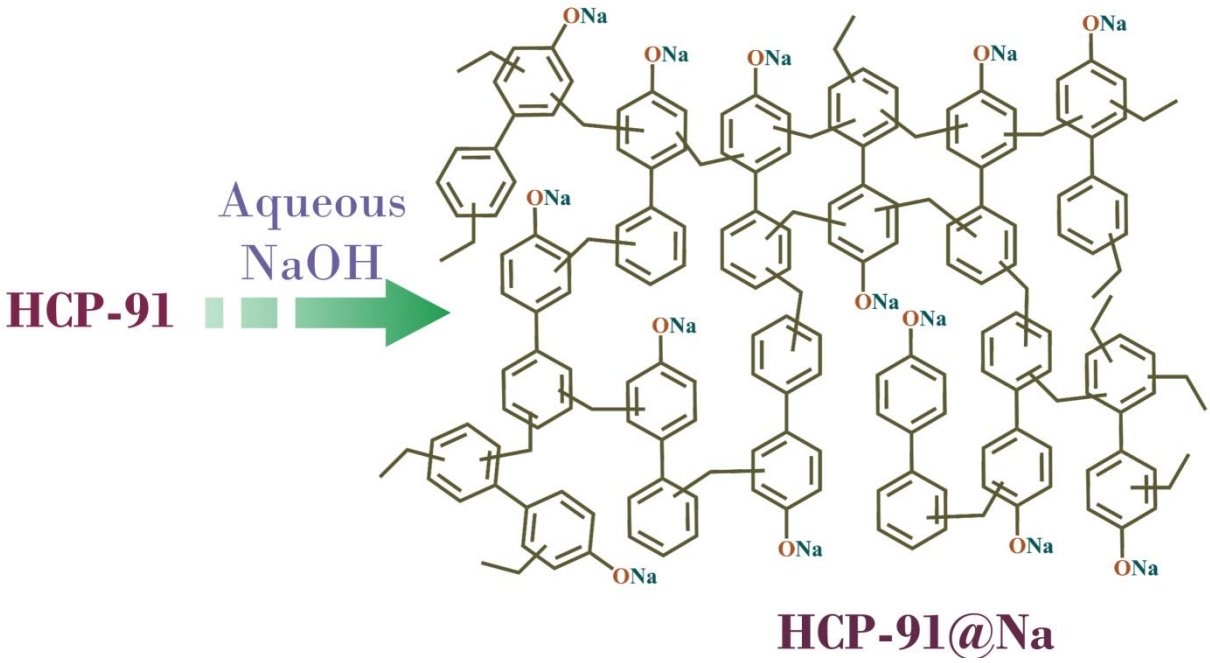
HCP-91 has been synthesized from cross-coupling of 4-phenylphenol (Scheme-1) by following our previous report.[1] To a round bottom flask 4-phenylphenol (300 mg, 1.7625 mmol) has been taken and to that 20 ml of dichloroethane ($C_2H_4Cl_2$) was added. Then to the reaction mixture formaldehyde dimethyl acetal (470 µl, 5.288 mmol) and $FeCl_3$ (860 mg, 5.288 mmol) were added respectively. The reaction mixture was heated at 50 °C for 5 hours and then was allowed to reflux at 80 °C for 20 hours (Scheme-1). On completion of the reaction brown coloured precipitate was filtered off and washed with DMF, methanol, water, chloroform, dichloromethane and tetrahydrofuran (THF) repeatedly. Thus obtained brown colored solid material was then kept in 1:1 $CHCl_3$-THF mixture (25 ml) for 3 days to remove the high boiling solvents from the porous network of HCP-91. Then the solvent exchanged phase of HCP-91 was heated at 100 ^oC under vacuum to obtain the guest free activated material and with this phase further works have been carried out. Yield: 335 mg.



.**Scheme S1:** Synthesis of HCP-91 from 4-phenylphenol.

Synthesis of HCP-91@Na:

Desolvated HCP-91 (100mg) was taken in a conical flask and to that 10 ml of distilled water has been added. Then to the reaction mixture NaOH (40 mg, 1mmol) was added and allowed stir overnight at room temperature (Scheme-1). On completion of the reaction dark brown coloured precipitate was filtered off and washed with water for several times to remove excess NaOH. Then precipitate was again washed DMF, methanol, water, chloroform, dichloromethane and tetrahydrofuran (THF) repeatedly. Thus obtained dark brown colored solid material (HCP-91@Na) was then kept inMeOH (25 ml) for 3 days and MeOH was changed two times in a day to remove the high boiling solvents from the porous network of HCP-91@Na. Then the solvent exchanged phase of HCP-91@Na was heated at 100 ^{o}C under vacuum to obtain the guest free activated material and with this phase further works have been carried out. Yield: 115 mg.



Scheme S2: Synthesis of HCP-91 from 4-phenylphenol.

.

Figures:

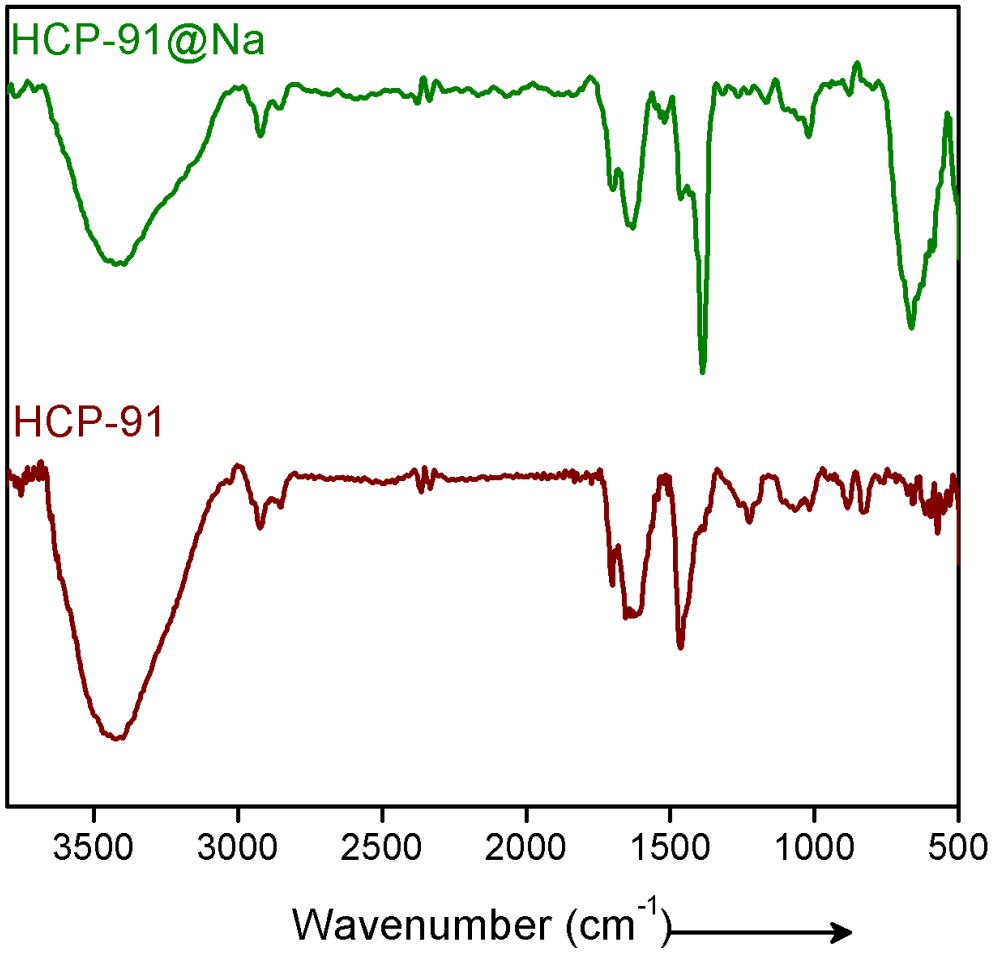


Figure S1: Infra-red spectroscopy of HCP-91 and HCP-91@Na.

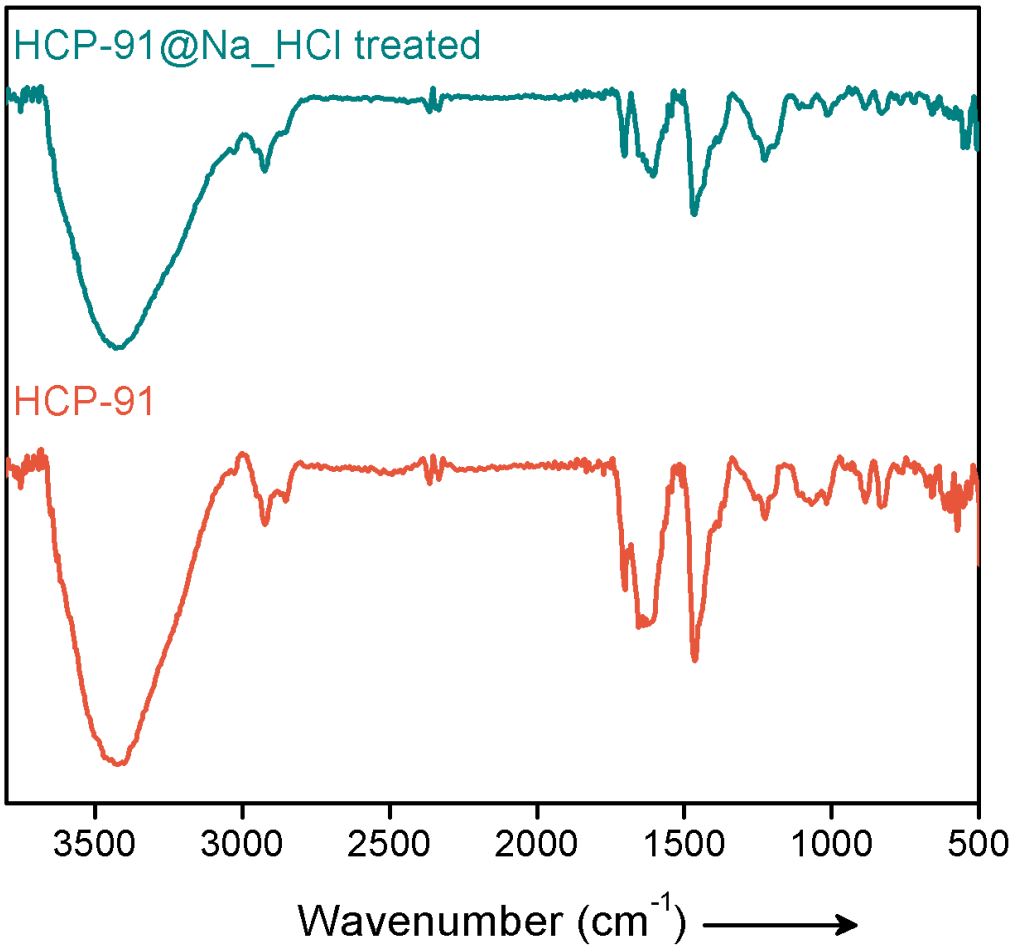


Figure S2: Infra-red spectroscopy of HCP-91 and HCP-91@Na after HCl treatment.

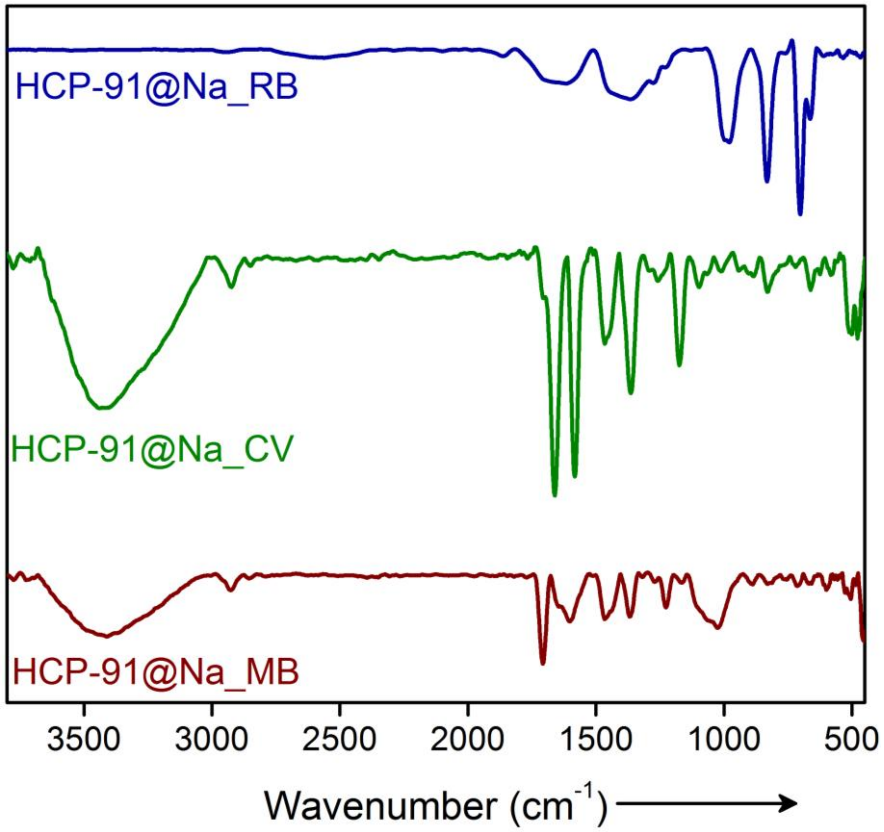


Figure S3: IR spectra of methylene blue encapsulated HCP-91@Na (wine red), crystal violet encapsulated HCP-91@Na (green) and rhodamine b encapsulated HCP-91@Na (blue).

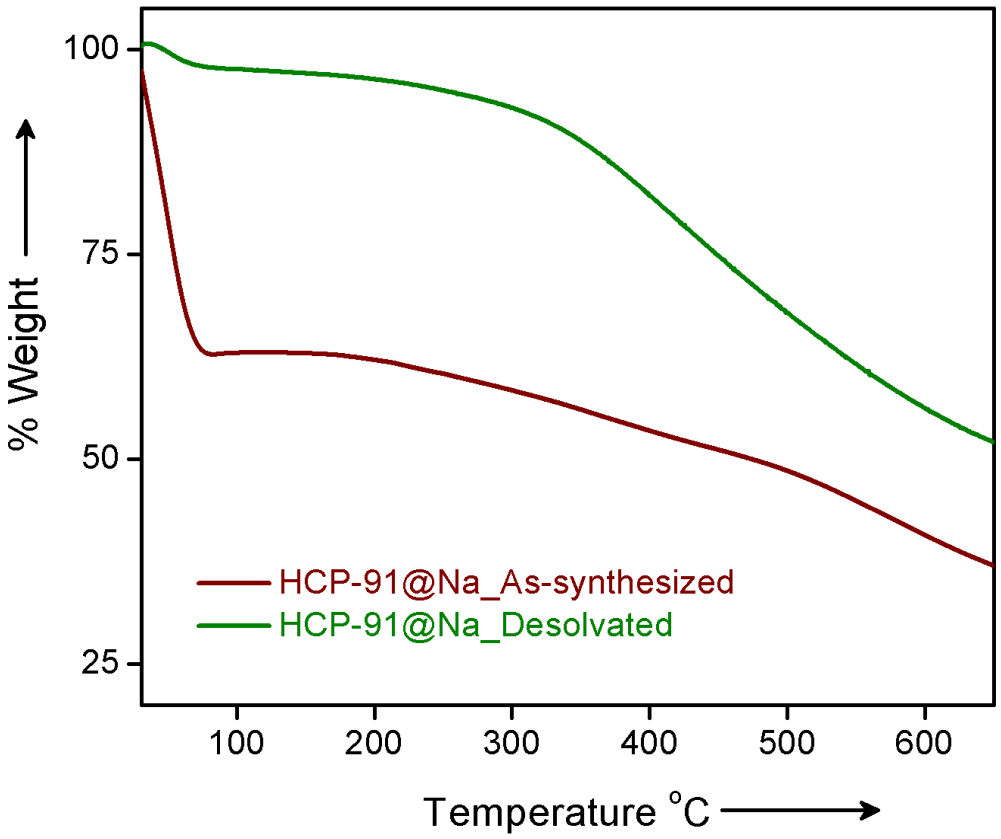


Figure S4: Thermogravimetric analysis profiles of as-synthesized HCP-91@Na (wine red) and desolvated phase of HCP-91@Na (green).

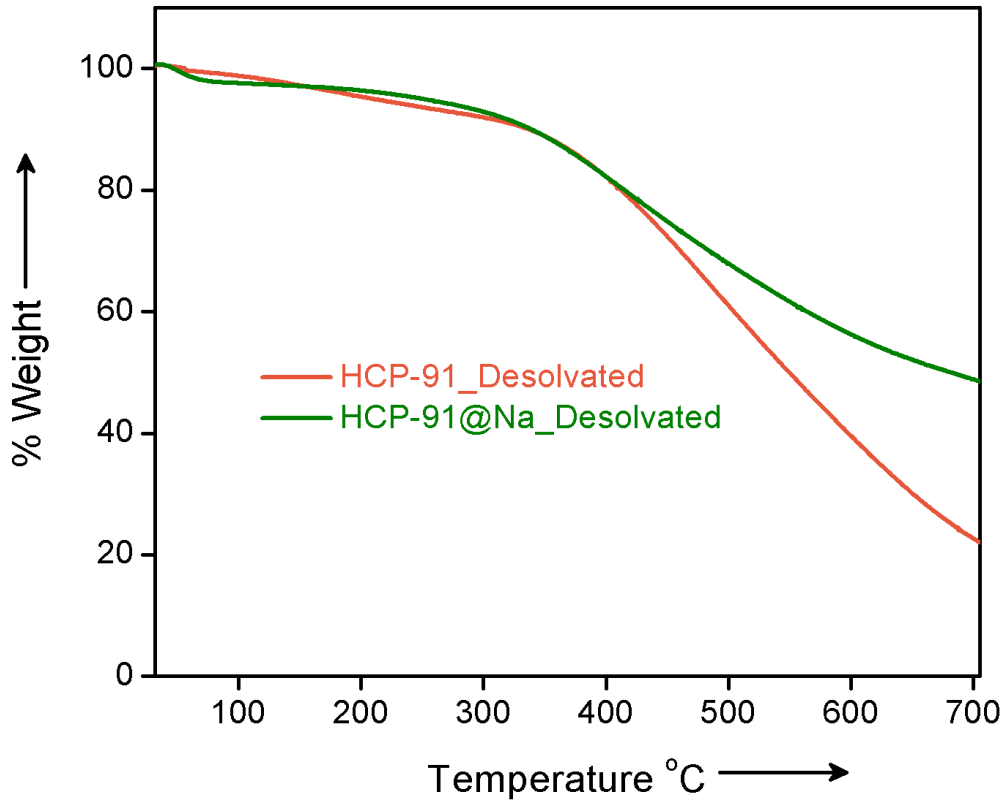


Figure S5: Thermogravimetric analysis profiles of desolvated phases of HCP-91 (orange) and HCP-91@Na (green).

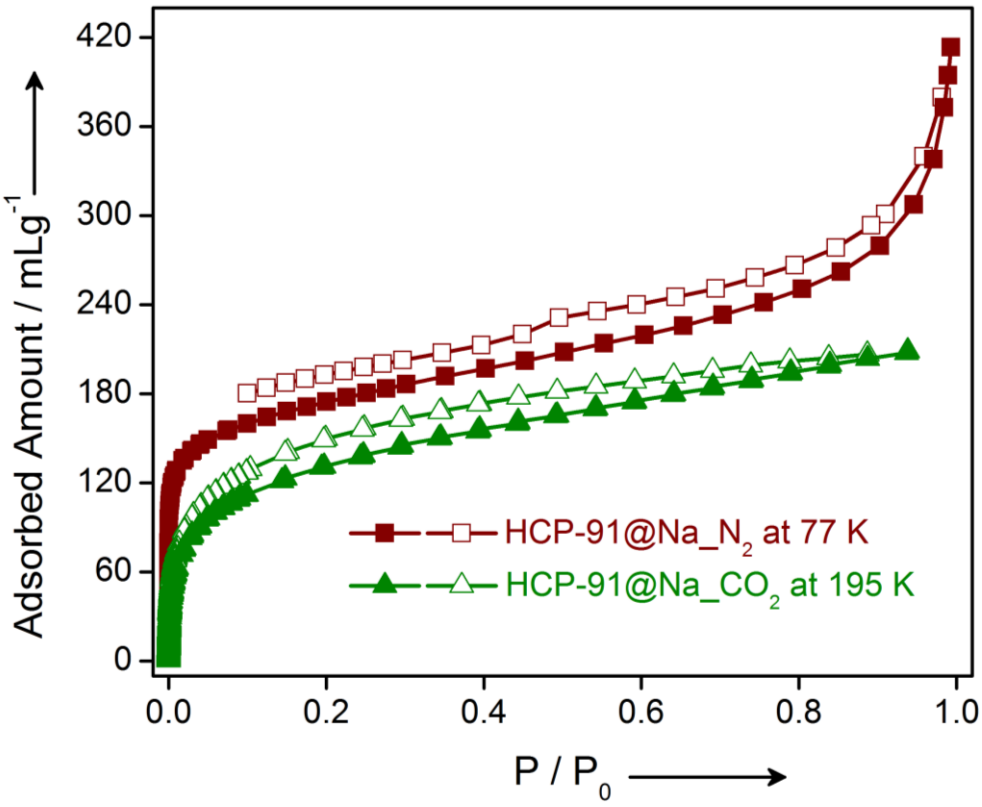


Figure S6: N_2 adsorption profile at 77 K (wine red) and CO_2 adsorption curve at 195 K (green) of HCP-91@Na.

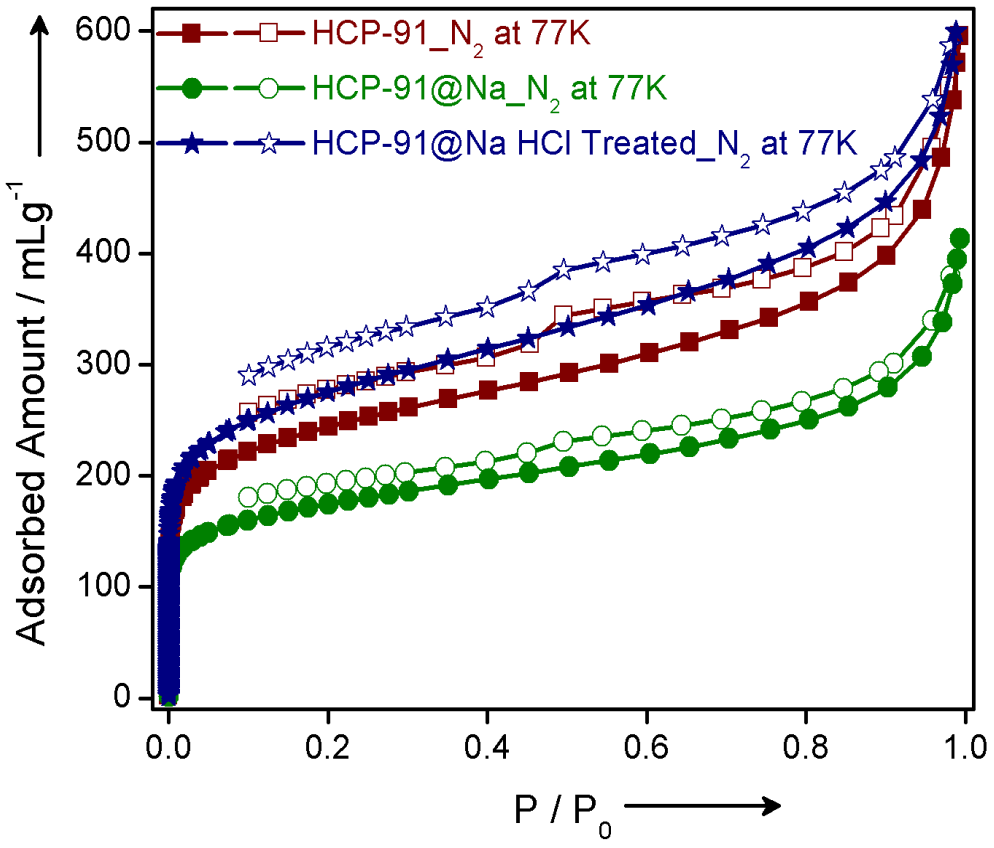


Figure S7: N_2 adsorption profile at 77 K of HCP-91 (wine red), HCP-91@Na (green) and HCl treated phase of HCP-91@Na (blue).

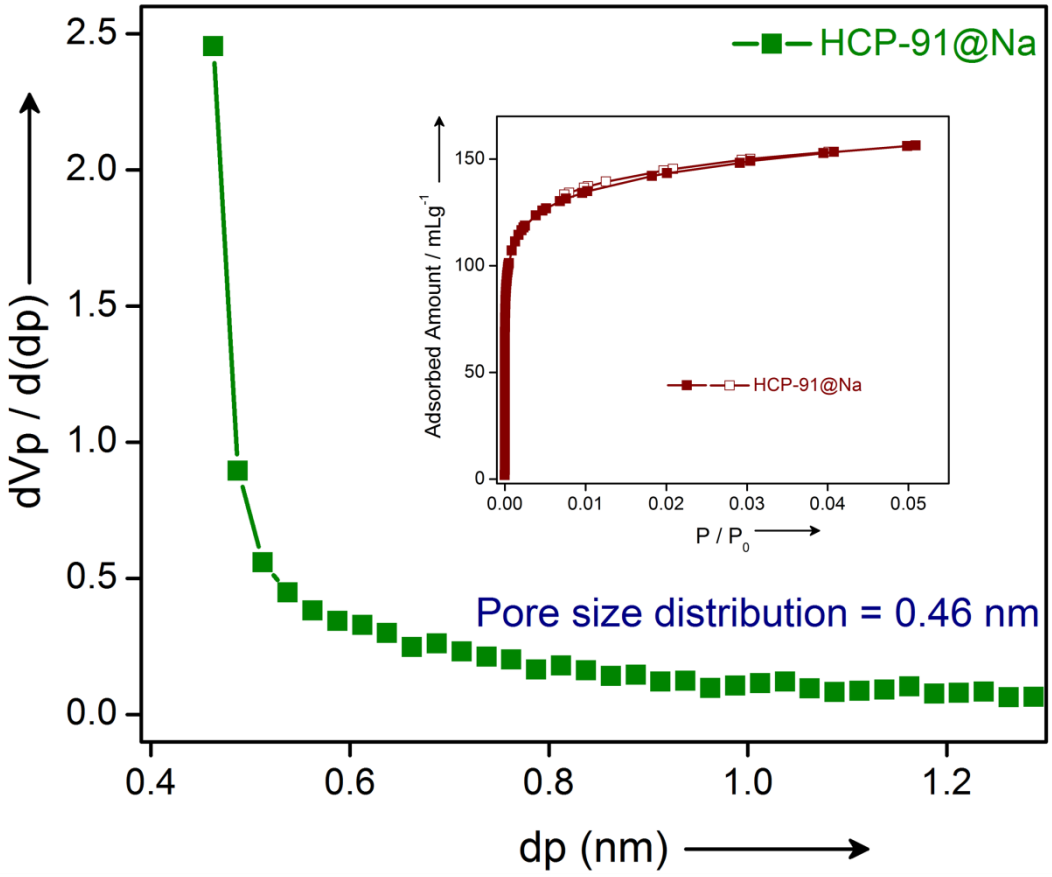


Figure S8: HK plot of HCP-91@Na from N_2 adsorption (at 77 K) at low pressure region.

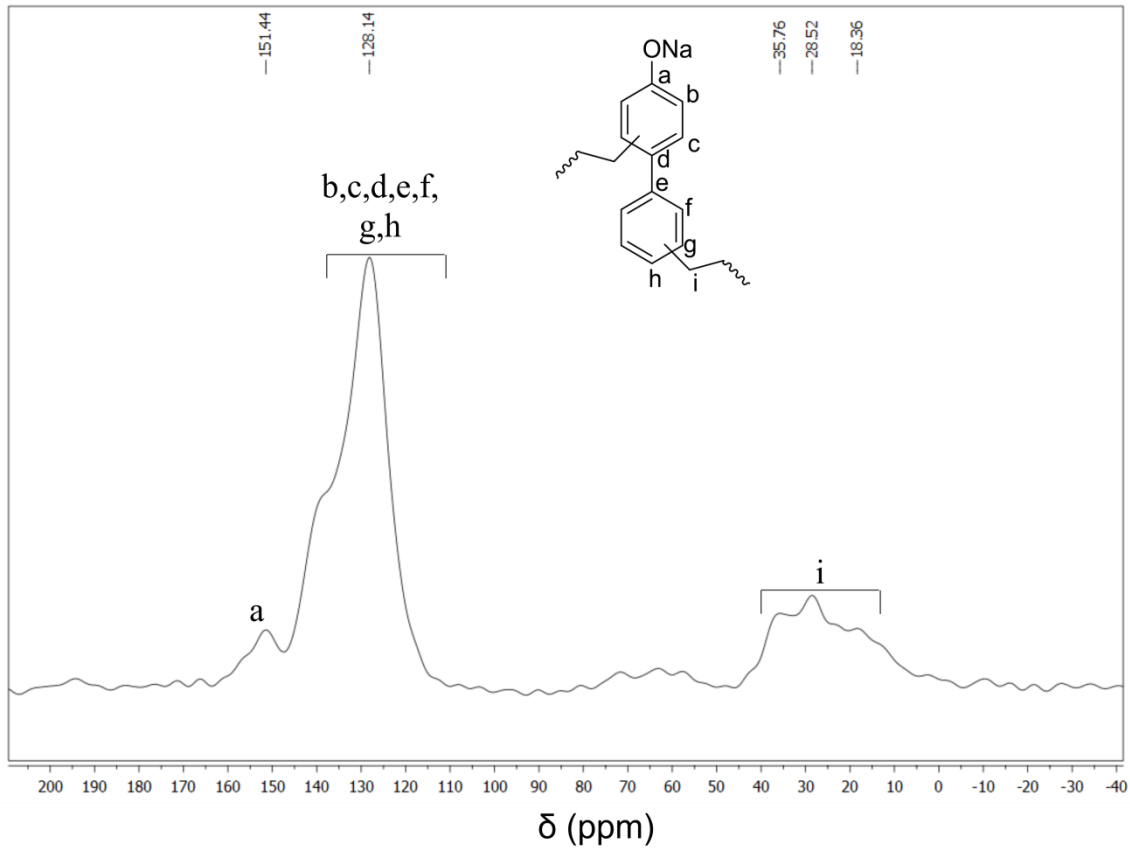


Figure S9: Solid state ^{13}C-NMR of HCP-91@Na.

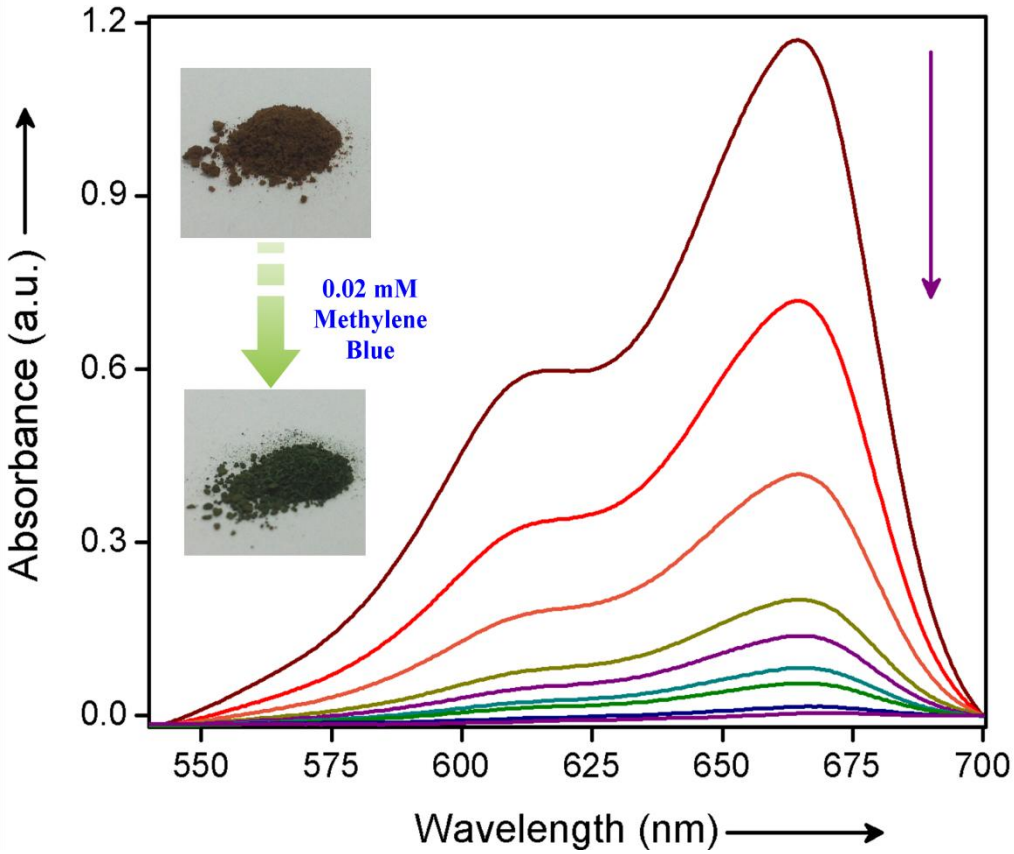


Figure S10:UV-Vis spectra of 0.02 mM methylene blue solution in presence of HCP-91@Na at different time.

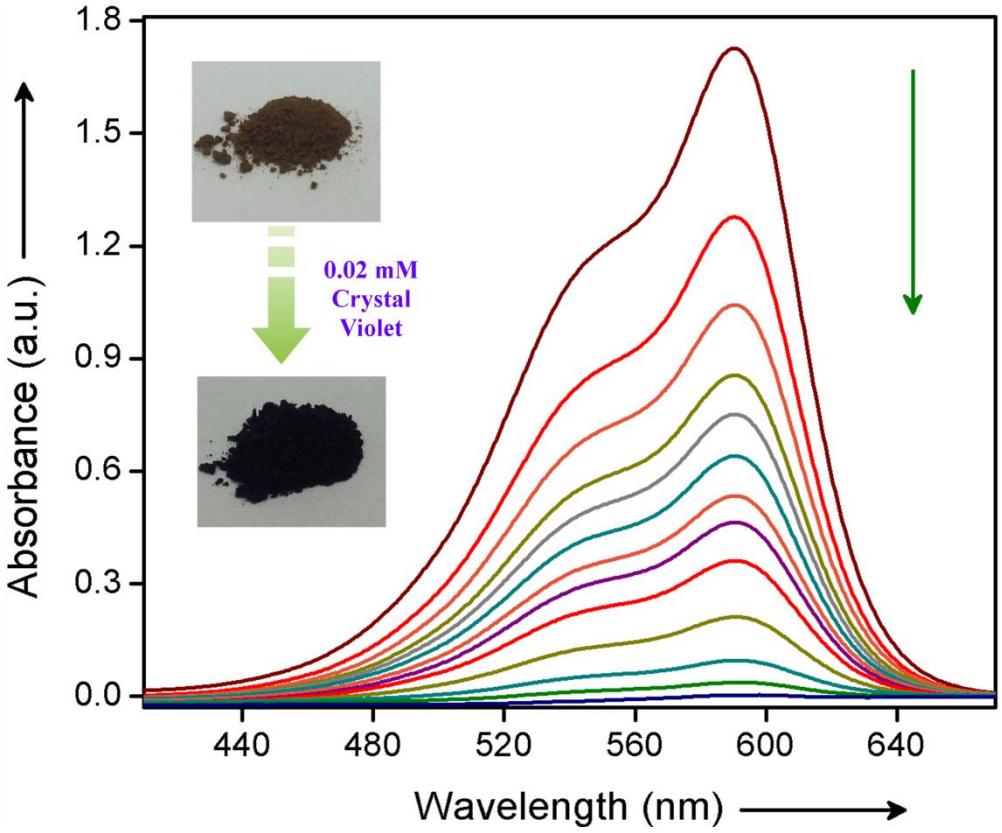


Figure S11: UV-Vis spectra of 0.02 mM crystal violet solution in presence of HCP-91@Na at different time.

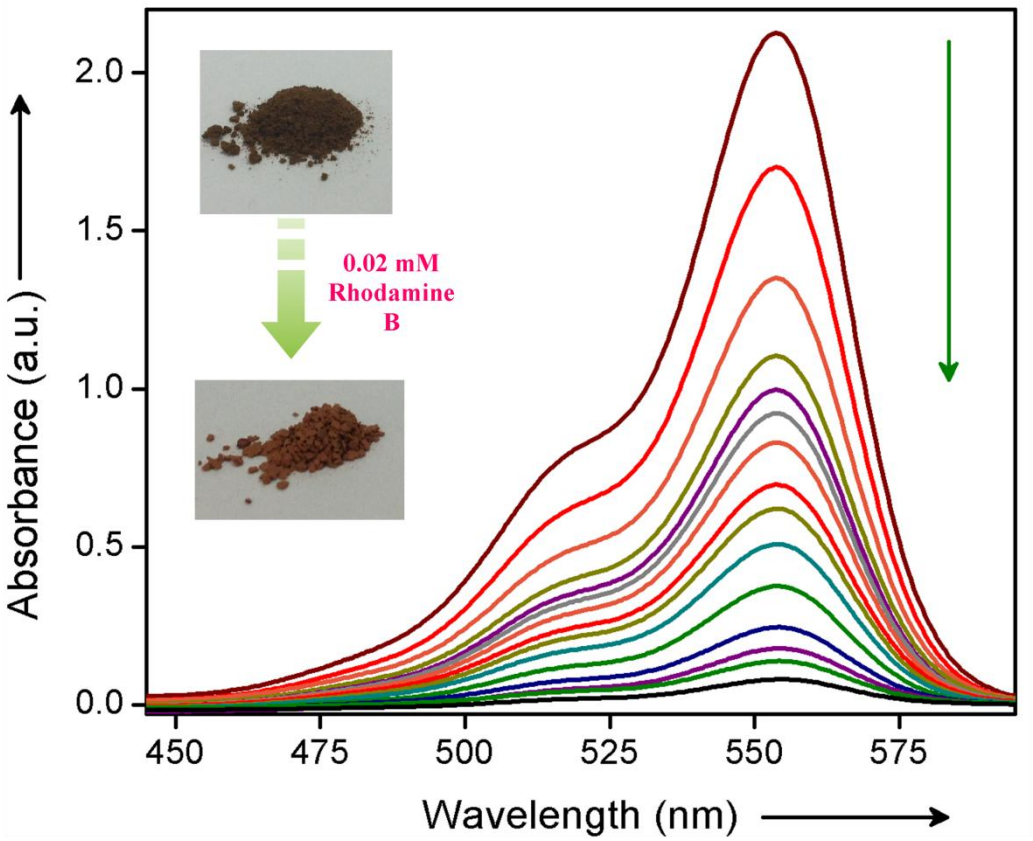


Figure S12: UV-Vis spectra of 0.02 mM rhodamine B solution in presence of HCP-91@Na at different time.

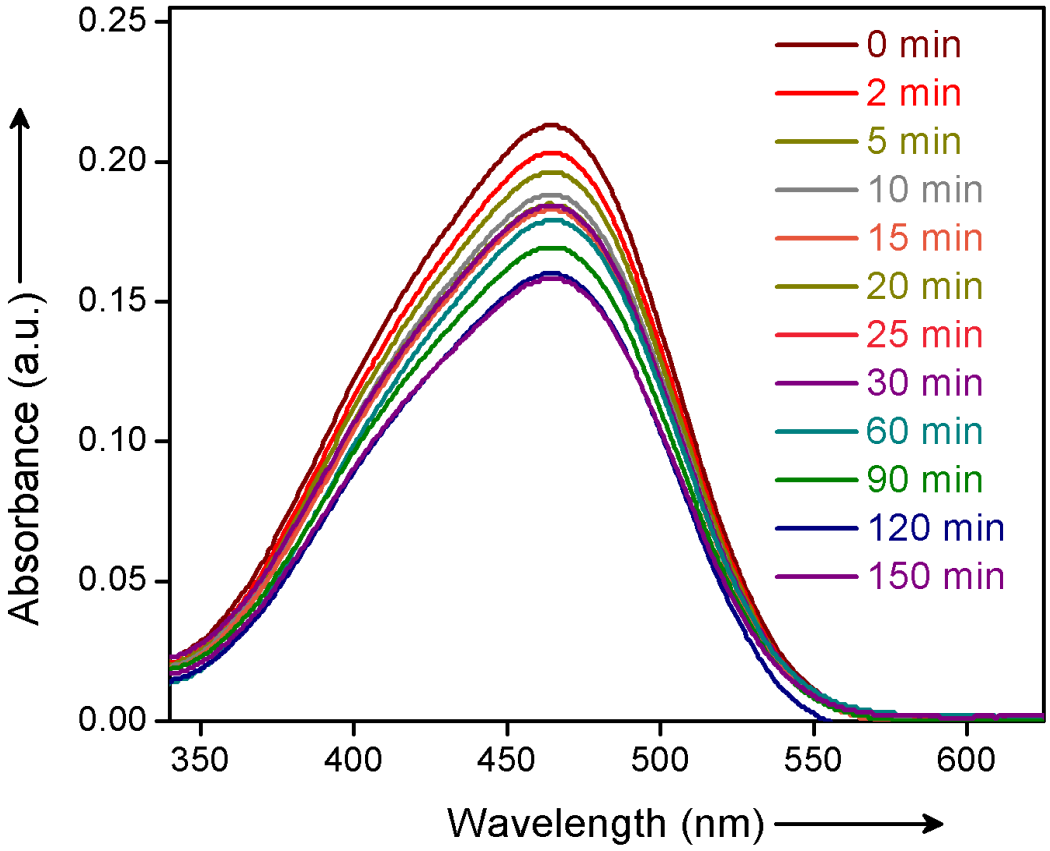


Figure S13: UV-Vis spectra of 0.02 mM methyl orange solution in presence of HCP-91@Na at different time.

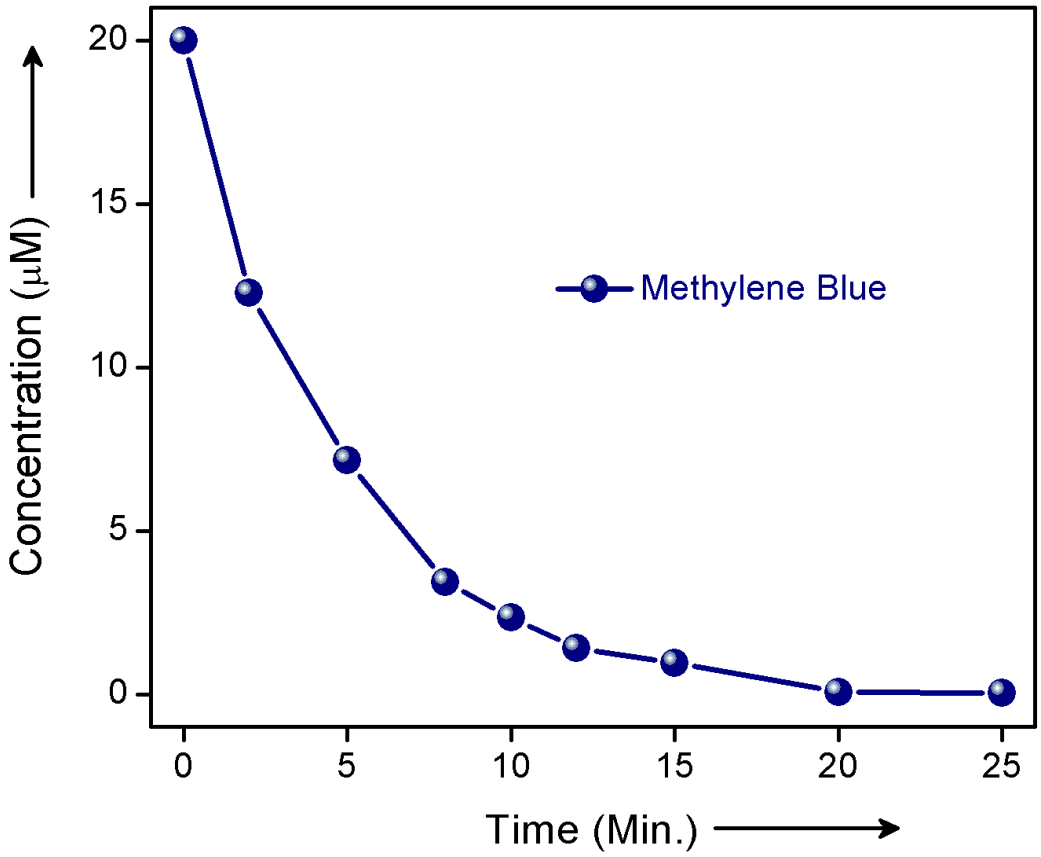


Figure S14: Change in concentration of methylene blue with time in presence of HCP-91@Na.

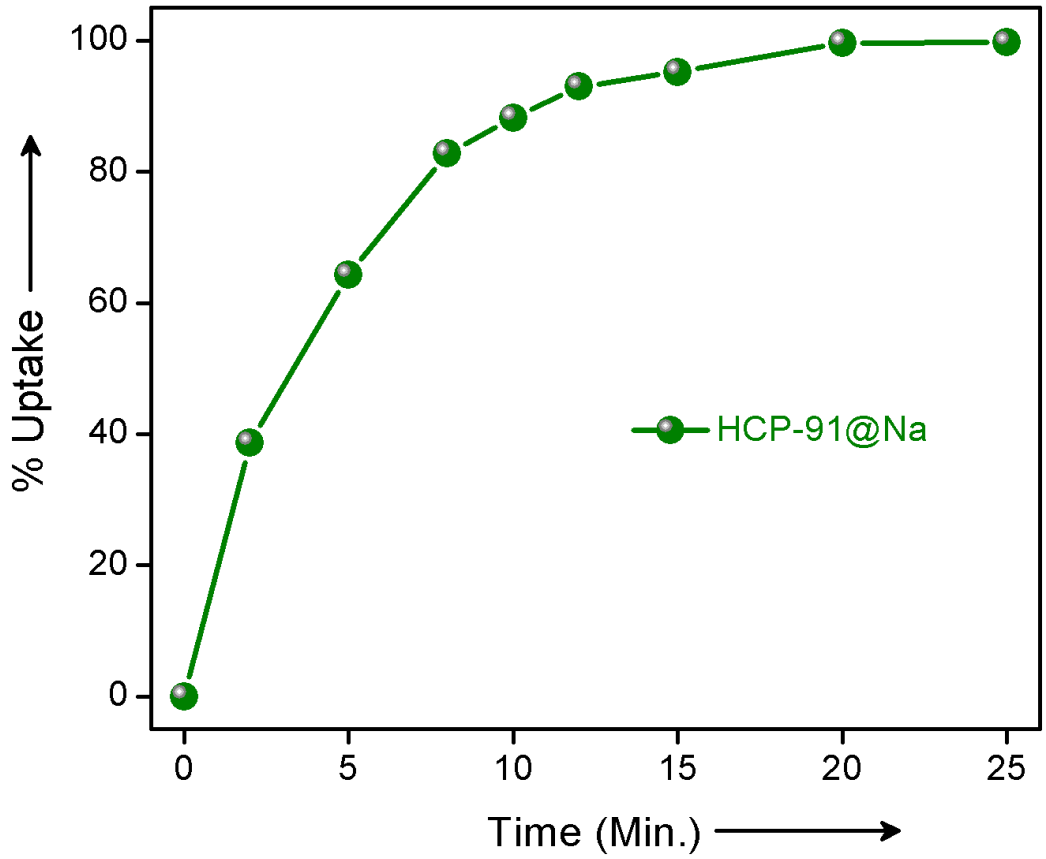


Figure S15: Uptake (in %) of methylene blue by HCP-91@Na with time.

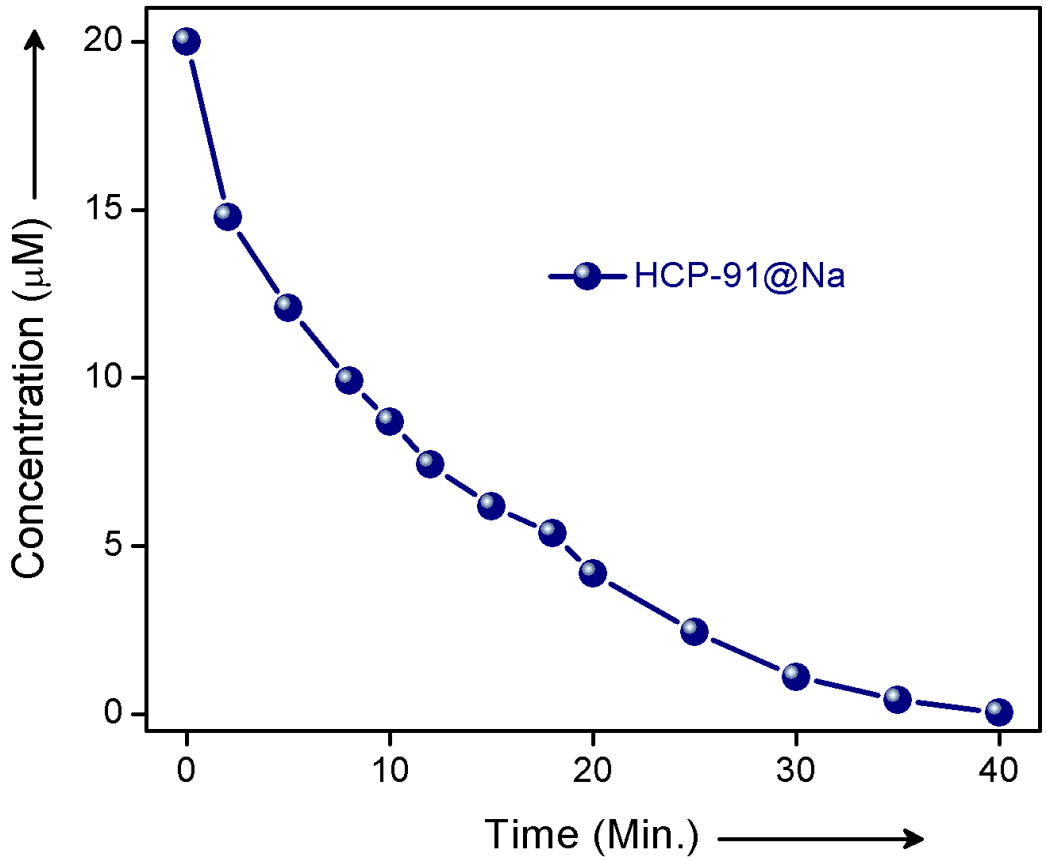


Figure S16: Change in concentration of crystal violet with time in presence of HCP-91@Na.

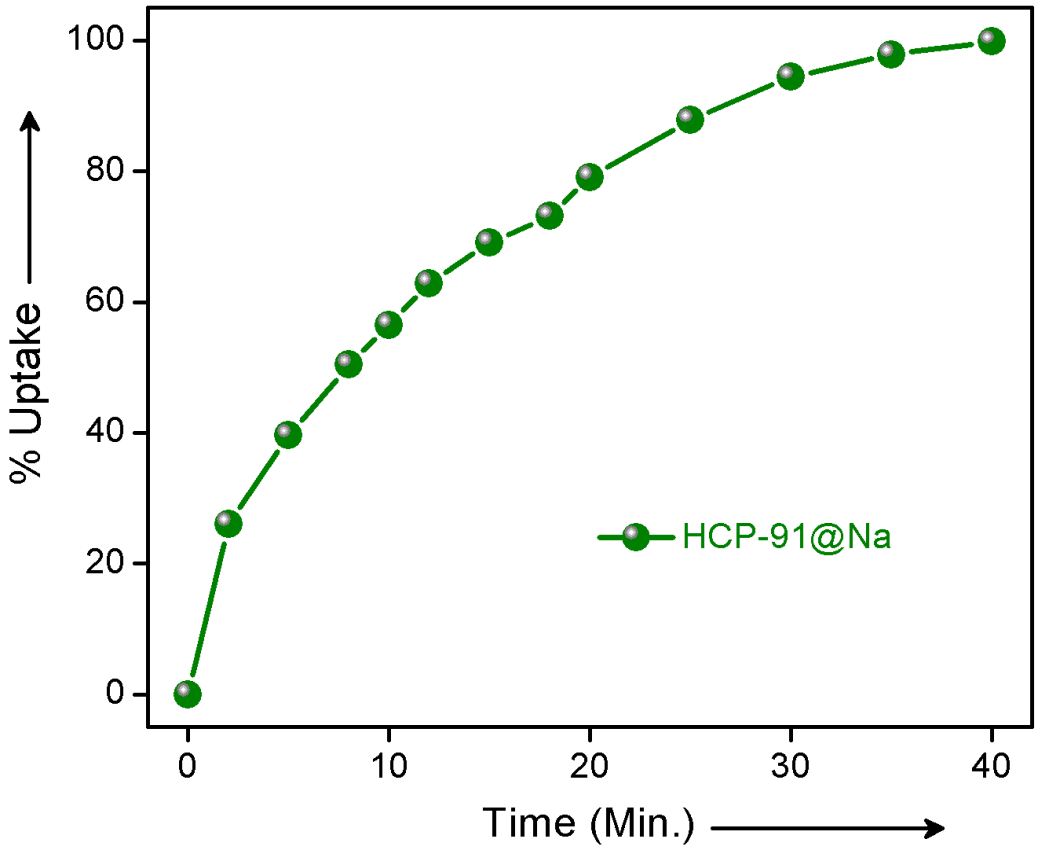


Figure S17: Uptake (in %) of crystal violet by HCP-91@Na with time.

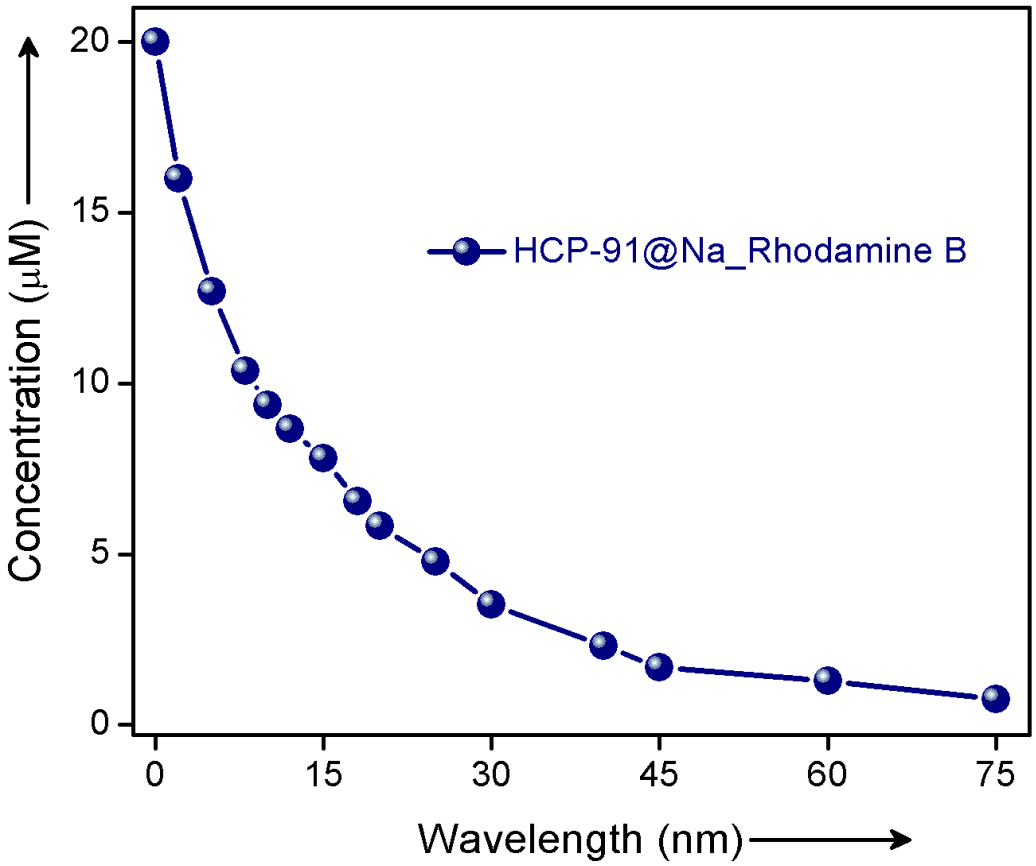


Figure S18: Change in concentration of rhodamine B with time in presence of HCP-91@Na.

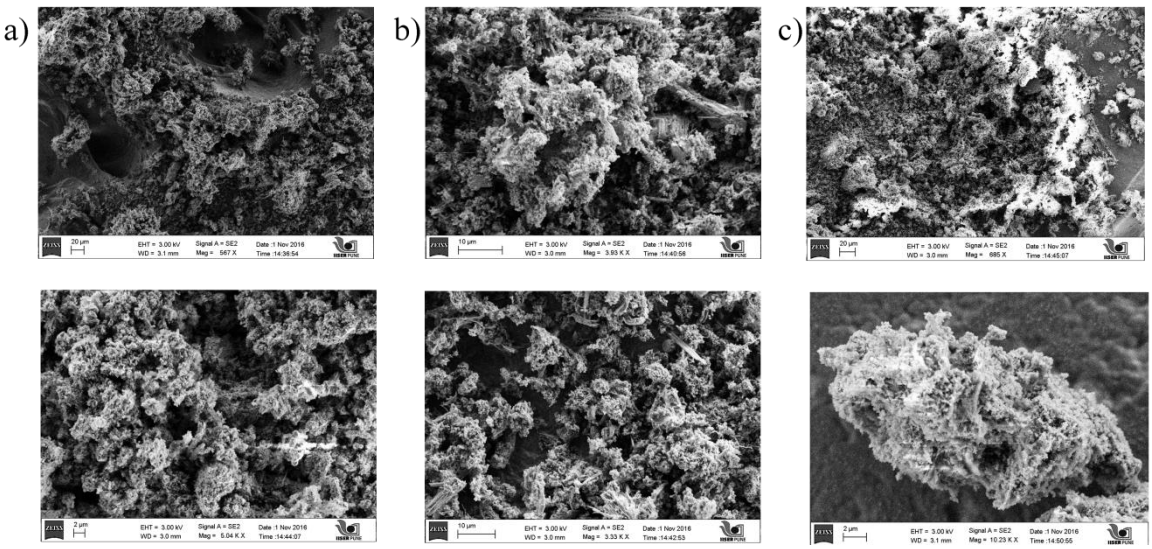


Figure S19: SEM images of a) HCP-91, b) HCP-91@Na and c) HCl treated HCP-91@Na respectively.

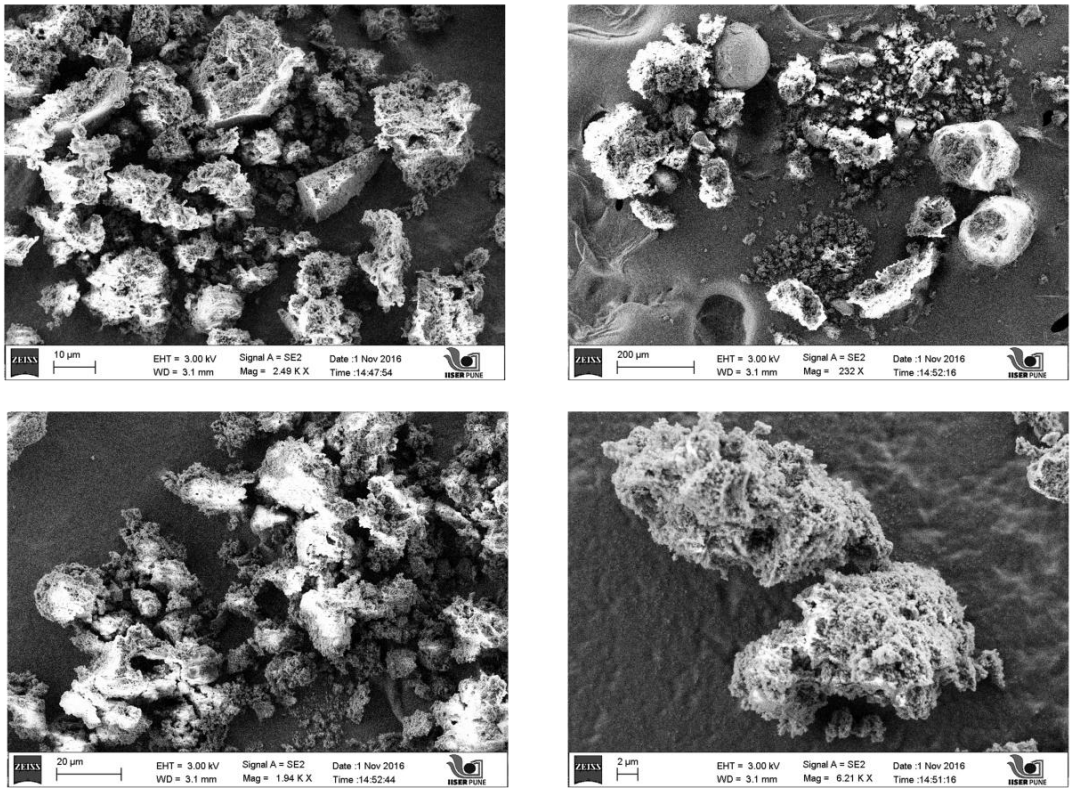


Figure S20: SEM images of methylene blue (MB) encapsulated HCP-91@Na.

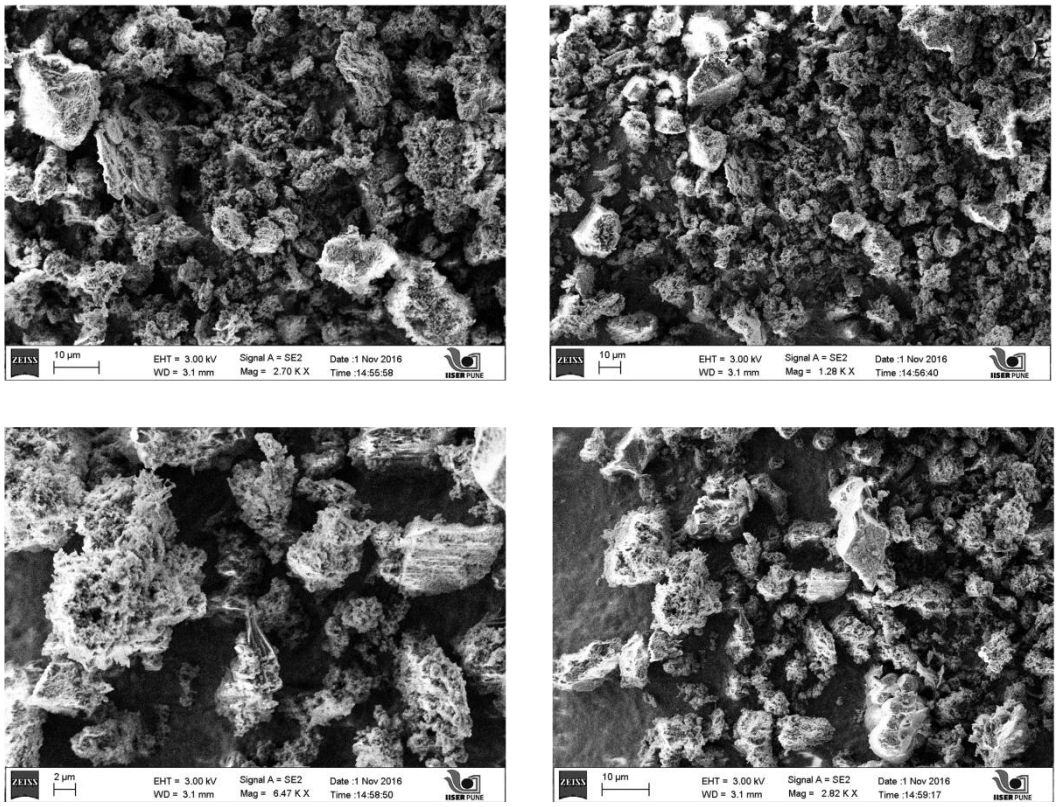


Figure S21: SEM images of crystal violet (CV) encapsulated HCP-91@Na.

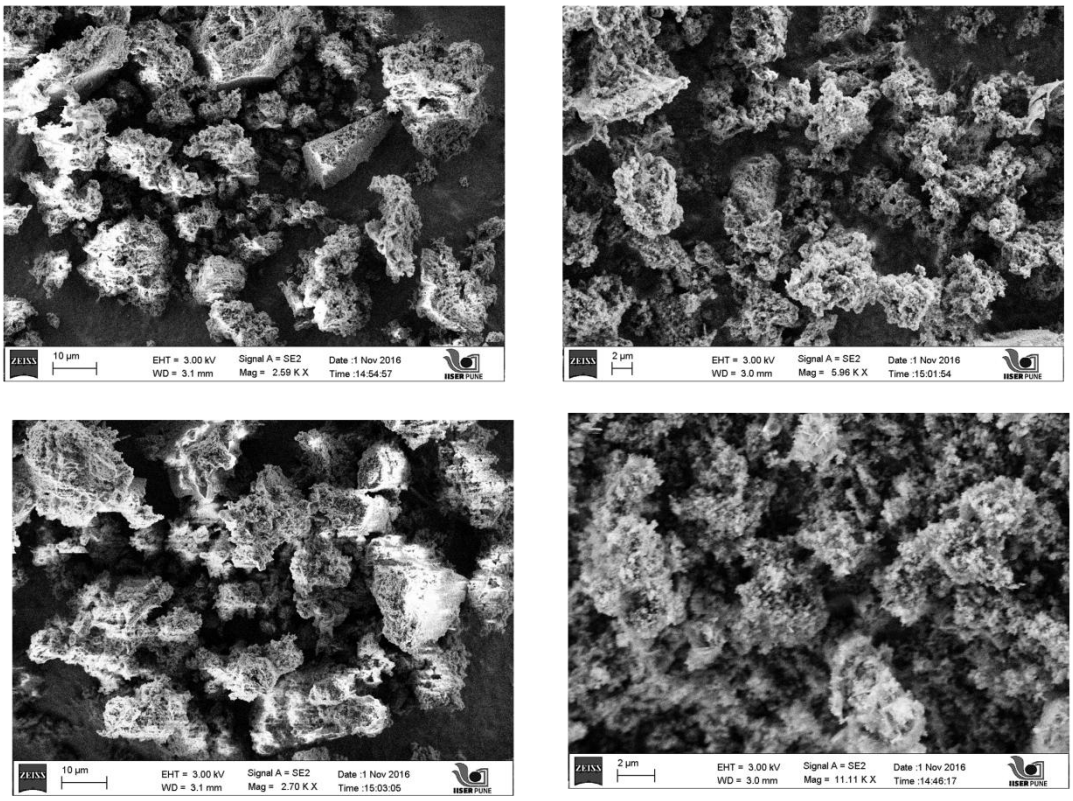


Figure S22: SEM images of rhodamine B (RB) encapsulated HCP-91@Na.

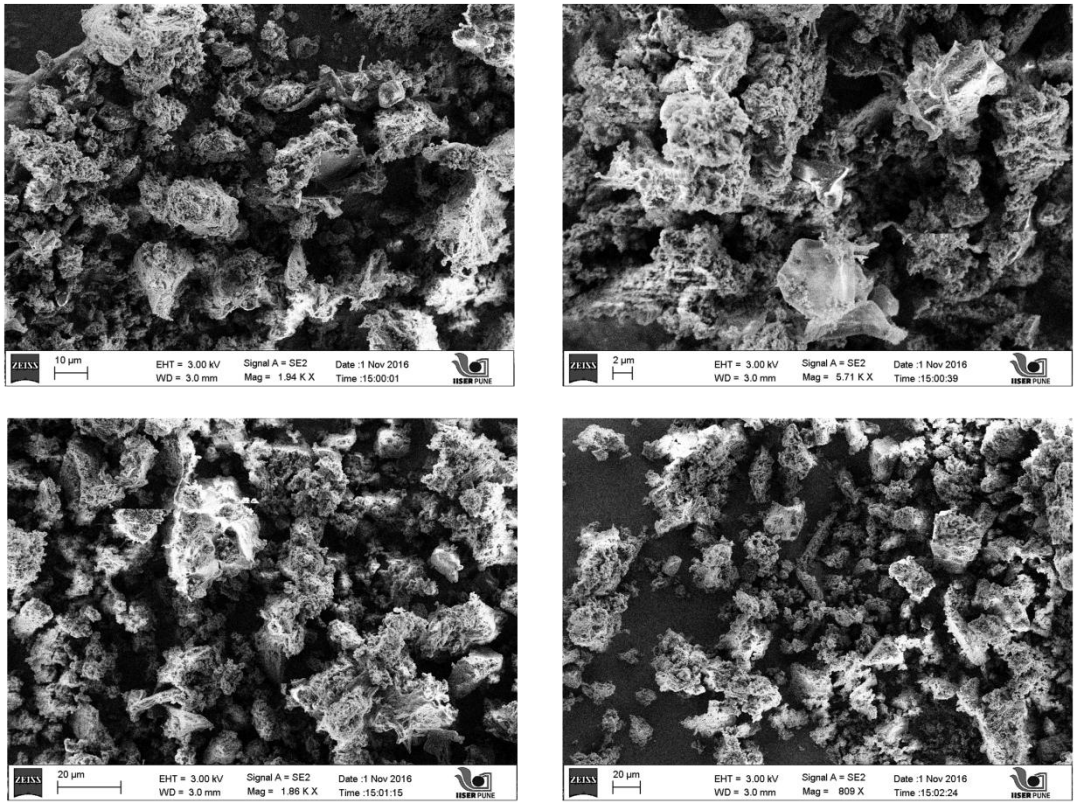


Figure S23: SEM images of methyl orange (MO) treated HCP-91@Na.

Compounds	% of C	% of H	% of N	% of S
HCP-91@Na	66.05	4.475	0.0	0.0
HCP-91@Na _MB	68.47	3.228	1.01	0.399
HCP-91@Na _CV	68.93	3.775	0.89	0.0
HCP-91@Na _RB	62.15	6.25	1.45	0.0

Figure S24: CHNS elemental analysis of HCP-91@Na and different cationic dye encapsulated HCP-91@Na.

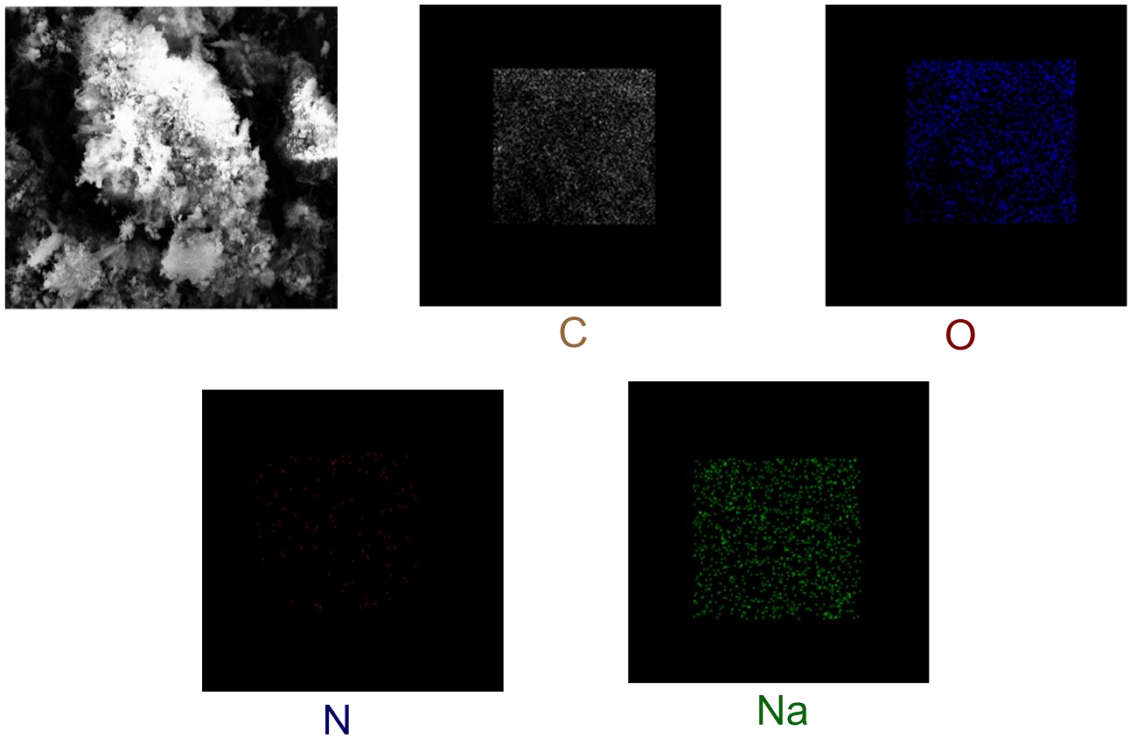


Figure S25: EDAX elemental imaging of HCP-91@Na.

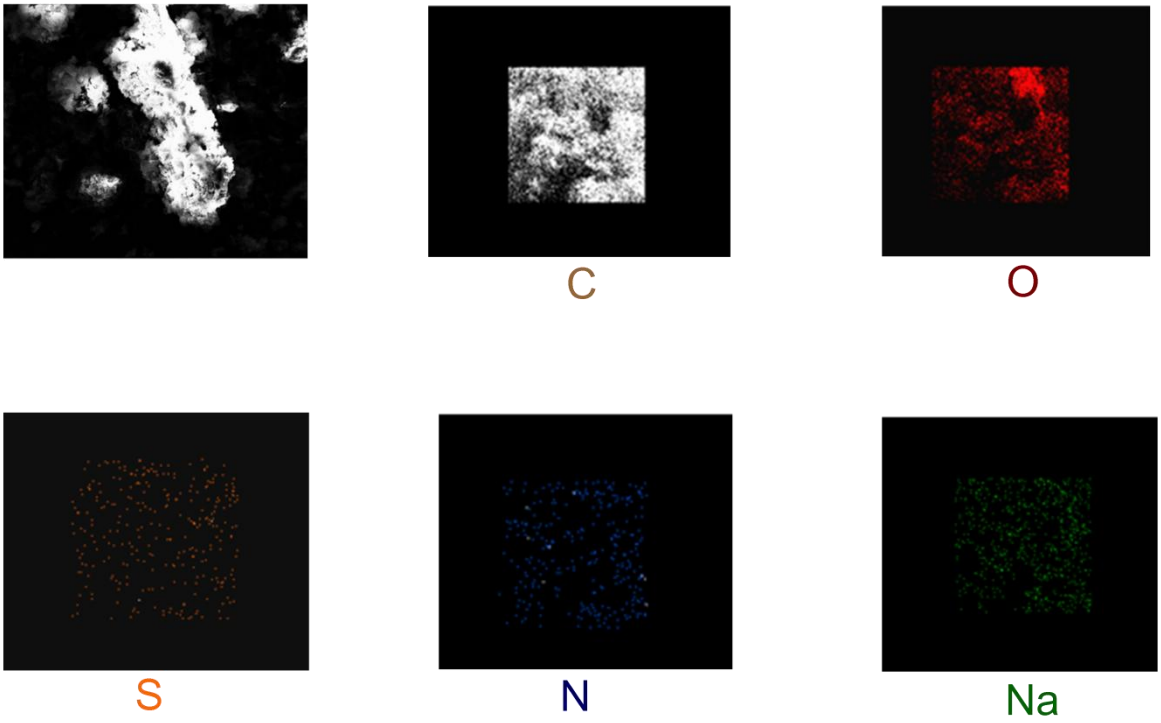


Figure S26: EDAX elemental imaging of methylene blue (MB) HCP-91@Na.

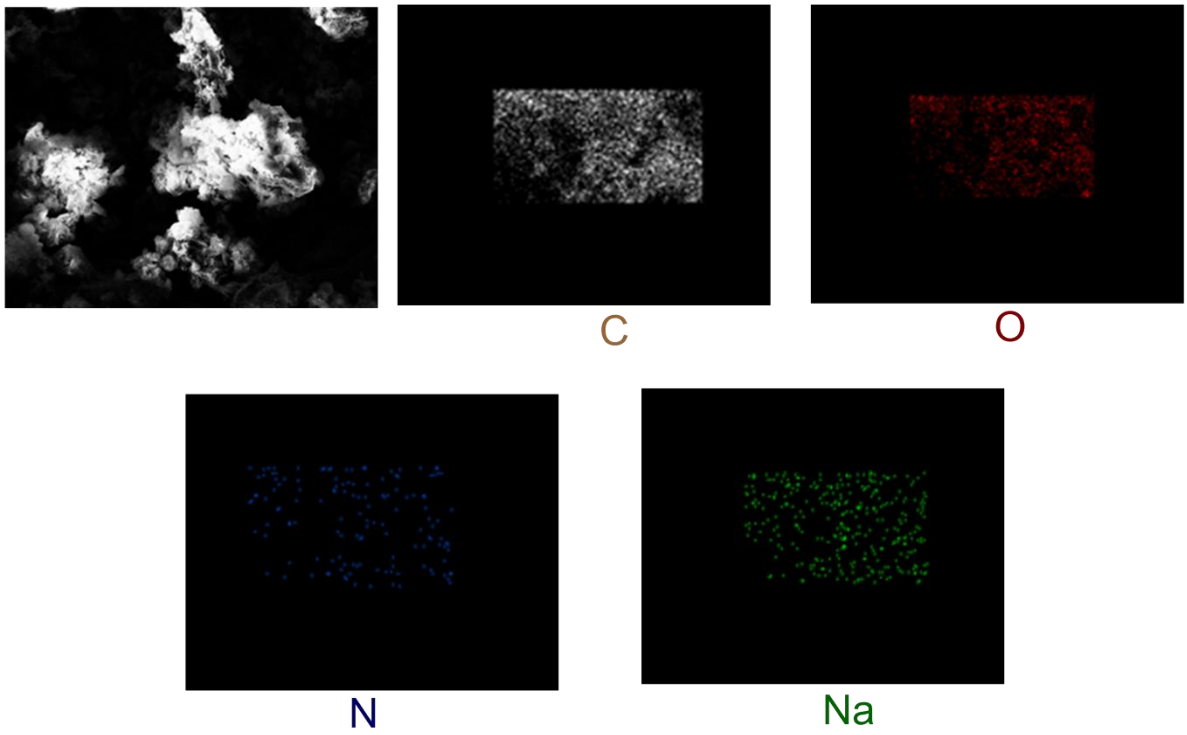


Figure S27: EDAX elemental imaging of crystal violet (CV) HCP-91@Na.

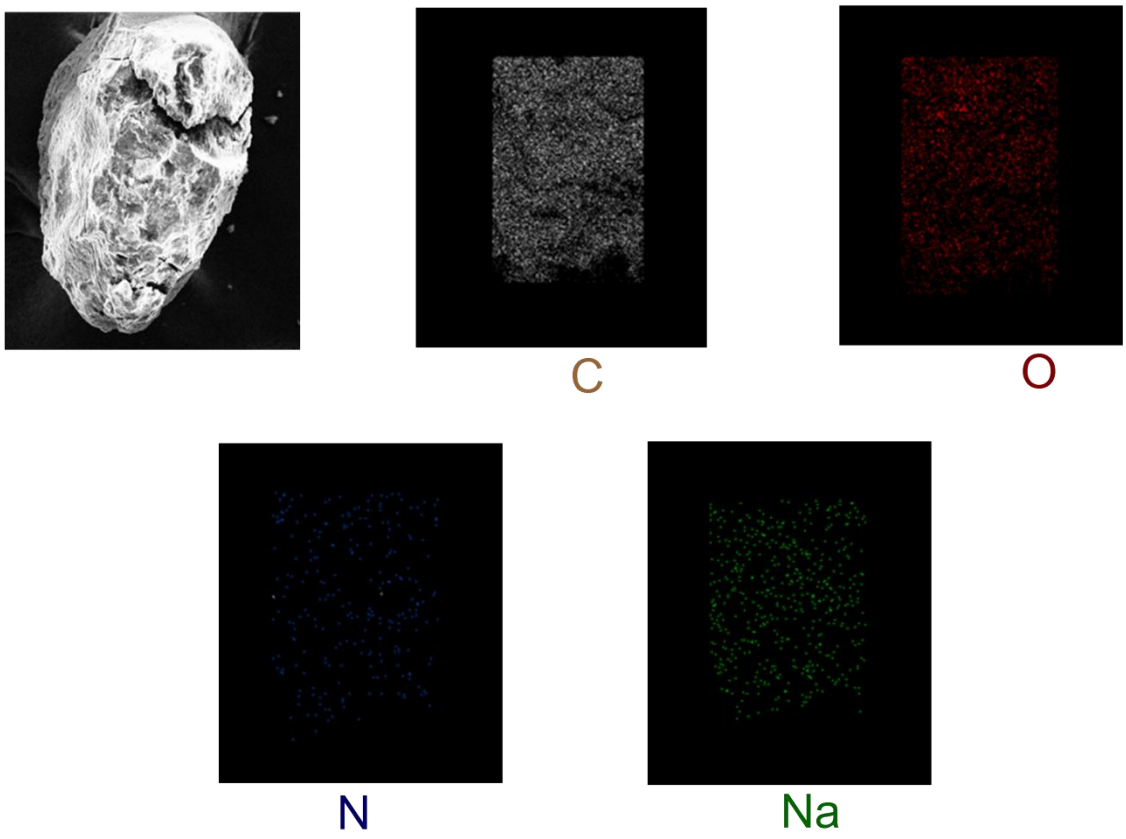


Figure S28: EDAX elemental imaging of rhodamine B (RB) HCP-91@Na.

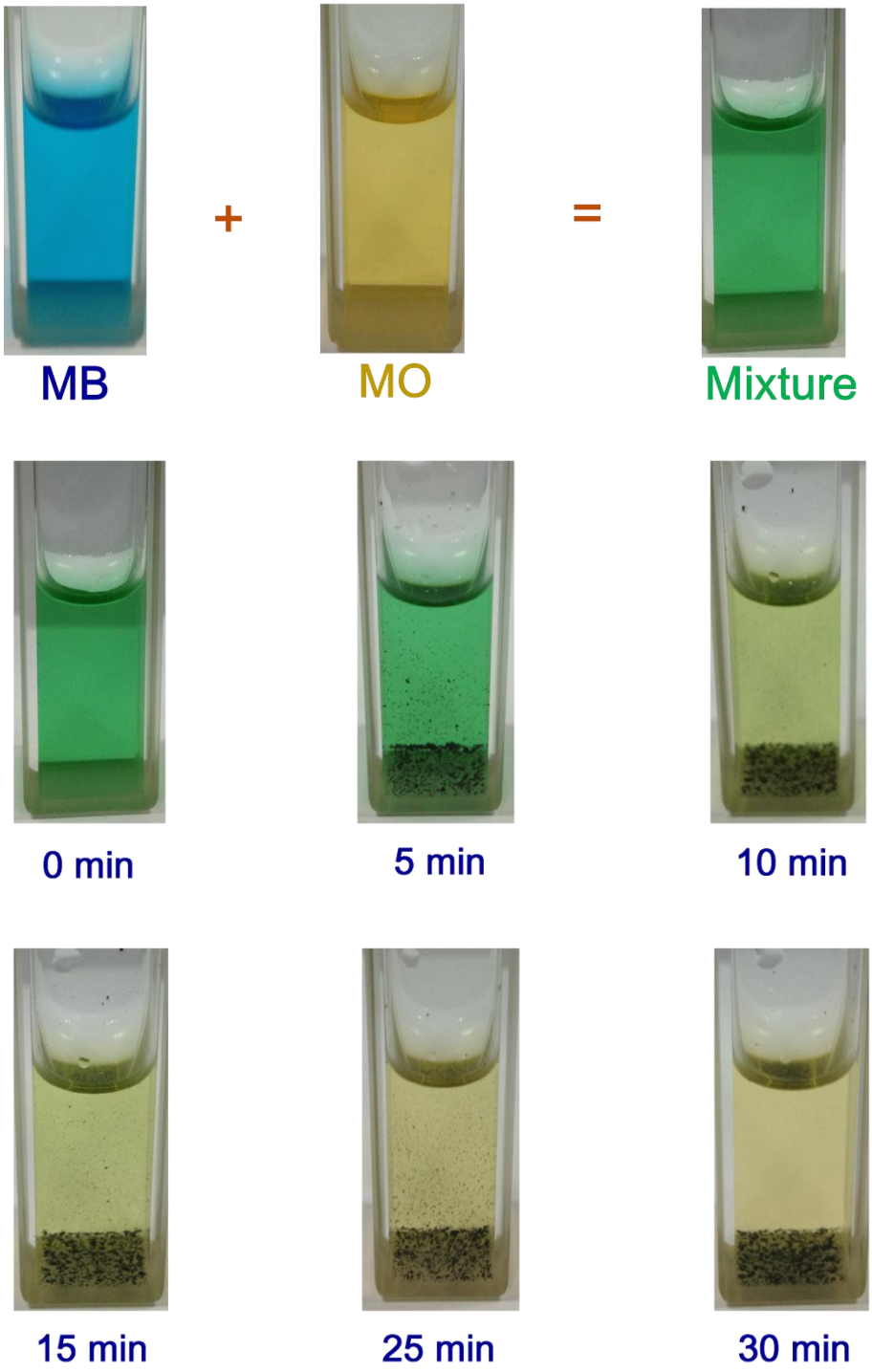


Figure S29: Images at different time of equimolar mixed solution of methylene blue and methyl orange.

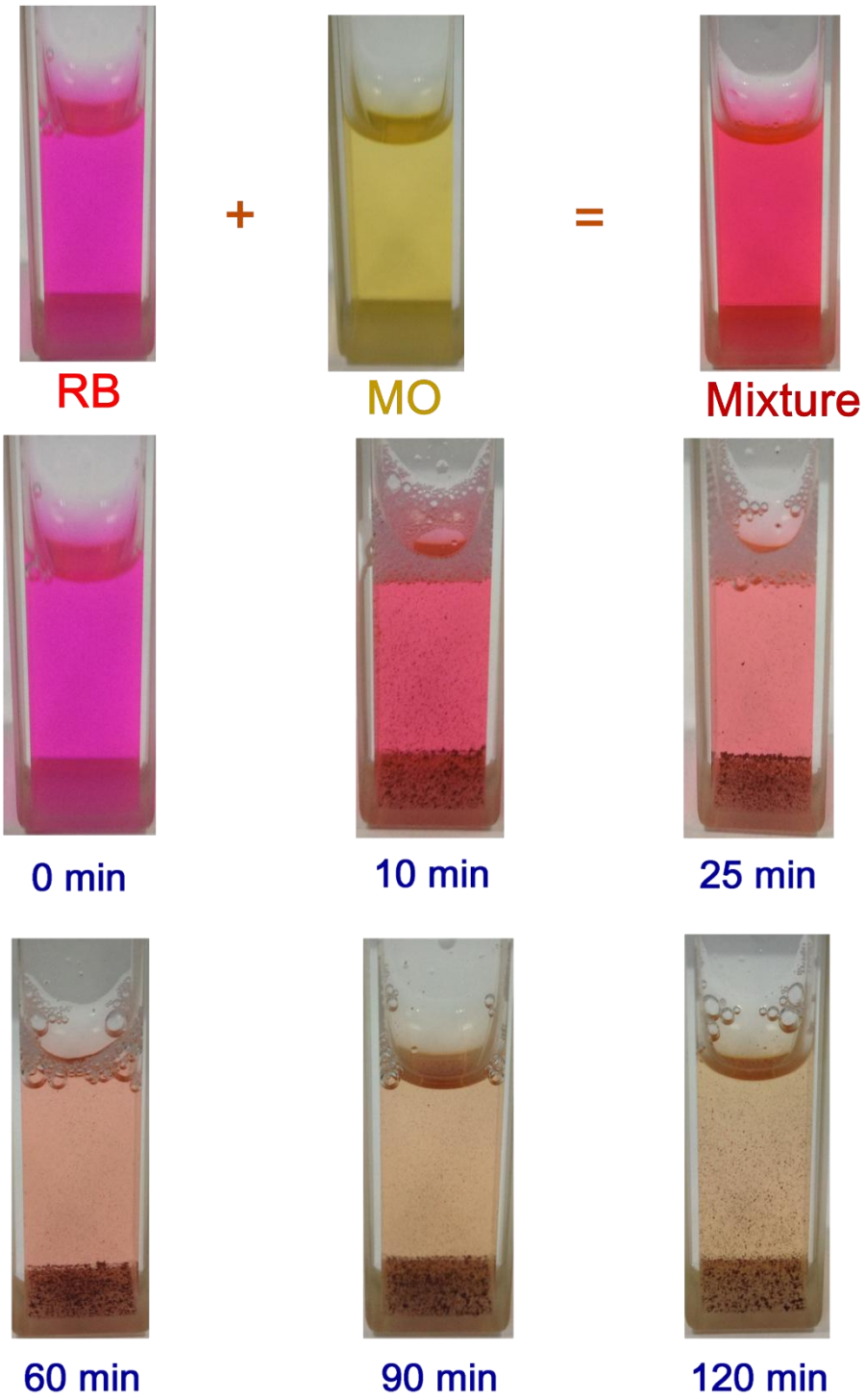


Figure S30: Images at different time of equimolar mixed solution of rhodamine B and methyl orange.

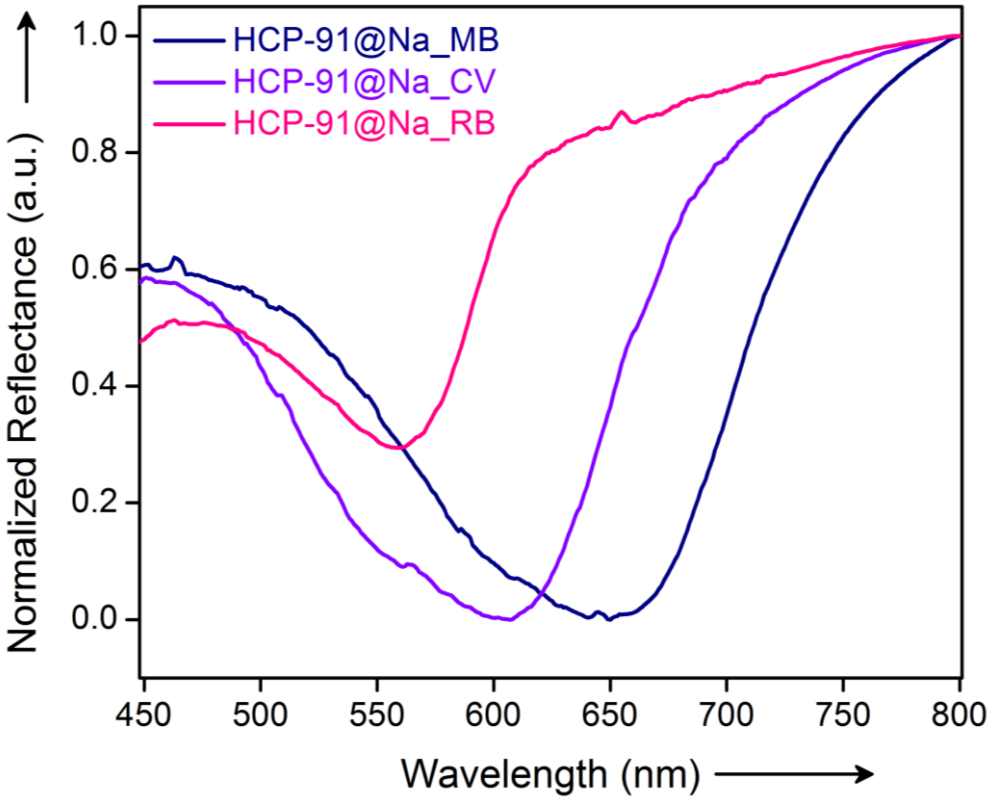


Figure S31: Solid state UV-Vis spectra of methylene blue encapsulated HCP-91@Na (blue), crystal violet encapsulated HCP-91@Na (violet) and rhodamine b encapsulated HCP-91@Na (pink).

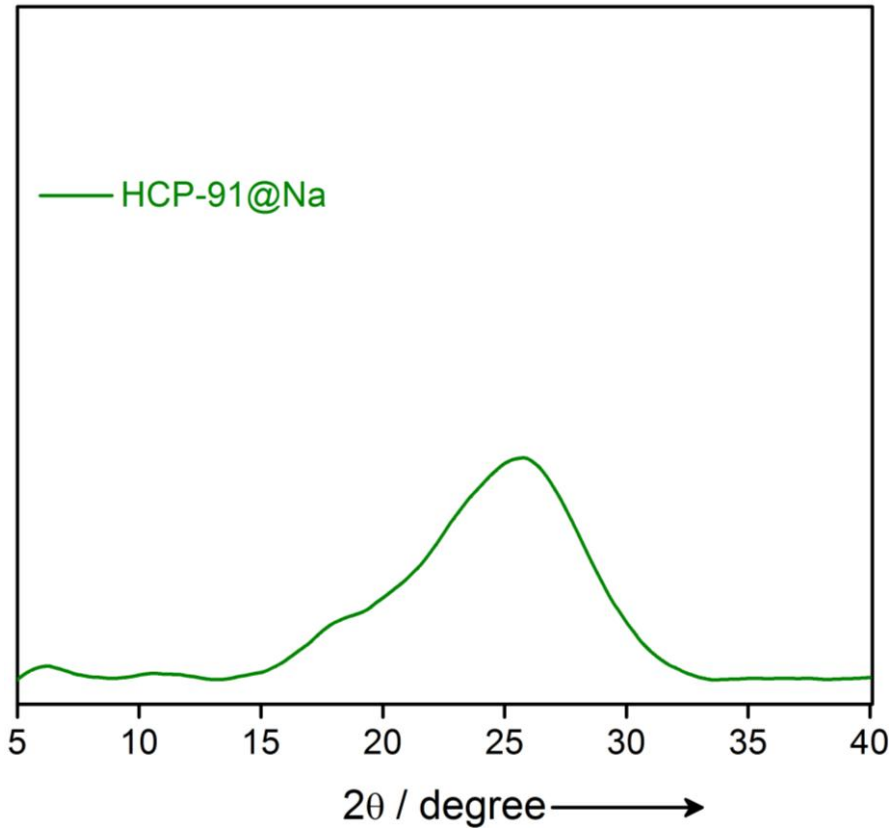


Figure S32: Powder X-ray diffraction (PXRD) pattern of HCP-91@Na.

References:

1. P. Samanta, P. Chandra and S. K. Ghosh, *Beilstein J. Org. Chem.*, 2016, **12**, 1981